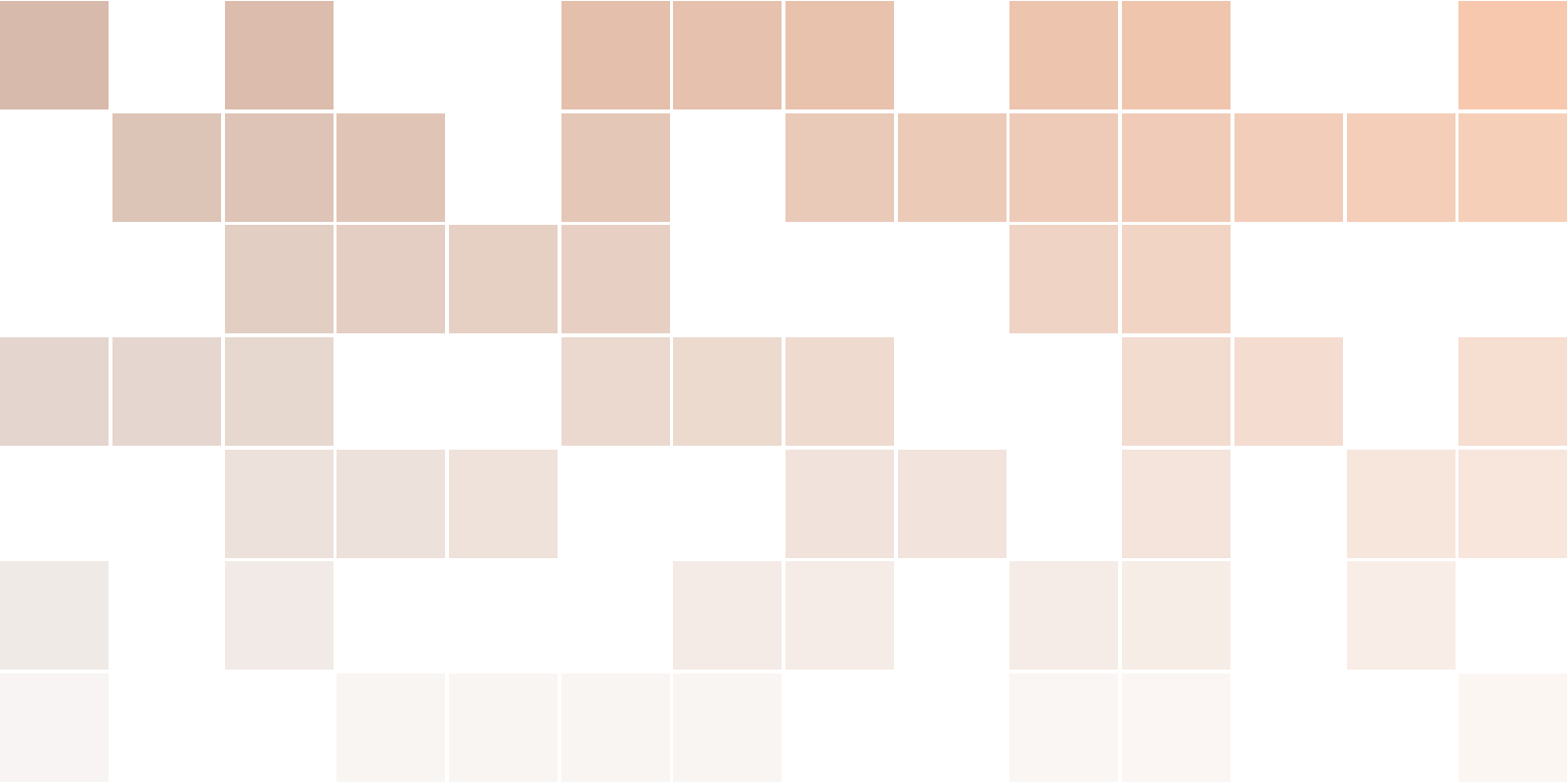
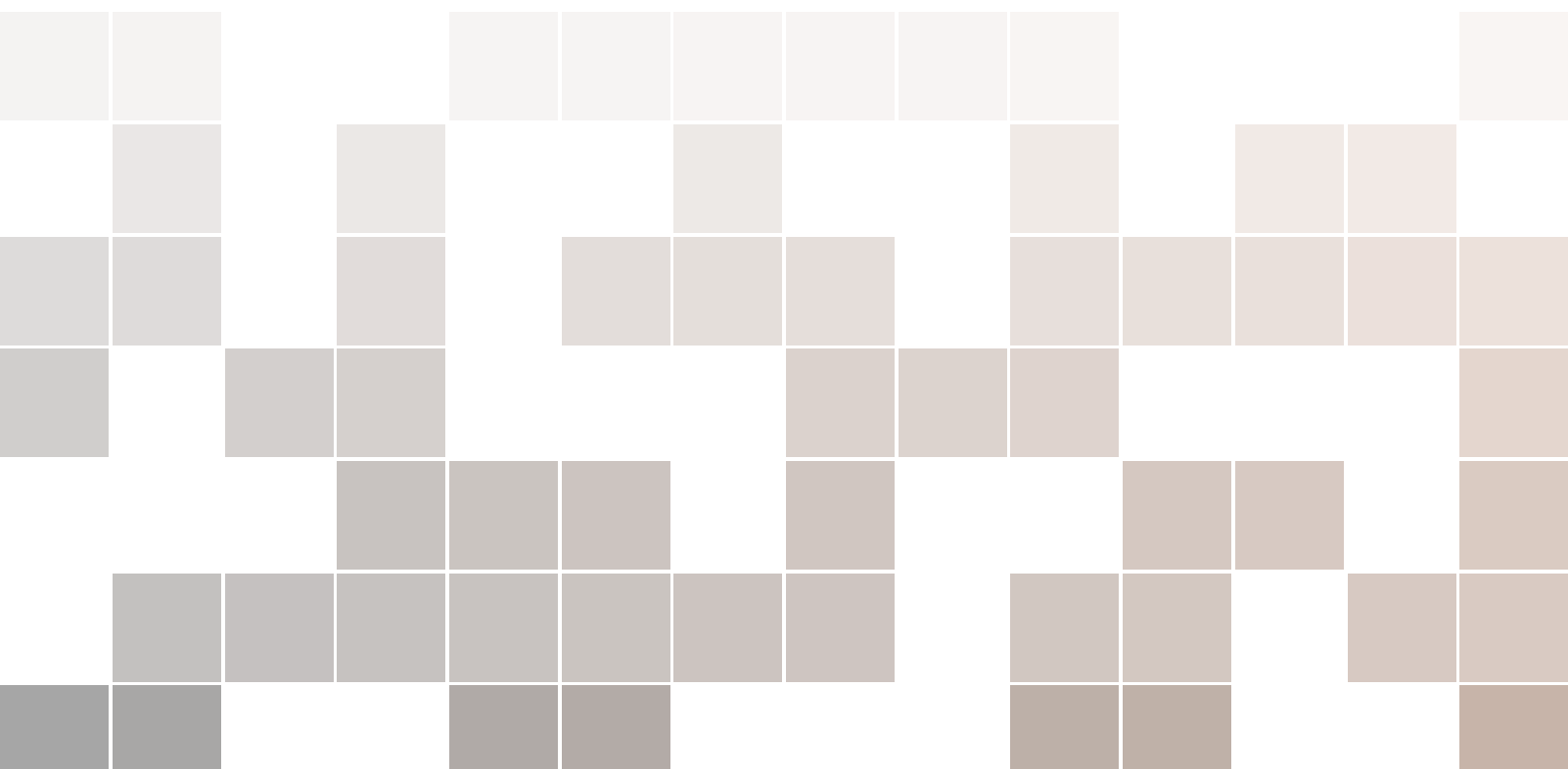




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Book of Abstracts



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0.1 Plenary

0.1.1 Indistinguishable single photons from a single Er³⁺ ion

Speaker: Thompson Jeff

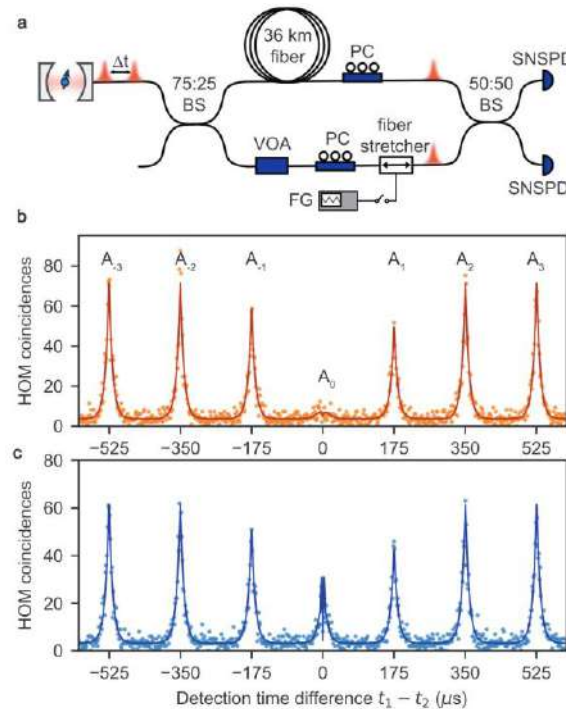
Indistinguishable single photons from a single Er³⁺ ion

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Atomic defects in solid-state crystals are widely explored as single-photon sources and quantum memories for quantum communications networks based on quantum repeaters. Rare earth ions, in particular Er³⁺, have several unique features including a telecom-band optical transition facilitating long-distance entanglement distribution, and compatibility with a broad range of materials and device structures. I will give an overview of recent work from our lab including fast photon emission from single Er³⁺ ions using silicon nanophotonic cavities [1], single-shot spin readout [2], sub-wavelength addressing based on spectral multiplexing [3] and coherent control of nearby nuclear spins [4]. Through systematic materials exploration, we have significantly extended the spin and optical coherence times of Er³⁺ ions, enabling indistinguishable single-photon emission [5]. I will conclude by discussing ongoing efforts to probe spin-spin interactions, and how these advances may be combined into a practical quantum repeater architecture.



Indistinguishable single photons from a single Er³⁺ ion: (a) Schematic of Hong-Ou-Mandel (HOM) interferometer with 36 km delay line, (b) HOM interference with visibility $V > 0.8$, (c) the interference vanishes when adding phase noise to one arm.

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0.1.2 Light-field Imaging: Capturing 3D in One Snapshot

Speaker: Liu Xiaogang

Light-field Imaging: Capturing 3D in One Snapshot

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Imaging technology has completely transformed our understanding and perception of the world, with advancement in medical imaging and astronomical observations. Imaging devices and methods have paved the way for significant breakthroughs in a variety of fields. Whether it is detecting cancer at an early stage or capturing the beauty of distant galaxies, imaging has become an indispensable tool for researchers and practitioners alike. As we continue to push the boundaries of what is possible, the field of imaging is constantly evolving, leading to increasingly sophisticated devices and techniques. One such technique is light-field imaging, which captures all light rays passing through a certain point in space, allowing for the creation of a four-dimensional data set. Unlike traditional images, light fields include information about the scene in all dimensions, including vector representations of light direction and intensity over time. During this talk, I will introduce the latest advancements in light-field imaging and present a new method that uses color-encoding to convert viewing angles into specific colors. This microlens-free approach to light-field imaging and absolute spatial positioning has the potential to revolutionize various fields, including 3D phase-contrast imaging, robotics, autonomous navigation, and satellite navigation.

0.1.3 Random Lasers

Speaker: Cao Hui

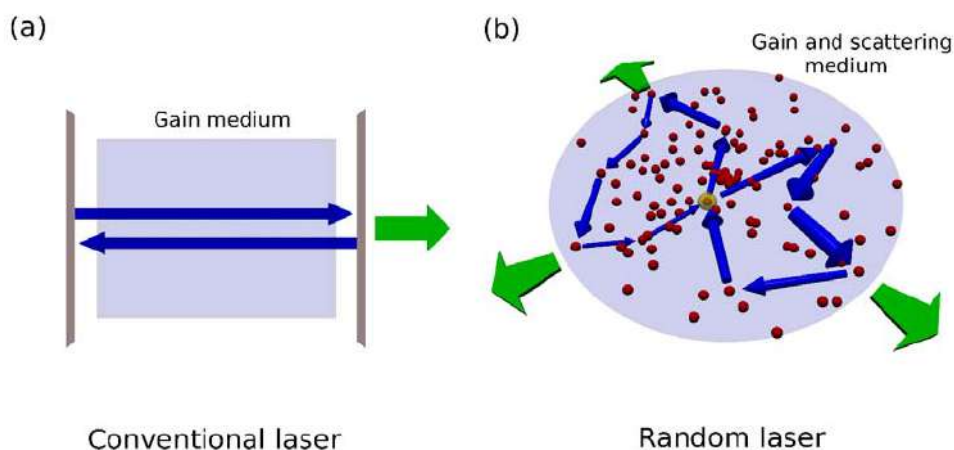
Random Lasers

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Unlike conventional lasers relying on mirrors or periodic structures to trap light, random lasers utilize multiple scattering in disordered gain media for optical confinement and feedback. They have been realized in many material systems, including powders, colloids, biological tissues, polycrystalline films, polymers, optical fibers, and cold atomic vapors. The lasing frequencies range from ultraviolet and visible to infrared and Tera-Hertz. This section will cover some applications of random lasers. Over the past three decades there have been extensive experimental and theoretical studies on random lasers. I will review the history of random laser development and introduce the lasing mechanism. I will also discuss the applications that benefit from the unique characteristic of random lasers.



0.1.4 Single-photon emitters at telecom wavelength in silicon

Speaker: Dréau Anaïs

Single-photon emitters at telecom wavelength in silicon

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The boom of silicon in semiconductor technologies was closely tied to the ability to control its density of lattice defects [1]. After being regarded as detrimental to the crystal quality in the first half of the 20th century [2], point defects have become an essential tool to tune the electrical properties of this semiconductor, leading to the development of a flourishing silicon industry [1]. At the turn of the 21st century, progress in Si-fabrication and implantation processes has triggered a radical change by enabling the control of these defects at the single level [3]. This paradigm shift has brought silicon into the quantum age, where individual dopants are nowadays used as robust electrical quantum bits to encode and process quantum information [4]. Fluorescent defects recently isolated at single-defect scale in silicon [5,6] could follow suit. These new artificial atoms in silicon have the advantage of an optical interface at telecom wavelengths, and for some, combined with a non-zero electron spin state that could be used to locally store quantum information [7].

In this talk, I will present the latest developments on the isolation and control of single fluorescent defects in silicon. These individual color centers feature a single-photon emission directly in the telecom bands adapted for long-distance propagation in optical fibers. They are observed at single-defect scale in silicon-on-insulator wafers at 10K-30K using confocal microscopy. This technique makes it possible to isolate not only well-known defects from the literature [8,9], but also to detect unreported color centers in optical spectroscopy measurements on ensembles [10]. We will discuss the prospects and challenges of these promising systems for Si-based quantum technologies, including integrated quantum photonics and quantum communications.

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0.2 Invited

0.2.1 Advancing Human-Centric Lighting with Phosphor Converted Violet LEDs

Speaker: Brgoch Jakoah

Advancing Human-Centric Lighting with Phosphor Converted Violet LEDs

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The concept of human-centric lighting stems from the evolution of sunlight's intensity and color temperature throughout the course of a day. This natural progression of bright cold-white light during the middle of the day to a softer warm-white light in the evening stimulates intrinsic photosensitive retinal ganglion cells that control our circadian rhythm. The blue-hue of daylight activates these cells to produce dopamine and cortisol while suppressing melatonin, the sleep hormone, to keep humans awake and alert. The current generation of energy-efficient LED lights reproduces daylight by converting a blue-emitting LED into a broad-spectrum white light using inorganic phosphors. Unfortunately, the resulting intense blue-hue generated by cheap LED bulbs and the underlying blue light from even the most expensive bulbs have been shown to cause macular degeneration, cataract formation, mood disorders, and circadian disruption, resulting in insomnia and fatigue. This talk will investigate alternative solutions to reduce the amount of blue light generated by modern LED lights. The core change will require identifying new luminescent phosphors that pair with violet-emitting LED chips while still producing high-quality white light. As a result, we have been developing materials like blue-emitting $\text{Na}_2\text{MgPO}_4\text{F}:\text{Eu}^{2+}$ and $\text{K}_3\text{AlP}_3\text{O}_9\text{N}:\text{Eu}^{2+}$, and the green-emitting $\text{NaBaB}_9\text{O}_{15}:\text{Eu}^{2+}$ that meet all of the necessary requirements, including a high quantum yield, thermally robust emission, and strong violet absorption. Incorporating these materials into prototype devices demonstrates that it is possible to produce a warm-white light with a higher color rendering index than a commercially purchased LED light bulb while significantly reducing the blue component.



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0.2.2 Are non-radiative transitions so different from radiative transitions?

Speaker: Suta Markus

Are non-radiative transitions so different from radiative transitions?

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Non-radiative transitions are usually considered a problematic decay channel for excited states of potent emitters. Based on the elementary work of Struck and Fonger, non-radiative transitions of inorganic luminescent compounds are categorized into multi-phonon- or thermal crossover-type non-radiative transitions [1]. While thermal crossover is typical for crossing excited state potentials with different equilibrium geometries and is thus, very sensitive to temperature to overcome a thermal activation barrier, multi-phonon-type transitions are usually comparably more inert towards temperature changes and typical for narrow-line emitters such as the trivalent lanthanoid ions. Multi-phonon transitions can be particularly effectively tuned by the famous energy-gap law [2]. The better control over non-radiative transitions in the case of multi-phonon-type transitions has been successfully employed in the structural design of narrow-band emitting LED phosphors with high quantum yields and quenching temperatures [3]. However, since the advent of luminescence thermometry, it has been realized that non-radiative transitions are not always disturbing but play a crucial role for their performance and working range [4]. A better understanding of non-radiative transitions is thus mandatory for a targeted design of luminescent compounds.

In this talk, the basic principles governing radiative and non-radiative transitions will be reviewed and demonstrate that non-radiative transitions do also follow a certain set of selection rules just like radiative transitions. It will be demonstrated how both structural effects and fundamental selection rules can control the order of magnitude of non-radiative transitions, what consequences may arise out of this and why crossover-type transitions are usually connected to higher intrinsic non-radiative transition rates than multi-phonon-type transitions. Finally, a perspective on potential interesting effects and the impact for phosphor design in general will be given.

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0.2.3 Bidirectional, Indefinite Near Infrared Nanocrystal Photoswitching

Speaker: Schuck James

Bidirectional, Indefinite Near Infrared Nanocrystal Photoswitching

P. James Schuck^{1*}, C. Lee¹, Emma Z. Xu¹, N. Fardian-Melamed¹, S. H. Nam², Y. D. Suh³, B. E. Cohen⁴, E. M. Chan⁴

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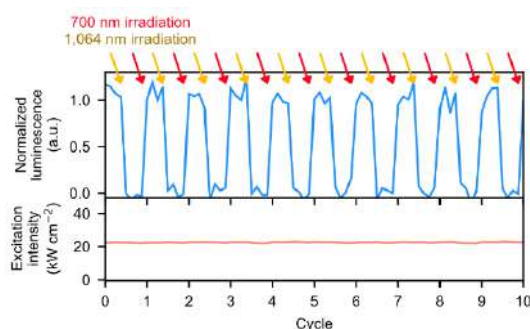
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Materials whose luminescence can be switched by optical stimulation drive technologies ranging from superresolution imaging, nanophotonics, and optical data storage, to targeted pharmacology, optogenetics, and chemical reactivity. Here, we present 2-way, NIR photoswitching of avalanching nanoparticles (ANPs) [1], showing full optical control of upconverted emission using phototriggers in the NIR-I and NIR-II spectral regions useful for subsurface imaging. Employing single-step photodarkening and photobrightening, we demonstrate indefinite photoswitching of individual nanoparticles (>1000 cycles over 7 h) in ambient or aqueous conditions without measurable photodegradation. Critical steps of the photoswitching mechanism are elucidated by modeling and by measuring the photon avalanche properties of single ANPs in both bright and dark states. Unlimited, reversible photoswitching of ANPs enables indefinitely rewritable 2D and 3D multi-level optical patterning of ANPs, as well as optical nanoscopy with sub-Å localization superresolution that allows us to distinguish individual ANPs within tightly packed clusters.



Perfectly stable NIR photoswitching of a single ANP

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0.2.4 Bottom-up assembly of nanocrystals for nonlinear, electro-optic, and quantum devices

Speaker: Grange Rachel

Bottom-up assembly of nanocrystals for nonlinear, electro-optic, and quantum devices

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Nonlinear and electro-optic devices are present in our daily life with many applications: light sources for microsurgery, green laser pointers, or modulators for telecommunication. Most of them use bulk materials such as glass fibres or high-quality crystals, hardly integrable or scalable. Even the fast developments of thin film lithium niobate face the challenging etching of metal-oxides [1]. Therefore, the quest for a non-centrosymmetric material system, easy to fabricate and to scale up while maintaining its functionality is still ongoing. Here we will present our recent advances on bottom-up photonic assemblies of randomly oriented nanocrystals and how we can produce electro-optic, nonlinear and parametric down conversion signals [2]. First, barium titanate metalenses synthesized by a sol-gel technique will be demonstrated. Then, we will show how the electro-optic response in assembled nanostructures can be as strong as certain other perfect crystalline structure. Finally, we will demonstrate spontaneous parametric down conversion from single nanostructures. The field of metal-oxides at the sub-wavelength scale is developing fast with potential applications in integrated optics and quantum photonics.

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0.2.5 Brighter, Better, Faster: Pushing the limits of luminescence thermometry with silver sulfide nanocrystals.

Speaker: Marin Riccardo

Brighter, Better, Faster: Pushing the limits of luminescence thermometry with silver sulfide nanocrystals.

R. Marin,^{1,2*} E. Ximendes,^{1,3} I. Zabala-Gutierrez,⁴ L. Ming,¹ Y. Shen,¹ J. Lifante,³ N. Fernandez,³ A. Benayas,^{1,2} J. Rubio-Retama,^{3,4} D. Jaque^{1,2,3}

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In the biomedical context, luminescence thermometry can afford remote, real-time thermal readout where classical thermometric approaches like thermocouples and infrared thermal cameras fall short. Indeed, the use of luminescent nanoprobe makes it for a minimally invasive approach with spatial resolution at the subcellular level.¹ Silver sulfide nanocrystals, with their benign composition and temperature-dependent near infrared emission, are ideally suited nanothermometers. Yet, they suffer from a poor photoluminescence quantum yield, and hence limited brightness: a crippling feature in luminescence thermometry and sensing broadly speaking.² This feature exacerbates the issue of low signal-to-noise ratio encountered in situations of, e.g., short acquisition times or heavy extinction of the luminescence signal by biological tissues. The result is a suboptimal thermal readout in terms of precision and accuracy.

In this talk, we will showcase some strategies we developed to tackle this issue in silver chalcogenide nanocrystals at two levels: *i*) optimization of the material for increased brightness^{3,4} and *ii*) inspection of the calibration datasets via machine learning techniques to maximise the performance of the thermometric approach⁵. Discussion of these complementary strategies will also set the stage for highlighting critical points in luminescence thermometry. Lastly, possible future research directions in nanoparticle-assisted luminescence thermometry for biological applications will be presented.

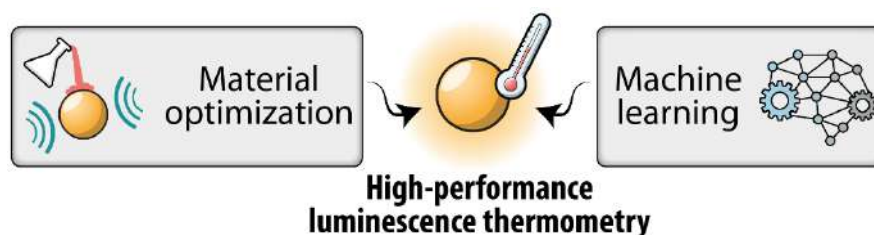


Figure 1. Artistic representation of the two families of strategies used to increase the performance of silver sulfide nanocrystals in luminescence thermometry.

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0.2.6 Chemical and mechanical pressure influence on luminescence properties of near-infrared phosphors

Speaker: Mahlik Sebastian

Chemical and mechanical pressure influence on luminescence properties of near-infrared phosphors

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Investigating the optical properties of inorganic compounds doped with optically active transition metal ions is one of the main themes in high-pressure studies using the diamond anvil cell. By exposing the material to high pressure, we directly influence the interaction of the crystal environment to luminescent centres and cause significant changes in the studied systems' energy structures. The overall conclusion from the structural point of view is the same effect that mechanical pressure can also be observed when chemical pressure is applied. Namely, incorporating the ions with a bigger ionic radius in the crystal lattice causes an increase in the atomic distance in the crystal, decreasing the crystal field strength around the optically active ion. Opposite, incorporating the ion with a smaller ionic radius causes a decrease in the atomic distance in the crystal lattice, increasing the crystal field strength.

In this study, we aim to compare the changes in the luminescence properties of the modified $\text{Ga}_2\text{O}_3:\text{Cr}^{3+}$ by Al or Sc ion substitution (chemical pressure) and hydrostatic pressure. Our study of two reference series of samples: $\text{Ga}_2\text{Al}_x\text{O}_3:0.02\text{Cr}^{3+}$ (GAOC) and $\text{Ga}_{2-x}\text{Sc}_x\text{O}_3:\text{Cr}^{3+}$ (GSOC), has shown that GAOC has qualitatively the same, while GSOC has different behaviour in the chemical and mechanical pressure dependences of the luminescence properties. In the case of Al doping, we can consider it as ion substitution in the neighbour unit cell, which changes the crystal properties like mechanical pressure dose. When Ga_2O_3 is co-doped with the Sc ions, it causes lattice distortion in the Cr^{3+} local environment. By applying pressure for GSOC, we reduce the volume of the cell; however, we cannot reverse the distortion caused by the co-doping.

0.2.7 Chlorosomes in the Light of Single-Molecule Spectroscopy

Speaker: Köhler Jürgen

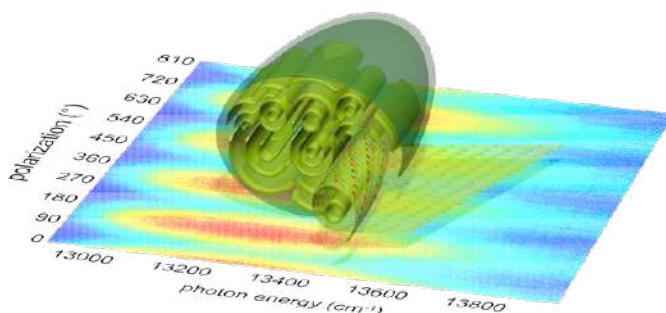
Chlorosomes in the Light of Single-Molecule Spectroscopy

Jürgen Köhler

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The light-harvesting apparatus of green sulfur bacteria - so called chlorosomes - is highly efficient and allows these species to grow photosynthetically under extremely low light conditions. The chlorosomes contain supramolecular structures comprising hundreds of thousands of bacteriochlorophyll molecules, and details of the structural organization of the molecular aggregates are the subject of ongoing debates. Since the electronic energies and the photophysical properties of a molecular aggregate are imposed by its geometrical structure, spectral information obtained can be compared with predictions derived from structural models. Thereby, the single-particle approach is particularly suited for the elucidation of specific, distinctive spectral features that are key for a particular model structure, and that would not be observable in ensemble-averaged spectra due to the heterogeneity of the biological objects. In other words, spectroscopy can search for the presence (or lack) of spectral signatures that are characteristic of specific structural features and thereby test whether a proposed structural model is compatible with the experimentally observed spectra. The talk will discuss these topics on the example of natural chlorosomes as well as biomimetic light-harvesting nanotubes. Employing quantum-chemical molecular modelling, the spectra of the individual artificial nanotubes can be explained consistently only for a molecular packing model that is fundamentally different from those considered so far for the natural systems. Subsequent theoretical simulations reveal that the remaining spectral variations between single nanotubes can be traced back to small variations of the mutual orientations of the monomer transition-dipole moments that are far beyond the resolving power of high-resolution electron microscopy imaging techniques.



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0.2.8 Controlling the emission of rare earth ions by plasmonic chains: spatial coherence and subwavelength waveguiding

Speaker: Bausá Luisa

Controlling the emission of rare earth ions by plasmonic chains: spatial coherence and subwavelength waveguiding

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Controlling the properties of rare earth emitters (RE) in solid-state platforms in the absence of an optical cavity is highly desirable for quantum light-matter interfaces and photonic networks. A promising approach is to combine plasmonic nanostructures with RE doped crystals, which can provide robust solid-state platforms with emergent functionalities at subwavelength scales.

Here, we show the capability of inducing directionality and spatial coherence in the emission of Nd³⁺ ions distributed into a solid-state platform in the absence of photonic cavity [1]. To that end, we have used a plasmonic chain formed by closely-spaced Ag nanoparticles, which transforms the incoherent emission from Nd³⁺ ions into spatially coherent light. In addition, we demonstrate the possibility of ultra-long-range waveguiding Nd³⁺ fluorescence by means of the plasmonic chain. Namely, sub-diffraction fluorescence waveguiding is demonstrated over several tens of microns in the technologically relevant NIR spectral range of 900–1100 nm. The spatial coherence and the long-range energy transport originate from the coherent near-field coupling of the Nd³⁺ emitters with the plasmon mode of the chain and the low dissipative losses displayed by this mode.

The work provides fundamental insights for controlling the coherence properties of quantum emitters offering new avenues for the design of integrated photonic circuits, as well as imaging, quantum technologies or sensing devices on solid-state platforms.

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0.2.9 Crown-Ether-Coordination Compounds: A New Class of Luminescent Materials with NLO Effects

Speaker: Feldmann Claus

Crown-Ether-Coordination Compounds: A New Class of Luminescent Materials with NLO Effects

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Crown ethers are unique ligands able to coordinate almost all types of metal cations.¹ Despite of their rich coordination chemistry, however, luminescence is not a salient property of crown-ether coordination compounds until now. Thus, the emission of crown-ether coordinated cations is weak or even only observed at low temperatures.^{1,2}

With our studies on ionic-liquid-based synthesis, we recently obtained a range of novel crown-ether coordination compounds by reaction of ZnX_2 , MnX_2 , EuX_2 (X : Cl, Br, I) with crown ethers.²⁻⁴ Some show unexpected and unprecedented luminescence properties with intense emission and high quantum yields of 85-100% (e.g., $\text{EuI}_2(18\text{-crown-6})$, $\text{Mn}_3\text{I}_6(18\text{-crown-6})_2$, Figure 1).² Compounds such as $\text{Mn}_2\text{I}_4(18\text{-crown-6})$, moreover, show intense second-harmonic generation (SHG) and allow efficient up-conversion, e.g., from infrared to orange light (Figure 1).² With these features, crown-ether coordination compounds can become a new class of compounds for up-conversion and non-linear optics (NLO).

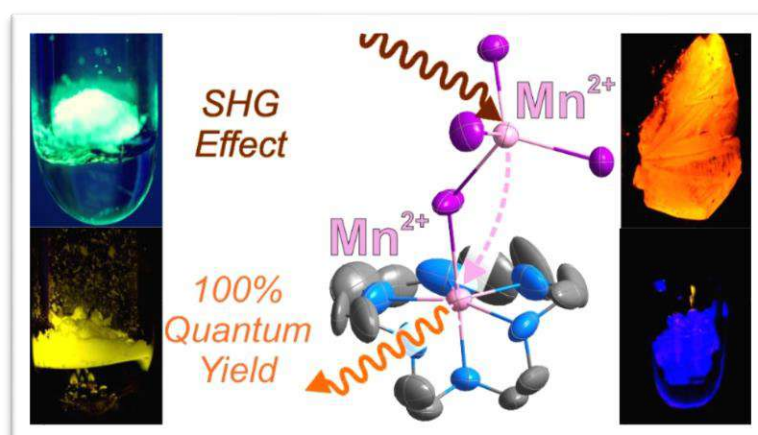


Figure 1. Emission and NLO effects of selected crown-ether coordination compounds.²

With this presentation, we discuss the synthesis and promising optical properties – including emission, up-conversion, and NLO effects – of the novel crown-ether coordination compounds and the theoretical and structural background of these unique compounds.

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0.2.10 Emerging Eu²⁺-doped/based phosphors for advanced lighting sources applications

Speaker: Zhiguo Xia

Emerging Eu²⁺-doped/based phosphors for advanced lighting sources applications

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4f–5d transitions in Eu²⁺-doped/based phosphors generally possess broad absorption and emission spectra with versatile spectral profiles that are strongly influenced by the chemical compositions and crystal structures of the hosts, as the 5d orbitals are sensitive to the surrounding environment. Therefore, Eu²⁺-containing luminescent materials, as an example, with optical tunability are more suitable for the lighting and display applications. Accordingly, many new and promising Eu²⁺-doped phosphors have been discovered, including oxides, sulfides, halides, and nitrides, etc..

In this talk, I will firstly summarize our recent progresses to manipulate Eu²⁺ emission in oxide-based phosphors exhibiting narrow-band blue/green emission, red and near-infrared emissions under blue light excitation (Fig. 1a). More importantly, we recently found a series of emerging Eu²⁺-based hybrid halides representing a new family, showing narrow-band blue, cyan and green emissions with highly thermal stability (Fig. 1b-c). One can expect and further adopt proper structural engineering to tune the Eu²⁺ luminescence. We hope this talk will be helpful for controlling photoluminescence by theory-structure-property relationships and guide scientists discover the next generation of Eu²⁺ doped phosphors for advanced lighting sources applications.

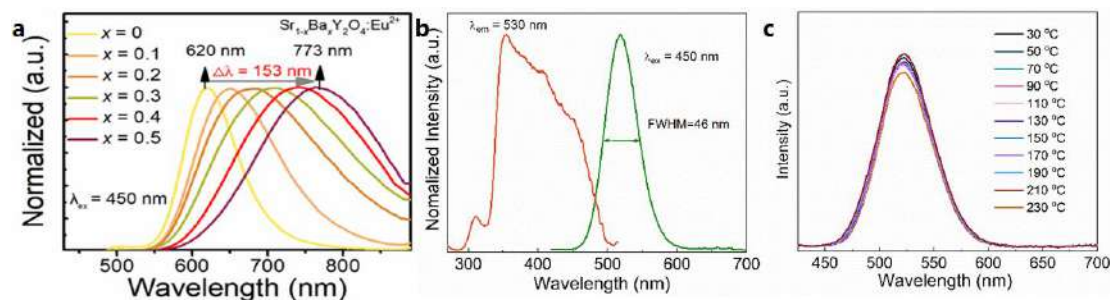


Figure 1 (a) Red-near-infrared emissions in oxide-based phosphors, Sr_{1-x}Ba_xY₂O₄:Eu²⁺; Unpublished results on the newly-discovered narrow-band green phosphors in Eu²⁺-based hybrid halides (b) and their thermal stable emissions (c).

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0.2.11 Fabrication of AlGaN-Based UVC-LEDs with high Performance

Speaker: Wang Xinqiang

Fabrication of AlGaN-Based UVC-LEDs with high Performance

Xinqiang Wang^{1,2,*}, Shangfeng Liu¹, Duo Li¹, Tai Li¹, Ye Yuan², Wei Luo², Junjie Kang² and Bo Shen¹

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Over the past decade, notable advancement has been made in the development and broad utilization of portable and eco-friendly AlGaN-based ultraviolet-C (UVC) light emitting diodes (LEDs). Despite these notable strides, AlGaN-based UVC-LEDs still encountered several challenges, such as low wall-plug efficiency (WPE), efficiency droop at high current injection, short lifetime and so on. To address these difficulties and facilitate the broader application of AlGaN-based UVC-LEDs, we have made the following efforts:

1) We realized high-quality AlN templates with threading dislocation densities less than $1 \times 10^9 \text{ cm}^{-2}$ on the hole-type nano-patterned sapphire substrates (NPSS), providing a good foundation for the growth of UVC-LEDs.^[1] Through a series of structural and MOCVD growth optimization, the fabricated $20 \times 20 \text{ mil}^2$ UVC-LED chip (Fig. 1a) with a peak wavelength at 276 nm exhibited a high WPE (5.7% at 100 mA) and low light output power (LOP) degradation.

2) To minimize the inner light absorption loss and improve homogeneous injection current distribution, a parallel-arrayed planar (PAP) DUV μ -LEDs structure was proposed and fabricated.^[2] The μ -LEDs achieved a significantly enhanced WPE at high current injection, which showed a peak value of 4.7 % at 775 Acm^{-2} (Fig. 1b).

3) Moreover, we demonstrated a monolithic dual-wavelength UV-LED with a simultaneous emission at wavelengths of 278 nm and 307 nm, respectively (Fig. 1c). This innovative design exhibited not only a high WPE but also a stable and controllable spectral profile, which offers versatility and opens up new possibilities for UV-LEDs in a wide range of fields.

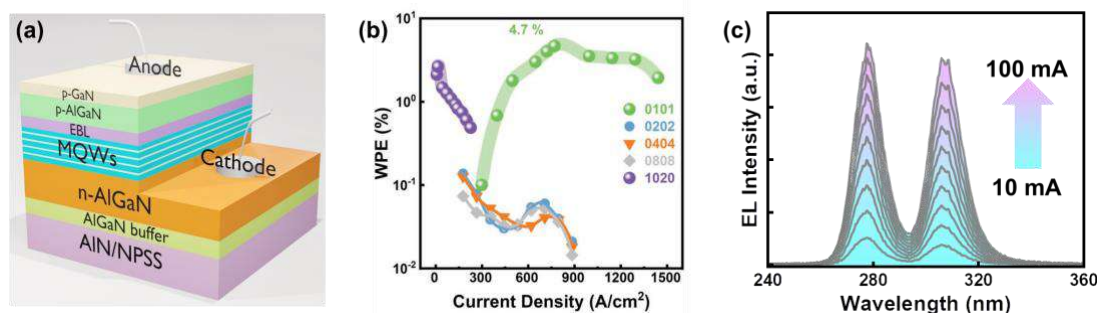


Fig 1. (a) Schematic diagram of the UVC-LED. (b) Current-density-dependent wall-plug efficiency of PAP-0101, PAP-0202, PAP-0404, PAP-0808, and conventional device 1020 (mil $\times$ mil). (c) Current-dependent electroluminescence (EL) spectra of dual-wavelength UV-LED.

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0.2.12 Fundamental optical properties of excitons in diamond

Speaker: Naka Nobuko

Fundamental optical properties of excitons in diamond

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Diamond is an ultrawide bandgap material and is known for its high breakdown voltage, thermal conductivity, radiation hardness, and chemical inertness, suitable for power electronics [1]. The mid-gap states, such as nitrogen-vacancy centers, in diamond have been attracting intense research focus toward the realization of quantum sensors and single-photon emitters. Meanwhile, the large indirect bandgap of diamond at 5.5 eV leads to fundamental optical responses, such as absorption and luminescence, in the deep ultraviolet (DUV) region, for which excitation light sources are very limited.

We have been investigating the optical properties of high-purity synthetic diamond across the bandgap using one-photon and two-photon excitation methods [2]. We have developed space- and time-resolved photoluminescence spectroscopy in the DUV region to reveal the transport properties of diamond [3]. We also demonstrated that mid-infrared dielectric response [4] and broadband terahertz time-domain spectroscopy on the excitonic Lyman transitions [5,6] allow new access to highly excited or highly dense carrier states in diamond.

In the presentation, I will review the recent understanding of the extreme optical properties of diamond [7,8] and the charm of diamond as a unique arena to explore a quantum many-body system consisting of charge carriers, excitons, polyexcitons [9], and electron-hole droplets.

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0.2.13 How to control the degree of reduction from Eu^{3+} to Eu^{2+} and obtain a phosphor with the high quantum efficiency

Speaker: Dereń Przemysław

How to control the degree of reduction from Eu^{3+} to Eu^{2+} and obtain a phosphor with the high quantum efficiency

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This work aims to understand the factors leading to the synthesis of high-quantum efficiency (QE) phosphors doped with Eu^{2+} ions. Such phosphors always require the reduction of Eu^{3+} to Eu^{2+} ions. The degree of reduction and consequently the value of QE can vary depending on the synthesis process and the presence of defects in the matrix. In order to control the amount of Eu^{2+} ions and obtain a stable phosphor, one needs to deeply understand the reduction process, what is the source of the additional electrons for Eu reduction. A simple method for measuring the amount of Eu^{2+} ions would be very helpful.

The samples, doped with Eu, presenting an intense emission in the whole visible region were studied: $\text{Ca}_2(\text{Al}_{0.5}\text{Mg}_{0.5})(\text{Al}_{0.5}\text{Si}_{1.5})\text{O}_7$ [1]. They were synthesized by two different methods (sol-gel and solid state) and annealed in different atmospheres (H_2/N_2 mixture and vacuum). We investigate the role of defects in the reduction process and show how to control the degree of reduction to obtain the greatest possible amount of Eu^{2+} ions. Defects were added by co-doping the samples with Li^+ , and Zr^{4+} , and adding Ca vacancies V_{Ca} .

The highest degree of europium reduction (90%) was obtained for annealing in the H_2/N_2 atmosphere for the sol-gel samples codoped with Zr or with V_{Ca} . However, the highest reduction degree of Eu^{3+} does not directly translate into a high quantum efficiency of emission. The highest quantum efficiency (78%) was exhibited by the samples in which no Eu^{2+} clustering occurred, i.e., synthesized by the solid-state method.

Our work demonstrates that by carefully controlling the synthesis procedures, samples with desired properties, such as varying magnetic susceptibility or blue-shifted emission bands, can be obtained. Our findings provide insights into the development of high-performance phosphors for WLED applications. A simple method for measuring the amount of Eu^{2+} ions is proposed, which can be used for the development of high-QE phosphors doped with Eu^{2+} ions. Overall, the study provides important information for optimizing the synthesis of high-performance phosphors for various applications.

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0.2.14 In-vivo Ultrasound-modulated Optical Tomography using a spectral filter in a rare-earth-doped crystal

Speaker: Louchet-Chauvet Anne

***In-vivo* Ultrasound-modulated Optical Tomography using a spectral filter in a rare-earth-doped crystal**

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The local optical properties of a biological tissue can yield valuable information for medical diagnosis such as early cancer detection. Extracting such information from deep inside the tissue is, however, a challenging task due to multiple scattering, resulting in a dramatic loss of resolution at depths larger than a few mm. Ultrasound-modulated optical tomography (UOT), combining optical and ultrasound (US) illumination, is a promising approach to solve this problem [1]. Yet the holographic methods developed for isolating the tagged light diffracted off the US-induced grating have up to now been unable to cope with the rapid speckle decorrelation inherent to *in-vivo* imaging, and all demonstrations have been limited to artificial phantoms.

Spectral filtering has recently emerged as a promising approach to tackle *in-vivo* UOT imaging, due to its incoherent nature making it inherently robust to speckle decorrelation. In this work, we design a spectral filter obtained by spectral holeburning in a rare-earth doped crystal cooled down to a few K. Using this filter combining a narrow linewidth (2MHz), large contrast (20dB) and large optical etendue (45 sr.mm²), we achieve the very first demonstration of *in-vivo* UOT imaging.

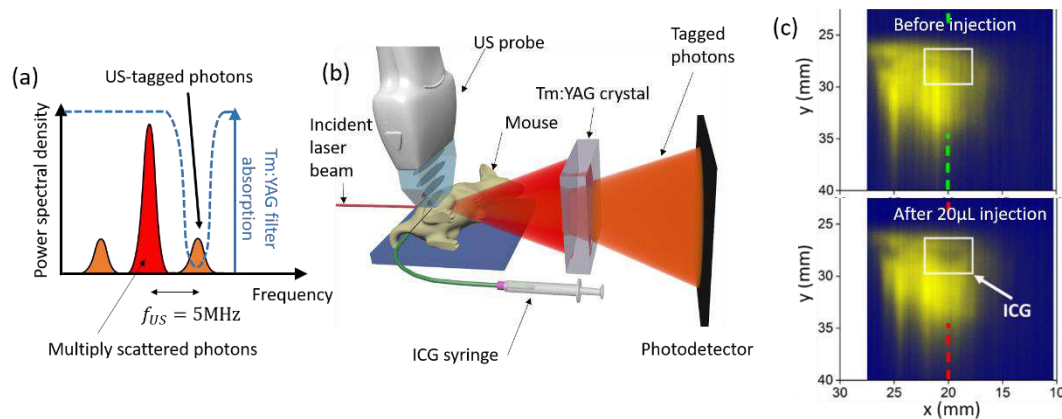


Figure: (a) Spectral filter built in a Tm:YAG crystal, selecting the US-tagged photons. (b) Simplified view of UOT setup. A mouse's thigh muscle is injected with indocyanine green (ICG) to form an imaging target. The 793nm light scattered through the mouse body is filtered through the Tm:YAG filter. (c) UOT image captured before and after injection, showing a local change in contrast due to ICG absorption of light.

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0.2.15 Luminescence Quenching via Electron and Hole Photoionization Processes

Speaker: Ueda Jumpei

Luminescence Quenching via Electron and Hole Photoionization Processes

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Phosphors doped with lanthanoid (*Ln*) and transition metal ions have played an essential role in many luminescent devices. In order to develop high-performance phosphors, it is crucial to investigate the luminescence quenching mechanisms. It is known that those phosphors show some quenching processes such as crossover quenching, multi-phonon relaxation, concentration quenching, photoionization and so on. So far, we have focused on and demonstrated the (thermally assisted) photoionization quenching process by using photoconductivity¹ and thermoluminescence excitation (TLE) spectroscopy² in Ce³⁺-doped Y₃Al_{5-x}Ga_xO₁₂^{1, 2} and Pr³⁺-doped Y₃Al_{5-x}Ga_xO₁₂³. These luminescent centers show the quenching process via the photo-oxidation process; that is, the *Ln*³⁺ ion loses one electron by light excitation (Figure 1a, 1c)^{4, 5}. On the other hand, the photo-reduction quenching can also exist. In this case, the hole can transfer to the valence band by the excitation process (Figure 1b, 1d). Recently, the thermally assisted photo-reduction quenching via the 4f excited state was demonstrated using TLE spectroscopy in the Eu³⁺-doped Y₂O₂S phosphor. In the presentation, the luminescence quenching via the electron and hole photoionization processes will be discussed.

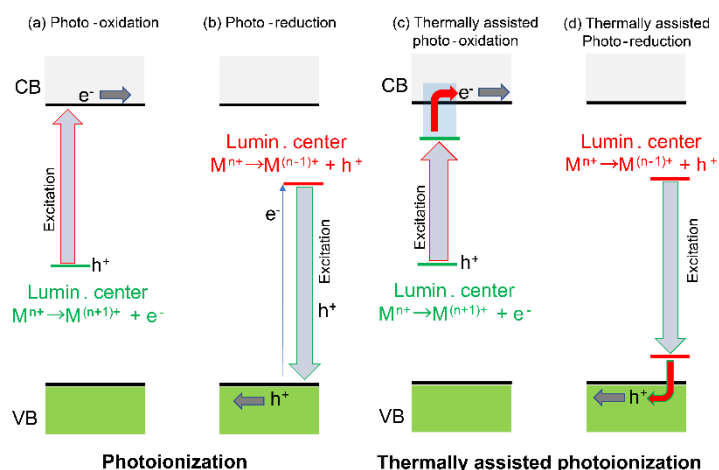


Figure1. Photoionization and thermally assisted photoionization via electron and hole transfer.⁴

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0.2.16 Luminescence thermal enhancement of NaYF₄: Ho³⁺/Yb³⁺ upconverting nanocrystals in vacuum

Speaker: Zhang Jiahua

Luminescence thermal enhancement of NaYF₄: Ho³⁺/Yb³⁺ upconverting nanocrystals in vacuum

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The phenomenon of luminescence thermal enhancement (LTE) has been observed in some lanthanide-doped upconverting nanocrystals (UCNCs), has attracted extensive attention for its applications in anti-counterfeiting, temperature sensing and so on. Some mechanisms for LTE were proposed including thermally induced desorption of quenchers from the surface of UCNCs, but conclusive evidence is still absent. Here, vacuumizing is employed in the experiment for the LTE in NaYF₄:Ho³⁺/Yb³⁺ UCNCs and significantly promoted LTE is observed. The 300-450-300 K temperature cycling experiment in vacuum shows continuous luminescence enhancement without luminescence intensity reduction as observed in the cooling process in air. This feature indicates that the desorption of quencher dominates the mechanism of the LTE in the present work. Therefore, no luminescence intensity reduction is observed in the cooling process because quencher re-adsorption to the surface of the UCNCs is blocked in vacuum. The quencher is considered to be water molecules. It was also found that Ho³⁺ ⁵I₆ level can be deexcited by direct long-rang energy transfer to water adsorbed at the surface of nanocrystals due to resonant coupling between Ho³⁺ ⁵I₆→⁵I₇ transition and -OH vibration of water. As a result, water desorption suppresses ⁵I₆ depopulation and thus enhances luminescence of Ho³⁺. Finally, the regulation of upconversion LTE is realized by controlling the dopand concentration, size and structure of the UCNCs. Our findings will deepen the understanding of LTE and offer insight into the regulation of LTE.

0.2.17 Luminescence-structure relationships in Bi³⁺-doped solids

Speaker: Boutinaud Philippe

Luminescence-structure relationships in Bi³⁺-doped solids

P. Boutinaud

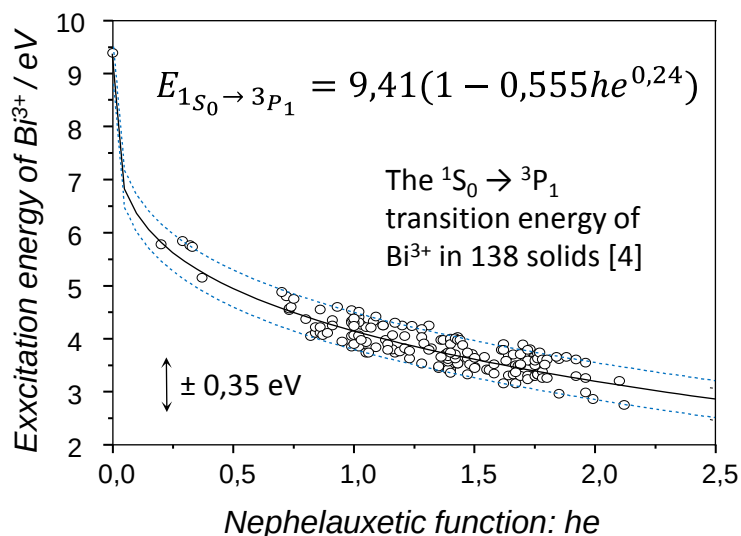
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We introduce a method allowing an easy and rapid estimation of the energy corresponding to the $^1S_0 (6s^2) \rightarrow ^3P_1 (6s^1p^1)$ transition of Bi³⁺ in solids. The method derives from the model introduced in the 70's by Duffy and Ingram [1,2] and was preliminarily reported in [3]. Tested on 138 Bi³⁺-doped compounds it demonstrates a convergence with experimental data within ± 0.35 eV, see Figure below.

The method is based on the calculation of the nephelauxetic function, he , at the crystal site occupied by Bi³⁺ in the compound and only requires the knowledge of the crystal structure. A robust he calculator has been designed for compounds containing up to 6 different cation sites and 8 different anion sites. This calculator is available for free on request. We show how easy and fast it is to calculate he at the Y³⁺ and Al³⁺ crystal sites of Y₃Al₅O₁₂, taken here as an example.

Finally, we re-inspect the optical properties of Bi³⁺ in a few phosphates, and especially YPO₄:Bi³⁺, at the light of these new calculations.



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0.2.18 Luminescent multifunctional nanostructures for sensing and theranostics applications

Speaker: De Camargo Andrea

Luminescent multifunctional nanostructures for sensing and theranostics applications

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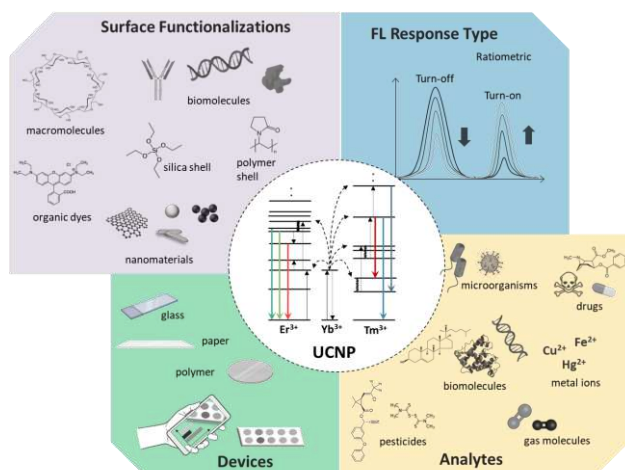
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The research carried out at the *Laboratory of Spectroscopy of Functional Materials* at IFSC/USP, in Brazil, is focused on the synthesis and structural-property correlation of luminescent materials including rare-earth (RE) doped glasses, ceramics and hybrid host-guest materials. For the past five years, we have been particularly interested in the development of single- and multifunctional nanosystems based on core-shell upconversion nanoparticles (UCNP) associated with dyes, organometallic complexes and other organic molecules, for biophotonic and sensing applications. In these systems, we take advantage of energy transfer between the UCNP and the molecules to either suppress or enhance luminescent response. Examples include the possibility of bioimaging and photodynamic therapy of bacteria and cancer cells [1], simultaneous magnetothermia and thermometry, localized O₂ sensing [2], fast detection and quantification of biological markers (e.g. kidney disease) and microorganisms. On what concerns the development of luminescent sensors - a recently started project [3], our aim is to develop paper-based platforms for point-of-care devices. In this presentation, an overview of our contributions for the past years and our future aims will be presented with several examples.



Scheme 1: Possibilities for the design of UCNPs-based sensors on solid substrates.

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0.2.19 Magnetic data as an aid to understanding electronic structure of rare-earth ions in crystals and nanoparticles

Speaker: Reid Michael

Magnetic data as an aid to understanding electronic structure of rare-earth ions in crystals and nanoparticles

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Photonic applications of rare-earth doped materials require accurate modelling of electronic states. Many potential materials for quantum-information applications have low-symmetry sites, where measurements of electronic energy levels alone do not give enough information to obtain crystal-field fits. However, we have shown that measurements of magnetic splitting along several magnetic field directions provides the necessary information to obtain unique solutions. [1,2].

Nanocrystals doped with rare-earth (lanthanide) ions also have considerable potential for photonic technologies, from quantum computing to biomedical applications, including imaging, nano-thermometry, and photodynamic therapy. There has been recent interest in using magnetic fields to modulate energy transfer between lanthanide ions in nanocrystals to enhance these applications [3]. Making use of such magnetic field effects requires a better understanding of the magnetic splitting of rare-earth ions in nanocrystals. Though the particles are randomly oriented, we have recently shown that useful information may be obtained by Zeeman spectroscopy of rare-earth-doped nanoparticles [4] and this data provides a more accurate analysis of the electronic structure of the rare-earth ions in the nanoparticles than zero-field data.

In this paper, we will discuss how magnetic splitting measurements can be used to provide the geometrical information essential to accurate crystal-field modelling in both bulk crystals and nanocrystals. We will discuss some outstanding issues and the potential for future improvements.

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0.2.20 Making rotaxanes sparkle

Speaker: Bui Anh-Thy

Making rotaxanes sparkle

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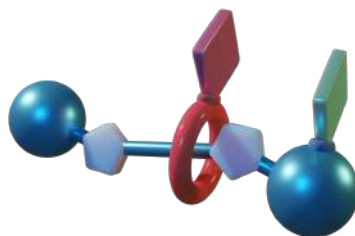
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Among the sophisticated interlocked supramolecular architectures that have emerged during the past decades, [2]rotaxanes, consisting of a ring threaded onto an axle, have notably attracted the interest of synthetic chemists as prototypical molecular machines, wherein light could be used to trigger mechanical or chemical processes.^[1] On the other hand, unique photophysical properties arise from the spatial arrangement of the components within these molecules. For instance, ring–thread reversible electronic energy transfer (REET)^[2] and enhancement of thermally-activated delayed fluorescence (TADF) emission^[3] were recently demonstrated in rotaxanes.

In this contribution, our approach to the conception of luminescent blinking rotaxanes that take advantage of submolecular intercomponent interactions will be presented, in the light of spectroscopic investigations. Finally, the development of new microscopy methodologies based on the designed dyes will be briefly outlined.



Schematic representation of a rotaxane bearing two chromophores that can interact by energy transfer processes.

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0.2.21 Modeling energy transfer rates between transition metals and lanthanides in luminescent bimetallic complexes

Speaker: Malta Oscar

Modeling energy transfer rates between transition metals and lanthanides in luminescent bimetallic complexes

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Luminescent lanthanide compounds can have a wider range of applications if they have chromophores that absorb at longer wavelengths and present the necessary requirements to act as efficient sensitizers. Transition metals (M) are relevant chromophores because of their spectral features. Thus, many bimetallic M-lanthanide ions (Ln^{3+}) have been synthesized and investigated.

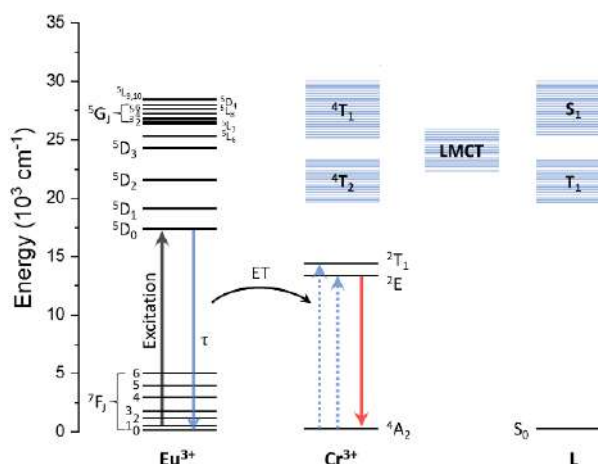
However, despite the importance of theoretical models for developing more efficient M- Ln^{3+} complexes, few works have devoted efforts to describe and elucidate the energy transfer (ET) processes between the M and Ln^{3+} ions.

In this context, this work presents efforts toward calculating the ET rates between M and Ln^{3+} ions, in bimetallic complexes, based on an adaptation of the nonradiative intramolecular energy transfer models developed by Malta and collaborators.

As an example, the ET rates between Eu^{3+} and Cr^{3+} ions in the $[\text{CrEuL}_3]^{6+}$ complex (where $\text{L} = 2\text{-}\{6\text{-}[\text{N,N-diethylcarboxamido}]\text{pyridin-2-yl}\}\text{-1,1'-dimethyl-5,5'-methylene-2'-(5-methylpyridin-2-yl)bis[1H-benzimidazole]}\}$) were estimated. The calculated rates ($930 - 1200 \text{ s}^{-1}$) are in excellent agreement with the available experimental data ($750 - 1200 \text{ s}^{-1}$) [1].

This agreement is achieved by further developments from the pioneering treatment of phonon-assisted energy transfer process based on the Miyakawa-Dexter model. In this way the present model provides a more general character and may be useful in describing photo-physical properties driven by the energy transfer between M and Ln^{3+} ions. In addition to the cited example, other cases of bimetallic complexes will be briefly presented.

Schematic energy levels diagram illustrating the Eu^{3+} , Cr^{3+} and the ligand (L) levels for the $[\text{CrEuL}_3]^{6+}$ complex and the most relevant energy transfer (ET) pathways.



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0.2.22 Multiphonon-assisted emissions of rare-earth ions: Towards pulse shortening in mode-locked lasers

Speaker: Loiko Pavel

Multiphonon-assisted emissions of rare-earth ions: Towards pulse shortening in mode-locked lasers [Invited]

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Electron-phonon interaction is an interaction between charge carriers in solids and vibrations of the crystalline lattice – phonons. It is relevant for the description of optical properties of dielectric crystals with impurity centers being responsible for such effects as spectral broadening / phonon sidebands, multiphonon non-radiative relaxation, phonon assisted energy-transfer / cross-relaxation, cooperative processes, etc. Phonon sidebands can lead to broadband emission and gain properties favoring broadly tunable operation and generation of ultrashort pulses. Vibronic lasers based on color centers and transition-metal ions featuring strong electron-phonon coupling are well known. In contrast, laser operation on rare-earth (RE³⁺) ion-doped materials typically occurs on 4fⁿ electronic transitions with narrow spectral bandwidths. In the present work, we review the recent achievements in the development of phonon-terminated rare-earth ion lasers.

The coupling of intraconfigurational 4fⁿ transitions of RE³⁺ ions with the lattice vibrations can vary by three orders of magnitude depending on the ion and the chemical nature of the ligand. The strength of electron-phonon interaction increases at the beginning and end of the lanthanide series [1]. We thus focused on three promising laser-active rare-earth ions: Yb³⁺ (emission >1 μm), Tm³⁺ and Ho³⁺ (emission > 2 μm), and identified promising crystalline matrices with a strong electron-phonon coupling, incl. sesquioxides, tungstates, borates and aluminates.

For the spectroscopic basement of this work, we studied the phonon sidebands of RE³⁺ ions in ordered and disordered crystals revealing two types of behavior: structureless exponential sidebands and well-resolved peaks assigned to dominant Raman-active modes, and verified the applicability of the reciprocity (absorption / emission) relations to these bands, as well as determined the electronic level structure based on low-temperature spectroscopy and crystal-field analysis. It is shown that multiphonon-assisted emissions can bridge the gap between different intermanifold transitions of RE³⁺ ions [2] leading to ultrabroadband emission capabilities, in particular, optical gain across 1.7 – 2.6 μm for Tm³⁺ ions. Phonon-terminated Yb and Tm-lasers are described.

Finally, it is shown that the optical gain due to multiphonon-assisted emissions can be responsible for the generation of ultrashort (few-optical-cycle) pulses from mode-locked lasers based on rare-earth-doped disordered dielectric crystals / ceramics [3].

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0.2.23 Nanodiamonds for optical sensing and their applications

Speaker: Plakhotnik Taras

Nanodiamonds for optical sensing and their applications

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Over the past decades, colour centres (nitrogen-vacancy, silicon-vacancy, and others) in diamond have attracted interest in a wide range of applications, from optical sensing to quantum computing. I will consider how these nanodiamonds may help to resolve a complex and controversial problem of intracellular thermometry. I will also discuss difficulties and apparent limitations on manufacturing of such diamonds.

It has been assumed that the temperature of single isolated cells is determined by their environment due to little heat produced internally. However, there is a growing body of controversial observations of hot temperatures near reaction centres that seemingly defy the laws of physics. We challenged one of the dominant beliefs postulating that thermal conductivity inside cells, even at the scale of about 100 nm, is close to that of water [1]. Because further progress in this field requires ever smaller, more selective (responding only to variations in temperature), sensitive and reliable probes, the second part of my talk is focussed on problems of making diamonds smaller and brighter.

The size of the crystals and their luminescence intensity are the two key parameters which we wish to control in the process of diamond manufacturing. For some applications, it is desirable to have only one centre per crystal but in other cases more centres are better because this makes the individual crystals brighter. The crystal size is less important if one needs just a centre in a proximity to the surface but in other cases the crystals should be small. For example, for intracellular applications a size useful for many purposes is less than 100 nm and sometimes the crystal should be smaller than 10 nm, for example, to enter a nucleus [2], but it should also generate a strong signal.

We have used luminescence to obtain an estimate for the number of centres and elastic scattering to obtain the size of particles. Naively, one expects that the intensity of photo luminescence is proportional to the volume of the particle. However, the experimental results were quite surprising. Luminescence was increasing with size approximately as fast as the intensity of scattering which is proportional to the sixth power of sizes for small particles. It is much harder to make small particles with many centres than suggested by the scaling with volume. This puzzle has been solved by considering several effects.

The first two effects are related to electrodynamics which predicts that the high refractivity of diamonds affects both, the photo excitation efficiency and the rate of the radiative transition from the electronically excited state to the ground state. The third effect is interesting dynamics of the crystal growth. Our model predicts that the number of centres in high temperature high pressure diamonds is proportional to the fourth power of the crystals size. These results explain difficulties of making ultra-small crystals sufficiently bright to facilitate their applications for optical sensing.

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0.2.24 Nanoporous scintillators for radioactive gas detection

Speaker: Dujardin Christophe

Nanoporous scintillators for radioactive gas detection

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The measurement of pure beta emitting radioactive elements such as ^3H and ^{85}Kr , is a major and a mandatory measurement for nuclear safety authorities issue for the monitoring of the territory, in particular for the monitoring of the expending nuclear activities for the carbon-free production of electricity. The short penetration length of these electrons in the air makes their detection very difficult. It requires mixing the radioactive gas with the sensitive element which is done with ionization chamber (gas-gas mixture) or liquid scintillation (gas-liquid mixture for ^3H only). However, these two methods do not meet all the needs since neither of them combines sensitivity to both gases, real-time analysis, and ease of wide deployment on the territory. Here we demonstrate that the new approach, based on the gas-solid mixture, allows to combine all the criteria allowing the efficient and real time detection of tritium and ^{85}Kr , and more generally of pure beta radioactive elements. We show that by synthesizing a transparent and scintillating nanoporous material, here a highly porous aerogel based on doped inorganic scintillators, we detect in real time with an efficiency of 95% and 20% the ^{85}Kr and the ^3H (illustrative results are presented Figure 1). We achieve sub-Bq.cm⁻³ in 100 s of accumulation, which is the best performance obtained so-far in real time. In this contribution, the latest results in terms of new materials characteristics including time-resolved luminescence, and detection performances will be presented.

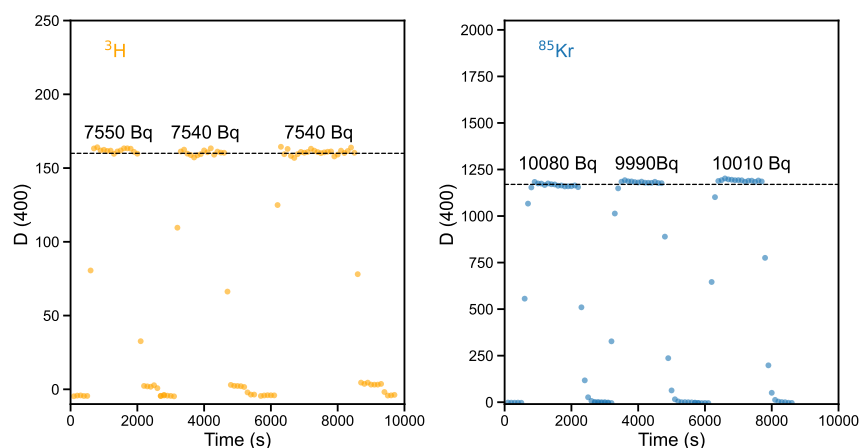


Figure 1: Typical measurements and their reproducibility for ^3H and ^{85}Kr detection. D(400) corresponds to the number of double coincidences measured in 400ns.

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0.2.25 Nd³⁺ ion spectroscopy as a tool in structural studies of nano/micro-crystalline phosphates

Speaker: Guzik Malgorzata

Nd³⁺ ion spectroscopy as a tool in structural studies of nano/micro-crystalline phosphates

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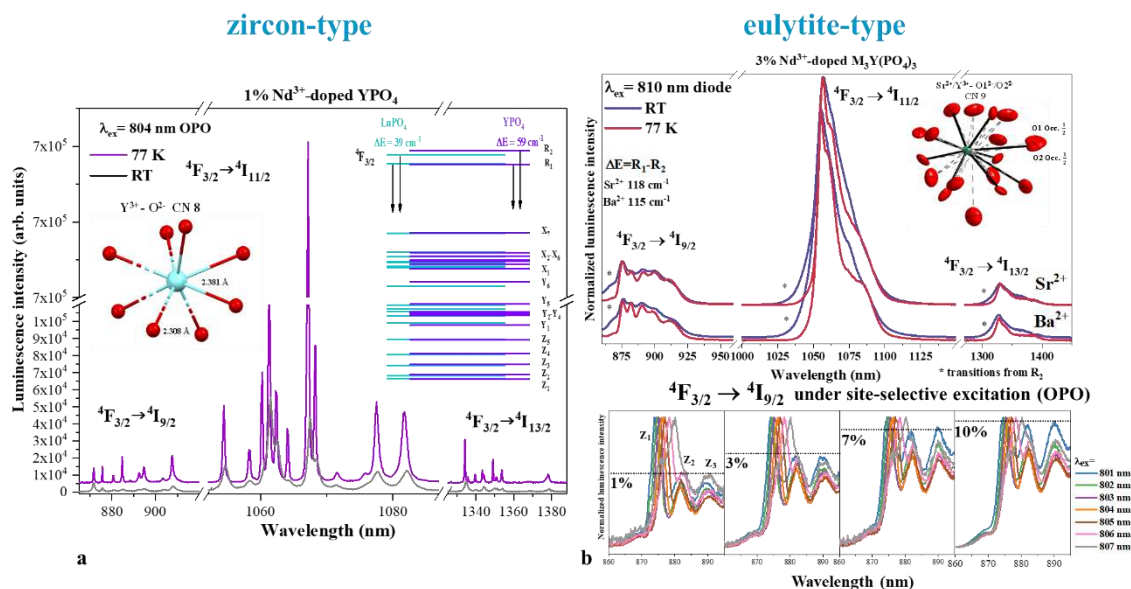
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Here we present a part of the extensive research conducted within the program targeted to obtain new optical transparent ceramics, a very difficult goal, which depend on many parameters. To studies were selected highly symmetrical phosphates from two families *i.e.* tetragonal LuPO₄/YPO₄ of zircon-type and eulytite-type M₃Y(PO₄)₃ (M=Sr²⁺, Ba²⁺) with a cubic structure - an important parameter to fabricate sintered ceramics of high density and in result transparency. The results of the tests with SPS (Spark Plasma Sintering) method for phosphates will be also shown. Nd³⁺ and Yb³⁺ dopants were chosen for two reasons, *i.e.* laser application and their role as a structural probe. As an example, significant differences in Nd³⁺ ion spectroscopy of both types of phosphates as presents in Figure) resulting from different structure ordering were demonstrated by complementary techniques such as X-ray studies combined with low-temperature high-resolution emission at 77K and absorption (4.2K) ones.



Differences of behaviour of Nd³⁺ ion in zircon (a) and eulytite-type phosphates (b).

The energy level diagram for the main D_{2d} symmetry site of Nd³⁺ ion in zircon-type hosts was proposed. Narrow 4f–4f lines with crystal field fine structure of Nd³⁺ transitions point out on a high degree of order in the network, whereas for eulytite-type host a huge disorder was observed. An abnormal temporal behavior at low temperature for Nd³⁺ ion in zircon-type phosphates will be discussed including different hypotheses.

The multisite character and inhomogeneous distribution of Nd³⁺ ions in eutyrites are confirmed by the spectroscopic measurements under site-selective excitation at 77K.

0.2.26 Novel primary and self-referencing thermometers based on the excitation spectra of lanthanide ions

Speaker: Longo Ricardo

Novel primary and self-referencing thermometers based on the excitation spectra of lanthanide ions

K. M. N. de Souza,^{1,2,3} R. N. Silva,^{1,2} J. A. B. Silva,³ C. D. S. Brites,² S. E. P. da Silva,¹ R. A. S. Ferreira,² L. D. Carlos,² and R. L. Longo^{1*}

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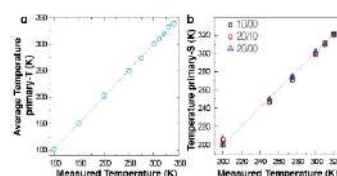
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Novel primary thermometers based on the excitation spectra of lanthanide ions are presented [1]. Simple Boltzmann-type thermometric equations $\Delta_i = A_i \times \exp(-a_i/T)$ were derived from first principles based on a general set of rate equations. For each thermometric parameter Δ_i , the a_i constant is related to the energy difference between the thermally coupled initial levels and can be obtained directly from the excitation spectrum. The factor A_i can be determined from measurements at a known temperature yielding primary-T thermometers or from data obtained from the emission spectrum providing primary-S thermometers, which are relevant for systems or situations where temperature calibration is difficult or impossible. For transitions starting at the same initial level, $a_i = 0$, the thermometric parameters are constant (independent of the temperature) and provide self-referencing thermometers. Seven self-referencing, 21 primary-T, and three primary-S novel thermometers were implemented for the [Eu(hfa)₃bpyO₂] complex. A subset of these primary thermometers is quite sensitive, ca. 2.4 to 1.3% K⁻¹ within 250 to 340 K.

The self-referencing thermometers have negligible average signed deviations from the mean (MSD) and unsigned deviations (MUD) as small as 1.26%. The temperature was predicted by 15 primary-T thermometers, which some were very accurate with MSD < 0.15% and MUD < 0.4% from the target temperature in the physiological range. They were also very precise with standard deviations as small as 0.5 K around the average temperature.

The primary-S thermometers were even more accurate, with MSD < 0.01% and MUD < 0.3%.

Implementations for another Eu(III)-complex without β -diketonate and doped nanoparticles (Y₂O₃ and BiF₃) were performed for solid samples as well as for Eu(III) complexes in aqueous solutions with a multiparametric thermometric function.



Predicted average temperature by 15 primary-T (a) and three primary-S thermometers.

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0.2.27 Opto-RF transduction in Er³⁺:CaWO₄

Speaker: Chanelière Thierry

Opto-RF transduction in $\text{Er}^{3+}:\text{CaWO}_4$

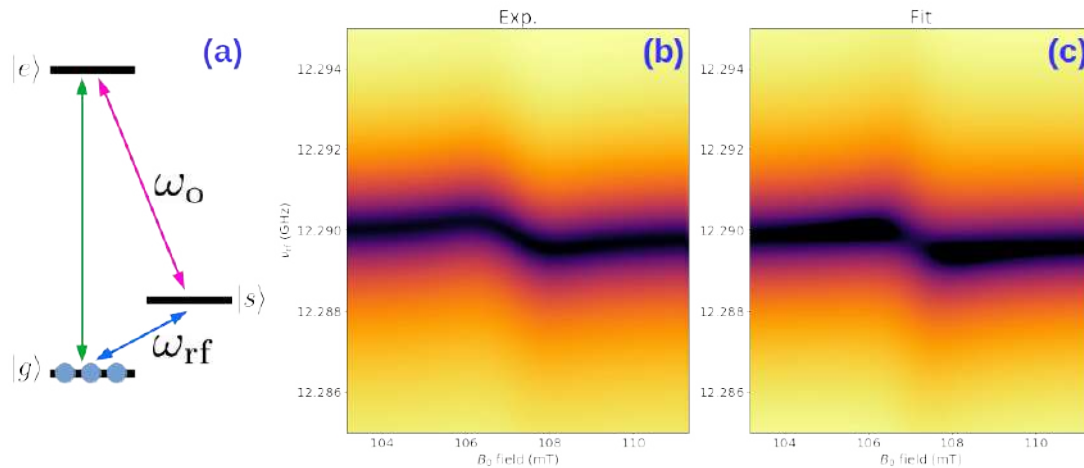
T. Chanelière^{1,*}, P. Bertet², R. Dardaillon¹, P. Lemonde¹, J. Viennot¹

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Quantum transduction between the RF and optical domains recently appeared as a choice morsel in the bestiary of quantum technologies [1]. The fundamental process can be seen as a non-linear mixing process using doubly resonant interactions on optical and spin transitions (see Fig.(a)) that is pushed at the extreme when a single RF photon generate and single optical photon, and vice versa. This physical process is called Raman heterodyne detection by the spectroscopists, at the frontier between optical and magnetic resonance techniques.



(a) Ideal levels scheme of Er^{3+} for opto-RF transduction mixing the optical (ω_0) and RF (ω_{rf}) excitations (b,c) Electron spin excitation when the Er^{3+} transition ($\sim 107\text{mT}$) crosses the RF resonator frequency (at 12.29GHz) (experiment, theory resp.)

I'll first discuss the mixing process and show how the transduction efficiency, a key feature for quantum technologies, can be inferred from a good knowledge of the optical and spin properties independently.

I'll then show preliminary results of opto-RF transduction in $\text{Er}^{3+}:\text{CaWO}_4$ obtained in the low efficiency regime (Fig.(b,c)). The well-know Er^{3+} optical transition in the fibered telecom range is particularly appealing for the development of quantum information. In the same context, this material has recently shown exceptional coherence properties [2]. Our demonstration of opto-RF conversion finally allows us to compare the theoretical predictions of the model with real experiments.

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0.2.28 Photochromism in crystallised inorganic luminescent compounds

Speaker: Jubera Véronique

Photochromism in crystallised inorganic luminescent compounds

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Photochromism is a phenomenon describing the irradiation-induced reversible transformation of a chemical compound's color between two states. While absorption photochromism is well known, few studies describe color modulations related to variations in emission properties. This can be initiated by the introduction of rare earth or transition metals as doping elements within the host lattice [1]. A widening of the colorimetric contrast in terms of intensity or spectral distribution can be observed. The processes involved are, either the emission of the doping element which competes with a photochromic absorbing center (PC), or the metallic cation being at the origin of the PC center. Quenching of the emission, or reversely, a new luminescence can be detected.

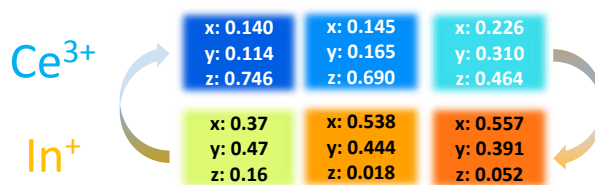


Figure1- Color contrast observed under UV irradiation of Ce³⁺ doped Indium fluorides

In addition, luminescent ions can be involved in intra-crystal redox reactions. This can be used to induce new photochromoluminescent properties, which are defined as the capacity to change the material's emission spectra from its previous regime. The discovery of bistable Ce³⁺ doped Indium fluorides (Figure 1), with the capacity to achieve huge contrast changes in the emission spectra (i.e., from orange to blue) in a reverse manner, has opened the window for new advanced applications [2]. The luminescence tuning as function of the chemical composition as well as the kinetic mechanism involved in the Ce/Indium redox processes will be discussed.

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0.2.29 Photoluminescence from heavily-doped graphene

Speaker: Tan Ping-Heng

Photoluminescence from heavily-doped graphene

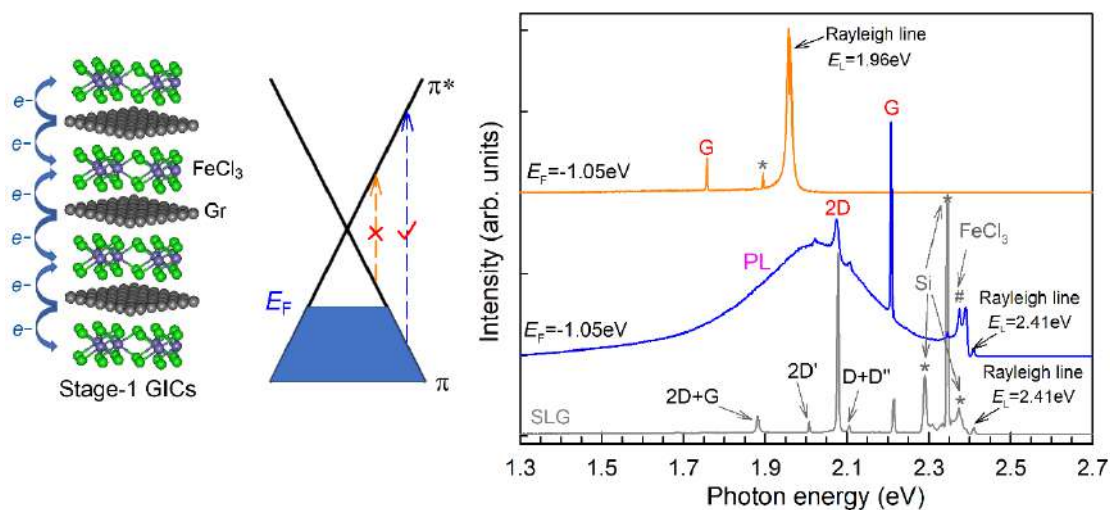
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The ability to tune the optical response of a material via doping is crucial for optoelectronic applications. For semi-metallic graphene with linear band structure, the natural advantage lies in that the Fermi level energy (E_F) could be readily controlled through chemical doping, possibly affecting the optical properties. Here, we report the observation of photoluminescence with the emission energy slightly below $2E_F$ in heavily-doped graphene under continuous-wave laser excitation higher than E_F . As the excitation energy lines below the $2E_F$, the broadband photoluminescence can be switched off by the Pauli-blocking of one-photon interband transition. The laser power and temperature dependence of the broadband photoluminescence are also investigated, suggesting the distinctive photoluminescence in heavily-doped graphene in comparison to that in semiconductor. This will help us gain insight into the fundamental optical processes of semiconductors.



Schematic illustrations of monolayer graphene in FeCl_3 -based stage-1 graphite intercalation compounds and Pauli-blocking of one-photon interband transition in heavily-doped graphene. The corresponding photoluminescence spectra of heavily-doped graphene with $E_F \sim -1.05$ eV excited by 1.96 eV and 2.41 eV with intrinsic graphene as a reference sample. Broadband photoluminescence emerges when excitation energy larger than $2|E_F|$.

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0.2.30 Precise engineering of luminescent lead-halide quantum dots: from single photons to coherent collective states

Speaker: Kovalenko Maksym

Precise engineering of luminescent lead-halide quantum dots: from single photons to coherent collective states

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Colloidal lead halide perovskite (LHP) nanocrystals (NCs), with bright and spectrally narrow photoluminescence (PL) tunable over the entire visible spectral range, are of immense interest as classical and quantum light sources. Severe challenges LHP NCs form by sub-second fast and hence hard-to-control ionic metathesis reactions, which severely limits the access to size-uniform and shape-regular NCs in the sub-10 nm range. We show that a synthesis path comprising an intricate equilibrium between the precursor (TOPO-PbBr₂ complex) and the [PbBr₃-] solute for the NC nucleation may circumvent this challenge [1]. This results in a scalable, room-temperature synthesis of monodisperse and isolable CsPbBr₃ NCs, size-tunable in the 3-13 nm range. The methodology is then extended to FAPbBr₃ (FA= formamidinium) and MAPbBr₃ (MA= methylammonium), allowing for thorough experimental comparison and modeling of their physical properties under intermediate quantum confinement. In particular, NCs of all these compositions exhibit up to four excitonic transitions in their linear absorption spectra, and we demonstrate that the size-dependent confinement energy for all transitions is independent of the A-site cation. We then discuss the size-dependent single-photon emission across the LHP NC compositions. We achieve 98% single-photon purity ($g(2)(0)$ as low as 2%) from a cavity-free, nonresonantly excited single 6.6 nm CsPbI₃ NCs, showcasing the great potential of CsPbX₃ NCs as room-temperature highly pure single-photon sources for quantum technologies [2]. In another study, we address the linewidth of the single-photon emission from perovskite NCs at room temperature. By using ab-initio molecular dynamics for simulating exciton-surface-phonon interactions in structurally dynamic CsPbBr₃ NCs, followed by single quantum dot optical spectroscopy, we demonstrate that emission line-broadening in these quantum dots is primarily governed by the coupling of excitons to low-energy surface phonons. Mild adjustments of the surface chemical

composition allow for attaining much smaller emission linewidths of 35-65 meV (vs. initial values of 70-120 meV) [3]. NC self-assembly is a versatile platform for materials engineering, particularly for attaining collective phenomena with perovskite NCs, such as superfluorescence [4, 5]. Collective electronic states arise at low temperatures from the dense, periodic packing of NCs, observed as sharp red-shifted bands at 6 K in the photoluminescence and absorption spectra and persisting up to 200 K. Perovskite SLs exhibit superfluorescence, characterized, at high excitation density, by emission pulses with ultrafast (22 ps) radiative decay and Burnham-Chiao ringing behaviour with a strongly accelerated build-up time.

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0.2.31 Quantifying (accessible and useful) traps in persistent phosphors

Speaker: Smet Philippe

Quantifying (accessible and useful) traps in persistent phosphors

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Considering the main application areas of glow-in-the-dark materials (or persistent phosphors) - such as safety signage, autofluorescence free bioimaging or X-ray imaging - one will typically strive for an as high as possible trap density [1,2]. Indeed, the more traps that are available, the more energy can be stored per unit volume of the phosphor. This stored energy can then be thermally released during the afterglow (in the case of persistent luminescence), upon mechanical stimulation (in the case of mechanoluminescence) or upon photostimulation (for instance, in the case of X-ray imaging [3]).

Consequently, a key characteristic is the trapping capacity (expressed as the number of traps per gram) in the phosphor under investigation. In this presentation, different strategies will be discussed to quantify this capacity, including photon counting approaches [4], X-ray absorption spectroscopy [5] and electron paramagnetic resonance techniques.

Finally, a special emphasis is given to the fraction of this total trapping capacity which is really accessible and useful for applications, such as in the case of glow-in-the-dark road markings, optical dosimeters [6] or flickerfree LEDs [7]. The relevant parameters are discussed, including the presence of a thermal barrier for charging, losses induced by optically stimulated luminescence, the trap depth distribution, the role of thermal quenching and the quantum efficiency for the recombination process.

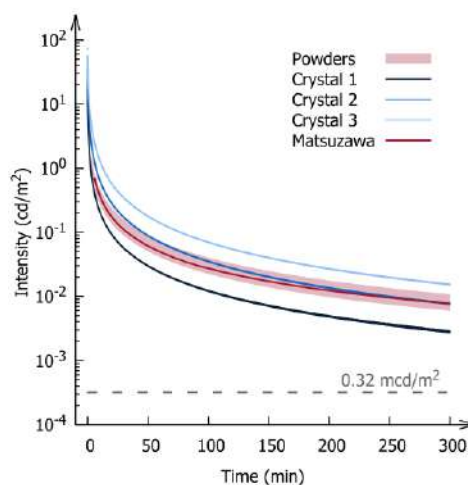


Figure. Benchmarking [8] of $\text{SrAl}_2\text{O}_4:\text{Eu,Dy}$ powders and single crystals after excitation with 1klux of white light from a Xe-arc lamp for five minutes.

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0.2.32 Quantum diamond magnetometry for high pressure sensing

Speaker: Adam Marie-Pierre

Quantum diamond magnetometry for high pressure sensing

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Diamond anvil cell (DAC) technology is widely used to study materials under high pressure. These materials can exhibit exotic phases of matter such as superconductivity with exceptionally high critical temperatures. The main difficulty with using the DAC lies in the challenge to measure magnetic properties at high pressure (above 100 GPa) due to the minute sample size.

In our work, we perform high-pressure magnetometry by using nitrogen-vacancy (NV) centers implanted at the anvil culet surface of the DAC. Using a confocal microscope, we observe the spin dependent luminescence of NV centers, to perform a mapping of the magnetic field at the diamond anvil tip. Expulsion of magnetic field lines due to the Meissner effect in a superconductor results in a clear drop of the magnetic field in the close vicinity of the sample, where the NV sensors are located¹. This detection provides an

unambiguous diagnosis of superconductivity that does not rely on questionable electrical contacts or indirect probes once implemented at high pressure. This procedure can be performed on any magnetic sample and is compatible with synchrotron X-ray diffraction for structural characterization².

Finally, we demonstrate that NV micro-sensing can be implemented above 100 GPa by machining a micropillar on the anvil tip to create a quasi-hydrostatic stress environment for the NV centers³. This result increases the pressure range of NV micro-sensing. It enables the undisputable detection of the Meissner effect of super-hydrides that is currently under stifling debate.

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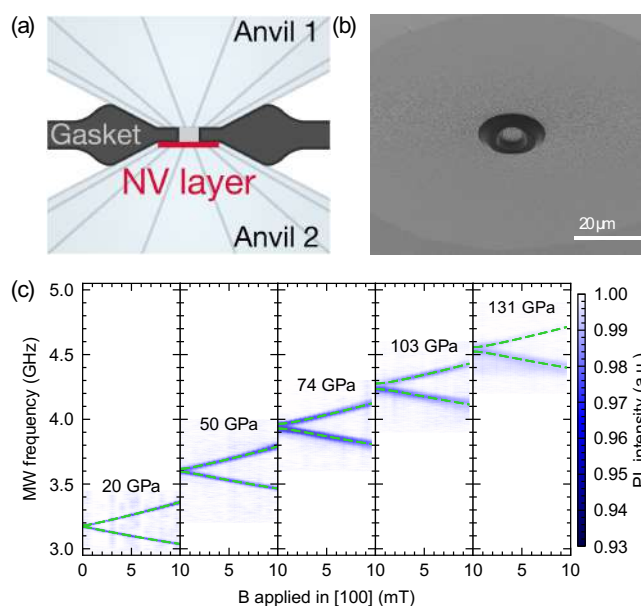


Figure 1 – (a) Schematic cross-section of the NV-DAC. (b) SEM of the diamond anvil tip with the micropillar. (c) ODMR spectrum of the NV centers as a function of pressure and applied magnetic field.

0.2.33 Quantum optics with single quantum emitters coupled to nanophotonic waveguides

Speaker: Le Jeannic Hanna

Quantum optics with single quantum emitters coupled to nanophotonic waveguides

Hanna Le Jeannic,^{1,2}

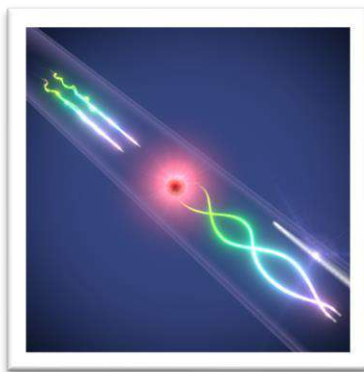
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In recent decades, advancements in nanofabrication and nanostructuring have enabled quantum optics protocols that were previously limited to large and complex atom-light experimental setup, to be carried out on small chips. These developments have led to the creation of new methods for generating optical quantum states, including single photons, and performing quantum operations.

During this presentation, we will discuss recent research on single photon sources that utilize single solid-state quantum emitters coupled to nanophotonic waveguides^{1,2}. From state of the art self assembled InGaAs quantum dots³ to new types of perovskites nanocrystals⁴, we will explore the different advantages and challenges faced by solid-state emitters. Additionally, we will explore the quantum operations that can be achieved through the coupling of a single quantum emitter to a few photon propagating field in a photonic waveguide^{1,5}, and explain how it can be applied to quantum computing. We will also emphasize how nanophotonics designs can help overcome some of the remaining challenges in photonic quantum computing.



A single quantum emitter in a nanophotonic waveguide can make two single photons interact, in a deterministic fashion⁵

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0.2.34 Ratiometric, temperature invariant luminescence manometry based on the Cr³⁺ ions emission

Speaker: Marciniak Lukasz

Ratiometric, temperature invariant luminescence manometry based on the Cr³⁺ ions emission

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The capability to precisely and accurately read and image pressure changes remotely is fundamental for the design of tools that enable rapid diagnostics across various application domains. Consequently, the development of luminescence manometers with high sensitivity to pressure changes that provides temperature invariant readout is imperative. In this context, a methodology utilizing the pressure-induced spectral shift of the $^4T_2 \rightarrow ^4A_2$ emission band of Cr³⁺ ions in inorganic materials has been proposed and evaluated [1,2]. The approach leverages ratiometric readout based on the analysis of the ratio of luminescence intensities of Cr³⁺ ions integrated in two spectral ranges. The proposed technique enables temperature independent pressure measurement with unprecedented relative sensitivities surpassing 120 %/GPa and facilitates temperature-invariant pressure readout. This presentation outlines the core principles of this approach and performs a comparative analysis of its advantages over conventional luminescence manometers which are based on the spectral shift of the $^2E \rightarrow ^4A_2$ line and the luminescence intensities ratio of $^2E \rightarrow ^4A_2$ to $^4T_2 \rightarrow ^4A_2$.

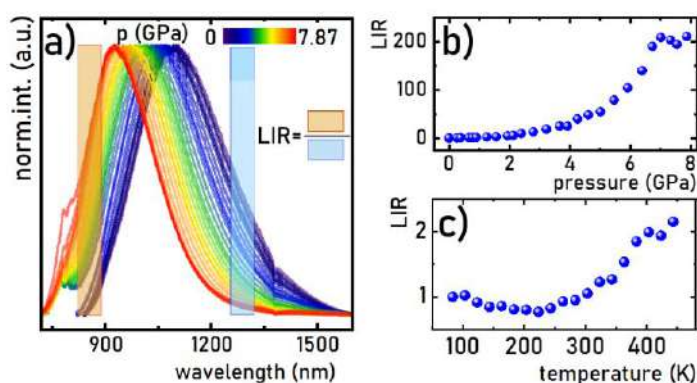


Figure 1. Schematic representation of a proposed ratiometric pressure readout: the pressure-induced spectral shift of the $^4T_2 \rightarrow ^4A_2$ emission band of Cr³⁺ ion and with the indication of the spectral gates used for LIR calculation-a); representative LIR as a function of pressure-b) and temperature -c)

Acknowledgements

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0.2.35 Relating thermal quenching and thermoluminescence involving lanthanides with level location in the band gap

Speaker: Dorenbos Pieter

Relating thermal quenching and thermoluminescence involving lanthanides with level location in the band gap

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The thermal quenching of lanthanide 5d-4f luminescence (Eu^{2+} , Ce^{3+}) and 4f-4f luminescence (Pr^{3+} , Eu^{3+} , Tb^{3+}) may proceed by means of charge carrier transfer from the excited state to the host bands. The reversed transfers to the ground states occur in trapping of electrons by trivalent lanthanides (Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} , Yb^{3+}) or holes by trivalent lanthanides (Ce^{3+} , Pr^{3+} , Tb^{3+}). Both processes are of crucial importance for the performance of luminescence, scintillator, dosimetry, afterglow, and storage phosphors. Data on quenching temperatures [1] and thermoluminescence gathered from literature involving 36 different compounds have been analyzed to obtain the quenching energy barriers ΔE_q and the electron trapping depths $\Delta E_{e\text{-trap}}$ and hole trapping depths $\Delta E_{h\text{-trap}}$. This will be compared with the energy barriers and trapping depths read from the Vacuum Referred Binding Energy diagram constructed for each compound. On the one hand very good correspondence was found, on the other hand systematic differences were revealed. This means that the validity of the VRBE diagrams is further confirmed but also that accuracy is limited to few 0.1 eV.

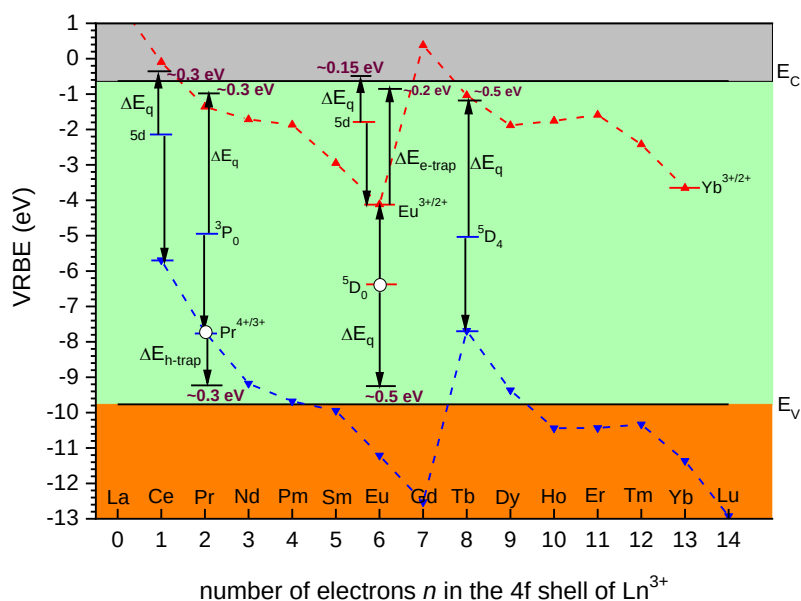


Fig. 1 VRBE diagram of hypothetical compound illustrating the average differences (in purple colour) between VRBE prediction and experimental quenching barriers and carrier trap depths

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0.2.36 Single particle spectroscopy of colloidal nanoparticles by optical tweezers: from fundamentals to applications

Speaker: Jaque Daniel

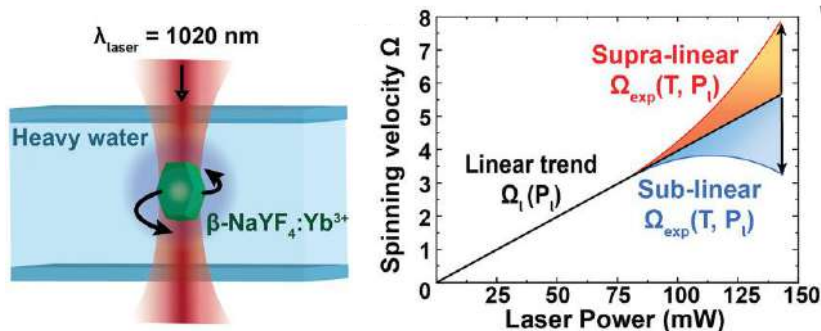
Single particle spectroscopy of colloidal nanoparticles by optical tweezers: from fundamentals to applications

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Achieving a full understanding about the physics governing the luminescence of nanoparticles requires to work at the single particle level. Studying an individual and isolated nanoparticle make possible to rule out the possible presence of particle-particle interactions. Traditionally, single particle studies have been conducted on dry samples, where nanoparticles are deposited on a substrate. In the case of colloidal nanoparticles, this traditional approach implies removing the liquid medium and, consequently, it makes not possible the study of single particle-medium interactions. Optical Tweezers (OTs) allow isolation, immobilization and spectroscopic characterization of individual nanoparticles suspended in liquids by using simple experimental set-ups. In this work we will overview some representative examples revealing the potential of OTs for single-particle studies in liquids. These examples include the use of OTs to elucidate plasmon-induced luminescence enhancement in individual nanoparticles, laser cooling by individual colloidal particles, or the use of an optically trapped single luminescent particle to determine the properties of cytoplasm in live cells.



0.2.37 Spectral Multiplexing for Scalable Quantum Applications

Speaker: Berger Perrine

Spectral Multiplexing for Scalable Quantum Applications

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Many quantum applications require spectral multiplexed control to achieve the targeted high performances: for example, high fidelity for quantum memories [1], large band radiofrequency processing [2,3] or multi-qubits for quantum computing [4]. We will focus on rare earth ions, as they naturally offer a large inhomogeneous linewidth, tailorable by spectral hole burning, and we will discuss the main challenges involved by the spectral multiplexing.

The first challenge is to optically address spins in solid over a large bandwidth. Complex and high bandwidth excitation waveforms [4,5] could be generated in the VIS/NIR range using acousto-optical modulators, but the limited bandwidth sets severe limitations in the bandwidth and frequency agility (few MHz). Electro-optic LiNbO₃ modulator have also limited bandwidth and optical power handling in the VIS/NIR and generates harmonics that can perturb the experiment, reducing the fidelity and/or the efficiency of the protocol [6]. Here we present and describe the performances of a laser source able to deliver high-bandwidth optical signals at multiple frequencies over 10 GHz (scalable to 100 GHz), while keeping a good stability. The architecture is based on the combination of multiple fixed-frequency laser sources at 1.5 μm , IQ optical modulators and tunable optical filters to obtain the required performances in terms of bandwidth, low noise and spurious suppression. A sum frequency generation stage allows then to address any emitters in the visible/near infrared (cold/trapped atoms, colour centers...).

The second challenge is to maintain the coherence at cryogenic temperature under large band optical programming, which involves the excitation of a large number of atoms, creating heat through non-radiative relaxations, and decreasing the coherence. We will present a local measurement of the hole lifetime, which enables to extract the temperature distribution in the sample, and can be compared to a simple heat diffusion model.

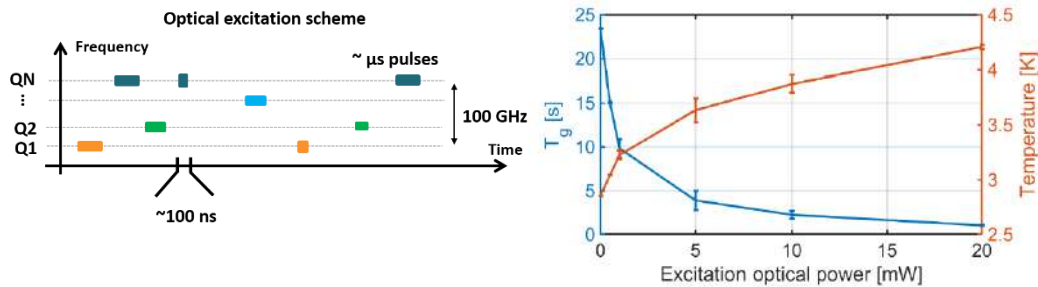


Figure 1 : (a) Example of an optical excitation scheme for optical Qubit quantum processing. (b) Lifetime T_g of Zeeman levels of $^3\text{H}_6$ in Tm:YAG and corresponding local temperature under 20 GHz wide optical excitation, for several optical powers.

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0.2.38 Stimulus-Responsive Luminescence in Doped Metal Halides

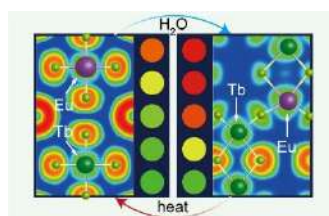
Speaker: Wang Feng

Stimulus-Responsive Luminescence in Doped Metal Halides

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Impurity doping represents an appealing strategy for creating highly tunable luminescence properties within a single host material. In this talk, I focus on our recent efforts to incorporate lanthanide and transition ions into metal halide perovskites for achieving tunable emissions that can be modulated by external stimuli, such as water and heat. We demonstrate rational control over luminescence processes and properties by leveraging characteristics of the host materials and their complex yet manageable interactions with various dopant ions. We show that these doped luminescent materials hold promise in many exciting applications in sensing, information security, and biomedical sciences.



Multicolor luminescence switching by dopant engineering in a lanthanide-based hydrochromic perovskite

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0.2.39 Synchrotron radiation in the luminescence research: comparative study of the luminescence of single crystals and single crystalline films of Ce^{3+} doped $\text{Gd}_3\text{Al}_5\text{-xGa}_x\text{O}_{12}$ garnets and $\text{Lu}_{2-\text{x}}\text{Y}_\text{x}\text{SiO}_5$ orthosilicates

Speaker: Zorenko Yuriy

Synchrotron radiation in the luminescence research: comparative study of the luminescence of single crystals and single crystalline films of Ce³⁺ doped Gd₃Al_{5-x}Ga_xO₁₂ garnets and Lu_{2-x}Y_xSiO₅ orthosilicates

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Substantial differences in the methods and conditions of material preparation from the melt (crystals) and melt-solution (films) of complex garnets and orthosilicates compounds result in the significant differences in their luminescent properties. Such differences are caused by various types of intrinsic defects, their concentration, different distributions of the dopant ions between the cation sites and by interaction of dopants with defect centers in the crystal and film phosphors.

For crystals of well-known mixed garnets and orthosilicates, the contribution of defect centers to the intrinsic luminescence or to the emission of dopants can be so important that it can significantly mask the native luminescent properties of dopants in them. The intrinsic defects concentration can be strongly reduced in the film of these oxides prepared by low-temperature LPE growth from the melting fluxes. Furthermore, the preference distribution of the dopant ions between the various cation sites can be substantially different from the distribution in crystals. At the same time, the LPE grown films can contain the flux components which also may influence their luminescent properties.

Thus, only the detailed comparison of the luminescent properties of garnets and orthosilicates, prepared in the film and crystal forms, gives the possibility to detect the “authentic picture” of the intrinsic and dopant luminescence in these oxides from the background of the luminescence of defect-related centers. Using for this purpose combination of the conventional spectral methods and synchrotron radiation (SR) excitation with the energy in the range of fundamental absorption of these compounds opens a unique possibility for correct comparison of the luminescent properties of complex oxides in the different crystalline forms.

The aim of presentation is to show the characteristic examples of comparison of the structure of luminescent centers in crystals and films of Ce³⁺ doped mixed Gd₃Al_{5-x}Ga_xO₁₂ garnets and Lu_{2-x}Y_xSiO₅ orthosilicates using the conventional spectral methods as well as time-resolved luminescent spectroscopy under excitation by synchrotron radiation in the exciton range and the range of fundamental absorption of these oxide hosts.

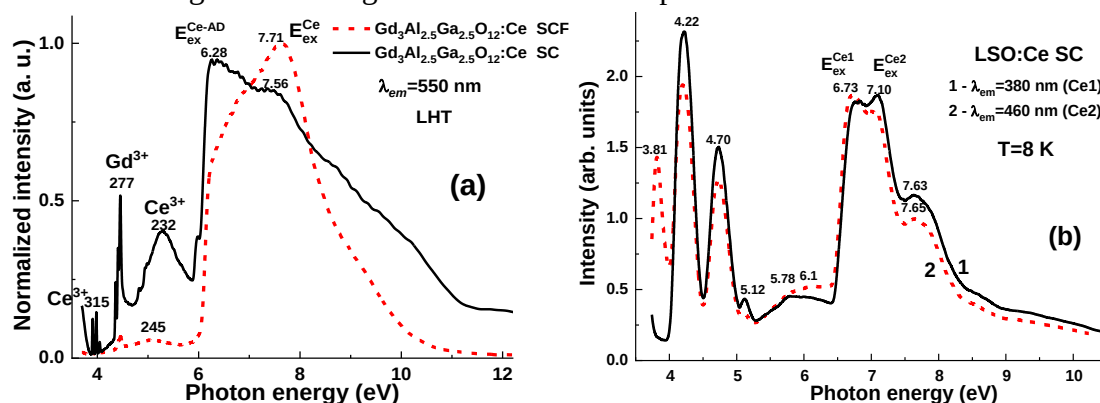


Figure. Excitation spectra of Ce³⁺ luminescence in the Gd₃Al_{2.5}Ga_{2.5}O₁₂:Ce SC and SCF (2) and Ce1 and Ce2 centers in Lu₂SiO₅ crystals (b) at 10 K.

Acknowledgments. This work was supported by Polish NCN 2019/33/B/ST3/00406 projects. Investigation with SR at Superlumi station at DESY were performed in the frame of project.

0.2.40 The $\text{K}_2\text{SiF}_6:\text{Mn}^{4+}$ (pfs/ksf) phosphor for led lighting and displays

Speaker: Cohen W.e.

The $\text{K}_2\text{SiF}_6\text{:Mn}^{4+}$ (PFS/KSF) phosphor for led lighting and displays

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In the modern-day phosphor-converted light emitting diodes (pc-LEDs), white-light for general illumination is generated by combining blue light from the InGaN chip with the yellow-green emission of Ce doped garnet phosphor and a red emitter. The red emitter is required to induce a “warm-white” color temperature (2700–3500 K). The optical properties of the red emitter are critical to achieving high luminous efficacy (lumens per watt or LPW) and high color rendering index (CRI) of the white light. The red emitter must display both strong absorption at 450 nm and sharp line emission in the range of 610 nm - 650 nm.

In the 1970's, scientists were exploring the optical properties of octahedral MnF_6 moiety in various fluorides [1-3]. A class of materials, of which K_2SiF_6 is a member, satisfied the requirements of a red emitter for a blue pumped LED [3]. This lead the General Electric company to commercialize the $\text{K}_2\text{SiF}_6\text{:Mn}^{4+}$ (PSF/KFS) phosphor [4].

In this talk we will provide a historical prespective of the PFS phosphor development, discuss the basic spectroscopic properties of the Mn^{4+} ion in K_2SiF_6 and focus on the manufacturing procedures with particular emphasis on post-synthesis processes that are required to produce phosphor with acceptable reliability. We will also discuss the development of $\text{Na}_2\text{SiF}_6\text{:Mn}^{4+}$ phosphor aimed at the display market segment. Future improvements, and challenges will also be discussed.

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0.2.41 Upconversion nanothermometry to unravel the phase diagram of liquid water

Speaker: Carlos Luís

Upconversion nanothermometry to unravel the phase diagram of liquid water

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Water is essential for all life on Earth and is the most common liquid. However, its behaviour is unique exhibiting a range of anomalous properties, including increased density upon melting, a density maximum at 277 K (4 °C), reduced viscosity under pressure at below 306 K (33 °C), high surface tension, and decreased isothermal compressibility and heat capacity with the temperature at ambient conditions, with minimum values at 319 K (46 °C) and 308 K (35 °C), respectively.[1] The hypothesis of two competing organizations of hydrogen bonds competing at thermal equilibrium has been proposed to explain its behaviour.[2] These two organizations manifest as two phases, namely the low-density liquid (LDL) and the high-density liquid (HDL), in the supercooled regime.[3] However, the existence of these two distinct structural organizations and their implications remain elusive and controversial under ambient conditions, despite the emergence of a recent possible pseudo-phase diagram for water.[2]

Here, we show how experimental measurements of the instantaneous Brownian velocity of NaYF₄:Yb/Er upconversion nanoparticles (UCNPs) dispersed in water through upconversion thermometry can support some of the assumptions of the proposed pseudo-phase diagram of liquid water under ambient conditions. The method can assess the size distribution of the LDL motifs in liquid water using different-sized UCNPs with the advantage of mimicking the effect of pressure on the hydrogen-bonding network by simply varying the pH of the aqueous suspension, with the benefit of working under ambient conditions. This experimental approach offers a new way to investigate the two-state model of water and gain deeper insights into the organization of the hydrogen bonds in liquid water by examining the effects of environmental conditions on the motion of UCNPs, such as distinct pH values and solvents.

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0.2.42 “Current advances in lanthanide doped nanostructures as Theranostic Platforms”

Speaker: Gonçalves Rogéria

“Current advances in lanthanide doped nanostructures as Theranostic Platforms”

R. R. Gonçalves

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The application of light and light-based technologies is now widespread in a significant number of human activities and leads to research in many technological areas. The development of photonic materials has not only revolutionized the area of Information and Communication Technology but has influenced widely in strategic global areas such as health, environment, lighting and energy. Our recent work on photonic and theranostic applications will be discussed, specifically, concerns about the synthesis and optical properties of rare earth doped nano and microstructured inorganic materials based on fluoride and oxides as theranostic agents for glioblastoma multiforme. Spheres, hollow spheres, cubes, rods, nanoparticles prepared by different methodologies will be presented, demonstrating high visible upconversion (UC) or near infrared (NIR) emission intensity after NIR excitation at transparent biological windows, radioluminescence and photoacoustic features for imaging. In vitro assays of UC nanoparticles have been performed, and cell viability has been evaluated for glioblastoma cells, making them promising materials for bioimaging and photodynamic therapy using as an excitation source near infrared radiation. Ensemble and Single Particle were evaluated as primary nanothermometer with relatively high thermal sensitivity.

Acknowledgments: FAPESP, CNPq, CAPES and University of São Paulo (USP), USP-Cofecub, CAPES-Cofecub, INCT-INFO, all researchers, undergraduate and graduate students at the Mater Lumen Laboratory and collaborating researchers from other institutions.

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0.2.43 “The photonic cannon shot”: sequential up- and down- spectral conversion processes with a luminescent solar concentrator for optimizing photovoltaic solar cell response

Speaker: Méndez-Ramos Jorge

“The photonic cannon shot”: sequential up- and down-spectral conversion processes with a luminescent solar concentrator for optimizing photovoltaic solar cell response

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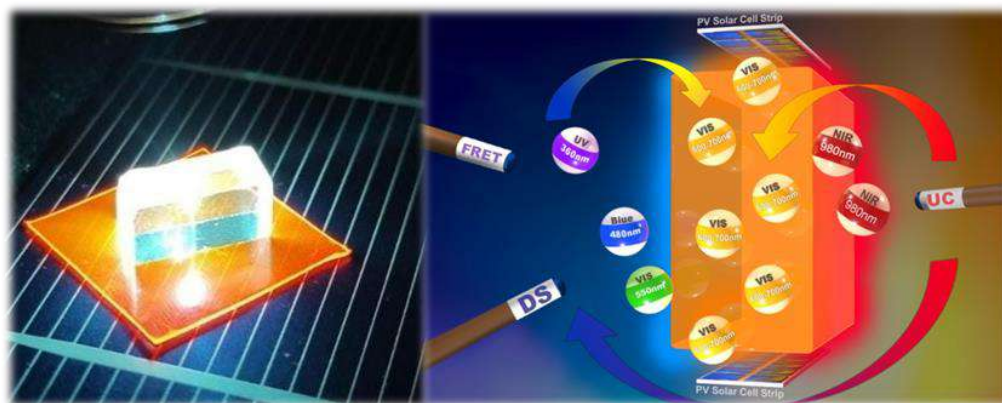
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Increasing the overall solar spectrum utilization is of crucial interest and stands up as a frontier-of-research approach in the photovoltaic sector, since typically the full potential of each photon of whole solar spectrum is not efficiently used in the generation of electricity [1,2]. Here we present an innovative ultra-broadband absorption and multiple spectral conversion approach, by means of rare-earth doped materials [3] together with organic dyes embedded in a luminescent solar concentrator (LSC). In this work, a simultaneously combined effect of up-conversion and down-shifting of light is aimed to optimal spectral matching with conventional photovoltaic silicon solar cells response. Thus, UV-visible photons coming from the incoming sunlight, together with UV-visible up-converted photons coming from near-infrared radiation, can be all shifted to the orange-red part of the spectrum. To the best of our knowledge, this represents the first reported proof-of-concept using LSCs with up-conversion and down-shifting photonic processes working together and sequentially.



Ultra-broadband absorption and simultaneously combined effect of up-conversion and down-shifting of light aimed to optimal spectral matching with conventional photovoltaic silicon solar cells response. First reported proof-of-concept using LSCs with up-conversion and down-shifting processes working together and sequentially with an $\text{Yb}^{3+}\text{-Er}^{3+}\text{-Tm}^{3+}$ doped ZBLAN glass.

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0.3 Oral

0.3.1 3D printing of photoluminescence in transparent organic materials by femtosecond laser direct writing

Speaker: Que Ruyue

3D printing of photoluminescence in transparent organic materials by femtosecond laser direct writing

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The quest for smaller optical components continues as smart terminals, wearable devices or lab on chips demand implementing photonic functions at the microscale. The femtosecond laser direct writing (FLDW) technology through multiphoton absorption can be a widely usable tool to perform flexible 3D transformation inside transparent materials, such as refractive index change[1], nanogratings[2], nanocrystallization[3] and other molecular or structural transformations. In our research, we focus on the generation of luminescence property, as it is an important part of optical devices, especially in the display field, sensors, labelling or data storage. For example, Kallepalli et al.[4] have created local photoluminescence (PL) in PMMA, showing its promising data storage applications. In our study, we have demonstrated that using an infrared fs laser with a dedicated parameter range, guided by analytical thermal models, PL in visible range can be created at the focus of the laser beam (a few microns) in several organic materials, including glycine single crystal (α and γ phase), sucrose single crystal, cyclo olefin polymer (Zeonex®), perfluorinated polymer (CYTOP®) and polycarbonate. Laser parameters such as pulse energy can influence to some extent the ratio of produced luminescent species [5]. Besides, through various characterizations, we found commonalities in this laser-induced luminescence among these materials, despite the differences in their structures and chemical compositions. Therefore, we presume that the mechanisms of the PL formation end up similarly, a point very interesting to study. FLDW for the implantation of luminescent functions in transparent organic substrates is demonstrated to be a universal and efficient technique.

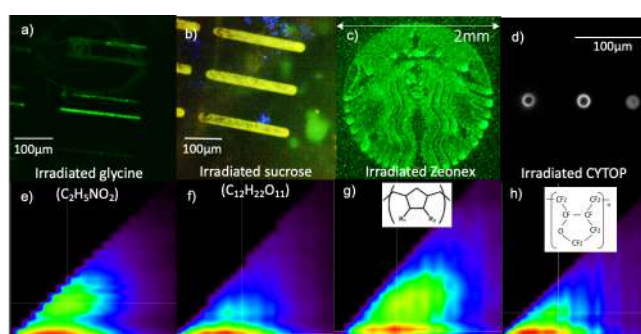


Figure.1 (a)-(d) fluorescence images of laser irradiated regions (examples) in glycine, sucrose, cyclo olefin polymer and perfluorinated polymer, respectively. (e)-(h) Excitation-Emission Matrix (EEM) of irradiated regions in each materials, no correlation with above irradiated regions.

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0.3.2 A soft-template route for molecular encapsulation in luminescent YVO₄:Ln³⁺ nanoporous particles

Speaker: De Sousa Filho Paulo

A soft-template route for molecular encapsulation in luminescent $\text{YVO}_4\text{:Ln}^{3+}$ nanoporous particles

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Engineered cavities in colloidal oxide particles can act as nanocontainers for encapsulation and transport of dyes, which can be selectively activated via the light emitted by the particles.^[1] In turn, these systems offer novel prospects for theranostic applications, where different selected wavelengths can provide orthogonal sensing and photoactivation of encapsulated molecules. Although template-mediated^[2] routes have been widely used to produce hollow metal and oxide nanoparticles, limited examples explore cavity functionalisation combined to luminescence in lanthanide (Ln)-doped particles, especially in vanadates. We have therefore investigated the formation of tetragonal ~ 35 nm $\text{YVO}_4\text{:Ln}^{3+}$ particles with functionalisable $\sim 7 \pm 3$ nm nanopores via the control of phase separation of VO_4^{3-} and rare earth precursors in reverse microemulsions soft-templates at 25 °C (Fig. 1A-D). The particles showed downshift (Ln=Eu) and upconversion (Ln= Yb/Er) luminescence despite the mild synthesis conditions, with high concentration of defects and partial carbonation.^[3] Eu^{3+} luminescence spectroscopy combined to multiple techniques (*e.g.*, XRD, SAXS, XPS) was used as a tool to probe the interfacial crystallisation of the vanadate phase (Fig. 1E-I), while xylenol orange absorption confirmed molecular encapsulation in particle cavities. These systems are therefore promising for further development of new multifunctional systems for luminescent sensing

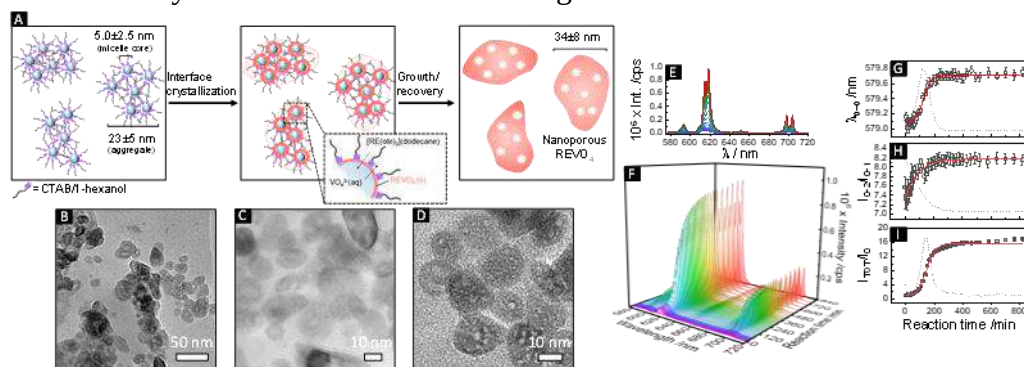


Figure 1. (A) Schematic illustration of the formation of nanoporous $\text{YVO}_4\text{:Ln}^{3+}$ particles by interface crystallization over micellar aggregates in water-in-*n*-dodecane reverse microemulsions. (B-D) TEM images of (Y,Eu) VO_4 nanoparticles. (E-I) *In situ* luminescence monitoring of the formation of (Y,Eu) VO_4 particles in $\text{H}_2\text{O}/n\text{-C}_{12}\text{H}_{26}$: (E,F) emission spectra ($\lambda_{\text{exc}}=288$ nm) at different reaction times, (G) position of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ barycentre, (H) $^5\text{D}_0 \rightarrow ^7\text{F}_2 / ^5\text{D}_0 \rightarrow ^7\text{F}_1$ intensity ratio, and (I) total integrated intensity normalised at $t=0$.

The authors thank **CAPES, CNPq, FAPESP (2018/08334-9, 2022/03442-3) and University of Warwick** for financial support and scholarships.

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0.3.3 Alkali luminescent lanthanide-free polyoxometalates as new sustainable and reusable sensors of humidity

Speaker: Dessapt Rémi

Alkali luminescent lanthanide-free polyoxometalates as new sustainable and reusable sensors of humidity

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The detection and quantification of water either as trace in organic solvents, or as relative humidity (RH) in air have attracted wide interest over the past years, because of their great significance in industrial process controls, batteries life extension and indoor air quality improvement [1]. In the last years, photoluminescent (PL) solid sensors for water molecules [2] have been considered as an attractive potential alternative to traditional analytical technics due to their faster response, higher sensitivity and ability of *in situ* detection. Many of investigated PL sensors incorporate lanthanide (Ln^{3+}) ions, but considering rising costs associated with the difficulties of extracting or recycling rare earths, new robust Ln-free sensors are still highly desirable.

We have recently elaborated and structurally characterized a new series of water-responsive luminescent anhydrous alkali salts of the $[\text{SbW}_6\text{O}_{24}]^{7-}$ polyoxometalate (Fig. 1a) [3]. These materials are capable to detect water at room temperature with high sensitivity and selectivity, based on a PL turn-off mechanism. Indeed, upon exposure to humidity, they are fully converted into crystallized hydrates, and the rehydration processes are accompanied by strong PL quenching effects (Figs. 1a and 1b). The anhydrous phases quantitatively sense RH with limit of detection values around 2% (Fig. 1c) which are among the best reported values [2]. Moreover, the regeneration of the PL-active anhydrous phases can be achieved by soft thermal dehydration, making them highly relevant for the development of new sustainable and reusable solid sensors.

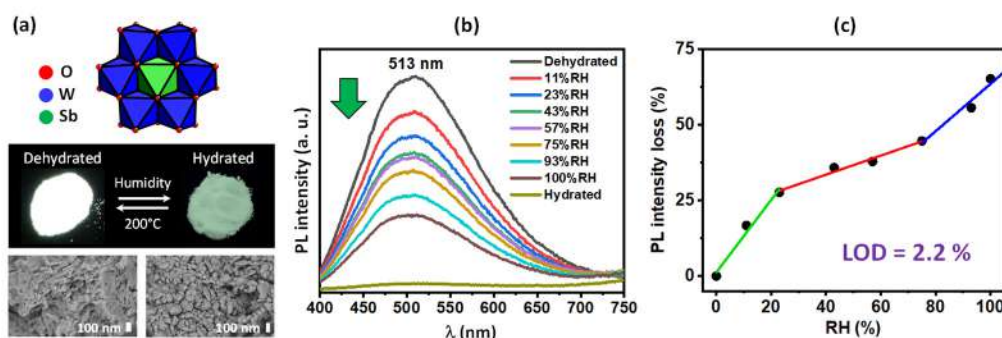


Fig. 1 (a) The $[\text{SbW}_6\text{O}_{24}]^{7-}$ unit, PL properties ($\lambda_{\text{ex}} = 254$ nm) and particle morphologies of $\text{Na}_7[\text{SbW}_6\text{O}_{24}]$ (left) and $\text{Na}_7[\text{SbW}_6\text{O}_{24}] \cdot 16\text{H}_2\text{O}$ (right). (b) PL intensity of $\text{Na}_7[\text{SbW}_6\text{O}_{24}]$ at different RH levels. (c) % PL intensity loss vs RH variation, and limit of detection (LOD) value.

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0.3.4 Application of photoluminescence to study the hydrodynamics of electrons

Speaker: Pusep Yury

Application of photoluminescence to study the hydrodynamics of electrons

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Photoluminescence (PL), photoconductance and time-resolved PL are applied to study strongly correlated electron-hole plasma formed in a high-mobility n-doped mesoscopic GaAs channel. We address our investigation to the diffusion processes which take place in the hydrodynamic regime. In particular, we report on a photocurrent (PC) study of diffusion of the photo-generated holes within a viscous electron fluid. Scanning PC microscopy was performed at the temperature 3.7 K in a channel with the 5 μm width and 100 μm length, fabricated on the basis of a 14 nm thick GaAs/AlGaAs quantum well. The sheet electron density and the mobility were $9.1 \cdot 10^{11} \text{ cm}^{-2}$ and $2.0 \cdot 10^6 \text{ cm}^2/\text{Vs}$, respectively. The diffusion profiles measured at various temperatures are shown in Fig.1.

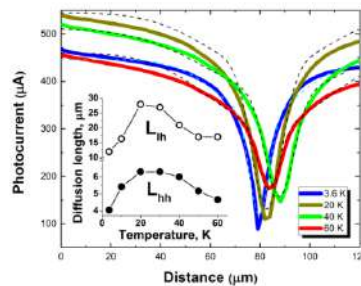


Fig.1. Photocurrent measured at various temperatures as a function of the distance along the channel (solid lines). The dashed lines were calculated diffusion profiles with the contributions of both heavy and light holes. The insert shows the diffusion lengths of heavy and light holes as a function of temperature.

It was shown that the observed diffusion is due to photo-generated heavy and light holes, which cause depletion of electrons leading to a PC minimum. Two diffusion regimes were observed: hydrodynamic regime at temperatures below 30K, where the diffusion length was found increasing with temperature, and Drude diffusion at higher temperatures. The obtained results were analyzed within the framework of ambipolar diffusion. In such a way, the ambipolar diffusion coefficient and the effective viscosity of the electron-hole system were determined. Moreover, the effects of the magnetic field were studied. The results of this study were partially published in [1].

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0.3.5 Artificial intelligence-assisted optical nanothermometry for more accurate temperature detection

Speaker: Jacinto Carlos

Artificial intelligence-assisted optical nanothermometry for more accurate temperature detection

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In recent years, many nanomaterials have been proposed as probes for thermometry and, despite their applicability in a diversity of fields, they have found some stumbling blocks when it comes to biomedicine. After all, achieving remote subcutaneous thermal sensing is yet a very difficult approach to implement. To circumvent such complexities of biological systems, luminescent nanothermometers (LNThs), operating in the so-called physiological temperature range (20-50 °C), have then emerged. The operational principle of LNThs is to have a well-characterized temperature dependence of one or more spectroscopic properties of a given nanostructure and utilize it as a means of inferring thermodynamic processes. Among such thermally-dependent properties one could mention the broadband intensity of a given transition, the intensity ratio between two transitions, the lifetime, the peak position, and the polarization. In the past decade, several works were published on their good performance when injected into small animals. The detection of incipient diseases such as ischemia and tumors, for instance, have been made possible by the study of thermal transients acquired through the luminescence of such materials. In spite of this recent success, some issues have also caught the attention of those working in the field. The most troublesome being the existence of spectral distortions even in the so-called Biological Windows (BW), where light attenuation is expected to be locally minimized in the electromagnetic spectrum. Recent works have widely demonstrated that this could be a serious issue for intensity-based LNThs operating in the BW-II (1000-1370 nm). Hence, it has forced the community to develop new materials, analysis procedures and protocols to reach more reliable thermal readings [1,2]. In this work we investigate the potential of LNThs operating in an almost unexplored spectral region (BW-III, 1500-1900 nm). The LNTh we developed emitted in the 1.5-2.1 μm spectral range by combining two rare-earth ions (Er^{3+} and Tm^{3+}). It is shown that its emission is minimally perturbed by the presence of a biological tissue and that the different quenching mechanism of Er and Tm ions provide the NPs with a thermal sensitivity that opens the path towards reliable *in vivo* thermal sensing using this spectral range. Furthermore, the potential application of these LNPs for fluorescent/thermal imaging was demonstrated through subcutaneous *ex vivo* experiment, evidencing greater efficiency in fluorescent/thermal imaging in the BW-III.

Acknowledgements

We acknowledge the financial support from Brazilian Agencies: FINEP, CNPq and CAPES. This work was also financed by the Spanish Ministerio de Innovación y Ciencias under project NANONERV PID2019-106211RB-I00.

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0.3.6 Au nanorods combined to vanadate particles as potential tools to investigate thermal effects in plasmonic catalysis

Speaker: Oliveira Tamires

Au nanorods combined to vanadate particles as potential tools to investigate thermal effects in plasmonic catalysis

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Plasmonic catalysis enables to promote chemical reactions using light as a fuel, thus being a growing relevance way to green chemistry¹. However, from a fundamental perspective, separating thermal effects from hot carriers to describe reaction mechanisms is still a challenge, demanding new systems capable to measure temperature at the nanoscale². Hence, in this work, we proposed to combine optical nanothermometers based on rare earth orthovanadates (REVO₄) with gold nanorods (AuNRs) as a platform to measure temperature around plasmonic nanoparticles in catalysis assays. Upconverting (Y,Yb,Tm,Er)VO₄ were prepared by aqueous precipitation followed by a protected annealing at 900 °C.³ Comparing bare and AuNR-functionalized (Y,Yb,Tm,Er)VO₄ particles revealed changes in the profile of Er³⁺ ²H_{11/2} → ⁴I_{15/2}, ⁴S_{3/2} → ⁴I_{15/2} upconversion emissions under λ_{exc}=808 nm, where the high energy band was intensified due to the increase of the local temperature caused the metal NPs. This effect was suppressed when this sample was dispersed in water, thus indicating a higher degree of energy dissipation. Bilogarithmic intensity vs. power profiles also showed the effects of AuNRs on upconversion mechanisms, with a decrease in the slopes when AuNRs interact with the vanadate particles. This local heating effect was also confirmed by *in situ* luminescence measurements monitoring progressive deposition of AuNRs over (Y,Yb,Tm,Er)VO₄ particles. Catalysis assays of 4-nitrophenol reduction by NaBH₄ under λ_{exc}=740 nm demonstrated a positive interaction between the (Y,Yb,Tm,Er)VO₄ support and AuNRs, with improved catalytic activities in comparison to pure AuNRs. These results point toward multifunctional systems to potentially provide detailed information on temperature fluctuations around the AuNRs and on the effects of REVO₄ as catalytic supports in plasmonic catalysis reactions.

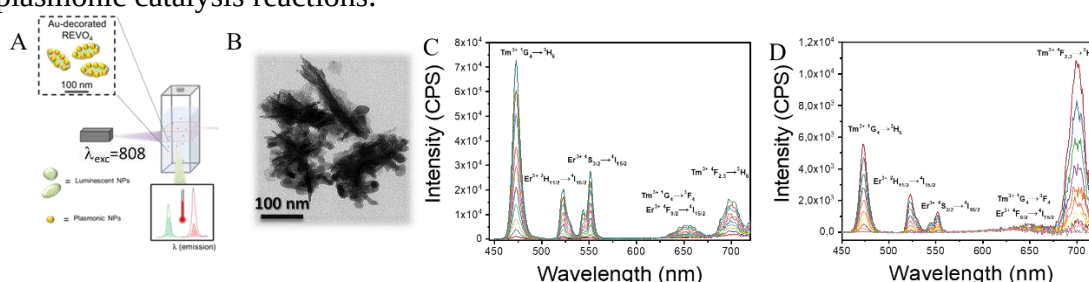


Figure 1. A. Illustration of the proposed nanoplateform (REVO₄-AuNRs) and B. TEM image of the real system. Power-dependent (3.16 – 34.9 W cm⁻²) emission spectra (λ_{exc}=808 nm) of C. (Y,Yb,Tm,Er)VO₄ and D. (Y,Yb,Tm,Er)VO₄-AuNRs.

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0.3.7 Bismuth-doped rare earth orthovanadates as tunable luminescence decay-time thermometers

Speaker: Fond Benoît

Bismuth-doped rare earth orthovanadates as tunable luminescence decay-time thermometers

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The unique electronic configuration of Bi^{3+} allows tuning of the optical and thermometric properties by carefully controlling the chemical composition of the host lattice. Previous studies on $\text{ScVO}_4:\text{Bi}^{3+}$ revealed that the phosphor exhibits an impressive relative temperature sensitivity of 2.2%/K at 37°C [1]. However, it has a low thermal quenching temperature ($T_{50\%}$) of about 342 K, resulting in a low emission signal at room temperature. In this work, we aim to tune the onset of thermal quenching by introducing Y^{3+} into the host matrix. The emission spectra of these Bismuth-doped orthovanadates have already been reported to shift with host composition modulation [2]. Thus, the aim of this work is to study the influence of the $\text{Y}^{3+}/\text{Sc}^{3+}$ ratio around the Bi^{3+} activator ion on the material's thermometric performance. In this work, we have synthesized a set of Bi^{3+} -activated orthovanadates with different $\text{Y}^{3+}/\text{Sc}^{3+}$ ratios. The XRD analysis revealed that the bond lengths steadily expand upon introducing more Y^{3+} into the host lattice, leading to a weaker crystal field intensity and a higher thermal quenching activation energy. The temperature-dependent lifetime curves shown in Figure 1 reveal that the onset of thermal quenching for these optical thermometers experiences a regular shift towards higher temperatures with a higher $\text{Y}^{3+}/\text{Sc}^{3+}$ ratio. From this work, we can tune the host composition to achieve an optimum luminescence signal and temperature sensitivity over a temperature range of -20°C to $+150^\circ\text{C}$.

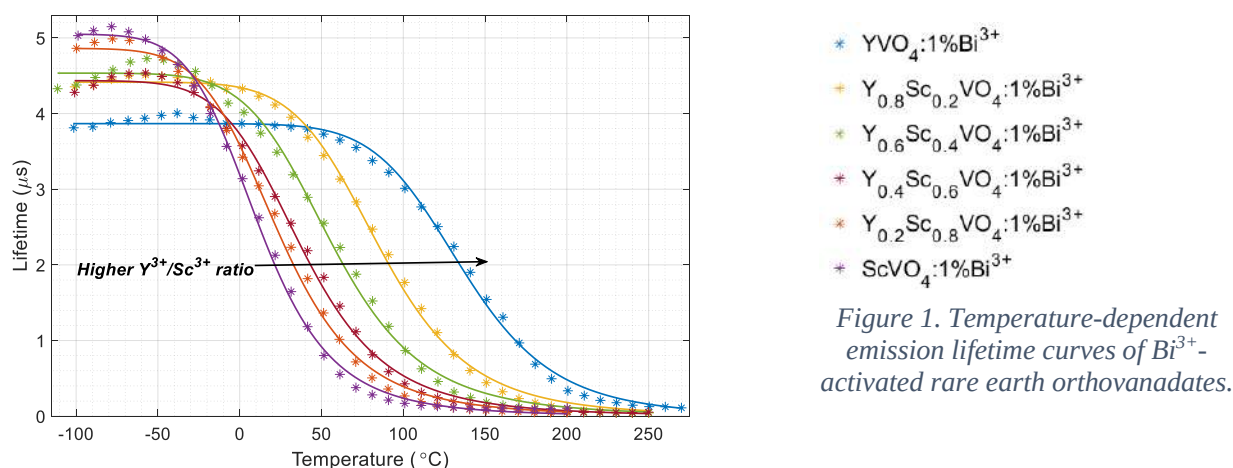


Figure 1. Temperature-dependent emission lifetime curves of Bi^{3+} -activated rare earth orthovanadates.

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0.3.8 Boltzmann Thermometry in Cr³⁺-Doped Oxides: The Structure Matters!

Speaker: Tanabe Setsuhisa

Boltzmann Thermometry in Cr³⁺-Doped Oxides: The Structure Matters!

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The performance of luminescent Cr³⁺-doped thermometers is strongly influenced by the locally surrounding ligand field. A universal relationship between the thermometric performance and structural/chemical parameters is highly desirable to drive the development of effective Cr³⁺-based thermal sensors avoiding trial-and-error procedures. In this view, as prototypes, the electronic structure and the thermometric performance of Cr³⁺-doped α -Ga₂O₃ and β -Ga₂O₃ polymorphs are compared. Combining a detailed theoretical and spectroscopic investigation, the electronic configuration and the crystal field (CF) acting on the Cr³⁺ in α -Ga₂O₃ are described for the first time and compared with β -Ga₂O₃: Cr³⁺ polymorph to discuss the thermometric behavior. A linear relationship between the ⁴T₂–²E energy gap (directly linked to the relative sensitivity) and the CF strength *Dq* is demonstrated for a wide variety of materials. This trend can be considered as a first step to set guiding principles to design effective Cr³⁺-based Boltzmann thermometers. In addition, as a proof of concept, particles of β -Ga₂O₃: Cr³⁺ thermometer are used to locally measure in operando thermal variations of Pt catalysts on β -Ga₂O₃: Cr³⁺ support during a catalytic reaction of C₂H₄ hydrogenation in a contactless and reliable mode, demonstrating their real potentials.

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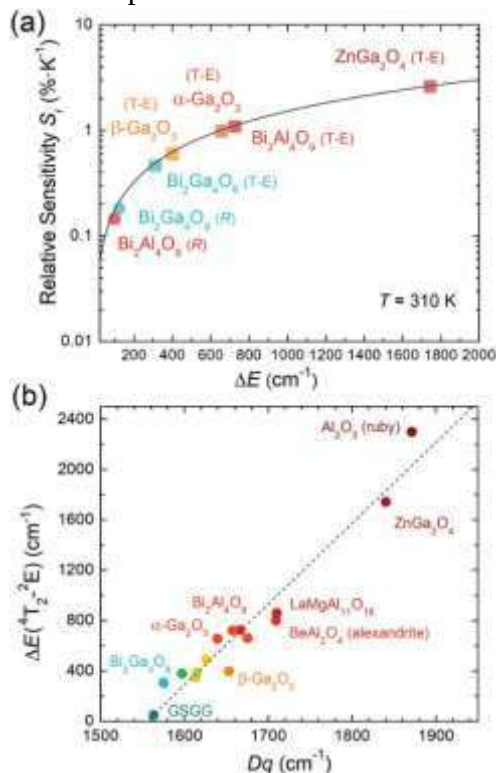


Fig.1. Performance of Cr³⁺-Boltzmann thermometers. **a)** Relative sensitivity as a function of the ⁴T₂–²E (squares) and R₁–R₂ (circles) energy gaps ΔE of Cr³⁺-activated thermometers and **b)** ⁴T₂–²E energy gap ΔE as a function of the experimental crystal field strength *Dq* for Cr³⁺-doped phosphors along with a linear fit.

0.3.9 Ce:LYSO as a blue luminescent concentrator

Speaker: Lopez Lisa

Ce:LYSO as a blue luminescent concentrator

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Luminescent concentrators (LC) allow to design new light sources combining high power and high brightness. So far, they have been developed from Ce:YAG [1]. It is possible to extend the luminescent concentrator concept to other wavelengths. Cerium-doped lutetium-yttrium oxyorthosilicate (Ce:LYSO) is a well-known single crystal scintillator used in medical imaging and security scanners. Recent developments of high power UV LED, matching its absorption band, opens the possibility to use Ce:LYSO in a new way: as LED-pumped solid-state light source. Since Ce:LYSO is available in large size crystals, we investigate its potential as a luminescent concentrator. Pumped by 768 UV LEDs which emit a peak power of 3400 W in pulsed regime (40 μ s, 10 Hz), a Ce:LYSO crystal delivers a broadband spectrum (60 nm FWHM) centred at 430 nm.

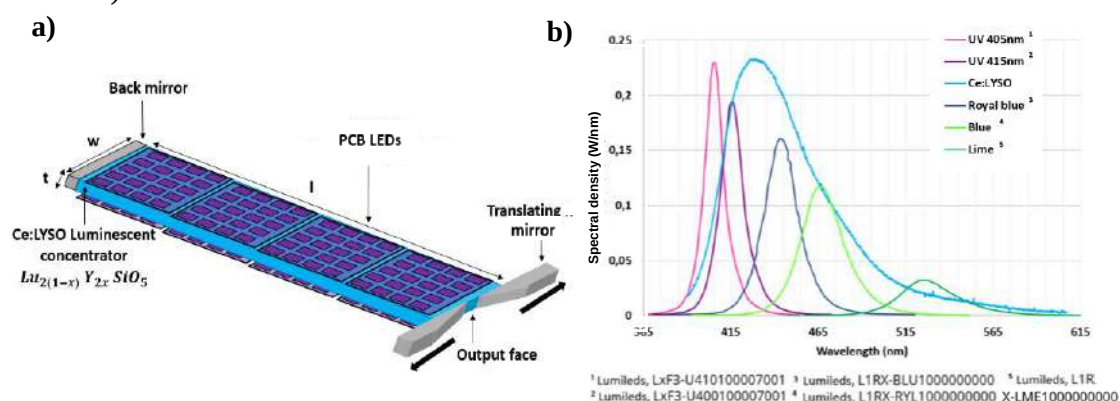


Fig. 1 a) Experimental setup of the LED pumped Ce:LYSO luminescent concentrator. The b-cut Ce:LYSO dimensions are $t=1$ mm, $w=22$ mm and $l=105$ mm. Beveled translating mirrors on the output face are used to adjust the output surface and the brightness [2]. **b)** Spectral density of Ce:LYSO LC (square output surface of 1 mm²) compared to different LEDs.

Ce:LYSO luminescent concentrator combines power and brightness at a level that is not reachable by any geometrical assembly of blue LEDs (Fig.1 b). This new powerful and bright source could address applications in the field of LED illumination. As LEDs, a Ce:LYSO concentrator is an incoherent source providing speckle noise free-illumination with a larger acceptability than laser sources regarding light safety limits. So, Ce:LYSO luminescent concentrator could be seen as an interesting way to "magnify" the blue LED in terms of brightness and spectrum.

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0.3.10 Coherent optical spectroscopy of $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ transparent ceramics

Speaker: Liu Shuping

Coherent optical spectroscopy of $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ transparent ceramics

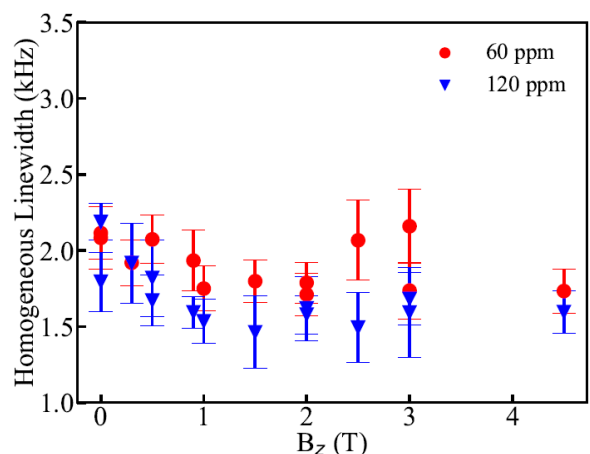
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Rare earth ion doped solid state materials possess stable physicochemical properties and excellent coherence properties, thus displaying unique potential in quantum information applications, especially in developing quantum storage devices. Compared with rare-earth doped single crystals, transparent ceramics have lower growth difficulty and more manipulation flexibility in size, shape and composition. In this work, we conduct an in-depth study on the high resolution and coherent spectroscopy of $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ transparent ceramics, in which the concentration of Eu^{3+} is 60 ppm and 120 ppm, respectively. Inhomogeneous linewidths as narrow as 4.7 GHz for the $^7\text{F}_0$ - $^5\text{D}_0$ transition are obtained, showing good crystalline quality of the ceramics. The homogeneous linewidth of both $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ ceramics is decreasing with applied magnetic field, reaching to ~ 1.5 kHz when magnetic field is 1.5 T at the temperature of 88 mK. This result is about 2 times narrower when compared to previously reported values¹. Furthermore, spectral hole lifetime more than 30 hours at 6.5 K is observed, which is long enough and comparable to $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ single crystals ever reported².



Magnetic field dependence of Γ_h for the $^7\text{F}_0$ - $^5\text{D}_0$ transition in $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ transparent ceramics.

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0.3.11 Coinage metal coordination polymers as luminescent sensors

Speaker: Ledoux Gilles

Coinage metal coordination polymers as luminescent sensors

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Coordination polymers made of coinage metals (Cu, Ag or Au) and thiolate linkers can form a wide variety of structures^[1-7] which implies strong changes in their optical properties.

The changes in linker functionality can generate a huge variety of 1D or 2D structures where the metal environment and the thiolate molecule disposition give rise to different optical transitions partly due to the metalophilic interactions. The change of metal can give rise to shifts in the luminescent spectra. Moreover, those systems can attain QY up to 90 % and show a strong dependency to temperature and to pressure making them interesting wireless sensors.

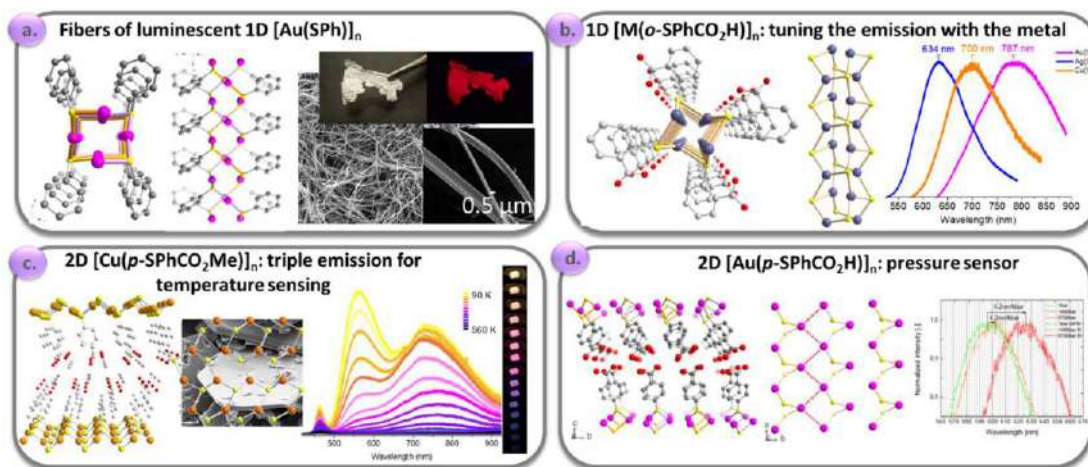


Figure 1 :examples of different structures of obtained coordination polymers: a. $[\text{Au}(\text{SPh})]_n$, b. $[\text{M}(\text{o-SPhCO}_2\text{H})]_n$ $\text{M} = \text{Cu}, \text{Ag}, \text{Au}$, c. $[\text{Cu}(\text{p-SPhCO}_2\text{Me})]_n$, and d. $[\text{Au}(\text{p-SPhCO}_2\text{H})]_n$ and examples of sensor applications: c. temperature sensing and d. pressure sensing.

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0.3.12 Combined multiconfigurational and TDDFT studies on the luminescence of f- and d-block metal complexes embedded in cyanido-based molecular materials

Speaker: Zychowicz Mikolaj

Combined multiconfigurational and TDDFT studies on the luminescence of f- and d-block metal complexes embedded in cyanido-based molecular materials

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In this contribution, we will present the fruitful conjunction of relativistic multiconfigurational and TDDFT-based *ab initio* methods for predicting luminescent properties of f- and d-block metal ions incorporated in functional molecular materials based on cyanido ligands.^{1–3} Both above-mentioned methodologies have proven their significant usefulness for investigating excited states and spectral properties of many molecular materials containing metal ions.^{3–7} However, both have their characteristic limitations and strengths compared to each other. By combining them we aimed to eliminate deficiencies in a particular area using the strength of the other method. Comprehensive studies on the successful conjunction of the multiconfigurational and TDDFT approaches will be presented using the following examples: a family of NIR-emissive [Yb^{III}(2,2'-bipyridine-1,1'-dioxide)₄]³⁺ complexes crystallizing with diverse cyanidometallates, various molecules based on [Re^V(N-nitrido)(L)(CN)₄]^{2–} moieties (**1** – with L of 1,2-diaminoethane, **2** – with L of 1,3-diaminopropane), and [Ir^{III}(R,R-pinppy)₂(CN)₂][–] (R,R-pinppy of 2-phenyl-4,5-pineno-pyridine) complex ions. Thus, we will present our approaches in the context of both f- and d-block metal complexes.

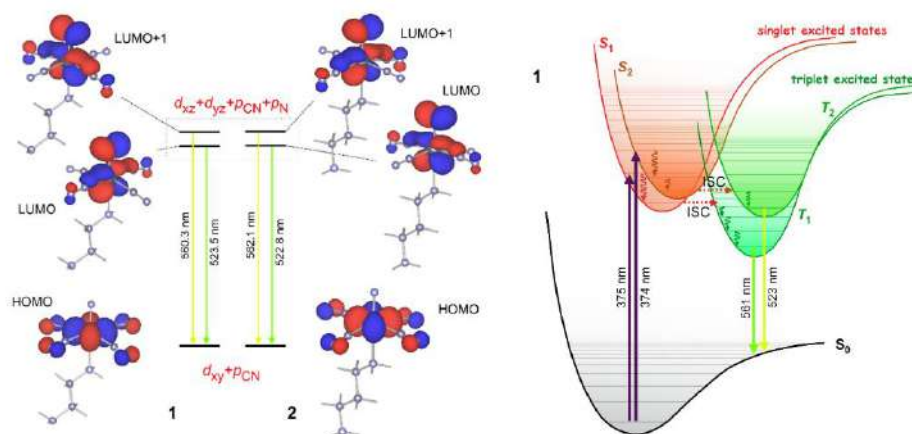


Fig. 1 Theoretical emissive properties of **1** and **2** with the postulated mechanism of excitation.

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0.3.13 Comparison of the luminescence response of porphyrins and ruthenium complex-based pressure sensitive paints under nanosecond laser pulses and microsecond LED pulses

Speaker: Le Bourgeois Orian

Comparison of the luminescence response of porphyrins and ruthenium complex-based pressure sensitive paints under nanosecond laser pulses and microsecond LED pulses

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Surface pressure measurements are to improve the aerodynamics of vehicles, i.e. to minimise their drag. Pressure is usually measured locally by pressure taps but the multiplication of these taps to achieve acceptable pressure fields is costly and not always possible depending on the models tested. Pressure Sensitive Paint (PSP) is an optical measurement technique using luminophore molecules that provides global pressure distribution with high spatial resolution. After the diffusion of oxygen molecules in the paint binder the luminescence is quenched by energy transfers, thus, the intensity and life-time of the luminescence are pressure dependent [1]. For excitation, LEDs are commonly used. However, for measurements on rotating engine blades, the light pulse has to be short ($<20\mu\text{s}$) to avoid motion blurring [2]. Under this restriction, nanosecond pulse lasers are able to deliver two orders of magnitude higher pulse energies but at fixed wavelengths (355 and 532 nm). The goal of this study is to compare the pressure sensing performance under both type of excitation, this includes the emission intensity, pressure sensitivity and photostability. As presented in Figure 1, the laser excites the platinum porphyrin PSP 8 times less efficiently than the blue LED. This is partially due to the different wavelengths, but the duration of the pulse also plays a role as shown in the comparison with the green LED. The laser excitation can however provide far higher fluence levels and the PSP emission intensity only starts to exhibit a weak saturation behaviour at $0.5\text{mJ}/\text{cm}^2$. The study also compares the impact of the pulse duration at fixed energy on the photodegradation and investigates whether the laser provides the same pressure sensitivity as the LEDs.

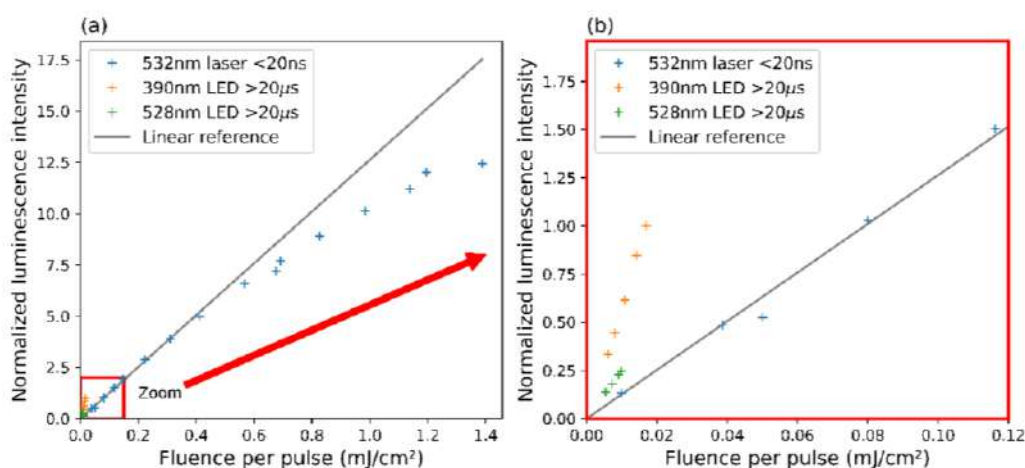


Figure 1: Luminescence intensity of platinum porphyrin-based PSP under different sources of illumination (UV LED 390nm, green LED 528nm and green laser 532nm). (a) represents the whole energy range while (b) is a zoom at low energy.

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0.3.14 Composition engineered Sc-admixed GGAG:Ce single crystal

Speaker: Zapadlík Ondřej

Composition engineered Sc-admixed GGAG:Ce single crystal

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Very recently, the Sc-admixed garnets have become of interest as the Sc energy levels shift down the edge of conduction band similarly to the Ga ones, i.e., the band-gap engineering is accessible with the supposed similar favourable effect on electron traps. Additionally, the ongoing rapid surge in the price of iridium significantly increased the production cost of GGAG:Ce [1], one of today's most competitive oxide scintillation material.

The substitution of Ga with Sc in GGAG host allows in principle the use of cheaper Mo crucible-based technology and by applying similar approach of band-gap engineering with fine stoichiometry tuning we focus on the development of such a novel GSAG-based scintillator to find its performance limits.

In our work [2], we managed to grow the GSAG:Ce single crystal from Mo crucible in the hydrogen-containing reduction atmosphere and evaluate it for the first time. We also compared the properties with the Ir-crucible grown crystal. We have further conducted studies to improve the scintillation performance of GSAG:Ce by Mg²⁺ codoping and fine-tuning through Ga-admixture.

We present an overall characterization of the optical and scintillation properties of various Sc-admixed multicomponent single crystals grown using the micro-pulling-down method.

Acknowledgement.

This research is supported by Czech Science foundation project no. 21-17731S.

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0.3.15 Controlling the luminescence of two-dimensional materials using tunnelling electrons

Speaker: Le Moal Eric

Controlling the luminescence of two-dimensional materials using tunnelling electrons

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A scanning tunneling microscope (STM) is used to electrically activate the luminescence of two-dimensional (2D) materials within a nanoscale tunnel junction, in order to spatially resolve the variations of the excitation quantum efficiency on the nanometer scale. An optical microscope and spectrometer is used to spatially, angularly, and spectrally resolve the emitted light, in order to investigate the emission processes and identify the involved excitonic species (see Fig. 1a-c). In this way, we demonstrated the STM-induced generation of neutral and charged excitons in monolayer transition metal dichalcogenides (MoSe₂ and WS₂) [1,2]. Recently, we showed that the tip and tunneling current of an STM can also be used to control the quantum yields of photoluminescence in 2D semiconductors [3] (see Fig. 1d,e).

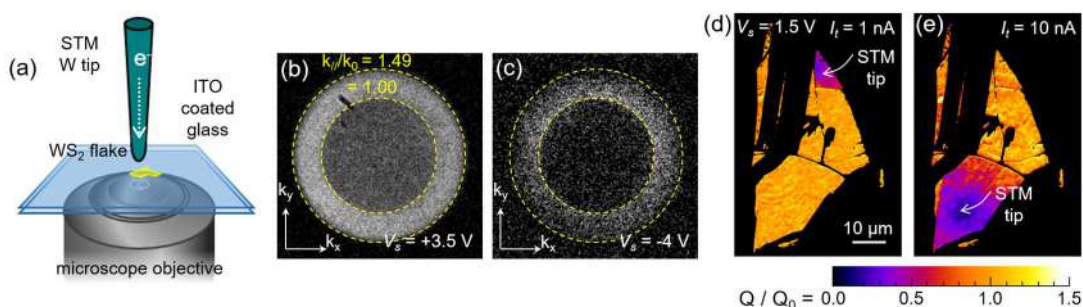


Figure 1. (a) Schematics of the experiment, showing the STM tip and the objective of the optical microscope. (b,c) Angular distribution of the STM-induced luminescence of monolayer WS₂ at positive and negative sample bias, respectively [2]. (d,e) False-color optical microscopy images showing the STM-controlled modification of the quantum yield of photoluminescence (Q) of monolayer WS₂ [3].

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0.3.16 Cooperative states of pair Nd^{3+} optical centers in crystals with fluorite structure and their use for CNOT quantum gate

Speaker: Orlovskii Yuri

Cooperative states of pair Nd³⁺ optical centers in crystals with fluorite structure and their use for CNOT quantum gate

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Pair optical centers or dimers are formed in a significant amount in crystals with fluorite structure like CdF₂, CaF₂, and SrF₂ doped by Nd³⁺ ions at a total concentration of dopant ions less than one percent. They consist of two closely spaced Nd³⁺ ions and two charge-compensating F⁻ ions in the nearest interstitials. The distances between the Nd³⁺ ions are 0.381, 0.386, and 0.410 nm, respectively [1, 2]. The quadrupole and forced dipole electronic transitions between the ground ⁴I_{9/2} and excited ⁴G_{5/2} states of the Nd³⁺ ion have a very high rate due to very large reduced matrix elements $U^{(2)}$ and $U^{(4)}$. This makes it possible to form quantum-entangled cooperative states of pair optical centers of the Nd³⁺ ion.

The oxygen-free 0.1%Nd³⁺:CdF₂, 0.6 and 0.03%Nd³⁺:CaF₂, and 0.5%Nd³⁺:SrF₂ crystals were grown by the Bridgman-Stockbarger technique in fluorine atmosphere. Exciting these crystals by pulsed tunable laser with narrow line of 0.15 cm⁻¹ and using time-resolved site-selective fluorescence laser spectroscopy, we measured the fluorescence excitation spectra of the quantum entangled one-exciton ⁴G_{5/2}(1) x ⁴I_{9/2}(1) cooperative state of the pair centers of Nd³⁺ at $T = 6.5$ K monitored in the near IR. Using two-color laser excitation, we measured the excitation spectra of non-entangled two-exciton ⁴G_{5/2}(1) x ⁴G_{5/2}(1) cooperative states monitored in the near UV. We observed a large splitting of the one-exciton state from 1.9 to 3 cm⁻¹ depending on the type of the host. Unexpectedly, the largest splitting was found in Nd³⁺: SrF₂ [3] with the largest distance between the ions in the pair, and the smallest in Nd³⁺: CdF₂ with the shortest.

We found that the large splitting of the one-exciton cooperative state of the pair centers is due to the exchange of electronic excitation between the excited and ground states ⁴I_{9/2}(1) ↔ ⁴G_{5/2}(1) with spin flip determined by quadrupole-quadrupole and forced dipole-dipole interactions. The rate of excitation exchange depends on the distance between the ions in the pair as R^{-5} for quadrupole-quadrupole and as R^{-11} for forced dipole-dipole interaction. Their contributions are differ in sign. This explains the experimentally observed dependence of the splitting of the one-exciton state on the distance R opposite to the expected one.

The pair centers in the one-exciton state, in contrast in the ground and two exciton states, have a nonzero dipole moment and interact strongly. This allows using two pair centers in Nd³⁺-doped fluorite-type crystals as fast (GHz) CNOT quantum gates.

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0.3.17 Core-multishell luminescent nanoparticles for asynchronous excitation and detection at 800 nm

Speaker: Passini Luan

Core-multishell luminescent nanoparticles for asynchronous excitation and detection at 800 nm

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One of the challenges of recent years in *in vivo* imaging is the development of probes that are sufficiently effective for in depth exploration of biological tissue while instigating little to none biological harm. Due to the absorption properties of the *in vivo* terrain, the near infrared portion of the spectrum is extremely advantageous, especially for fluorescent imaging. This region is known as the maximum transparency of the biological window, i.e., good penetration depth, reduced auto-fluorescence and tissue scattering.^[1] Potentially multifunctional, nanoparticles (NPs) are great candidates for imaging technologies. Upconverting nanoparticles (UCNPs), Ln³⁺-based NPs, are very attractive candidates due to narrow emission bands, long-lived lifetimes, and their anti-Stokes emission. Herein, we have proposed Ln³⁺-based core-multishell UCNPs towards excitation and emission at 800 nm. To achieve such an ambitious goal, multilayered UCNPs were engineered, relying on the Nd-Yb-Tm triad embedded in NaYF₄ matrix.^[2] These UCNPs were strategically designed as a three-layer structured material; Yb-Tm (core); Yb (shuttle); Nd-Yb (outer shell) to prevent cross relaxations between Nd and Tm.^[3] Thus, the energy collected upon Nd excitation at 808 nm migrates to the core carried by Yb throughout the nanoparticle, and eventually feeds Tm's excited states, among which ³H₄ leads to the most intense emission at 802 nm. In this presentation, we will show the synthesis of the core-multishell UCNPs and the time-gated detection analysis setup and the time-resolved luminescence analysis, which allowed us to reconstruct the entire emission spectrum between 300 and 1000 nm (thus overlapping the excitation wavelength) (Figure 1a and 1b respectively). Finally, we will present the first application of this concept in a microscopic cellular imager.

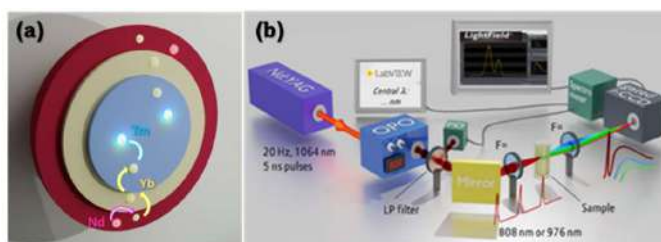


Figure 1. The core-multishell structure showing the segregation of Nd and Tm ions, with Yb ions acting as energy shuttles (a), time-gated detection setup illustration (b).

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0.3.18 CTH:YAG as a luminescent concentrator in the SWIR

Speaker: Lopez Lisa

CTH:YAG as a luminescent concentrator in the SWIR

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CTH:YAG is a laser medium known for many years. Thanks to efficient energy transfer between Cr^{3+} , Tm^{3+} and Ho^{3+} , CTH:YAG has often been pumped in the visible by flashlamps. Sensing and inspection applications are growing with the emergence of low-cost image sensors in the SWIR (Short Wave InfraRed) range. The purpose of this work is to show that CTH:YAG opens opportunities for innovative, high-brightness, spectrally-broadband and incoherent sources in the SWIR. As visible pump source, we used a Ce:YAG luminescent concentrator (LC) [1], since CTH:YAG absorption band matches the Ce:YAG yellow emission. A Ce:YAG is pumped by 2240 blue LEDs (Fig.1a). A $1 \times 3 \times 14 \text{ mm}^3$ CTH:YAG is bonded on the output surface by an UV-curing optical adhesive. Total internal reflections are preserved by the index difference between CTH:YAG ($n=1.82$) and the adhesive ($n=1.5$). Therefore, we have a cascade of concentrators and CTH:YAG can be considered as a secondary LC. To enhance the brightness and the extraction efficiency an edge face ($1 \times 1 \text{ mm}^2$) is used with mirrors on the lateral faces [2] (Fig.1 a).

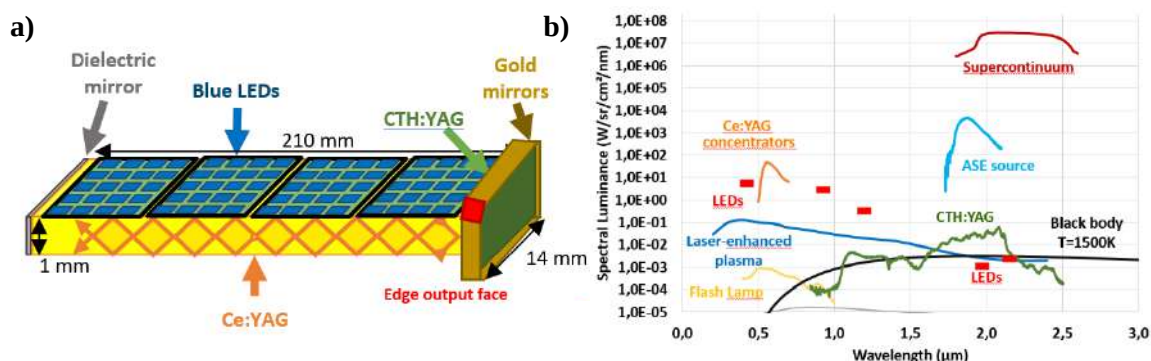


Fig. 1 a) Scheme of the cascade of concentrators with blue LEDs pumping Ce:YAG slab that pumps CTH:YAG crystal with an edge face (in red) and gold mirrors coated on all other lateral faces (in brown). **b)** State of the art of incoherent sources spectral luminance in the SWIR.

The first Ce:YAG LC delivers a peak power of 730 W towards the 2nd CTH:YAG LC. The spontaneous emission from the output face has a peak power of 340 mW on a spectrum extending from 1.6 μm to 2.1 μm (Fig.1 b). Despite a low efficiency, the spectral brightness is 20 times higher than the one of a black body at $T=1500 \text{ K}$ and approximately 25 times higher than commercial LEDs operating in this wavelength range. Performance are still far below ASE source. This first result proves that a LED pumped cascade of concentrators has a potential for alternative SWIR incoherent sources with applications like sensing and inspection.

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0.3.19 Cyanido metal complexes as a source or support for multifunctional molecule-based luminescent materials

Speaker: Chorazy Szymon

Cyanido metal complexes as a source or support for multifunctional molecule-based luminescent materials

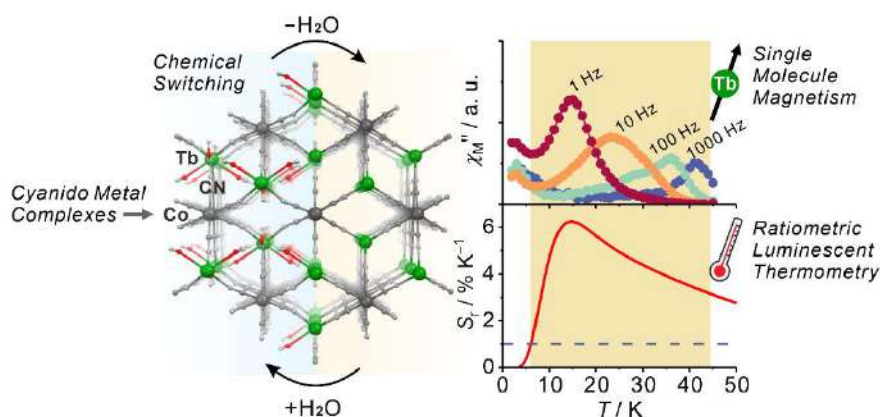
Szymon Chorazy,¹ Jakub J. Zakrzewski,¹ Mikołaj Zychowicz,¹ Junhao Wang,² Yue Xin,² Koji Nakabayashi,² Shin-ichi Ohkoshi,² Robert Jankowski,¹ Michal Liberka,¹ Maciej Wyczęsany,¹ Jan Rzepiela,¹ Tomasz Charytanowicz,¹ Paweł Bonarek,¹ Agnieszka Puzan,¹ Aleksander Hoffman,¹ Kseniia Boidachenko,¹

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Multifunctional molecule-based materials combine various physical functionalities, including optical, magnetic, mechanical, or electrical ones, within a single phase. They are promising candidates for highly efficient and miniaturized devices, offering also the perspectives for new coupling physical effects that come from the conjunction of a few different at the molecular level. The trend of multifunctionality concerns also the luminescent materials based on molecules, such as metal complexes. We present our recent findings in the design of multifunctional luminescent materials linking optical effects, such as sensitized tunable photoluminescence and optical thermometry, with other physical functionalities, including chirality, single-molecule magnetism, and switching of physical properties by chemical stimuli. We present our synthetic strategy relying on the application of diverse transition metal cyanido complexes as a source or support for the construction of solid luminophores of multifunctional character.^{1–5} This will be shown on a few representative examples, e.g., the combination of Tb(III) centers with hexacyanidocobaltate(III) ions leads to the novel coordination framework showing the chemically switchable conjunction of high-performance single-molecule magnetism and ratiometric luminescent thermometry (figure below).



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0.3.20 Design of hybrid optical temperature sensors based on luminescent and thermochromic materials

Speaker: Pawłów Jakub

Design of hybrid optical temperature sensors based on luminescent and thermochromic materials

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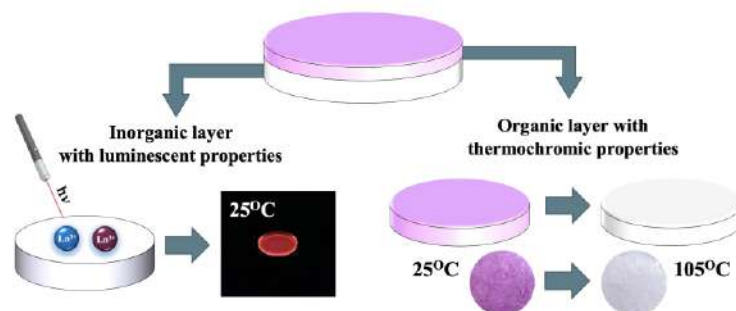
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Temperature is one of the fundamental physical quantities and is used for measuring the internal thermal energy state of a substance. Unfortunately, most temperature-measuring devices, like pyrometers or thermal imaging cameras, are characterized by low resolution and accuracy of the temperature reading or the need to connect the temperature sensor with the recording system.

The alternatives to these devices are well-known luminescent thermometers, based on inorganic nanoparticles doped with lanthanide ions [1], however, luminescence detection is still required for precise temperature readings. The solution to this problem is an innovative concept of fusing them in a hybrid combination with thermochromic organic dyes. The use of organic dyes will visually show whether the temperature of the measured object is still within limits or has reached critical values, while the accurate measurement of the temperature is ensured by recording the luminescence of doped inorganic nanoparticles.



The idea behind a hybrid temperature sensor, consisting of luminescent inorganic and thermochromic organic layers.

In this research, we present the design, preparation, and analysis of structural as well as spectroscopic properties of inorganic nano-particles fused with thermochromic materials. Combining these two types of materials on one platform will enable quick temperature measurement using the advantages of the luminescent inorganic component in the form of inorganic nano-sized phosphates REPO_4 co-doped with Nd^{3+} and Yb^{3+} ions, and the thermochromic organic dyes, from the group of fluoranes or spirolactones. The combination of thermochromic mixtures that show a color change under the influence of temperature and inorganic phosphates doped with lanthanide ions is still unexplored, while it may change perspective in designing future hybrid optical temperature sensors.

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Acknowledgements

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0.3.21 Determining the Luminescence Quantum Yields of Molecular, Nanocrystalline, and Particle Emitters in the UV/vis/NIR/SWIR

Speaker: Resch-Genger Ute

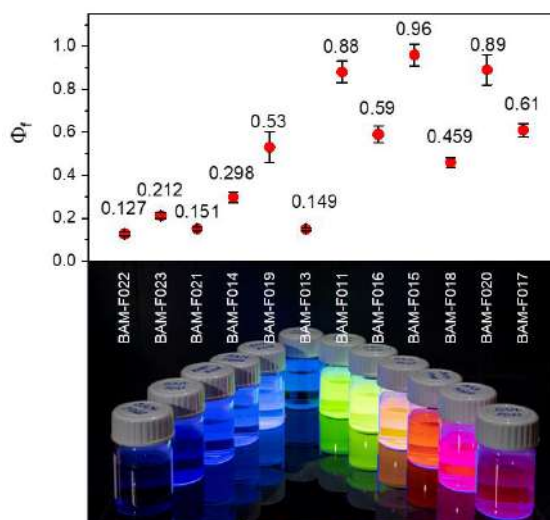
Determining the Luminescence Quantum Yields of Molecular, Nanocrystalline, and Particle Emitters in the UV/vis/NIR/SWIR

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The rational design of molecular and nanoscale reporters and functional luminescent materials, photophysical and mechanistic studies, and the comparison of different emitters rely on accurate and quantitative photoluminescence measurements. Particularly the reliable determination of the key performance parameter luminescence quantum yield (Φ_f), the number of emitted per absorbed photons, and the brightness are of special importance for luminescence applications in the life and material sciences and nanobiophotonics.[1] In this context, examples for absolute measurements of luminescence quantum yields of UV/vis/NIR/SWIR emissive organic dyes, semiconductor quantum dots, and lanthanide upconversion nanocrystals in transparent matrices are presented including excitation wavelength and power density dependent studies.[2,3] Also, procedures for the determination of luminescence quantum yields of scattering particle dispersions and solid luminescent materials like perovskites are shown.[4] Thereby, pitfalls, achievable uncertainties, and material-specific effects related to certain emitter classes are addressed. Moreover, a set of UV/vis/NIR quantum yield standards is presented including their certification with a complete uncertainty budget.[5]



Set of certified UV/vis/NIR luminescence quantum yield standards.

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0.3.22 Development of Red-emitting Garnet Nanoparticle Scintillators

Speaker: Koshimizu Masanori

Development of Red-emitting Garnet Nanoparticle Scintillators

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Scintillators are phosphors that emit scintillation upon irradiation and widely used for radiation detection in combination with photon detectors such as photomultiplier tubes. Recently, novel applications have emerged for scintillators in addition to the conventional use for radiation detection. One application is the use of scintillators in living bodies to achieve efficient emission inside the living bodies induced by irradiation from outside: an example of such applications is use of scintillator microparticles coupled to neurons to control the behavior of mouse using X-ray irradiation from outside [1]. In this study, to widen the use of scintillators inside living bodies, we have developed red-emitting scintillator nanoparticles for two reasons: one is to deliver scintillators inside living bodies in a less invasive manner, and the other is to use in combination of various photoreceptors which have absorption in the red wavelength region. We chose $\text{Gd}_3\text{Al}_{5-x}\text{Ga}_x\text{O}_{12}$ (GAGG) and $\text{TbAl}_y\text{Ga}_{5-y}\text{O}_{12}$ (TbGG) as the host compounds and Eu, Pr, or Sm as the dopants. The excitation-emission contour plot of Eu 5mol%-doped GAGG nanoparticles is presented in Figure 1. Among the samples with different host compositions, dopant ions, and dopant concentrations, the highest photoluminescence quantum yield of 98% was obtained for the nanoparticles.

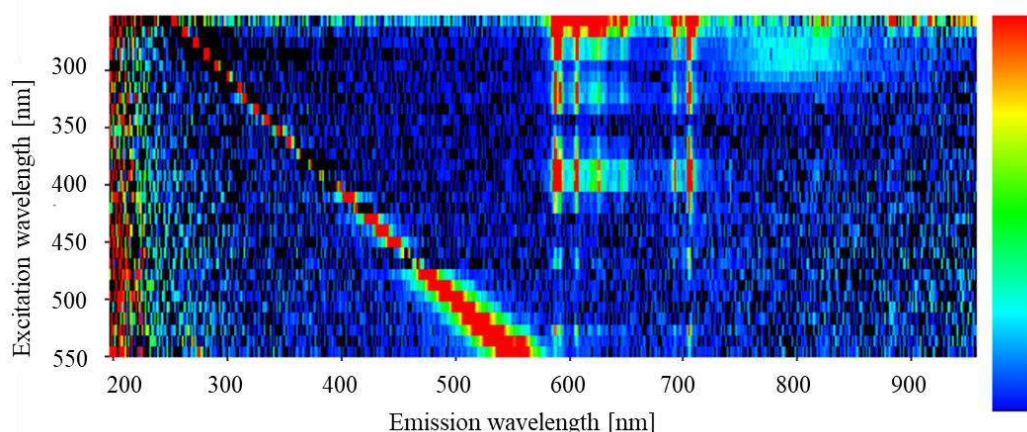


Figure 1. Excitation-emission contour plot of Eu 5mol%-doped GAGG nanoparticles.

Reference

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0.3.23 Dual chromogenic and fluorogenic detection of organophosphorus pesticides: Application of luminescence for organophosphorus pesticides prohibited by European Union, comparison between fluorogenic and chromogenic response on impregnated substrates

Speaker: Termeau Lucile

Dual chromogenic and fluorogenic detection of organophosphorus pesticides

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Despite the ban on most organophosphorus pesticides at European Union level, their use throughout the world is still a public health issue. They are mostly used as insecticides in agriculture, in home and garden, for maintenance of public spaces and forests, or for veterinary practices. Chlorpyrifos, malathion, parathion and many other organophosphorus compounds are classified by the ONG Pesticide Action Network (PAN) as highly hazardous pesticides (HHPs).[1] Just like organophosphorus chemical warfare agents, organophosphorus pesticides are inhibitors of acetylcholinesterase enzyme (AChE) what makes them neurotoxic agents. The use of organophosphorus pesticides is likely to lead to long-term effects such as endocrine disruption, asthma, carcinogenicity or chronic neuropsychological dysfunction. [2,3] Moreover, organophosphorus pesticides are implied in many cases of self-poisoning suicide in rural areas.[4]

These last years, chromogenic and fluorogenic sensors have attracted great attention due to low cost, portability, and easy operation. Recent publications highlight the interest of using both colorimetry and luminescence as a tool for sensing and identifying organophosphorus compounds.[5,6]

The interaction between an organophosphorus pesticide and a luminescent probe can cause either a disappearance (“turn-off”) of the luminescence signal, either the appearance (“turn-on”) of a new luminescence signal either a shift of the initial luminescence signal. The incorporation of the luminescent probe into a solid-state substrate without degrading the sensing properties of the probe is a key point in the development of a detection system. The aim of this communication is to present luminescent probes that also present a color shift under daylight after exposition to liquid organophosphorus pesticides, and their incorporation into different solid-state substrates without degrading the luminescence features. The emission and excitation spectra will be presented and discussed. The results obtained with a portable system will be displayed. The colorimetric and fluorometric detection properties of the solid-state substrates will be compared.

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0.3.24 Dual-window Detection Using Persistent Nanophosphors for Anti-counterfeiting and Bio-imaging

Speaker: Cai Guanyu

Dual-window Detection Using Persistent Nanophosphors for Anti-counterfeiting and Bio-imaging

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Real-time fluorescence materials are susceptible to give interferences under constant excitation producing therefore high level background signal during the sensing and imaging applications¹⁻². Our previous works based on ZGO and ZGSO show persistent luminescence (PersL) property offering great potential for bio-imaging and anti-counterfeiting applications³⁻⁶. To further improve the efficacy of PersL materials, we prepared a new composition, Cr³⁺ and Ni²⁺ co-doped ZGSO and evaluated the effect of co-dopants on the signal intensity and emission wavelength. For this purpose, we propose spinel compound Zn_{1.3}Ga_{1.39}Ni_{0.005}Cr_{0.005}Sn_{0.3}O_{3.995} nanoparticles (ZGSO:Ni²⁺,Cr³⁺ NPs) prepared by hydrothermal synthesis. Their excitation spectrum broadly covers the UV and visible ranges (up to ~ 600 nm). ZGSO:Ni²⁺,Cr³⁺ NPs exhibit dual-emission at 700 nm and 1300 nm for several minutes after removal the UV or red LED excitation (see figure 1b). Due to a Cr/Ni energy transfer, ZGSO:Ni²⁺,Cr³⁺ NPs show stronger PersL in regard to ZGSO:Ni²⁺ NPs after UV/LED excitation, which could supports the use of ZGSO:Ni²⁺,Cr³⁺ for bio-imaging and anti-counterfeiting applications in dual-windows.

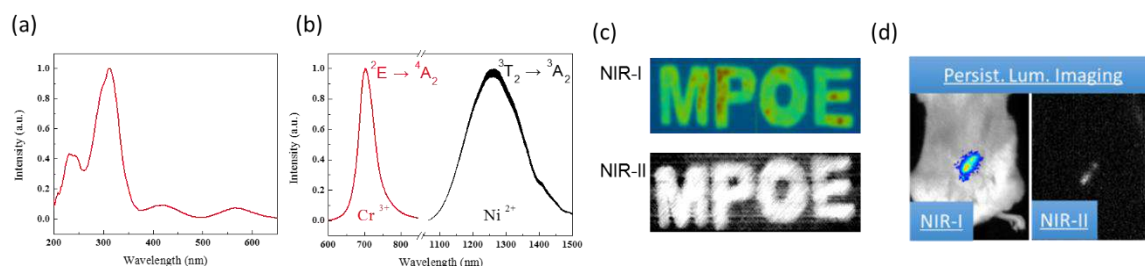


Fig 1. (a) PLE and (b) PersL spectra of ZGSO:Ni²⁺,Cr³⁺ NPs. (c) anti-counterfeiting application and (d) PersL imaging results based on ZGSO:Ni²⁺,Cr³⁺ NPs in NIR-I and NIR-II windows with Si and InGaAs camera respectively. PLE spectrum in (a) is obtained from dry NPs with emission at 700 nm. PersL spectra in (b) and images in (c-d) started 1 min after removal of excitation.

Dual-windows detection could be interesting for anti-counterfeiting and bio-imaging, as presented in Figure 1 (c and d). Unfortunately the sensitivity of the NIR detector is far below the Si-CCD and therefore the NIR PersL signal of the NPs should be further enhanced. Using Er³⁺ as co-dopants⁶ and other excitation source could be a possible strategy, for example, X-ray could be also tested as excitation source to enhance the signal⁷.

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0.3.25 Dynamics of Photocarrier in TiO₂ anatase: a collision process with a thermal activation

Speaker: Girault Adrien

Dynamics of Photocarrier in TiO₂ anatase: a collision process with a thermal activation

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When an anatase TiO₂ crystal is excited in the UV (3.8 eV) at low temperature (10K), a shifted broad photoluminescence emission band centered at 2.3 eV appears [1]. This signal is quenched when the temperature increases [2]. Several interpretations of this behaviour involving excitons or polarons have been proposed [3].

This work aims at clarifying the dynamics of the carriers within anatase TiO₂ by studying the time decay of the photoluminescence (PL). The emission of samples excited by 200fs pulses at 3.8eV is measured at different temperatures using a streak camera. Our data cover a large time range, from 10ps up to 10ms, with a PL intensity varying over 5 orders of magnitude. We observe that, at any temperature, nearly the whole decay profiles can be fitted with a power law: this is a clear signature that a collision process governs the carrier dynamics without involving any supplementary process. We analyse these results considering the specific features of TiO₂. First, a very large carrier-lattice interaction leads to the formation of polarons and self-trapped excitons and is responsible for the very large Stokes shift of the emission at 2.3eV. Second, the indirect gap of anatase TiO₂ allows a fast separation of electron and holes in the reciprocal space, avoiding direct recombination and creating a reservoir. We propose that recombination can occur only after spatial diffusion of the photoexcited carriers before their collision and recombination. The dynamics becomes faster when the temperature increases, showing that the collision process is thermally activated.

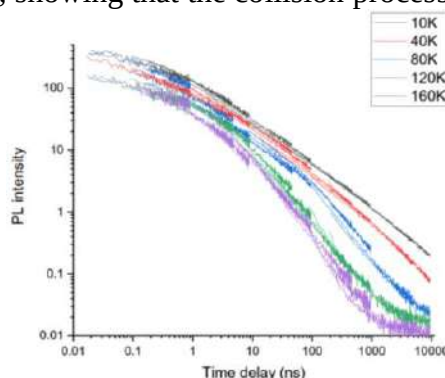


Fig. 1: Photoluminescence decay of TiO₂ anatase at various temperature

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0.3.26 Dynamics of the power-dependent up-conversion luminescence in Er³⁺/Yb³⁺ co-doped single nanocrystal

Speaker: Zebrowski Michal

Dynamics of the power-dependent up-conversion luminescence in Er³⁺/Yb³⁺ co-doped single nanocrystal

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This work analyzes the dynamics of the red up-conversion luminescence ($^4F_{9/2} \rightarrow ^4I_{15/2}$) in Er³⁺/Yb³⁺ co-doped single nanocrystals (NCs) under varying laser excitation power. A confocal luminescence microscope was used to collect the red luminescence transients of Er³⁺, which was activated at 980 nm. First, we noticed a strong correlation between the shape of the transient and the excitation laser power. For low laser power, c.a. 100 μ W, we observed a distinct rising part preceding a decay profile. However, for high laser power, c.a. 1 mW, the rising part was not present, and transient intensity peaked promptly. Interestingly, the estimated average luminescence decay time decreases with increasing laser power. Moreover, we observed modification of Yb³⁺-Er³⁺ energy transfer rates along with laser power.

In order to explain this phenomenon, we discuss a semi-empirical model of kinetic rate equations of the Er³⁺/Yb³⁺ system. We show that the dominant contribution in the excitation process comes from the nonradiative energy transfer from Yb³⁺ to Er³⁺, contributing to the rising part of the transient in the case of low laser power. However, for high laser power, up-conversion is mainly activated via direct absorption of photons in the ground and excited state absorption processes, causing a sharp increase in the emission intensity. To explain the shape of the decay curves, we introduced an additional nonradiative deexcitation channel depopulating the $^4F_{9/2}$ level. We attributed this effect to the interaction between Er³⁺ ions and surfactants stabilizing the NCs. We also verified this concept experimentally by coating NCs with an optically passive shell limiting surfactant activity. Eventually, we show that mentioned energy transfer rate variations can be explained by the local temperature changes activated by the laser, disturbing phonon statistics. Finally, the proposed model allowed us to estimate correct fits to the experimental luminescence decay profiles and extract the power-independent, pure radiative lifetime of $^4F_{9/2}$ level and energy transfer rates. We found the presented approach valuable for advanced analysis of the up-conversion processes dynamics.

This research was financed from Project no. 2017/26/E/ST3/00209 founded by the National Science Centre, Poland.

0.3.27 Effect of plasmonic chains on the photoluminescence of a MoS₂ monolayer

Speaker: Fernández-Martínez Javier

Effect of plasmonic chains on the photoluminescence of a MoS₂ monolayer

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Among low dimensional materials, monolayer (1L) Transition Metal Dichalcogenides (TMDs) are promising candidates for the development of next-generation optoelectronics due to their direct optical gap and atomic thinness. TMD electronic properties can be readily tuned employing strain or electrostatic gating, to name some examples.

Here, we analyse the photoluminescent properties of 1L MoS₂ deposited on top of plasmonic chains of closely spaced Ag nanoparticles (NPs) formed on the domain wall surfaces of a ferroelectric crystal. These NP chains support a spectrally broad plasmonic resonance centred at around 600 nm, overlapping the A and B excitonic transitions of MoS₂. Scanning photoluminescence (PL) microscopy is employed to elucidate the effect of plasmonic chains on the MoS₂ emission. The results show that the PL spectrum of 1L MoS₂ is altered in the vicinity of the plasmonic chains, causing a redshift of the A exciton along with an increase in the contribution of trions to the PL spectrum. The influence of both strain gradient and electron hot transfer are discussed to account for the observations.

The results show the potential of integrated plasmonic-ferroelectric-2D semiconductor platforms for the enhancement of strain driven quasiparticle confinement phenomena, opening a pathway for quantum emitters in 2D strained systems.

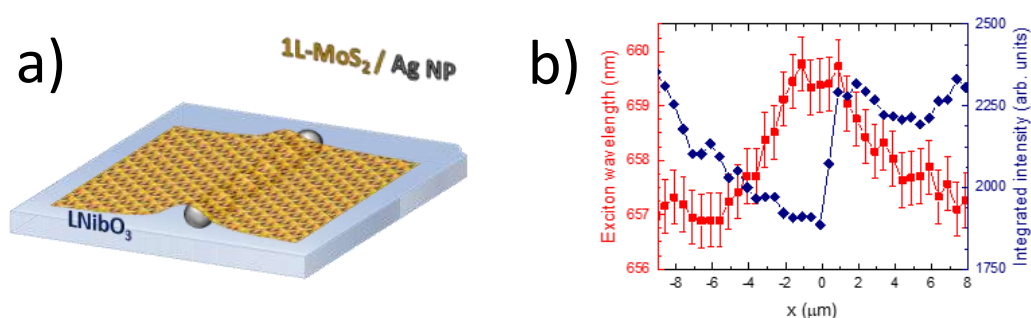


Figure: a) Schematic of the MoS₂ monolayer deposited on a plasmonic Ag NP chain. b) Redshift of the A exciton transition (red) and integrated intensity of MoS₂ emission (blue) in the vicinities of the plasmonic chain

0.3.28 Effects of alloy disorder and growth inhomogeneities on the luminescence of semiconductor nitride devices

Speaker: Fornos Camille

Effects of alloy disorder and growth inhomogeneities on the luminescence of semiconductor nitride devices

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Semiconductor nitrides are used in light-emitting diodes (LEDs) for lighting [1,2] since they emit over a wide spectral range with particularly high efficiencies in the blue. The active regions of these devices are InGaN quantum wells (QWs) which exhibit emission spectra much broader than expected. The cause of this broadening is widely debated in the literature but often it is attributed to spatial fluctuations of the emission energy which are due either to the intrinsic compositional disorder of the ternary alloys or to extrinsic growth inhomogeneities. These different causes of fluctuations occur on very different characteristic scales: a few nm for the alloy disorder and a few hundred nanometers (or more) for the growth inhomogeneities. To distinguish the different sources of broadening, it is therefore necessary to probe the radiative recombination processes down to the nanoscale. To do this, we have developed an approach based on tunneling electroluminescence micro-spectroscopy (STLM) [3].

In STLM electrons are locally injected from the STM tip into a QW located a few nm below the surface. The resulting electro-luminescence peak position (E_1) as a function of the tip position is shown in Fig. 1(a). It is thus possible to map in parallel the topography of the sample surface (see Fig. 1(b)) and the electro-luminescence spectrum (see Fig. 1(c)). From the obtained spectra, maps showing the spatial fluctuations of different quantities can be produced such as the emission energy (Fig. 1(b)). These maps are used to derive information about the structure and composition of quantum wells [4]. Measurements are performed on different samples composed of InGaN/GaN QWs with different Indium concentrations. Fluctuations in E_1 of a few tens of meV over characteristic scales of a few hundred nanometers correlate well with fluctuations in topography and can be attributed to extrinsic growth inhomogeneities.

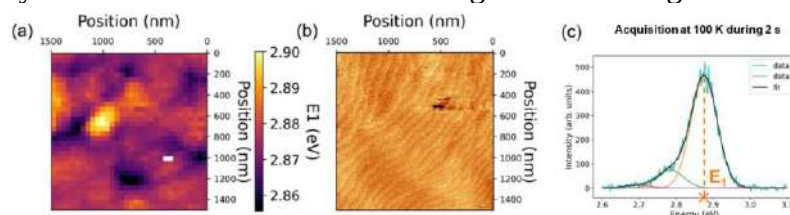


Figure 1: (a) Energy position map of the main tunnel electroluminescence peak. (b) GaN surface topography of the same area (GaN/InGaN/GaN QW with 15% of In). (c) Local electroluminescence spectrum under tunneling injection; a Gaussian fit of the main contribution gives the characteristic energy of optical phonons in InGaN.

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0.3.29 Electroluminescence from sub-gap emitters of step-bunched, oxidized 4H-SiC

Speaker: Natalia Alyabyeva

Electroluminescence from sub-gap emitters of step-bunched, oxidized 4H-SiC

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Since the invention of the scanning tunnelling microscope (STM), light induced by the locally injected current has been used as a spectroscopic nanotool to probe electronic and optical properties of matter down to ultimate scales. Different processes can be at the origin of light emission under the tip of an STM [1,2]. In semiconductors, scanning tunnelling electro-luminescence microscopy (STLM) involves the emission of light from within the sample due to the local injection of charge carriers. Its principal asset is the unique possibility to combine the selectivity of luminescence spectroscopy with STM's atomic-scale spatial resolution.

In the present work, STLM is used to study a step-bunched, oxidized 4H-SiC surface prepared on the silicon face of a commercial, n-type wafer using a silicon melt process [3]. The surface is composed by microscopic steps alternating large atomically flat terraces parallel to the [0001] crystal direction and step-bunched risers having a high amount of electrically active defects located at step edges and used as sub-gap single photon emitters [4]. Using the STM tip, charge injection and recombination processes followed by light emission have been probed simultaneously with topography, allowing for the correlation of emission spectrum variations related to composition fluctuations or crystal defects (Figure 1)[5].

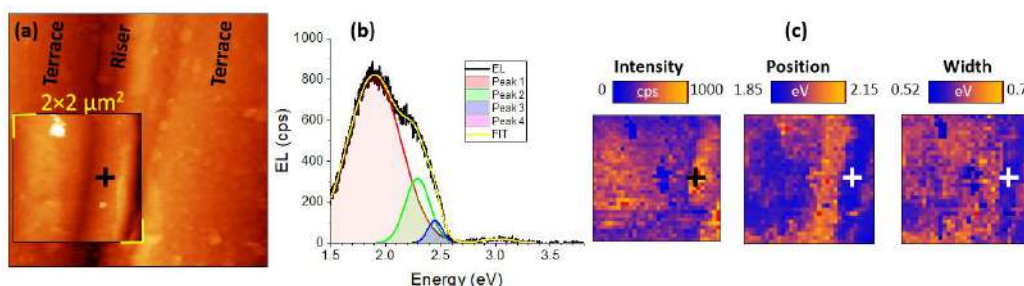


Figure 1. (a) Topography image ($V=-9V$, $I=-10$ nA) of 4H-SiC surface with close-up ($2 \times 2 \mu\text{m}^2$) image of terrace/riser zone; (b) Locally probed light emission spectrum in the zone marked by a cross and corresponding spectrum decomposition using Gaussian fit. (c) Light emission map of a peak 1 at 1.89eV: intensity, position and width corresponding to a close-up zone (a).

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0.3.30 Electroluminescence of high-mobility graphene transistors

Speaker: Baudin Emmanuel

Electroluminescence of high-mobility graphene transistors

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Krachmalnicoff², J-P. Hugonin⁶, R. Haidar³, B. Plaçais¹, C. Voisin¹, P.
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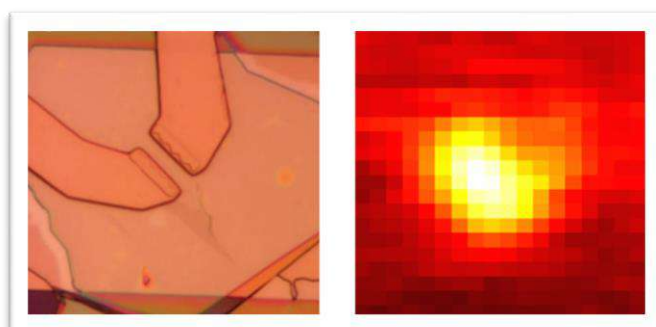
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Electroluminescence is ubiquitous in semi-conductors and gapped organic materials but fundamentally precluded in metals. In this talk, I'll show that this restriction can be circumvented in high-quality graphene. By investigating the radiative emission of high-mobility graphene field-effect transistors over a broad spectral range, spanning the near and mid-infrared, direct far-field electroluminescence from hBN-encapsulated graphene is demonstrated at $\lambda = 7.43 \mu\text{m}$ under large bias in ambient conditions. This mid-infrared electroluminescence results from the electrical pumping produced by interband tunneling. In addition to its significance from the fundamental point of view, electroluminescence in metals is of particular practical importance: In contrast to semi-conductors, the gapless electronic band structure of metals enables electroluminescent emission at arbitrary photon energy, paving the way toward innovative light sources.



6x10 μm graphene transistor micrograph (left), and corresponding image of its middle-infrared emission (right). The emission spot size is diffraction-limited by the MIR microscope objective.

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0.3.31 Embedding of YAG:Ce within 316L stainless steel matrix by additive manufacturing for corrosion monitoring

Speaker: Baslari Christina

Embedding of YAG:Ce within 316L stainless steel matrix by additive manufacturing for corrosion monitoring

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In most cases, metal components are exposed to harsh environments that are responsible for their degradation and premature failure. For instance, parts subjected to corrosion require extensive preventive maintenance which is time consuming and costly. Very often, these components are replaced before their end of life to prevent any risk of failure. Thus, corrosion-related degradations present environmental, economic and safety issues to high-tech industries. In a circular economy approach, it would be relevant to focus on extending the service life of metal components by proposing new eco-designed solutions and smart management of maintenance. The proposed solution consists in incorporating luminescent particles into metal parts by additive manufacturing in order to track their corrosion rate [1]. Monitoring of the luminescent signal enables to determine the extent of the degradation of the material. Additive manufacturing is a suitable process for this kind of operation as it allows the mixture of several materials without interrupting the construction cycle of the parts [2]. In this study, Laser Powder Bed Fusion (L-PBF) technology was used to incorporate Ce³⁺ doped yttrium aluminum garnet (YAG:Ce) into 316L stainless steel matrix. These luminescent pigments were successfully embedded within the metal matrix as assessed and identified by Scanning Electron Microscopy (SEM). Chemical composition and microstructure of the material were analyzed by energy dispersive spectroscopy (EDS) and backscatter diffraction (EBSD) respectively. Influence of process parameters (laser power, scanning speed) on the incorporation rate of phosphors as well as on the laser induced photoluminescence spectra (PL) were also studied. Interactions between the metal matrix and the luminescent particles during the process induce structural, physical and chemical modifications that reveal new optical properties to the precipitated luminescent phases.

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0.3.32 Energy transfer and ion clustering in Tm,Ho:CaF₂ crystals

Speaker: Eremeev Kirill

Energy transfer and ion clustering in Tm,Ho:CaF₂ crystals

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Holmium ions (Ho³⁺) are known for their emission slightly above 2 μm due to the $^5\text{I}_7 \rightarrow ^5\text{I}_8$ transition. A Tm³⁺,Ho³⁺ codoping scheme is often used to excite Ho³⁺ ions [1]. Tm³⁺ ions (donors) are pumped at 0.79 μm by AlGaAs diode lasers and non-radiatively transfer their energy to Ho³⁺ ones (acceptors), $^3\text{F}_4(\text{Tm}^{3+}) \rightarrow ^5\text{I}_7(\text{Ho}^{3+})$. Such codoping is also beneficial for combining the gain bandwidths of both ions [1]. Calcium fluoride (CaF₂) features strong clustering of the dopant rare-earth ions leading to “glassy-like” (smooth and broad) spectra and enhanced energy-transfer processes [2]. We have studied ion clustering and energy transfer in Tm,Ho:CaF₂ crystals.

A set of Tm,Ho:CaF₂ crystals was grown by the Bridgman method under controlled atmosphere to eliminate oxygen assisted sites. Low-temperature (12 K) spectroscopy of lightly doped Ho³⁺:CaF₂ revealed ions in isolated sites (trigonal C_{3v} , tetragonal C_{4v} and cubic O_h) together with small Ho ion clusters, while for codoped crystals, Ho³⁺ ions entered large rare-earth (Tm-Ho) clusters, Fig. 1(a). The codoped crystals excited at 0.77 μm exhibited broadband luminescence spanning from 1.6 to 2.2 μm due to two transitions, $^3\text{F}_4 \rightarrow ^3\text{H}_6$ Tm³⁺ and $^5\text{I}_7 \rightarrow ^5\text{I}_8$ Ho³⁺, with the Ho³⁺ emission being more intense. The relative intensity of Ho³⁺ emission raised when reducing the temperature. The luminescence dynamics for both ions were studied under resonant Tm³⁺ excitation, Fig. 1(c). The decay curves indicated efficient and predominantly unidirectional Tm³⁺ $\rightarrow$ Ho³⁺ energy-transfer. The observation of two different time scales for the rise of Ho³⁺ luminescence and the beginning of Tm³⁺ decay indicates the presence of two compositions of ion clusters: (i) clusters containing both dopants and (ii) those composed of only Tm³⁺ ions. The thermal equilibrium decay time was 11.0 ms. A rate-equation model accounting for two cluster compositions is proposed to explain the observed dynamics and to determine the energy-transfer parameters.

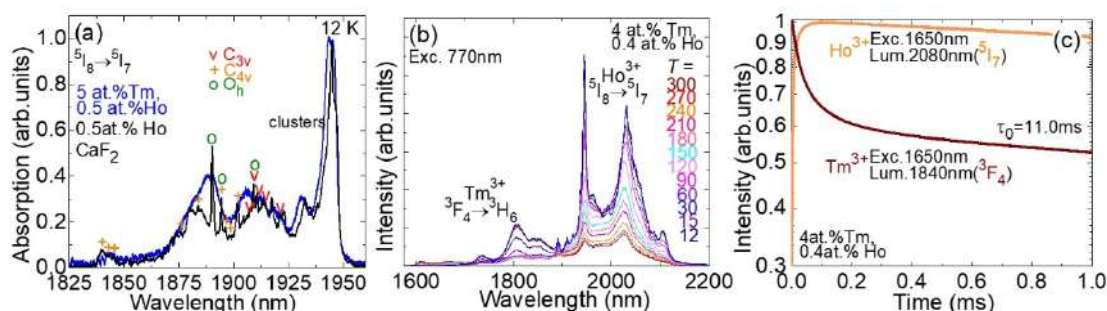


Figure 1. Spectroscopy of Tm³⁺,Ho³⁺-codoped CaF₂ crystals: (a) LT (12 K) absorption spectra, the $^5\text{I}_8 \rightarrow ^5\text{I}_7$ Ho³⁺ transition; (b) temperature-dependent luminescence spectra at 2 μm ; (c) RT luminescence decay from the $^3\text{F}_4$ Tm³⁺ and $^5\text{I}_7$ Ho³⁺ manifolds.

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0.3.33 Engineering the Spatial Assignment at Nanoscale Region for Photon Transfer Management in Luminescent Materials

Speaker: Mahata Manoj Kumar

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Nanotechnology aims to utilize chemical functional groups-conjugated nanoparticles for measuring physical and chemical quantities at the intracellular level. This demands the basic understanding of the interfacial energy transfer process in luminescent nanoparticles. Therefore, a new technique is introduced to engineer complex photon upconverting nanostructures and alter their photonic properties. In this study, an intraparticle-energy transfer process (i-ETP) is presented by a complex nanoarchitecture consisting of core-multiple shells, spatially separated Er^{3+} , Yb^{3+} , Tm^{3+} , and Nd^{3+} ions in a multi-layered NaYF_4 host structure. The main concept is by placing certain lanthanide ions (Ln^{3+}) in specific spatial positions of the special nanostructures, the luminescence profiles can be changed and energy transfer can be blocked or reversed based on need. Additionally, the study offers a qualitative analysis of how to regulate energy transfer at the nanoscale by engineering the core's structure along with double and triple shell layers by Ln^{3+} for their specific functions.

The findings enhance the understanding of Ln^{3+} ion behavior in intraparticle light management upon 980 nm light excitation. The intra-cellular compatibility of the nanoparticles is verified through cytotoxicity and cellular uptake investigation using multicolor 3D live-cell imaging.

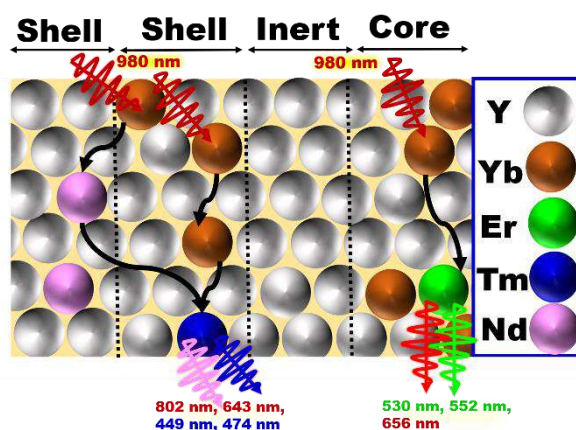


Fig. Symbolized presentation of lateral distribution of lanthanide ions and energy-transfer processes upon NIR light excitation.

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0.3.34 Enhanced PL properties in (Li⁺/Ca²⁺/Bi³⁺) ions co-doped NaLa(MoO₄)₂ : Eu³⁺ phosphors, Study on temperature sensing behavior and Judd-Ofelt analysis

Speaker: Sonali Sonali

Enhanced PL properties in (Li⁺/Ca²⁺/Bi³⁺) ions co-doped NaLa(MoO₄)₂: Eu³⁺ phosphors, Study on temperature sensing behavior and Judd-Ofelt analysis

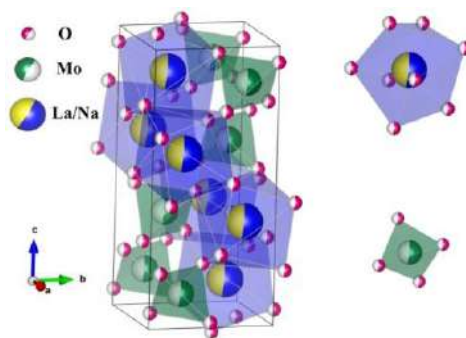
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In this work a series of monovalent, divalent and trivalent ions co-doped with Eu³⁺ activated NaLa(MoO₄)₂ phosphors were synthesized by the conventional solid-state method. Structural parameters were refined by the Rietveld method using powder X-ray data. All the compounds crystallized in the scheelite-type tetragonal structure with space group *I*4₁/*a* (No. 88). Upon excitation at 395 nm, the photoluminescence spectra exhibit characteristic luminescence ⁵D₀ → ⁷F_J (*J* = 1, 2, 3, and 4) intra-4f shell Eu³⁺ ion transitions. Among these transitions, electric dipole transition located at 615 nm (⁵D₀ → ⁷F₂) was stronger than the magnetic dipole transition located at 592 nm (⁵D₀ → ⁷F₁). Further, the effect of different ionic size and charge of the co-dopant ions, such as Li⁺, Ca²⁺ and Bi³⁺ ions co-doped luminescence properties have been examined. The PL results reveals that, enhanced luminescence intensity due to the distortion of their crystal lattice thus breaking the local site symmetry leading to a better color purity. In addition, to explore the thermal stability and temperature sensing, temperature-dependent down conversion photoluminescence has been performed. The activation energy was estimated with the help of Arrhenius plot and found to be 0.33 eV. Almost 57% of the initial intensity at room temperature is still maintained at 423K and the maximum sensitivity was observed about 0.66% K⁻¹ at 382 K. Apart from this, the intensity parameters (Ω_2 , Ω_4) and radiative properties such as transition probabilities (*A_r*), radiative lifetime (τ_{rad}), and branching ratio were calculated using the Judd-Ofelt theory. CIE color coordinates confirmed that the Eu³⁺ activated NaLa(MoO₄)₂ phosphors exhibit red luminescence. The above results point out that the aforementioned phosphors can be promising materials for the developing red component in solid state lighting, laser applications and non-contact optical temperature sensor.



Crystal structure of NaLa(MoO₄)₂

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0.3.35 Enhancing solar energy harvesting in space using spectral converters for photo-voltaics

Speaker: Correia Sandra

Enhancing solar energy harvesting in space using spectral converters for photovoltaics

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According to the United Nations 2030 Agenda for Sustainable Development, the use of clean and affordable energies, such as solar power, is a crucial challenge [1]. Nevertheless, the sun intermittence is a limitation, i.e., the energy is only available when/where the sun shines. As ‘the sun never sets in space’, the use of Solar Power Satellites (SPS) to harvest solar energy from space, convert it to electricity and transmit it to the Earth’s surface as microwaves was proposed [2].

In order to maximize the amount of energy reaching the Earth’s surface, the optimization of photovoltaic (PV) cells to increase the energy harvesting ability is of prime importance. This can be achieved by reducing the mismatch between the solar spectrum and the PV cells absorption through the use of spectral converters, such as downshifting layers (DSLs) [3].

In this work, DSLs were fabricated following previous results using highly efficient tri-ureasil t-U(5000) organic-inorganic hybrid modified by phenyltrimethoxysilane and doped with the Eu(tta)₃·2H₂O complex [4], with absolute emission quantum yield values of 0.57±0.06 at 365 nm and estimated potential to absorb ~3% of the solar photon flux on space [5].

The final prototype consisted on a c-Si PV panel with a total PV area of 276×320 mm² which was coated with the DSL by drop-casting. The PV prototype was tested under simulated AM0 solar spectrum revealing a relative increase in the generated electrical power of ~2.7% compared to the bare PV device.

Acknowledgments

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0.3.36 Er³⁺, Yb³⁺ codoped fluoride-based particles: luminescence and photoacoustic properties for nanomedicine

Speaker: De Oliveira Lima Karmel

Er³⁺, Yb³⁺ codoped fluoride-based particles: luminescence and photoacoustic properties for nanomedicine

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Rare Earth (RE) doped upconversion nanoparticles (UCNPs) have recently attracted great attention in nanomedicine due to their unique optical and physicochemical properties, enabling the use of UCNPs for luminescent imaging, temperature mapping, sensing, and medical therapies [1-2]. Er³⁺-Yb³⁺ codoped KGd₃F₁₀ cores were prepared by EDTA assisted hydrothermal synthesis, and core-shell Er³⁺-Yb³⁺:KGd₃F₁₀@SiO₂ particles, obtained through Stöber method. These spherical monodisperse UCNPs display strong green and red emission transitions under infrared excitation (at 980 and 1,550 nm), and intense NIR emission centered at 1,530 nm under 980 nm power pump. Er³⁺-Yb³⁺:KGd₃F₁₀ cores have been investigated for NIR bioprobes and accurate nanothermometers in the thermal range of biological interest [3], in this work this system is evaluated as contrast agents for photoacoustic (PA) images. Photoacoustic imaging experiments were performed upon excitation at 520 and 980 nm in core and core-shell ethanolic suspensions (6-15mg/mL). The obtained PA signal for Er³⁺-Yb³⁺:KGd₃F₁₀ cores is one order of magnitude more intense under excitation at 520 nm at lower fluence and even at lower concentration (7.5 mg/ml) compared to excitation at 980 nm and higher NP concentration (15 mg/ml). For the core-shell sample, a similar behavior concerning wavelength pump and incident fluence was observed at even lower particle concentration (6 mg/ml). Cytotoxicity evaluation of Er³⁺-Yb³⁺:KGd₃F₁₀ on glioblastoma multiform tumors (U87MG and KNS42 cells) was probed by using colorimetric resazurin assays. The obtained viability values remained close to 75 % for U87MG cells and 100% for KNS42 cells, for different NP concentrations in the biological medium, after 3-h incubation time. To the best of our knowledge, this is the first promising photoacoustic imaging results for Er³⁺-Yb³⁺:KRE₃F₁₀ and Er³⁺-Yb³⁺:KRE₃F₁₀@SiO₂ particles. These preliminary results suggest the potential application of RE doped fluoride based NPs in nanomedicine, acting in luminescent and PA imaging and as light converters in photodynamic therapy for brain tumor treatments.

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0.3.37 Eu²⁺ Site-Selective Occupation Driven Photoluminescence Modulation for Multi-Scenario White LED Applications

Speaker: Zhao Ming

Eu²⁺ Site-Selective Occupation Driven Photoluminescence Modulation for Multi-Scenario White LED Applications

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As light sources for illumination and liquid-crystal displays (LCDs), phosphor-converted white light-emitting diodes (*pc*-WLEDs) have penetrated into various products, including diverse lamps, mobile phones, computers, and more. To meet the different requirements for practical applications of LEDs, researchers need to develop novel phosphors with different emission peak and bandwidth^[1-2]. In this study, we selected the narrow-band cyan-emitting CsKNa₂(Li₃SiO₄):Eu²⁺ phosphor with three different cation sites that can be selectively occupied by Eu for spectral tuning^[3]. Depending on the variation of K/Na content, the phosphors exhibit controlled photoluminescence tuning from narrow-band cyan emission to cyan-green bimodal emission to narrow-band green emission (Figure 1). The narrow-band cyan phosphor CsK_{1+x}Na_{2-x}(Li₃SiO₄)₄:Eu²⁺ ($x = 0$) can be used to fill the cyan gap between blue and yellow emission for full-spectrum illumination; CsK_{1+x}Na_{2-x}(Li₃SiO₄)₄:Eu²⁺ ($x = 0.4$) exhibits cyan and green double peak emission with similar intensity, which can be combined with a red phosphor for general lighting; the narrow-band green phosphor CsK_{1+x}Na_{2-x}(Li₃SiO₄)₄:Eu²⁺ ($x = 1$) can be applied to LED backlight to realize wide color gamut display. The design principle of Eu²⁺ site-selective occupation provides a new approach to discovering multi-color phosphors suitable for multi-scenario white LED applications.

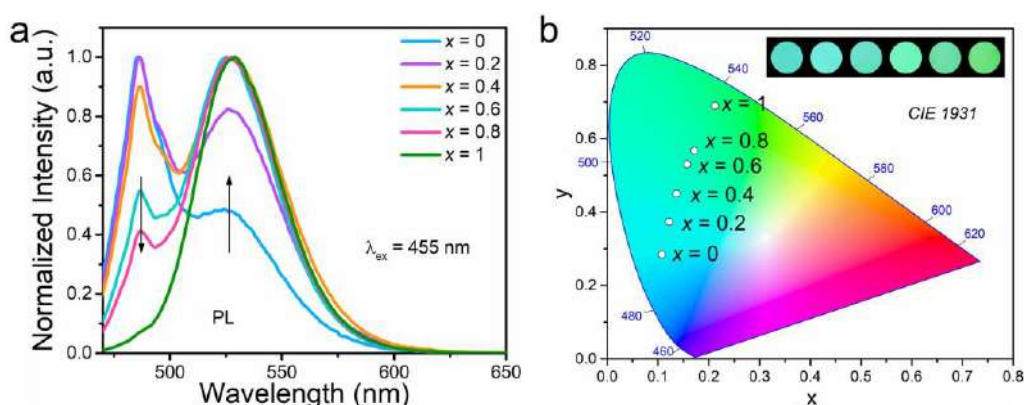


Figure 1. The emission spectra and CIE 1931 color coordinates of CsK_{1+x}Na_{2-x}(Li₃SiO₄)₄:Eu²⁺ ($x = 0-1$) phosphors.

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0.3.38 Eu³⁺ in high-charge micas: Dual functionality as radioactive waste encapsulation and in-situ luminescent sensor

Speaker: Martín-Rodríguez Rosa

Eu³⁺ in high-charge micas: Dual functionality as radioactive waste encapsulation and in-situ luminescent sensor

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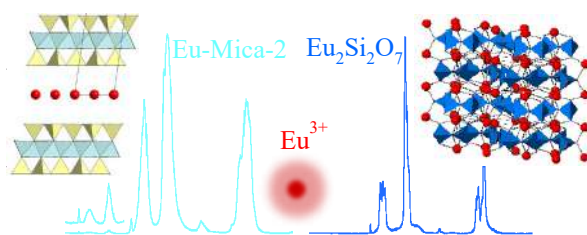
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Clay minerals are one of the most promising materials to be used in deep geological repositories, as engineered barriers for isolation of high-level radioactive waste. In particular, high-charge micas, which show extraordinarily large adsorption capacity, are an optimum candidate for radioactive waste decontamination through two different mechanisms: (i) ion exchange reaction and (ii) formation of new stable crystalline phases under hydrothermal conditions. In addition, these synthetic clays have some characteristic features that allow its use as an optical sensor by doping with luminescent lanthanides such as Eu³⁺ [1]. The incorporation of Eu³⁺ into the interlayer space of the mica originates well-resolved green and red luminescence, from both the ⁵D₁ and ⁵D₀ excited states, respectively.

Here we discuss an optical sensor based on the combination of Eu³⁺ and high-charge micas as a new approach for tracking the physical and chemical modifications of the radioactive waste under mild hydrothermal conditions [2]. The optical properties of different hydrothermally treated samples have been correlated with the interaction mechanisms between the lanthanide ions and the clay mineral at different temperatures and times. The most interesting features of Eu³⁺ luminescence to be used as an optical sensor are: (i) the presence or absence of the Eu³⁺ green emission from the ⁵D₁ excited state, (ii) the energy shift of the ⁵D₀ → ⁷F₀ transition, (iii) the crystal-field splitting of the ⁷F₁ Eu³⁺ level, and (iv) the observed luminescence lifetimes.



Correlation between Eu³⁺ optical properties and clay structural transformation mechanisms.

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0.3.39 Excitation of a magnetic dipole transition through a plasmonic nano-antenna

Speaker: Reynier Benoît

Excitation of a magnetic dipole transition through a plasmonic nano-antenna

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Light-matter interactions are often considered to be mediated by the optical electric field only, discarding half of the energy stored in the optical magnetic field. Although interactions between light and matter are very weak, they can be studied in a certain class of materials, such as metal ions. For instance, it was demonstrated in Eu³⁺ ions that magnetic emission could be manipulated by tuning the local magnetic quantum environment surrounding magnetic dipoles by means of dielectric or plasmonic nanostructures [1,2]. Along the same line, it is also possible to manipulate the electric and magnetic excitation of these ions by controlling the electric and magnetic fields distribution of the excitation light [3].

Here, by using a plasmonic nano-antenna placed at the end of a local probe (Figure 1), we demonstrate the localization and enhancement at sub-wavelength scales of the optical magnetic field (Figure 2). This magnetic hot spot is then used to excite a luminescent nanoparticle doped with Eu³⁺ ions, demonstrating an energy transfer from the optical magnetic field to matter at the nanoscale. Moreover, by selectively exciting an electric or magnetic transition of the particle, the nanoscale scanning capabilities of our near-field system allow us to image the spatial distribution of these fields of the localized plasmon in the antenna (Figure 2). This research opens the way to increasing the all-magnetic light-matter coupling, with applications in quantum optics, in studying chiral phenomena, or the generation of photon avalanches.

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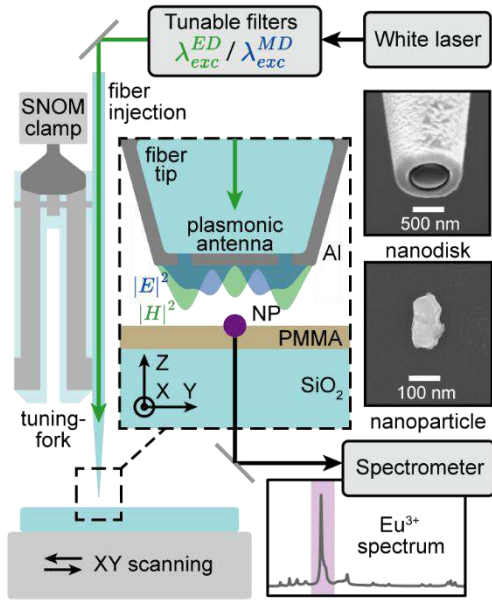


Figure 1 : Schematic of the experimental setup. A plasmonic nano-antenna, designed at the end of a tapered fiber is excited using an injected linear polarization. By means of a near-field setup, a Y₂O₃:Eu³⁺ doped nanoparticle can scan in the XY plan the electric and magnetic intensity distributions of the localized plasmon. The luminescence is then collected and analyzed by a spectrometer for each antenna-particle position.

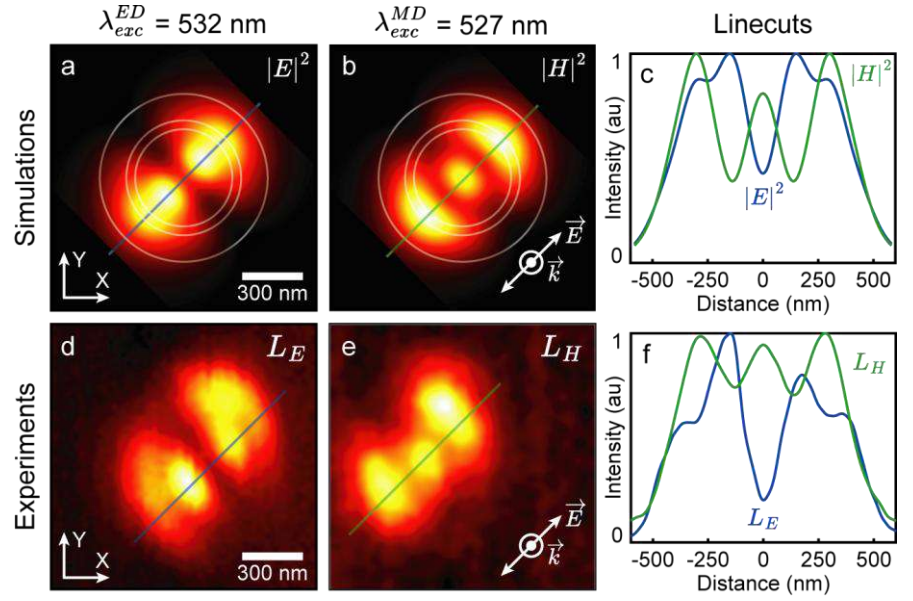


Figure 2 : Simulation results in the XY plan below the plasmonic antenna (white circles) of the (a) electric and (b) magnetic intensity distributions. (c) Linecuts along the polarization direction for the electric (blue) and magnetic (green) intensity distributions. Collected luminescence in the XY plan below the plasmonic antenna of the (d) electric and (e) magnetic field excitation. (f) Linecuts along the polarization direction for the electric (blue) and magnetic (green) excitation.

0.3.40 Exploring phase transitions by Raman spectroscopy and luminescent properties in Eu(III)-indandionate complexes

Speaker: Costa Israel Ferreira

Exploring phase transitions by Raman spectroscopy and luminescent properties in Eu(III)-indandionate complexes

Israel F. Costa,^{1,*} Lucca Bjois,¹ Vitor H. Paschoal,¹ Albano N. Carneiro Neto,² Renaldo T. Moura Jr.,³ Victor M. Deflon,⁴ Luís D. Carlos,² Wagner M. Faustino,⁵ Marja Claudia F. C. Felinto,⁶ Ricardo L. Longo,⁷ Ercules E.S. Teotonio,⁵ Hermi F. Brito,¹ Romulo A. Ando,¹ Oscar L. Malta.⁷

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This study investigates a series of tetrakis complexes that contain tetraethylammonium as counterions. The complexes are labeled as $\text{Et}_4\text{N}[\text{Ln}(\text{acind})_4]$, where Ln: Gd(III) and Eu(III) and acind: 2-acyl-1,3-indandionate ligands. The study includes synthesis, structural, vibrational (FTIR/Raman), theoretical and photoluminescence analyses. The coordination polyhedron of the $\text{Et}_4\text{N}[\text{Ln}(\text{acind})_4]$ may be described as a distorted triangular dodecahedron close to D_{2d} symmetry point group (Fig. 1a). One complex in the series has shown an exceptional intensity parameter value of $\Omega_2 = 73.5 \times 10^{-20} \text{ cm}^2$ and high photoluminescence quantum yields of $Q_{\text{Eu}}^L \sim 80\%$ at 300 K. In addition, this complex shows different solid-state phases at 367 and 460 K, observed in Differential Scanning Calorimetry, leading to significant changes in the band profile of the $^5D_0 \rightarrow ^7F_2$ transition (Fig. 1b). Furthermore, these phase transitions can be linked to cation's conformational changes from a pseudo- S_4 to a pseudo- D_{2d} symmetry, associated to the broadening and shifts of the bands in ca. $650\text{--}660 \text{ cm}^{-1}$, as shows the Raman scattering spectra in Fig. 1c. These changes in conformation can be related to a softening of the lattice as a whole, where the increased quasi-elastic scattering in the low-frequency Raman spectra (see inset in Fig. 1c) overcomes the lattices modes, indicating an onset of relaxational dynamics of the system before melting. These phenomena alter important structural characteristics of the compound and can be connected to the overall decrease in photoluminescence in experimental quantum yields (Q_{Eu}^L). These luminescent systems have shown very interesting and promising results for applications, such as in OLED devices and luminescent thermometers based on Ln(III) ions [1].

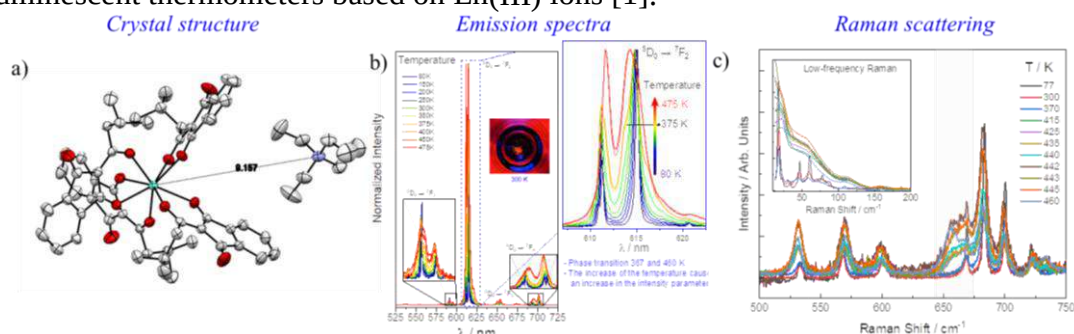


Figure 1. a) Emission spectra from 80 to 475 K, b) Raman scattering from 80 to 460 K, and crystal structure of $\text{Et}_4\text{N}[\text{Eu}(\text{isovind})_4]$ complex at 300 K.

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Acknowledgments

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0.3.41 Exploring trap depth distributions in Cr³⁺ - doped zinc gallogermanate solid solutions

Speaker: Matuszewska Celina

Exploring trap depth distributions in Cr³⁺ - doped zinc gallogermanate solid solutions

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Cr³⁺-doped zinc gallates and zinc gallogermanate solid solutions have recently attracted significant interest because of potential applications in bioimaging [1] and photodynamic therapy of cancer [2]. It is due to their long persistent luminescence of Cr³⁺ ions in the NIR region, which was first reported by Bessière *et al.* in 2011. Since then the structure of ZnGa₂O₄: Cr³⁺ was extensively modified and optimized in order to meet the requirements of real-life applications, including the substitution of Ga³⁺ by Ge⁴⁺/ Sn⁴⁺ ions and Zn depletion.

However, for more complex systems, such as zinc gallogermanate solid solutions, the relationship between a structure and the resulting persistent luminescence properties has not been studied to a large degree so far. Therefore, it is still very challenging to derive any physical models, which are necessary to develop more advanced persistent phosphors.

Thermoluminescence studies are ideally suited to provides a better understanding of the nature of trapping centres and their role in the mechanism responsible for persistent luminescence. In our recent findings, the relationship between the composition, the distribution of the trapping centres and the resulting persistent luminescence properties of the material was proposed for the two most common zinc gallogermanate solid solutions. [4] In the current work, the trap depth distributions in Cr³⁺ - doped zinc gallogermanate solid solutions were investigated in a systematic manner, based on the previously developed approach proposed by Van den Eeckhout *et al.* [5] and Feng *et al.* [6]. The series of thermoluminescence measurements under different charging conditions provided further insight into the detrapping kinetics and revealed the existence of a thermal barrier for charging.

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0.3.42 Facile Pechini screening of Nd³⁺-Yb³⁺ codoped oxide nanocrystals allows development of thermal bioprobes with phonon-tunable sensitivity

Speaker: Tsuchida Nogueira Camila

Facile Pechini screening of Nd³⁺-Yb³⁺ codoped oxide nanocrystals allows development of thermal bioprobes with phonon-tunable sensitivity

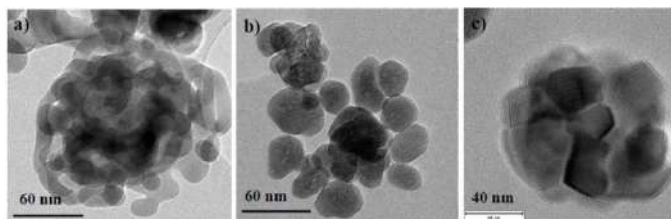
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Tumors and inflammatory areas are associated with local temperature rise. Therefore, the temperature mapping in organisms can contribute in early diagnosis of diseases and their treatments. Nanothermometers displaying high relative thermal sensitivity (S_r) and low thermal resolution (δT) are essential. Recent works show ratiometric luminescent thermometry is one of the most promising approaches for temperature sensing [1]. It is based on the intensity ratio of two luminescent peaks, which leads to a remote temperature readout. However, there is still a need of probes with suitable shape and size, operating with excitation and emission wavelengths within the biological windows (BW), where the absorption and scattering of the light by tissues are minimized in the near infrared region. Furthermore, the factors that influence S_r are not widely understood. To address these shortcomings, we conducted a global study of several oxide nanocrystals (NCs): Y₂O₃, Y₂Ge₂O₇, Y₃Al₅O₁₂ (YAG), Y₄Al₂O₉ (YAM), Y₃BO₆ and YBO₃ doped with Nd³⁺ and Yb³⁺, and associated, using 804 nm excitation and emission in II-BW. The Pechini method was first chosen to synthesize the oxides and screen their luminescent properties due to its generic character and flexibility. The NCs were firstly single-doped with Nd³⁺ and, then, co-doped with Nd³⁺ and Yb³⁺. For single-doped NCs, we observed that S_r and ΔE between thermally coupled Nd³⁺ levels are linearly related, as predicted by the Boltzmann's law. Likewise, our findings show that higher S_r of co-doped hosts, presenting low phonon energy, is favored. Then, we significantly increased S_r , up to 3-fold factor, by co-doping oxide NCs with Nd³⁺ and Yb³⁺, compared to single-doped oxide NCs. In addition, the screening revealed that YAG and Y₂O₃ are the most promising hosts. Currently, we've been optimizing the preparation of individual NCs through the solvothermal method to avoid agglomerated NCs, as usually obtained by Pechini route (**Fig. (a)**). We first obtained 60-nm YAG NCs of high crystal quality (Fig. (b)), functionalized and well dispersed in physiological solutions [2], to advance in coupled biological studies. The YAG thermal probes present $S_r = 0.47 \text{ \%} \cdot \text{K}^{-1}$ and $\delta T = 0.3 \text{ K}$, but the later parameter will be significantly reduced by improving our experimental set-up of photoluminescence measurement. Solvothermal routes are in development to synthesize Y₂O₃ individual nanocrystals with size < 100 nm. So far, Y₂O₃ clusters of 40 nm were obtained (**Fig. (c)**).



TEM images of a) YAG agglomerated NCs obtained by Pechini method, b) YAG individual NCs synthesized by solvothermal method, c) Y₂O₃.

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0.3.43 Fingerprint of quantum confinement in the photoluminescence of single perovskite nanocrystals

Speaker: Amara Mohamed-Raouf

Fingerprint of quantum confinement in the photoluminescence of single perovskite nanocrystals

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Lead halide perovskite NCs (LHP NCs) are an unforeseen class of materials with a singular combination of favourable optoelectronic properties. In contrast to wurtzite and zinc-blende NCs where even a small concentration of defects has a drastic impact on the photoluminescence efficiency, LHP NCs are defect-tolerant and remain bright without the need of core-shell structures. As in conventional NCs, the emission can be tuned over the entire visible range by a combination of size-engineering, i.e. quantum confinement and composition-engineering.

Early experimental studies of individual LHP NCs have revealed narrow lines grouped in doublets or triplets attributed to a bright triplet exciton with a fast radiative lifetime [1]. Several additional emission peaks have also been reported within a 20 meV range, attributed to the charged exciton, biexciton and phonon replicas [1]. Theoretically, the band-edge exciton fine structure has been the subject of debate in the community since the prediction that the Rashba effect should place the bright triplet exciton as the ground exciton state, in contrast to all other known semiconductors [2]. This prediction was since contradicted experimentally [3] and the discussion has shifted towards quantifying the influence of the exchange interaction and this potential Rashba effect on the exciton fine structure [4].

Here, we report on a statistical study of the spectral properties of individual CsPbBr₃ NCs at cryogenic temperatures over a wide range of NC edge lengths from ~5 to ~25 nm. Doing so, we reveal the spectral fingerprint of quantum confinement in the band-edge exciton fine structure emission via the size-dependent spectral features related to the emission of the bright triplet exciton, charged exciton, biexciton, and their respective phonon replicas. Notably, we find a general increase of bright-bright energy splittings, consistent with the expectations of a simple quantum confinement model with no signature related to the Rashba effect. Similarly, charged and biexciton binding energies and exciton-phonon coupling strength increase with confinement.

In a nutshell, we provide a comprehensive study of the emission of individual CsPbBr₃ NCs and reveal the size-dependent properties of the emission in these nascent materials.

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0.3.44 First-principles explanation of the luminescent lineshape of $\text{SrLiAl}_3\text{N}_4\text{:Eu}^{2+}$ phosphor for light-emitting diode applications

Speaker: Bouquiaux Julien

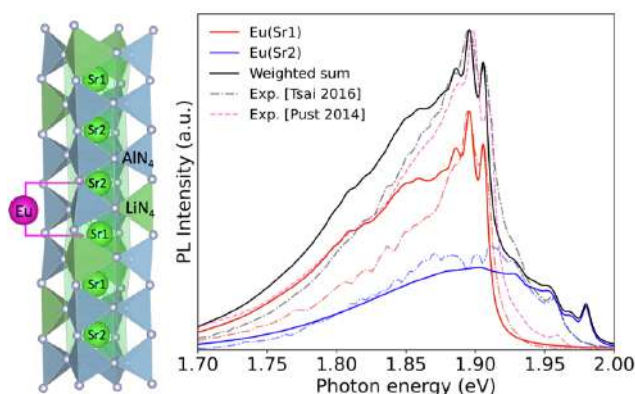
First-principles explanation of the luminescent lineshape of SrLiAl₃N₄:Eu²⁺ phosphor for light-emitting diode applications

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The red phosphor SrLiAl₃N₄:Eu²⁺ [1] is among the first promising phosphors with small bandwidth for the next-generation lighting but the microscopic origin of this narrow emission remains elusive. In the present work [2], density functional theory, the Δ SCF-constrained occupation method, and Huang-Rhys theory are used to provide an accurate description of the vibronic processes occurring at the two Sr²⁺ sites that the Eu²⁺ activator can occupy. The emission bandshape of Eu(Sr1), with a zero phonon line at 1.906 eV and high luminescence intensity, is shown to be controlled by the coupling between the 5d_{z²} - 4f electronic transition and the low-frequency phonon modes associated to Sr and Eu displacements along the Sr channel, as already observed in the similar SrLi₂Al₂O₂N₂:Eu²⁺ [3]. The good agreement between our computation and experimental results [4] allows us to provide a structural assignment of the observed total spectrum. By computing explicitly the effect of the thermal expansion on zero phonon line energies, the agreement is extended to the temperature-dependent spectrum. These results provide insights into the electron-phonon coupling accompanying the 5d-4f transition in similar UC₄C₄-type phosphors: they highlight the importance of the Sr channel in shaping the narrow emission of SrLiAl₃N₄:Eu²⁺, and shed new light into the structure-property relations of such phosphors.



Crystal structure of SrLiAl₃N₄:Eu²⁺ and simulated PL spectra of both Eu(Sr) sites.

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0.3.45 Fluorescent artificial seeds as luminescent thermometers for environmental sensing

Speaker: Nexha Albenc

Fluorescent artificial seeds as luminescent thermometers for environmental sensing

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Monitoring environmental parameters could tackle issues related to climate change. Current technologies for environmental monitoring are based on electronic materials that are costly, bulky, and lead to electronic waste.¹ We propose a new generation of self-deployable, biocompatible artificial flying seeds, inspired from nature, for a wireless environmental monitoring system. Optical communication enables the use of passive "robots" that communicate with drones.

We take inspiration from *Acer Campestre* seeds, which are carried passively by the wind and are dispersed in large distances and distinct areas. The artificial seeds are printed via 3D technologies and emulate the morphometric and aerodynamic characteristics of the natural seeds. These seeds are composed of fluorescent materials embedded into a polymeric host such as polylactic acid. We selected this polymer due to its thermoplastic and biocompatible nature and its renewable precursors such as corn starch. The PLA-based sensor material that we developed is compatible with 3D fused deposition modeling.²

Sensing is based on fluorescent, lanthanide-doped particles that contain Er³⁺, Yb³⁺ co-doped in hexagonal NaYF₄ host. They absorb eye-safe and cheap near infrared excitation sources at 980 nm due to the sensitizer Yb³⁺ and convert this energy into bright green emissions due to the activator Er³⁺.³ The intensity of their fluorescence spectra depend on temperature.

The fluorescent artificial seeds are deployed and optically read out from a distance using drones. The seeds then act as deployable luminescent thermometers for distributed monitoring of environmental temperatures in top soil. We will report on the ability of these seeds to sense temperature under different conditions, such as long exposure to near infrared irradiation or sunlight, and on their stability and reliability.

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0.3.46 Frequency-tunable single Er ions as telecom quantum emitters

Speaker: Yu Yong

Frequency-tunable single Er ions as telecom quantum emitters

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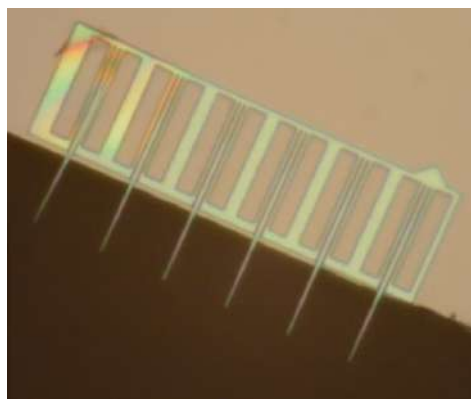
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During the past decade, rare-earth ions doped in crystals have emerged as promising candidates for optical quantum memories, owing to their long optical and spin coherence time [1]. Recently, advancements in high-quality factor and low-mode volume nanophotonic cavities have made individual rare-earth ions optically addressable [2, 3]. Furthermore, deterministic qubit detection [4] and nuclear spin control [5] have been achieved, marking a full-stack quantum node. Among all rare-earth ions, Erbium (Er) ions are of great interest in large-scale quantum networks due to their telecom light-matter interface.

Here, I will present our results on coupling single Er ions in a lithium niobate host with silicon nanophotonic cavities. Additionally, we have achieved linear Stark tuning of a single Er ion frequency for the first time, which is a crucial element in establishing a multi-node quantum network.



Silicon nanocavities on the Er:LiNbO₃

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0.3.47 Frequency-upconverted lasing from a whispering-gallery-mode microcavity

Speaker: Sun Ling-Dong

Frequency-upconverted lasing from a whispering-gallery-mode microcavity

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Lanthanide-based upconverted microlasers are attractive candidates for miniaturized optics, bio-sensing, and imaging. And upconverted microlasers usually operated in multi-modes, meanwhile, with a cavity size larger than 5 μm . The competing modes and large cavity dimension severely limit their prospects in practical applications. we investigated the upconverted lasing behavior and the confined lasing modes from a polystyrene (PS) whispering-gallery-mode (WGM) microcavity that is gained by monolayer upconversion nanoparticles (UCNPs). A uniform coating layer of UCNP benefits the amplified emission and a low threshold ($\sim 4 \text{ kW/cm}^2$) is expected. With a reduced cavity size, an enlarged free spectra range is feasible, and single-mode lasing output could be selected. The lasing wavelength can be adjusted from blue, green, to red and near-infrared with the integration of Ho^{3+} , Er^{3+} , or Tm^{3+} doped UCNPs. Our single-mode, small-cavity-size, and low-threshold upconverted lasing paves the way for 3D lasing display, high-precision bio-sensing, and imaging.

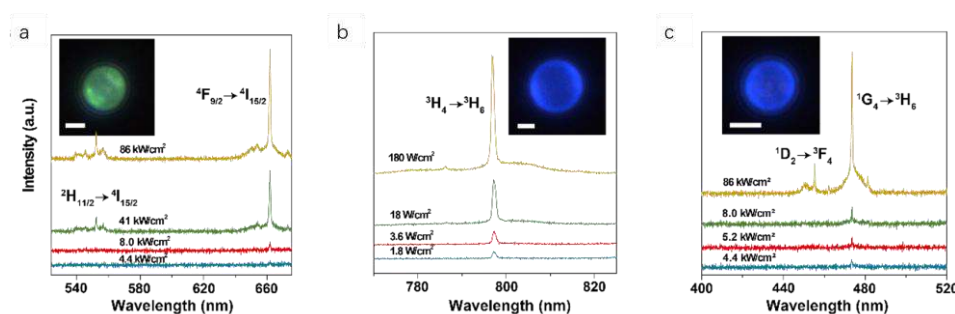


Figure 1 Extension of single-mode lasing wavelength and pump power dependent upconversion emission

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0.3.48 FRET-mediated collective blinking of self-assembled stacks of semiconducting nanoplatelets

Speaker: Coolen Laurent

FRET-mediated collective blinking of self-assembled stacks of semiconducting nanoplatelets

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Extensive studies have been performed since the 1980s and 1990s on semi-conducting colloidal nanoparticles, usually on isolated emitters in dilute solutions. However, for many opto-electronic applications such as quantum-dot-LEDs or quantum-dot-sensitized solar cells, densely-packed stackings of emitters are used. Interactions between them are then expected and must be understood. Colloidal CdSe nanoplatelets (NPL) can be self-assembled into chains of hundreds of NPLs (up to 4 μm length) [1], with constant platelet center-to-center distance of 6 nm and excellent linear order, therefore constituting a perfect platform for exploring these various collective effects.

We have imaged the fluorescence from individual NPL chains and found a FRET (Förster resonant energy transfer : dipole-dipole non-radiative exciton hopping) migration length of 500 nm (around 90 NPLs). From this, a diffusion-equation model leads us to estimate the characteristic time of FRET transfer between neighbour platelets to 1-2 ps, much shorter than all decay mechanisms known to occur in fluorescent semiconductor nanoparticles [2].

Densely-packed nanoparticles can thus be expected to present, because of FRET, totally new photophysical behaviour involving tens or hundreds of emitters collectively instead of each platelet emitting individually. Notably, we have demonstrated that some portions of NPL chains blink collectively, showing that a single intermittent quencher platelet is able to block the luminescence from an ensemble of a few tens of NPLs as excitons in these NPLs migrate by FRET and reach the quencher [3]. The luminescence decay curves also show signs of FRET-induced effects of quencher defects and metastable traps.

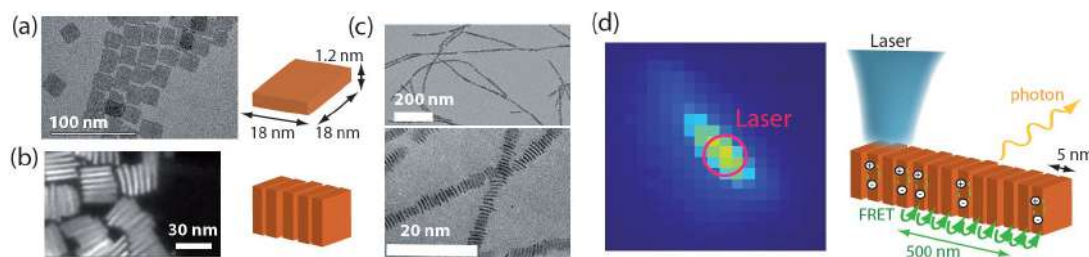


Figure 1 : TEM images of (a) CdSe nanoplatelets, (b) aggregated platelets and (c) self-assembled stacked nanoplatelets. (d) A laser excites a spot on the chain and energy propagates by FRET between around 100 platelets so that a 1- μm portion radiates light [1]

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0.3.49 From IRQC to APTE self-decontaminating printable surfaces: 40 years of Auzel Effect applications at LandFoton UFPE Lab

Speaker: Santa-Cruz Petrus

From IRQC to APTE self-decontaminating printable surfaces: 40 years of Auzel Effect applications at LandFoton UFPE Lab

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What contributed the most to enable applications based on the upconversion effect was the mechanism of photon addition by energy transfer (APTE, French acronym for "Addition de Photons par Transferts d'Énergie"), proposed by François Auzel in 1966. In memory of his fruitful visits to our institution, we intend to present some applications developed in the LandFoton laboratory at the Federal University of Pernambuco (UFPE) using this mechanism, here called the Auzel Effect. Forty years ago, during his first visit to UFPE, we performed the experiments that resulted in the very first practical application of this effect: an IRQC (Infrared Quantum Counter) at a time when the detection of the infrared radiation band used in third generation optical fibers was very poor, since only bolometers were available in that region. The development of the IRQC for detection of 1.5 μm infrared radiation resulted in a publication in 1985, which even included experimental measurements of the Noise Equivalent Power of the presented detector ($\text{NEP} = 10^{-11} \text{ W}/\sqrt{\text{Hz}}$) [1]. Two years later, we published a first paper on the effect of metallic nanoparticles on the APTE process [2], starting a series of works involving the enhancement of luminescence by plasmonic interactions with lanthanide ions. Twenty years ago, our group proposed the first material for the production of white light by additive synthesis exclusively by the Auzel Effect from the control of the chromatic coordinates of the three primary colors of light (RGB) produced by this mechanism in relative intensities controlled by the proportions of Tm^{3+} and Er^{3+} and Yb^{3+} ions, resulting in strong white light emission [3]. In the same period, our group produced UV radiation from the sum of four photons per APTE [4]. More recent work has been developed by our group involving printable photonic devices in hybrid materials that resulted in patents, such as printable photonic thermometers [5]. Currently, we are applying the Auzel Effect to the development of self-decontaminating surfaces that generate UV in situ by $\text{Ca}_2\text{LaF}_7\text{:Yb}^{3+}\text{-Tm}^{3+}$ upconversion nanoparticles as the active phase of polymer nanocomposites that can be printed by MSLA 3D printers. The printed parts generate a small flux of UV radiation on their surfaces, sufficient for the inactivation of viruses near the nanoparticles. Proof-of-concept has been conducted for $\text{IR} \rightarrow \text{UV}$ conversion on surfaces of solids printed on Phrozen Sonic Mini 8k printers, and here we propose $\text{VIS} \rightarrow \text{UV}$ conversion with APTE nanoparticles. Auzel awarded the title of Doctor Honoris Causa from UFPE in 2008. On the International Day of Light 2023, the LandFoton UFPE is renamed LandFoton François Auzel Lab in his honor, with the consent of his sons.

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0.3.50 From nanodots to continuous layers: mechanisms and applications of 2D MoS₂ photoluminescence

Speaker: De Andres Alicia

From nanodots to continuous layers: mechanisms and applications of 2D-MoS₂ photoluminescence

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MoS₂ is one of the most studied bidimensional transition metal dichalcogenides because of its excellent light absorption and emission properties. 2D-MoS₂ has excellent performance in a wide variety of applications related to its optical characteristics, from photodetectors to biosensors. Photoluminescence (PL) is a key feature for most applications but its quantum yield is maximum only for single-layers due to the direct to indirect bandgap transition occurring from one to two layers, being undetectable for few-layer samples. Therefore, high quality single-layers are required in many cases. Here we will present how the combination of Raman, PL and optical transmittance micro-spectroscopies can provide detailed information on the characteristics of 2D-MoS₂ over a wide range of sizes (from continuous films to nanoflakes) obtained by different techniques (CVD, PVT and mechanical exfoliation) [1]. Micro-transmittance spectroscopy is an optimum tool to reveal the changes in the electronic structure as the number of layers is reduced and much less sensitive to defects or doping than PL. Combining these optical techniques we show that it is possible to reveal relevant characteristics of single and few-layers MoS₂ nanoflakes, obtained by CVD and PVT and their dependence on size [2]. Regarding sensing applications, the enhancement of the PL signal for single and few-layer MoS₂ is a crucial point to lower the detection level. We show that Ga and MoO₃ nanoparticles on 2D-MoS₂ flakes provide PL and Raman enhancement by SERS and charge transfer processes [3]. Finally, we show that the modifications of the PL band of MoS₂ single-layer PVT flakes modified with a thiolated DNA probe complementary to the target biomarker can be used as a specific probe to detect the biomarker miRNA21c related to breast cancer [4].

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0.3.51 Ga-Modified YAG:Pr³⁺ - Tunable Luminescence Thermometers

Speaker: Bolek Paulina

Ga-Modified YAG:Pr³⁺ - Tunable Luminescence ThermometersP. Bolek¹, J. Zeler¹, C. D. S. Brites², J. Trojan-Piegza¹, L. D. Carlos², E. Zych¹¹ University of Wrocław, Faculty of Chemistry, 50-383 Wrocław, Poland² University of Aveiro, Physics Department, CICECO-Aveiro Institute of Materials, 3810-193 Aveiro, Portugal

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Luminescence thermometry is considered the most prospective technique for remote temperature measurement in so different areas as medicine, biology, technology, space research, engineering, and others. Its dynamic development in the last decade is related to great technological development, especially the miniaturization of devices or sensors in which traditional temperature measurement is useless or impractical [1,2,3].

In this presentation, we will discuss the properties of Pr-activated Y₃Al₅O₁₂ (YAG) and its Ga-modified versions in the context of luminescence thermometry. We will show the possibility to generate and manage two types of emissions: allowed broad-band resulting from the inter-configurational 5d→4f transition and narrow lines produced by intra-configurational 4f→4f transitions. We will show how such phosphors' properties may be tweaked by means of bandgap engineering to tune their thermometric performance. Finally, we will present a group of materials able to measure the temperature with high relative sensitivity, $S_r = 3.6\% \text{K}^{-1}$, in as broad operating range as 15-700 K, with accuracy reaching 0.02K or better.

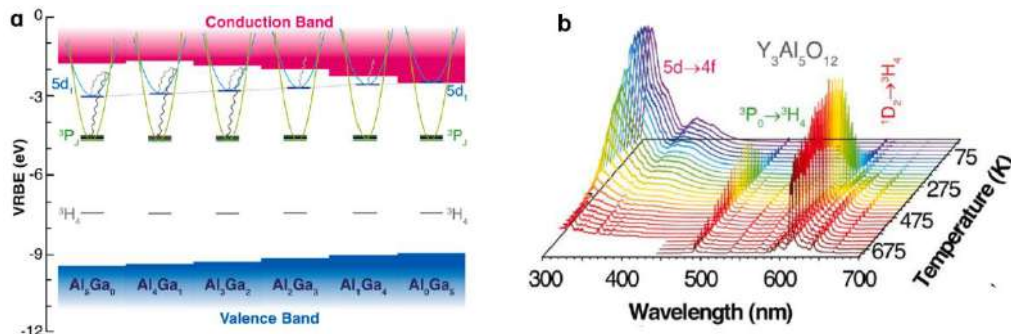


Figure 1 (a) Vacuum referred binding energy diagram of Y₃(Al,Ga)₅O₁₂:Pr containing energy levels of Pr³⁺ ion. (b) Emission spectra of Y₃Al₅O₁₂:Pr registered at various temperatures under 278 nm excitation [4].

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0.3.52 High Performance Photonic Physical Unclonable Functions based on luminescent materials

Speaker: Andre Paulo

High Performance Photonic Physical Unclonable Functions based on luminescent materials

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The enormous advances in digital systems and the Internet of Things (IoT) are causing an increase in concerns about security and safety, challenging the development of innovative authenticatable smart IoT labels [1]. The ability to perform authentication using smartphones appears as an exciting and affordable strategy to sustainably convert a signal from an optical label into a digital data sequence for the new generation of mobile optical (mOptical) authentication [2]. Hence, the development of strong cryptographic systems based on reliable methods to generate secure cryptographic keys is required. The Physical Unclonable Functions (PUFs) appear as a solution because they are based on a black-box challenge-response system, where an external stimulus (challenge) is applied to the device generating an unpredictable and unique response (challenge-response pair) [3]. The factors involved in the generation of the response are unidentified but result from the internal manufacturing variability of the device. This underlies the safety of PUFs as these factors are unknown and hard to estimate, and therefore to replicate. We propose the design of smart e-labels for real-time remote or in-situ authentication based on the all-optical interaction of luminescent bio-based inks printed virtually on any surface with low-power sources such as light-emitting diodes. The inks display emission features dependent on the excitation wavelengths spanning from the ultraviolet to the visible spectral regions providing a myriad of challenge-response pairs, opening new perspectives for developing a large variety of photoactive inks for smart labels for sensing and to further explore strong photonic PUFs.

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0.3.53 High pressure band structure modification for tunable cross-luminescence in wide band gap fluoride crystals

Speaker: Cadatal-Raduban Marilou

High pressure band structure modification for tunable cross-luminescence in wide band gap fluoride crystals

Marilou Cadatal-Raduban,^{1,2,*} Kohei Yamanoi,² Akira Yoshikawa,^{3,4} Yuui Yokota,⁴ Toshihiko Shimizu², Tadashi Togashi,^{5,6} Akira Kondo,⁷ Nobuhiko Sarukura^{2,3}, and Luong Viet Mui⁷

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Scintillators are widely used for radiation detection in various industries. Scintillators used in applications involving time-of-flight measurements need to have a fast decay time and a high photon yield. Scintillation decay time becomes faster when the emission wavelength of the scintillator becomes shorter. Therefore, scintillators emitting in the vacuum ultraviolet region (VUV, $\lambda = 100$ nm to 200 nm) using wide band gap materials doped with rare earth activator ions are being investigated to develop fast-response scintillators. However, there is a tradeoff between decay time and light yield such that fast scintillators suffer from a low light yield. In addition, the VUV emission wavelength imposes limitations to the detector unit that can be used to collect the scintillation light. The ability to shift the luminescence to a longer wavelength, for example in the ultraviolet region, will enable easier detection of the fast emission. We report on the potential of the potassium magnesium fluoride (KMgF) crystal as a fast-response scintillator with tunable cross-luminescence (CL) emission wavelength through high-pressure applications. By performing first-principles density functional theory calculations using the Perdew–Burke–Ernzerhof (PBE) hybrid functional including exact exchange (PBE0) and Green's function and screened Coulomb interaction approximation as implemented in the Vienna Ab initio Simulation Package using plane-wave basis sets within the projector-augmented wave method, we identify the specific valence-to-core band transition that results in the experimentally observed CL emission at 148 nm (8.38 eV) and 170 nm (7.29 eV) wavelengths with intrinsically fast decay times of 290 ps and 210 ps, respectively. Uniform volume compression through hydrostatic high-pressure applications could decrease the energy gap between the valence and core bands, potentially shifting the CL emission wavelength to the ultraviolet (UV) region from 200 nm (6.2 eV) to 300 nm (4.1 eV). The ability to tune and shift the CL emission to UV wavelengths allows for the detection of the CL emission using UV-sensitive photodetectors in ambient atmosphere instead of highly specialized vacuum UV detectors operating in vacuum while maintaining the intrinsically fast CL decay times, thereby opening up new possibilities for KMgF as a fast-response scintillator.

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0.3.54 High pressure cross-luminescence from BaF_2 as potential wavelength-tunable, fast-response scintillator

Speaker: Yamashita Masahiro

High pressure cross-luminescence from BaF₂ as potential wavelength-tunable, fast-response scintillator

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The luminescence from BaF₂ has a very fast and a slow component. The fast component is cross-luminescence (CL)[1]. The decay time of CL is 600 ps, which is 1/1000 that of the slow component called self-trapped exciton (STE) emission. However, the CL wavelength is in the VUV region. Numerical calculations predicted that the wavelength of CL can be shifted to longer wavelength by controlling the band gap energies through high pressure application to the crystal [2]. In this research, we observed experimentally the pressure dependence of the shift in the CL wavelength when pressure is applied to the BaF₂ crystal.

In the experiment, the luminescence and x-ray diffraction (XRD) were measured simultaneously under high pressure in a sapphire anvil. X-rays of 20 keV was used as excitation source for luminescence and diffraction evaluation.

Figure 1 shows the relationship between pressures and lattice constants of BaF₂. Experimental data reached 8.7 GPa because the sapphire anvil was broken when the pressure increased above 8.7 GPa. The crystal phase was changed at 3 GPa from cubic to orthorhombic. In this presentation, we will report about the luminescence properties of CL and STE emission.

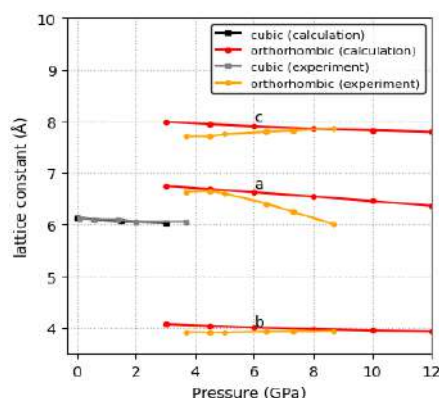


Figure 1. Pressure vs lattice constants.

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0.3.55 High-resolution cathodoluminescence on polycrystalline photovoltaic materials

Speaker: Frouin Bérengère

High-resolution cathodoluminescence on polycrystalline CdSeTe for photovoltaics: the role of selenium

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Adding Selenium in a CdTe thin film significantly improves the performances of solar cells, but a complete and quantitative physical understanding is still missing [1,2]. A systematic study with various Se concentration ($\text{CdSe}_x\text{Te}_{1-x}$, x from 0 to 0.4) allows us to quantify the passivation role of Se. We demonstrate a ten-fold luminescence enhancement between $x=0$ (CdTe) and $x=0.4$. CL spectra are fitted with the generalised Planck law coupled to a proper absorption model [3] (Fig.1(e)) to link the bandgap energy to the Se concentration. High-resolution CL is used to map polycrystalline CdSeTe films after thermal annealing (Fig.1(a,b)), and to map the Se concentration probed by the luminescence peak position (Fig.1 (c,d)). We evidence Se diffusion along CdTe grain boundaries, and we quantify the diffusion coefficients of Se atoms in both grain interior and grain boundaries [4].

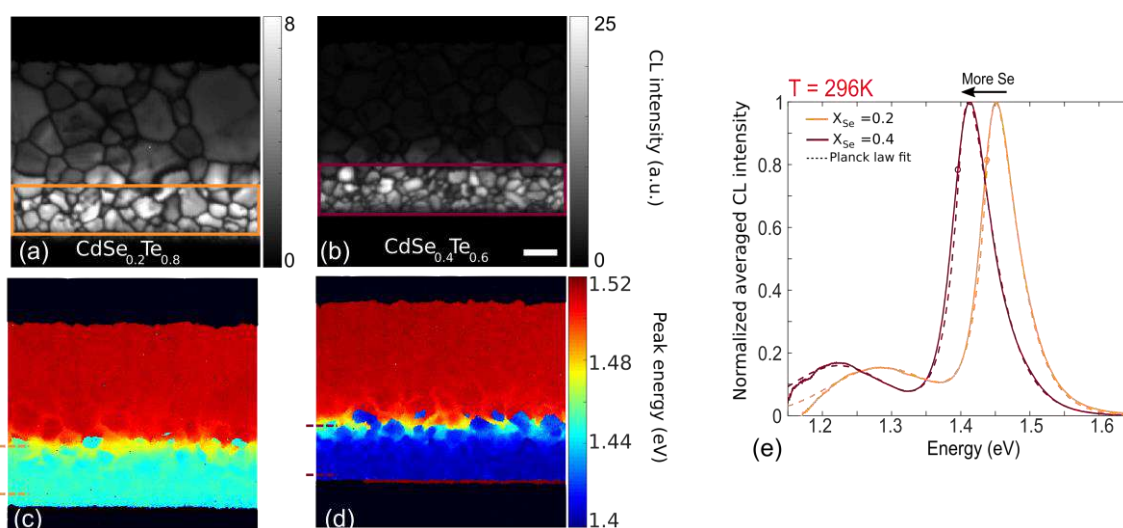


Figure 1: Panchromatic maps of CL intensity for $\text{CdSe}_x\text{Te}_{1-x}$ samples with nominal Se content of $x=0.2$ (a) and $x=0.4$ (b) along with the corresponding emission peak energy maps (c,d). (e)

Normalized CL spectra averaged over the area shown as colored rectangles in panels (a) and (b) (solid lines). Dashed lines correspond to the generalized Planck law fit, open circles on the CL spectra indicate the bandgaps determined from the fit.

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0.3.56 Impact of phosphor coatings optical and thermal properties on luminescence-based thermometry uncertainty

Speaker: Mendieta Aldo

Impact of phosphor coatings optical and thermal properties on luminescence-based thermometry uncertainty

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The use of luminescence thermometry has grown continuously over the last years. Its appeal lies in its ability to perform remote and minimally invasive temperature measurements in a wide range of applications (nuclear, steel processing, combustion, etc.), where conventional techniques are severely limited. However, to elevate it to a traceable temperature measurement technique, rigorous metrological validation is required. In luminescence thermometry, during or following excitation with UV light, selected ceramic materials emit temperature-dependent luminescence – changes in the luminescence emission spectra or lifetime. For surface thermometry, these materials are bonded to the surface of interest for remote temperature monitoring [1]. Although thin coatings are applied ($l_{phos} < 100 \mu\text{m}$), still the measured temperature T_{meas} (from the phosphor thermometry system) can be vastly different to that of the coating's surface (T_{surf}). To quantify such offset, we propose a highly accurate and traceable calibration prototype for luminescence thermometry as well as an in-house developed uncertainty modelling tool to quantify the sources of optical and thermal uncertainties. As such, a 1D steady-state heat transfer and optical extinction model (under LabView), together with a design for a prototype phosphor-based surface calibrator, operating up to 500 °C, are presented. All estimations are using thermophysical and optical properties of tested coatings made with $\text{Mg}_4\text{FGeO}_{5.5}:\text{Mn}$ and a ceramic binder (Aremco Ceramabind 643-2). The uncertainty evaluation showed here can easily be extended to other phosphors, substrates and/or temperatures. Fig. 1 Left shows the design of the prototype phosphor calibrator and, Fig. 1 Right shows the temperature difference ($T_{surf} - T_{meas}$) for three coating thicknesses l_{phos} , showing how the phosphor derived temperature is dependent on coating thickness due to the luminescence signal emanating from different coating depths.

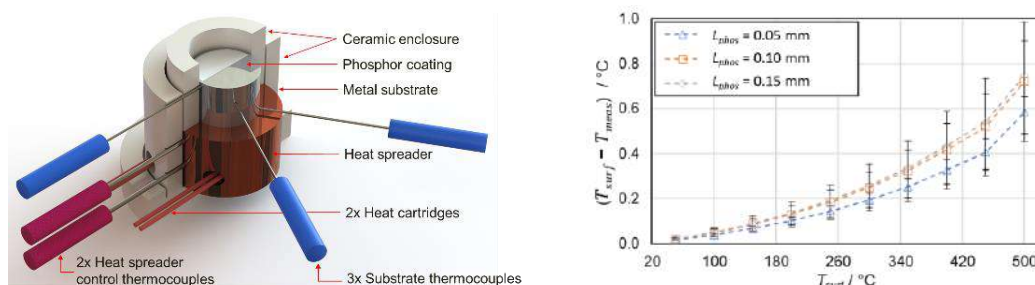


Fig. 1. Left. Design of the phosphor calibration system. Right. Calculated difference ($T_{surf} - T_{meas}$) for three coating thicknesses, for temperatures up to 500 °C. The error bars represent the change in values for a 1σ change of $\Delta = \pm 0.017 \text{ mm}$ (coating thickness).

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0.3.57 Improving sensitivity, signal intensity and operating range of luminescent pressure sensors based on lanthanide ions

Speaker: Runowski Marcin

Improving sensitivity, signal intensity and operating range of luminescent pressure sensors based on lanthanide ions

M. Runowski,^{1,2,*} T. Zheng,³ P. Woźny,¹ I. R. Martín,² M. Sójka,⁴ E. Zych,⁴
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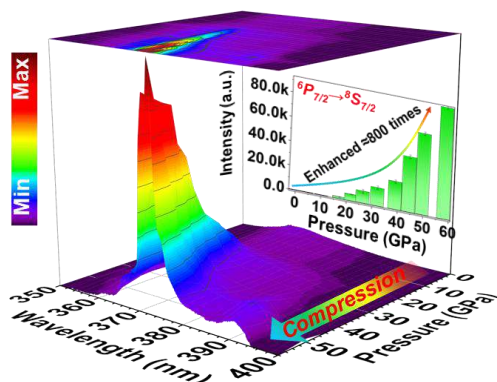
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Luminescent pressure sensors allow non-invasively monitor variations of pressure gradient in the system studied, including micron-sized and large-scale areas. Utilizing diverse manometric parameters, such as emission band shift, band intensity ratio, band width or luminescence lifetime, one can remotely read out the pressure values, alike in the low pressure (vacuum)^[1-3] and high-pressure ranges.^[4-7] However, the limiting factors for pressure readouts are often associated with deterioration of the optical signal with pressure (quenching), low sensitivity of the manometric parameters and limited operating range of the luminescent sensors.

Here we show how to enhance, improve and broaden the mentioned factors, applying various strategies, such as: I) inter-ionic energy transfer and temperature/pressure-induced configurational crossover processes;^[4] II) the use of lanthanide ions at different oxidation states in diverse host lattices;^[5-7] III) vacuum-enhanced light-to-heat conversion and thermalization of states for indirect pressure sensing,^[1-3] etc.



Pressure-enhanced $4f^7 \rightarrow 4f^7$ luminescence of Eu^{2+} in SrB_4O_7 crystals (${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition)

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0.3.58 Influence of the metal type on spectroscopic properties of organic-inorganic optical thermometer $[DMA]M1 - xCrx(HCOO)_3$ ($M = Zn, Mn, Mg$); $x \in (0, 0.01, 0.03, 0.05)$

Speaker: Kabański Adam

Influence of the metal type on spectroscopic properties of organic-inorganic optical thermometer [DMA]M_{1-x}Cr_x(HCOO)₃ (M = Zn, Mn, Mg); x ∈ (0, 0.01, 0.03, 0.05)

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Organic-inorganic perovskite-type materials with general formula ABX₃ attract increasing attention due to their unique properties, i.e. optical, magnetic, and ferroelectric. [1,2] However, temperature-dependent luminescence is one of the most crucial phenomena occurring in hybrid materials. [2,3] The composition of the host material, as well as dopant concentration are key parameters tuning the optical characteristics and enhancing implementation potential.

Among various hybrid materials, the single perovskite structure, herein, the series of [DMA]M_{1-x}Cr_x(HCOO)₃ where M = Zn, Mn, Mg, and x = (0, 0.01, 0.03, 0.05), exhibit outstanding temperature-dependent spectroscopic properties. The luminescence intensity is particularly affected by the substitute of the metal type (M). Changing the concentration of Cr³⁺ ion (x) affects the intensity of the narrow, spin-forbidden ²E_g → ⁴A_{2g} (around 698 nm) and the broad, spin-allowed ⁴T_{2g} → ⁴A₂ (around 769 nm) transitions. By analyzing these temperature-sensitive emissions, it is possible to develop a thermometric model for high-sensitive temperature detection. Moreover, the investigation of emission intensity as a function of temperature provides important insights into the relationship between crystal field strength and luminescence characteristics.

The presentation will be focused on the preparation of the series of investigated materials, structural analysis, and temperature-dependent optical studies. Particular attention will be paid to the influence of the crystal field strength on the spectroscopic and thermometric properties.

This research was supported by the National Science Center (Narodowe Centrum Nauki) in Poland under the project SONATA 16 no. 2020/39/D/ST5/01289

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0.3.59 Insights into the mechanisms of persistent luminescence provided by electron paramagnetic resonance

Speaker: Antuzevics Andris

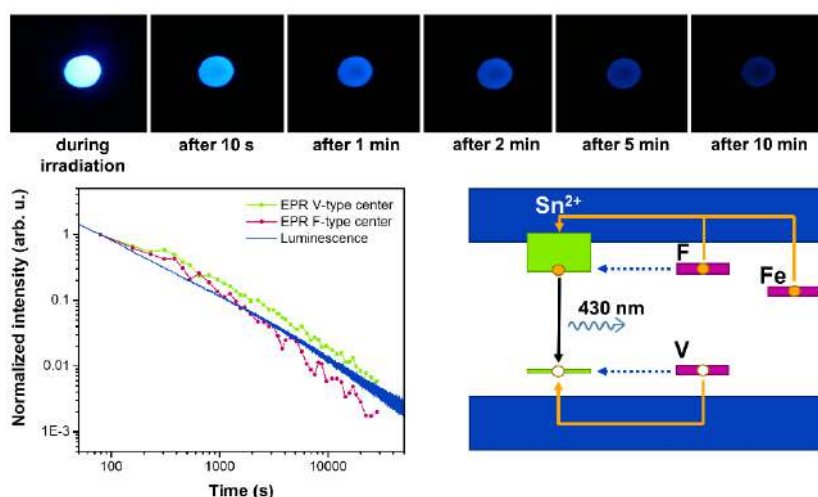
Insights into the mechanisms of persistent luminescence provided by electron paramagnetic resonance

A. Antuzevics,^{1,*} G. Krieke,¹ G. Doke,¹ D. Nilova,¹ P. Rodionovs,¹
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Persistent luminescence is a phenomenon with deep underlying physics whereby optical spectroscopy alone cannot reveal all the details. Application of complementary magnetic-resonance-based techniques is crucial for in-depth analysis of the oxidation state and site-occupancy of emission centers as well as the defects created during the excitation process.



The proposed mechanism of persistent luminescence in $\text{Ca}_2\text{SnO}_4:\text{La}^{3+}$ based on correlated decay of luminescence and EPR signals [1].

The presentation will overview the capabilities of electron paramagnetic resonance (EPR) in the analysis of persistent phosphors. The versatility and limitations of EPR spectroscopy will be highlighted based on recent results obtained in $\text{Ca}_2\text{SnO}_4:\text{La}^{3+}$ [1,2], $\text{MgGeO}_3:\text{Cr}^{3+}$ [3], $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Pr}^{3+}$ [4], and $\text{Mg}_3\text{Lu}_2\text{Ge}_3\text{O}_{12}:\text{Pr}^{3+}$ persistent phosphor materials.

Latvian Council of Science, project “Defect engineering of novel UV-C persistent phosphor materials”, project No. Lzp-2021/1-0118 is gratefully acknowledged.

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0.3.60 Isolated coordination polyhedral confinement to the analysis of structure-photoluminescence relationship of Mn²⁺ and Cr³⁺

Speaker: Qiu Zhongxian

Isolated coordination polyhedral confinement to the analysis of structure-photoluminescence relationship of Mn²⁺ and Cr³⁺

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Researches have focused on designing new inorganic phosphors to meet different application requirements. The structure-photoluminescence relationship between activator ions and matrix lattice plays an irreparable role in designing target phosphors. Herein, a series of ABP₂O₇-based phosphors (A = Ba/Sr, Li/K; B = Mg/Zn, Ga/Sc/In) are prepared for a detailed study on the relationship between the luminescence performance and spatial structure and symmetry of the doping site of Mn²⁺ or Cr³⁺. Due to the weak interaction between nearest B–B pairs, [BO_{5/6}] are defined as isolated coordination polyhedron whose structure and symmetry have direct influence on the photoluminescence of the activators. The Mn²⁺ shows red or deep red emission and the Cr³⁺ shows tunable broadband near infrared emission. We proposed the isolated coordination polyhedral confinement to clarify luminescence performance of Mn²⁺ and Cr³⁺ in the 5- or 6-fold coordination polyhedra with different geometries, which has a great theoretical research significance for designing different inorganic phosphors.

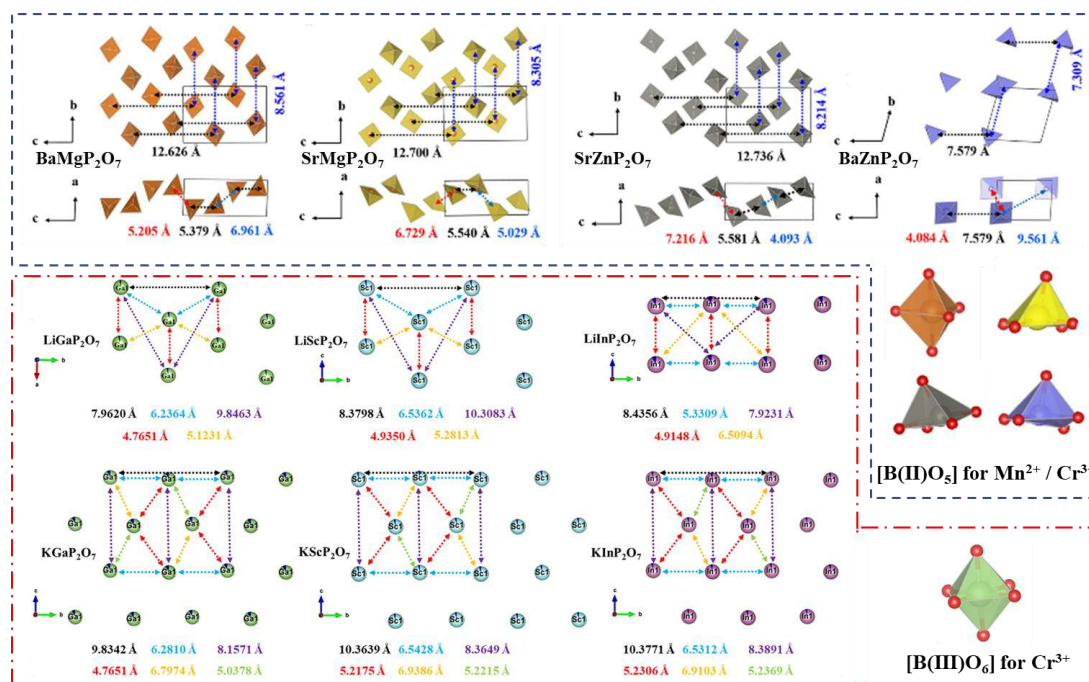


Figure 1 Schematic diagram of the isolated coordination [BO_{5/6}] in ABP₂O₇-typed structures

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0.3.61 Keep the quenching away: Quantifying the shielding effect over quantum yield of neodymium-doped near-infrared nanoparticles

Speaker: Benayas Antonio

Keep the quenching away: Quantifying the shielding effect over quantum yield of neodymium-doped near-infrared nanoparticles

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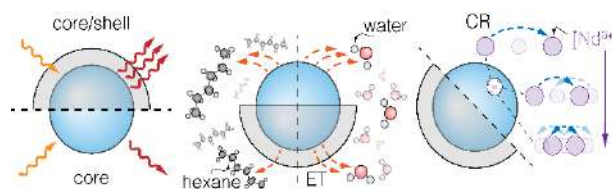
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Measure what is measurable and make measurable what is not so.
Galileo Galilei

Quantification of the photoluminescence quantum yield (PLQY, defined as the fraction of emitted photons against the number of absorbed photons),¹ constitute the most rigorous way to characterize the performance of luminescent nanoparticles for biomedical applications. Yet, it is a variable quantitatively missed in the literature, as frequently reports do not present absolute PLQY values. Between absorption and PLQY, physical parameters determining the brightness, the former is an intrinsic characteristic of the material, while PLQY depends on the architecture of the nanoparticle and its immediate environment. Even fewer absolute PLQY insight is available for nanoparticles operating in the near-infrared (NIR), a spectral range indeed where such probes operate deeper within tissues, grant better imaging contrast, and suffer less from background noise, i.e., autofluorescence.^{2,3} Among NIR-NPs, lanthanide-doped nanoparticles (LNPs) are widely used because of versatility, chemical and optical stability, and generally presumed nontoxicity.⁴

In this talk, we will identify the findings for Nd³⁺-doped NPs -the preferred LnNPs for many applications ranging from imaging to therapy- which cover the improvement of the PLQY upon inert shell coating of the NPs; the PLQY decrease with increasing Nd³⁺ doping despite the inert shell; and the major influence of solvent quenching on the PLQY of the LNPs, though it is relatively lessened for high Nd³⁺ doping. Later developments in the literature will be briefly discussed.



Schematic representation of the quenching factors (solvent molecules and cross relaxation) hampering luminescent (in particular NIR) nanoparticles.

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0.3.62 Lead-free manganese based perovskite inspired metal halides: from synthesis to (micro)-LED application

Speaker: Martin Pierre

Lead-free manganese based perovskite inspired metal halides: from synthesis to (micro)-LED application

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Inorganic lead halide perovskites, with a general formula CsPbX_3 ($\text{X}=\text{Cl}^-$, Br^- , I^-) have triggered a huge scientific interest, particularly since 2015. Even if they show excellent quantum yields, narrow and tunable emission band, their poor stability against oxygen, moisture, thermal and photonic stresses needs to be considered for application in LED devices. Moreover, lead (Pb) amount in electronic compounds is restricted to 1000 ppm by the RoHS, considering the risk for human health. Consequently, to overcome this major drawback, the development of stable and Pb free halides is currently attracting strong interest [1].

Herein, we employed a rapid and room-temperature synthesis to achieve Cs_3MnBr_5 micron-sized crystals (Figure A). Its strong green emission is attributed to manganese (II) ${}^4T_1 \rightarrow {}^6A_1$ transition, partially allowed in tetrahedral environment. A better air stability was achieved through zinc alloying. We show that an increase in x value in $\text{Cs}_3\text{Mn}_x\text{Zn}_{1-x}\text{Br}_5$ improved blue light absorption, but is also responsible for an internal quantum yield drop, which has been correlated to the occurrence of a quenching phenomenon, evidenced through time resolved emission measurements. Then, the stability under thermal and photonic stresses was investigated.

Through this work, we developed a narrow band (FWHM~40nm) green-emitting halide ($\lambda_{em} = 520\text{nm}$ – Figure B) with high internal quantum yield (~60%) under blue/UV light (Figure C), and good thermal and photonic stability, which is particularly promising for an association with (micro)-LED.

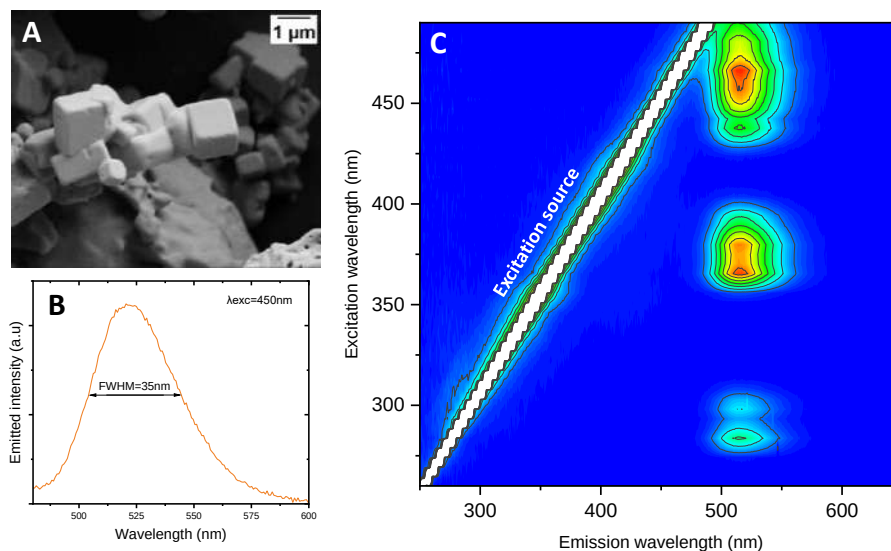


Figure – SEM picture (A), emission spectra under blue (450nm) excitation (B) and excitation-emission map (C) of $\text{Cs}_3\text{Zn}_{0.5}\text{Mn}_{0.5}\text{Br}_5$.

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Acknowledgements

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0.3.63 LED-pumped Ce:YAG luminescent concentrator for absolute calibration of a streaked optical pyrometer

Speaker: Nourry-Martin Maxime

LED-pumped Ce:YAG luminescent concentrator for absolute calibration of a streaked optical pyrometer

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LED-pumped Luminescent Concentrator (LC) has already demonstrated its performance to pump transition metal lasers [1]. This incoherent source of high brightness and high optical power can also be useful for direct emission instead of laser pumping [2]. Absolute calibration of streak cameras requires high optical power over the short sweep duration (from few ns to hundreds of ns). Traditional sources like spectral lamps or halogens are not powerful enough for this calibration. We demonstrate that a LED-pumped Ce:YAG luminescent concentrator is able to calibrate a streaked optical pyrometer (SOP) dedicated to temperature measurements of plasmas on high-energy laser facilities. The Ce:YAG concentrator is a parallelepiped with a high aspect ratio (200 mm x 2.5 mm x 1 mm). A small surface (2.5 mm x 1 mm) is used for the output whereas the large faces are dedicated for the pumping (Fig.1). Close to these two large faces of the Ce:YAG, there are two panels of 256 LEDs emitting at 440 nm. In order to increase the pump power, the LEDs operate in quasi-continuous wave regime, at 10 μ s with a current of 4A (4 times the nominal value in cw). The light generated inside the crystal by spontaneous emission is guided thanks to total internal reflection towards the output face. We chose to "fiber couple" the output with a light guide adapted to the large etendue of the concentrator (lambertian emission). To adapt the numerical aperture (NA) of the concentrator to the NA of the light guide, we have bonded a compound parabolic concentrator (CPC) at the concentrator output. Despite the transmission of the light guide (70%), this setup allows to achieve 36 W at the output of the light guide. The LC source made it possible to obtain signal over the complete temporal and spatial axis of the streak camera. Tests were carried out on Quartz as it acts as a reference for equation of states. We observed a good agreement between temperature measurements and the model.

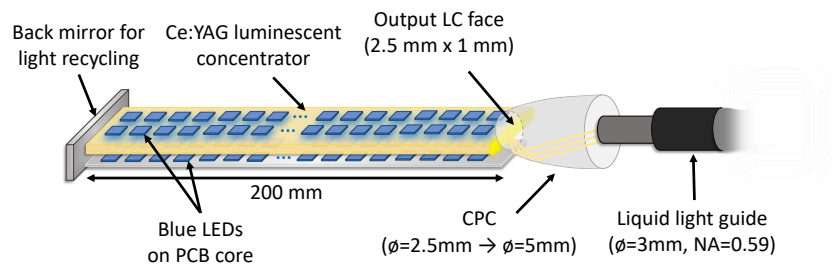


Fig.1: Experimental setup of the LED pumped Ce:YAG luminescent concentrator

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0.3.64 LED-pumped Er:Cr:YSGG

Speaker: Lopez Lisa

LED-pumped Er:Cr:YSGG

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Er:Cr:YSGG is a well known crystal with laser emission at 2.79 μm useful for medical applications. Energy transfer between Cr and Er allows to pump this crystal with flashlamps. In a search for new sources emitting in the SWIR, we propose to revisit this crystal with a new way of pumping: with LEDs. Er:Cr:YSGG generally operates on its $^4I_{11/2}$ - $^4I_{13/2}$ transition for laser emission at 2.79 μm . Its $^4I_{13/2}$ - $^4I_{15/2}$ transition around 1.6 μm can also be investigated for spontaneous emission. Indeed, this wavelength range is interesting for high-brightness, spectrally broadband and incoherent sources in the SWIR adapted for InGaAs cameras. In order to collect the spontaneous emission efficiently, a geometry of luminescent concentrator (LC) can be used [1].

As pump source, we use a Ce:YAG LED-pumped luminescent concentrator emitting a broadband spectrum between 550 nm and 650 nm matching the absorption band of Er:Cr:YSGG (Fig.1a). The Ce:YAG delivers 2 ms pulses at 10 Hz with an energy of 1.4 J in the Er:Cr:YSGG. The later operates as a second LC with a maximum brightness on its smallest face chosen as the output face of the system.

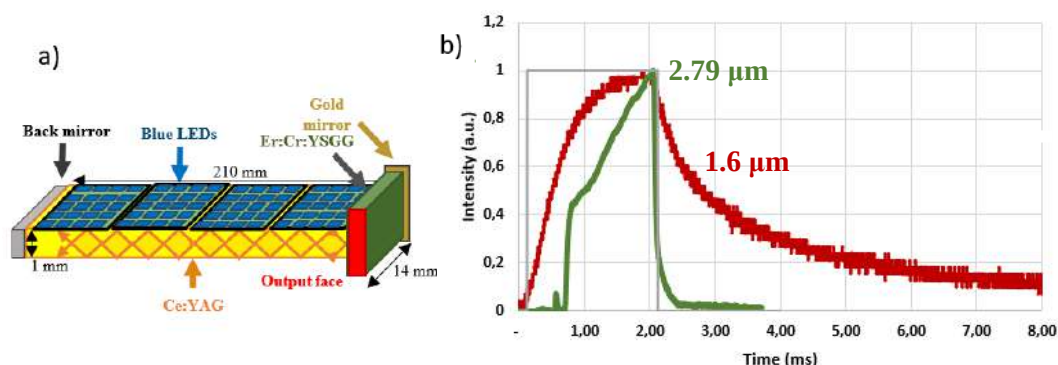


Fig. 1 a) Experimental setup for the cascade of concentrators **b)** Temporal evolution for the two wavelength ranges after optimization of each: in green laser signal at 2.79 μm , in red spontaneous emission signal at 1.6 μm and in grey pump signal.

At 1.6 μm , the spontaneous emission emitted by the output face represents an energy of 245 μJ (temporal profile fig.1b). It corresponds to a spectral luminance peak of 40 $\text{mW}/\text{sr}/\text{cm}^2/\text{nm}$, 10 times larger than the ones of SWIR LEDs available on the market. These performances show the relevance of a Er:Cr:YSGG LED-pumped luminescent concentrator as a source of spontaneous emission in the SWIR at 1.6 μm .

It is also interesting to note that we also have observed, a significant laser emission at 2.79 μm , for the first time under LED pumping, with an energy per pulse reaching 0.8 mJ and a duration of 1.5 ms (Fig.1b).

More work will be presented during the conference by optimizing the parameters.

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0.3.65 Lengthening of $\text{Sm}^{2+} 5d \rightarrow 4f$ decay times through interplay with the $4f6(5D0)$ level

Speaker: Van Aarle Casper

Lengthening of $\text{Sm}^{2+} 4f^5 5d \rightarrow 4f^6$ decay times through interplay with the $4f^6[{}^5D_0]$ level

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In literature, compounds with exclusively $\text{Sm}^{2+} 4f^5 5d \rightarrow 4f^6$ emission are reported to show decay times ranging from 1.5 μs to 35 μs [1, 2] whereas 1 to 2 μs is to be expected. Lengthening of the decay time can occur when excited Sm^{2+} spends part of its time in the $4f^6[{}^5D_0]$ configuration. The role of the $4f^6[{}^5D_0]$ level in the decay dynamics of Sm^{2+} has been previously studied for specific compounds [3], but the relation between compound and $4f^5 5d \rightarrow 4f^6$ emission decay time has not yet been studied.

In this work, a simple Boltzmann distribution using the energy difference between the excited $4f^5 5d$ and $4f^6[{}^5D_0]$ levels is employed to explain the decay dynamics of Sm^{2+} as a function $4f^5 5d \rightarrow 4f^6$ emission wavelength. Figure 1 shows that the resulting model predicts the room temperature $4f^5 5d \rightarrow 4f^6$ emission decay time. Its ability to predict the temperature dependence of the decay time will also be discussed. Additionally, the model gives insight in how experimental data on Sm^{2+} decay times may be prone to misinterpretation, where upon increasing temperature, shortening of the decay time can be falsely identified as thermal quenching and lengthening as self-absorption.

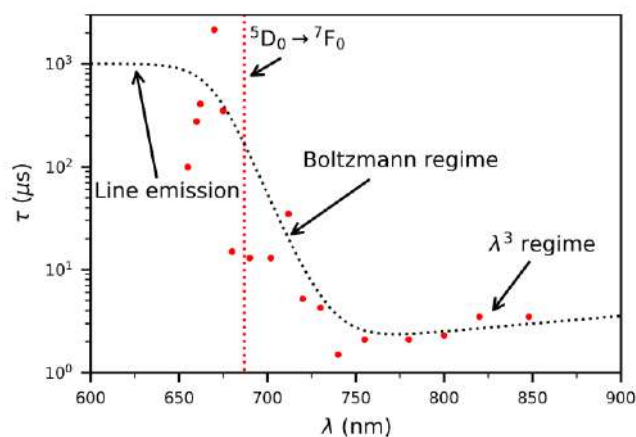


Figure 1. The observed decay time τ versus $4f^5 5d \rightarrow 4f^6$ emission wavelength λ . The red dots show data from literature, the black dotted curve is the simulated data using a Boltzmann distribution between the $4f^5 5d$ and $4f^6[{}^5D_0]$ states. The red dotted line indicates the emission wavelength of the ${}^5D_0 \rightarrow {}^7F_0$ transition.

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0.3.66 Levitodynamics with optically active nanocrystals

Speaker: Cyril Laplane

Levitodynamics with optically active nanocrystals

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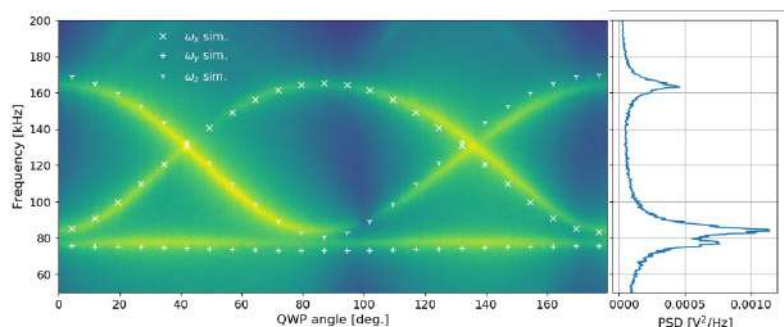
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Levitated mesoscopic particles, with their intrinsic low coupling to the environment, are ideally suited as hybrid quantum platforms of mesoscopic size and mass. In vacuum, the only coupling to the environment is the levitation field itself, resulting in a mechanical oscillator with a very high-quality factor. Optically levitated systems in vacuum have recently entered the quantum realm with demonstration of cooling to the motional quantum ground state using passive and active feedback methods [1 - 3]. The levitated particles in most of these experiments are optically inert such as SiO₂ nanospheres. Here we are interested in studying and developing techniques suitable for the stable levitation of optically active nanoparticles, in particular, rare-earth ion activated nanocrystals. Rare-earth ion doped crystals are one of the few materials enabling laser refrigeration through anti-Stokes fluorescence which is particularly relevant for levitation in vacuum as it enables control over the internal temperature of the levitated nanoparticle [4]. This is particularly relevant since the internal temperature of the particle will limit the coherence of the oscillator.



Oscillator spectroscopy of a 10% Yb³⁺:NaYF₄ nanocrystal in vacuum. By varying the polarization using a quarter-wave plate (QWP) we can orient the nanoparticle in the trap, effectively tuning the oscillation frequency of the motion.

We will present the spectroscopy of the oscillator and the optically active ensemble of different nanoparticle designs. In particular we will show refrigeration down to 150k from room temperature of a levitated nanocrystal. We will also show control of the temperature of the oscillator paving the way to the absolute cooling of a levitated nanoparticle. Our approach would enable access to advanced tools for the quantum manipulation of levitated mesoscopic systems, opening up new avenues for accessing fundamental physics.

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0.3.67 Light extraction and injection enhancement using metallic nanocubes

Speaker: Réveret François

Light extraction and injection enhancement using metallic nanocubes

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Phosphor materials are widely used as luminescent coating (LC) in lighting, display, illumination, marking or Li-Fi [1]. Due to the refractive index mismatch between LC and the air, a strong amount of light is trapped in the structure. Large part of photons is guided in both LC and substrate and escape mostly from the edge. This leak could represent up to 80% of the emitted photons [2]. After a brief review of the existing solutions in the literature to extract guided photons, the interest of using metallic nanoparticles (MNPs) will be presented. Most of published works report the improvement of light extraction by using plasmonic resonance of MNPs. In this study, we show that MNPs could be used efficiently as optical scatterers [3]. A light extraction enhancement by a factor of 1.8 has been evidenced (figure 1a) when silver nanocubes (NCs) are simply deposited on the LC surface. The role of the NCs density will be highlighted and compared with simulations. As shown in figure 1b, we can quantify a large light injection improvement when Ag NCs are dispersed on a transparent material (quartz substrate), a factor 50 is found. Moreover, we observe a strong light extraction enhancement of a feebly luminescent quartz material by a factor up to 200 depending on the Ag NCs density (figure 1c).

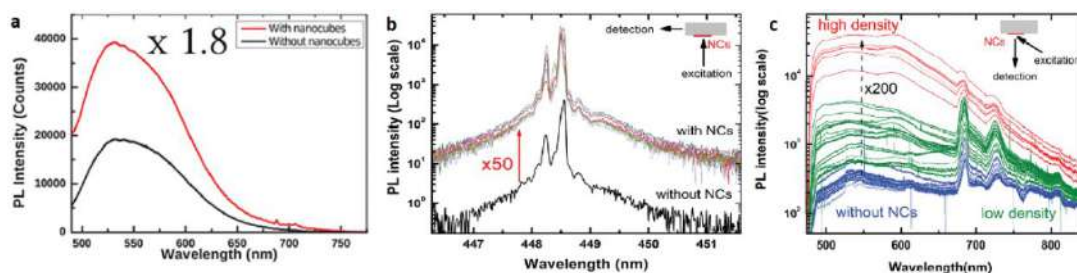


Figure 1: (a) Emission spectra of YAG:Ce LC with and without nanocubes. (b) Light injection improvement on a quartz substrate decorated with Ag nanocubes. (c) Enhancement of light extraction of a quartz substrate depending the Ag nanocubes density.

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0.3.68 Light harvesting and enhanced emission in core-shell dye-based fluorescent organic nanoparticles

Speaker: Blanchard-Desce Mireille

Light harvesting and enhanced emission in core-shell dye-based fluorescent organic nanoparticles

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In the search for ultrabright nanoparticles for bioimaging purpose, we have developed a promising class of luminescent nanoparticles via an original approach based on the design of dedicated **Polar and Polarizable Dyes** (PPDs). These PPDs spontaneously self-aggregate in water generating dFONs (i.e. PPDs-based fluorescent organic nanoparticles). Interestingly, thanks to the strong dipolar interactions promoted by molecular confinement, such dFONs may show sufficient structural stability in aqueous media. Yet we had to fulfill a number of key issues for dFONs to be of major interest for bioimaging. These include large brightness's, colloidal (and fluorescence) stability in biological media, tunable emission, photostability as well as biocompatibility. We showed that we could achieve all those goals via subtle engineering of the PPDs building blocks [1-3]. Strikingly we were also able to engineer the dFONs surface properties to yield tunable, hyper-bright and photostable dFONs that (i) either easily penetrate inside of cells while maintaining their integrity (allowing single particle tracking within cells)[2] or (ii) alternatively can be made naturally stealth [3]. Our next goal was to exploit surface interactions to create **core-shell dFONs**. We have recently shown that by using complementary dedicated PPDs (Figure 1) allowing Fluorescence Resonance Energy Transfer (FRET), we could achieve core-shell dFONs. Such binary dFONs show efficient **shell-to-core light harvesting** and generate much brighter red emission than single component dFONs. Interestingly, unusual *nanointerfacial effects* on the fluorescence quantum yield and color have been unveiled.

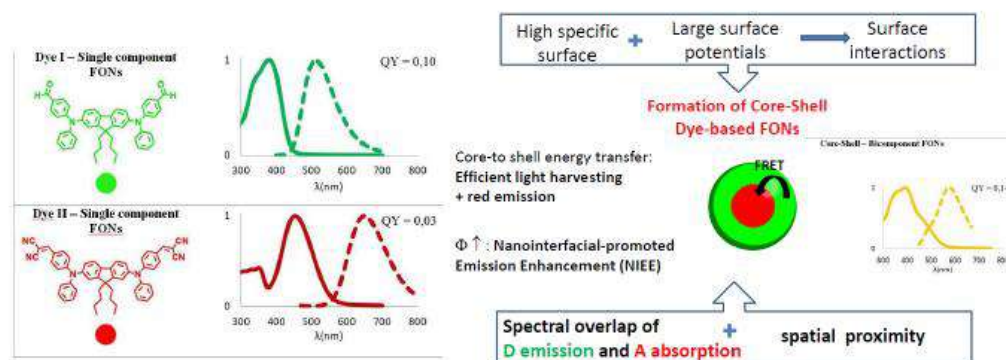


Figure: Luminescence properties of binary core-shell dFONs made from dyes I and II

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0.3.69 Luminescence based Circular Dichroism

Speaker: Markovic Obren

Luminescence based Circular Dichroism

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Sensitive and enantiomer-selective detection of chiral molecules is an important issue for many fields, including biology, chemistry, and the pharmaceutical industry. Indeed, chirality is a common property for both natural and synthetic molecules, leading to potentially very different effects depending on the enantiomer. Most of the current detection methods are based on circular dichroism (CD) spectroscopy – the quantification of the differential absorption of left and right-handed circularly polarized light – and consist in measuring the transmission of an incident beam through the chiral medium. However, this approach requires large volumes of solution and is intrinsically limited in sensitivity. Here, we propose a method to measure CD based on detecting the photoluminescence of chiral fluorescent emitters instead of absorption. Indeed, for low excitation powers, the differential emission of the two enantiomers is equal to their differential absorption, and therefore their CD spectroscopy can be performed on the luminescence signal. In this case, photoluminescence can be collected on very small volumes involving very small amounts of chiral objects, and consequently, very high sensitivity can be achieved. As an example, we show in **Figure 1**, the CD signals recorded in absorption, (c) and (d), and emission, (b) and (e), for fluorescent chiral nanoplatelets (1D confinement quantum dots) and compare them to the case of an achiral molecule, the rhodamine.

This circular dichroism detected by fluorescence can find applications in monitoring the grafting dynamics of chiral molecules, even at the single-molecule level. Moreover, it can be applied to molecules in their natural environment, such as living cells. Coupled with nanophotonics techniques to generate superchiral light, this new approach will also allow detecting CD in zeptoliter volumes [1]

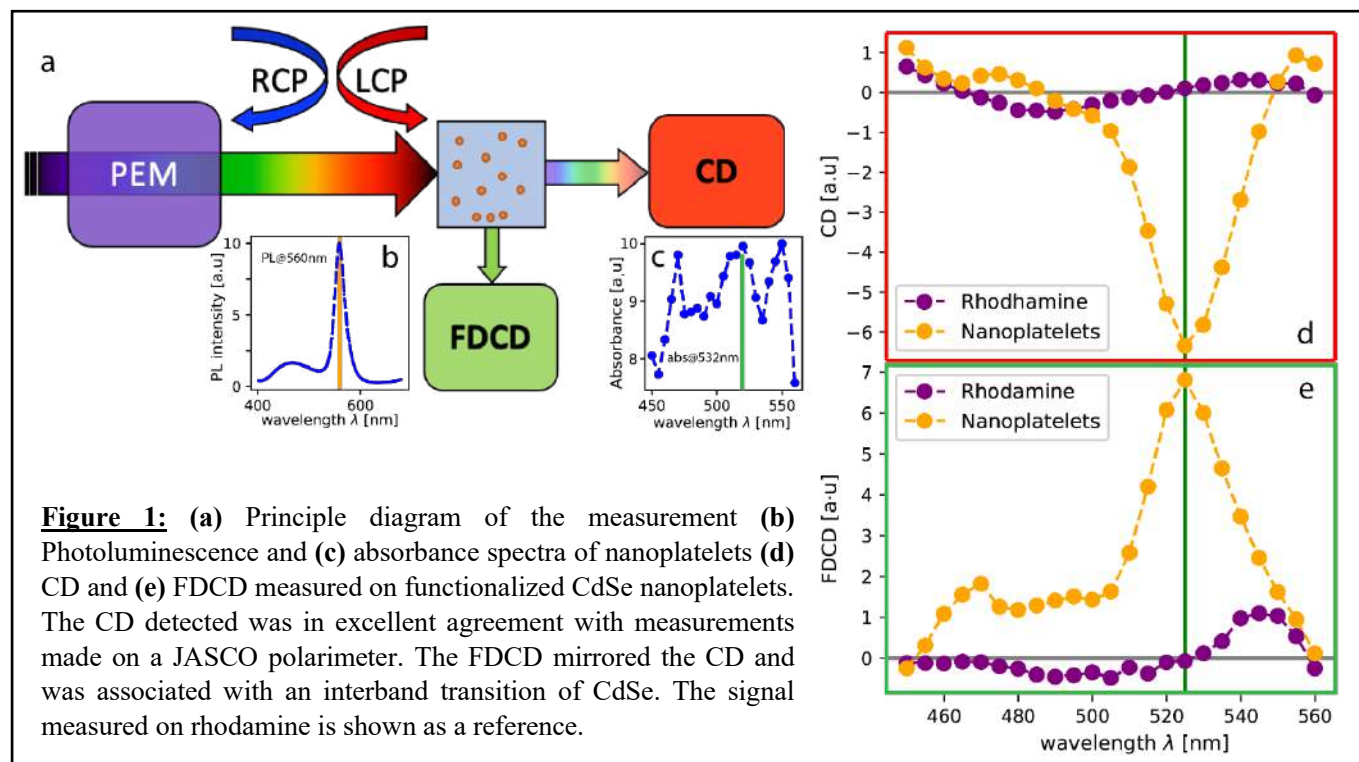


Figure 1: (a) Principle diagram of the measurement (b) Photoluminescence and (c) absorbance spectra of nanoplatelets (d) CD and (e) FDCD measured on functionalized CdSe nanoplatelets. The CD detected was in excellent agreement with measurements made on a JASCO polarimeter. The FDCD mirrored the CD and was associated with an interband transition of CdSe. The signal measured on rhodamine is shown as a reference.

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0.3.70 Luminescence of Bi₃TeBO₉ micro-crystals doped with Yb³⁺ and Er³⁺ ions

Speaker: Kasprowicz Dobrosława

Luminescence of Bi₃TeBO₉ micro-crystals doped with Yb³⁺ and Er³⁺ ions

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Bi₃TeBO₉ crystal is an excellent nonlinear optical material as well as an efficient host matrix for luminescent rare earth ions.^{1,2} Investigated Bi₃TeBO₉ crystalline powders were synthesized by means of the modified Pechini method. The results of μ -Raman investigations showed low phonon energy of Bi₃TeBO₉ matrix.³ Enhanced emission at 1531 nm of Er³⁺ ions in Bi₃TeBO₉:Yb³⁺/Er³⁺ system was excited by Bi³⁺ and/or Yb³⁺ ions upon their excitation at 327 or 975 nm, respectively. Moreover, it was found that the effective energy transfer from the excited Bi³⁺ ions directly to Er³⁺ ions or indirectly to Er³⁺ ions (via the excitation of Bi³⁺ ions in VIS range or excitation of Yb³⁺ ions in the NIR range) results in synergistic effect. As a result, the investigated Bi₃TeBO₉:Yb³⁺/Er³⁺ powders efficiently concentrate the ultraviolet/visible radiation in the near-infrared spectral range and can be potentially used as effective spectral converters in multi-functional miniaturized optical devices or new generation photovoltaic devices.

Acknowledgement

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0.3.71 Luminescence of Eu^{2+} centre in Eu-doped yttrium aluminate glasses: The effect of $\text{Gd}^{3+}/\text{Lu}^{3+}$ addition

Speaker: Klement Robert

Luminescence of Eu²⁺ centre in Eu-doped yttrium aluminate glasses: The effect of Gd³⁺/Lu³⁺ addition

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Yttrium-aluminium garnet, Y₃Al₅O₁₂ (YAG), is one of the most widely studied inorganic hosts due to its high application potential when doped with rare-earth (RE) ions. The excellent performance of YAG in terms of high rigidity, low thermal expansion, high optical transparency and chemical inertness predetermines YAG for its use in various fields of luminescence implementation such as scintillators, white light emitting diodes (w-LED) and laser media. The YAG:Eu³⁺ is known for its red light emission [1]. However, recently, efficient and stable Eu²⁺ blue photoluminescence (PL), excited in the broad UV band having a maximum at 300 nm was reported in YAG [2,3]. The presence of the stable Eu²⁺ responsible for the emission was unambiguously corroborated by optical and electron paramagnetic resonance techniques. In the present work, we report white light emission of Eu²⁺ centres from Eu-doped yttrium aluminate glasses and their crystalline, YAG-containing, analogues.

The Eu³⁺-doped yttrium aluminate glasses with eutectic composition were prepared by flame-spraying synthesis in the form of glass microspheres from precursor powders synthesized by the sol-gel method. The doping level ranges from 0.25 to 3.0 at. % of Eu³⁺. The as-prepared glasses contained both Eu³⁺ and Eu²⁺ ions in the equilibrium. To convert the Eu³⁺ to Eu²⁺ or vice versa in glass and glass-ceramic materials, the samples were heat treated in a reducing or oxidizing atmosphere at optimized temperature and dwell time. The prepared glass and glass-ceramic samples were characterized in terms of phase composition, microstructure, thermal properties and photoluminescence. The Eu³⁺-doped glasses and their crystalline analogues exhibit typical red emission due to the 4f-4f transitions within Eu³⁺ ions. In contrast, the samples containing Eu²⁺ ions emit cold white light under excitation at 345 nm, and PL spectra exhibit large broad-band emission in the 400-750 nm range with the emission maximum at ~520 nm. The temperature-dependent luminescence of the prepared phosphors and the lifetime using the TCSPC technique were studied in detail. Moreover, the effect of Y³⁺ substitution by Gd³⁺/Lu³⁺ on the luminescence properties of the phosphors was investigated.

Acknowledgement

This work was also supported by the Slovak Research and Development Agency under contract No. APVV-17-0049 and by grant VEGA 1/0476/22.

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0.3.72 Luminescence properties of multiscale nanostructured coatings combining ZnO nanowires and $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$

Speaker: Potdevin Audrey

Luminescence properties of multiscale nanostructured coatings combining ZnO nanowires and $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$

Aubry Martin^{1,2}, Audrey Potdevin^{1*}, François Réveret¹, Emmanuel Centeno³, David Riassetto², Michel Langlet², Geneviève Chadeyron¹

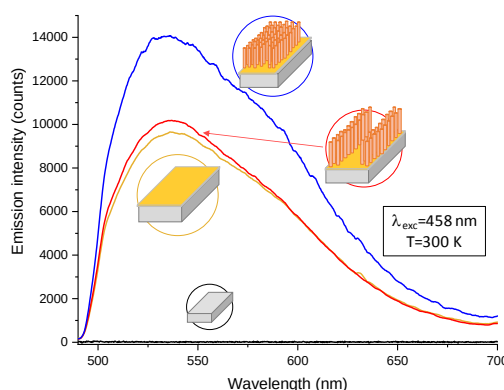
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Even if LED devices present very high efficiency, their performance could be further enhanced by increasing photon extraction or by controlling photons directionality. To attain this goal, we have developed heterostructures made of a $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ (YAG:Ce) coating combined with ZnO nanowires (NWs) coatings or gratings. NWs were obtained by hydrothermal growth on a photo-sensitive seed-layer and the selective growth came from the UV photo-engraving of the seed-layer directly deposited on the sol-gel derived YAG:Ce coating. The addition of NWs on the top of YAG:Ce coatings was expected to influence their optical properties. SEM, AFM and angle-dependent photoluminescence measurements have been carried out to study the morphological and optical properties of the obtained functional heterostructures. In particular, the optical study shows that this original design leads to a different angular distribution of light together with an increase in emission efficiency of YAG:Ce coating upon blue excitation compared to the flat coating (see Figure). This enhancement is very promising since a higher efficiency is obtained without using a superior amount of rare-earth ions, which are a critical resource. Simulation experiments have been carried out to unravel the involved mechanism. Results will be discussed in reliance on multiscattering and resonance events for photons within the structure, allowing them to escape from the phosphor layer by taking optical paths different from those of the flat coating.



Emission spectra of YAG:Ce coating and heterostructures YAG:Ce / ZnO NWs

Acknowledgment:

The authors acknowledge the French Agence Nationale de la Recherche for its financial support in the frame of the ANR SMARtLEDs project (ANR-19-CE08-0001).

0.3.73 Luminescence Thermometry Using Pr-Activated Garnets

Speaker: Kulesza Dagmara

Luminescence Thermometry Using Pr-Activated Garnets

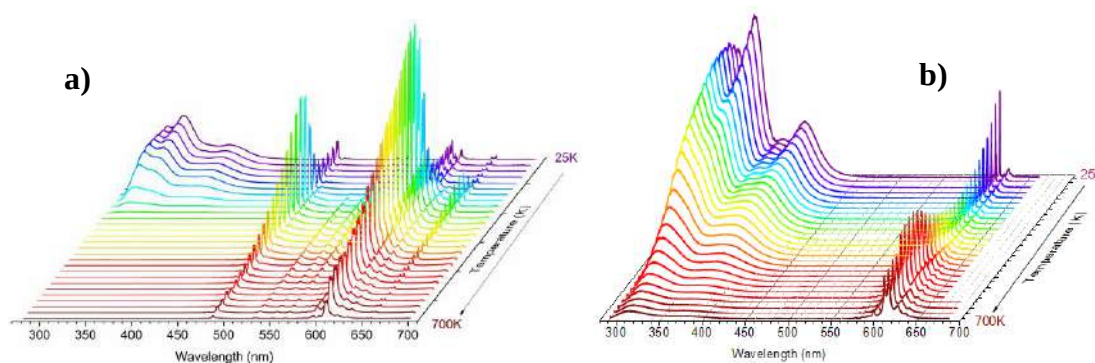
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Remote reading luminescence thermometry is of great interest to novel and emerging technologies. Nowadays, when high spatial resolution and/or harsh conditions are frequently faced, undisturbed measurements spanning a wide range of temperatures become continuously more difficult exploiting methods developed years ago. Luminescence thermometry addresses these challenges.

Pr-activated garnets are specific phosphors in which the Pr^{3+} ion can be efficiently excited optically by its $4f \rightarrow 5d$ allowed absorption transition around 300 nm and produce three types of emissions afterward. Thus, the $5d \rightarrow 4f$ broadband luminescence in the UV-blue part of the spectrum as well as narrow lines resulting from the $^3\text{P}_0 \rightarrow ^3\text{H}_J$ and $^1\text{D}_2 \rightarrow ^3\text{H}_J$ transitions in the bluish-green and red ranges respectively are generated. The three emissions have different properties. Among others their temperature dependence is diverse. Therefore, we considered the Pr^{3+} luminescence very attractive for luminescence thermometry. Since garnets are mostly thermodynamically stable oxides, they can withstand drastic changes in temperature from helium to above 1500 °C even. This makes them useful when measurements in harsh conditions are of interest.



T-dependence of luminescence spectra of a) $\text{Ca}_3\text{Sc}_2\text{Ge}_3\text{O}_{12}:\text{Pr}$ and b) $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Pr}$ garnets.

Acknowledgements: This research was supported by the Polish National Science Center (NCN) under the grant #UMO2018/29/B/ST5/00420.

0.3.74 Luminescent Imidazolium Salts as Bright Multi-Faceted Tools for Biology

Speaker: Berthiot Romain

Luminescent Imidazolium Salts as Bright Multi-Faceted Tools for Biology

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Light and cognate phenomena, e.g., luminescence are powerful tools endowed with great sensitivity to explore the infinitely small. Molecular salts, especially those based on imidazolium units, are granted with original properties and structural versatility, such as a tunable amphipatic character which promotes their self-organizations into liquid-crystal mesophases¹. Associated with fluorophores, their interactions with negatively charged species and biological membranes as well as their controllable cytotoxicity imparted them applications as anion receptors and cell imaging agents, but also as antibacterial and anticancer agents whose mechanism of action can be observed using luminescence, opening the possibility of theranostics (therapy and diagnosis)². In this presentation, we will describe the synthesis and design of new families of highly luminescent materials in the three states of matter (liquid, liquid crystal, crystalline) in a minimum of steps. We will describe their mesomorphic and photophysical properties and their activities as dyes for cell imaging, and as gene delivery agents.

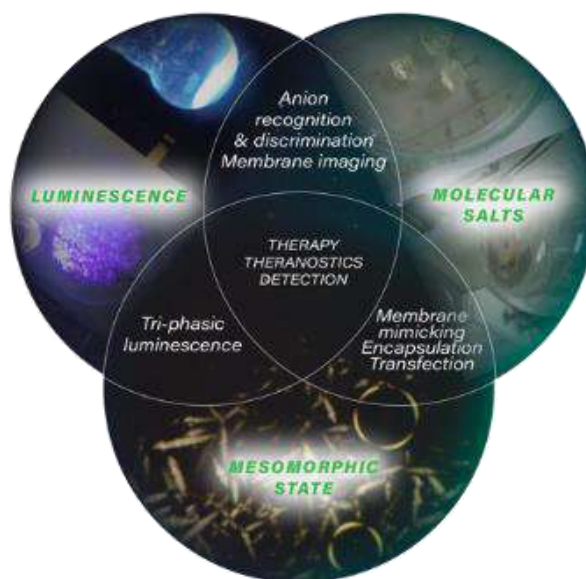


Figure: Imidazolium salts bearing fluorophore units can be easily tuned to encompass the desired properties to explore the biological world.

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0.3.75 Luminescent interphases in hybride nanocomposites

Speaker: Nedilko Serhii

Luminescent interphases in hybride nanocomposites

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Historically, an assessment of the role of phase separation in composite materials has changed over time. Phase separation (for example, in glasses) was considered as a negative phenomenon that affects the properties of materials and deteriorates their quality. At the same time, by changing the phase composition, it is possible to control and manage properties of the composite. Thus, this is a positive aspect of the phase separation phenomenon. In reality, certain intermediate regions (interphase layers) are formed in the composite between the "pure" original components. Thus, the composition and structure of these layers do not correspond to the composition and structure of the initial phases. The contribution of the interphase to the material properties and the interaction between the components of the composite can be clarified by the difference in the characteristics of the separated starting components and the composite materials.

The role of interphases in determining the macrocharacteristics of hybrid oxide nanocomposite materials is discussed in the contribution. Suitable literature data and the results of our own experimental and computer simulation studies were used..

The main direction of interphase behaviour in composite material study is a determination of the relationships between the properties of the material, on the one hand, and the atomic and energy structure, composition of the object, the size of its components, - on the other hand. Although the mechanisms of interaction between any possible components of the composite, in principle, are predictable, nevertheless, their role and contribution in the case of a particular type, especially - nanoscale composite material (nanocomposite) containing oxides fillers needs to be clarified.

These issues are discussed here on the base of results obtained for nanocomposites of three types, where nanocrystalline luminescent oxides fillers were embedded into: 1) the glass oxide dielectric matrices; 2) the polymer matrices, particularly, microcrystalline cellulose and nanocellulose; 3) carbon nanostructures (nanotubes, graphene and graphene oxide). Optical, electron and atomic force scanning microscopy methods as well as XRD, diffuse optical reflectance and photoluminescence methods were used to study mechanisms of phase interactions and their impact on optical and luminescent macro-characteristics of nanocomposite materials under study.

0.3.76 Luminescent ionic materials to detect neutrons

Speaker: Douce Laurent

Luminescent ionic materials to detect neutrons.

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Light and associated phenomena, such as luminescence, have proven to be powerful tools with great sensitivity for exploring the infinitely small, physical processes (energy and electron transfer, polarity, pressure, etc.) and physicochemical processes (concentration, visualization and localization of species...). Moreover, luminescent materials open up prospects for applications as scintillators in the detection and discrimination of ionising radiations. In this context, molecular salts, in particular those based on imidazolium units, have attracted the attention of the scientific community due to their original properties and structural versatility. In this presentation, we will describe the synthesis and design of new families of highly luminescent materials in the three states of matter (liquid, liquid crystal, crystalline) in a minimum of steps and without rare, expensive and strategic chemical elements. Finally, we will present the shaping of some luminescent imidazolium into centimetric photonic single crystals by crystallogenesis and their properties to detect neutrons of any energies. In the near future, these luminescent salts could replace helium (3) in the detection of low energy neutrons.

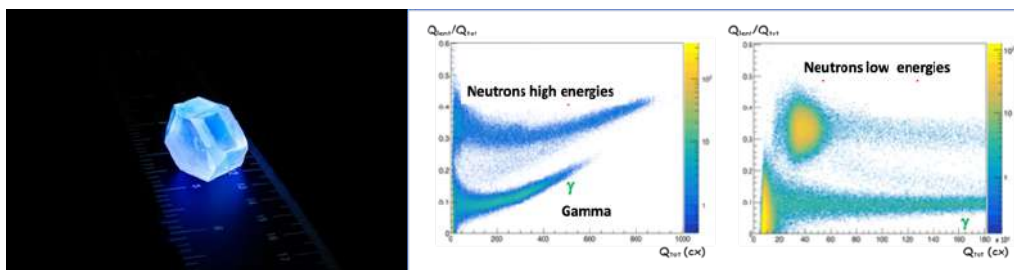


Figure: luminescent centimetric single crystal (left), fast and slow neutron detection (right)

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0.3.77 Luminescent lanthanide(III) molecular crystals under mechanical stimuli and photo-illumination

Speaker: Hirai Yuichi

Luminescent lanthanide(III) molecular crystals under mechanical stimuli and photo-illumination

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Stimuli-responsive luminescent materials have attracted attention for sensor applications and security marking techniques. In particular, triboluminescence (TL) is a unique phenomenon that occurs by fracturing solid-state materials without a light source. Despite its long history (> 400 years) and versatility, TL has not been elucidated in terms of the general molecular designs and the underlying photophysical processes. Bright TL has been reported for various lanthanide(III) (Ln(III)) complexes which also show strong photoluminescence (PL),^[1] and high ligand-excited PL quantum yields (Φ_{PL}) have reasonably explained the brightness of Ln(III) TL. On the other hand, we previously reported that Ln(III) TL does not always have the same characteristics of the corresponding PL by demonstrating clear TL/PL color differences.^[2]

This study aimed differentiate TL from PL. We prepared dinuclear Ln(III) complexes with quenching and enhancing processes in PL for Eu(III) and Tb(III) ions, respectively, and demonstrated that bright TL can be generated even when Φ_{PL} is negligible (Figure 1).^[3] It suggests the existence of direct Ln(III) excitation mechanisms under mechanical stimuli, while ligand-mediated photo-excitation is essential to efficiently sensitize Ln(III) ions in PL. Nanomechanical tests also indicated that ductility that allows crystals to accumulate the deformation energy could be critical for TL activity from a mechanical point of view. In addition, mechanochromic luminescence (MCL) was observed in a heterodinuclear Tb/Eu complex by mechanical grinding (*c.f.* fracturing for TL, grinding for MCL), being the first example of Ln(III) complex with dual TL and MCL properties. The presented strategy for Ln(III) mechanophores would trigger the development of new-generation mechano-responsive luminescent materials.

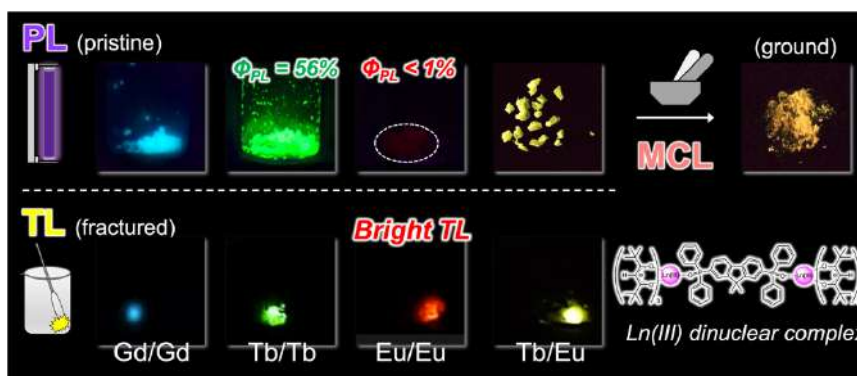


Figure 1. A schematic illustration of Ln(III) dinuclear complexes (Ln = Eu, Gd, Tb, or mixture thereof) with mechanically-responsive luminescence properties.

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0.3.78 Luminescent nanocrystals to measure complex dynamics of micro-organisms and bio-fluids

Speaker: Kim Jongwook

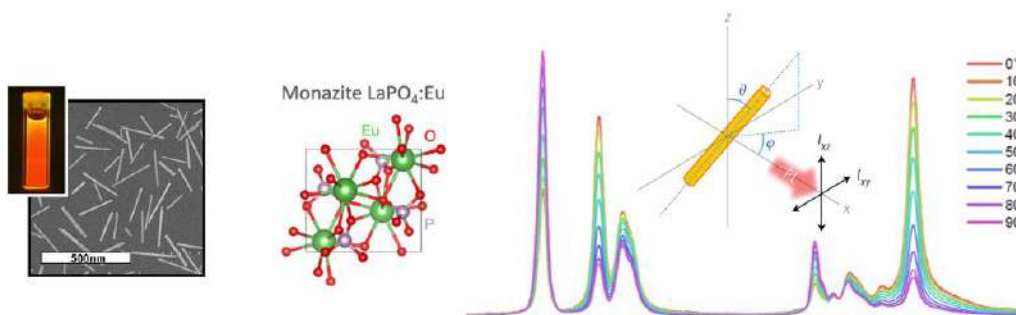
Luminescent nanocrystals to measure complex dynamics of micro-organisms and bio-fluids

Elodie Chaudan¹, Jeongmo Kim¹, Zijun Wang¹, Lilian Magermans¹,
Khalid Lahilil¹, Thierry Gacoin,^{1,*} and Jongwook Kim^{1,*}

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Luminescent probes are universally used to observe life and matter in small scale. However, many dynamic processes at the cellular and molecular levels remain unknown because they involve complex motions such as rotation, twisting, and bending that occur at scales below the optical diffraction limit.



Eu³⁺-doped LaPO₄ nanocrystals and their polarized emission spectra

We have developed novel fluorescent probes that emit light signaling the three-dimensional orientation of the probes. We utilized lanthanide-doped-nanocrystals, which emit peculiarly polarized luminescence. These nanocrystals exhibit a sharp emission spectrum, which varies dramatically as the probes rotate. The unique nature of lanthanides, including both electric and magnetic dipole transitions, allows to measure the orientations of individual probes as well as their ensemble [1]. We deliberately tune the host nanocrystal structure to maximize the efficiency of emission and the degrees of polarization, achieving unprecedented sensitivity to the orientation of nanoscale objects [2].

These nanocrystal probes can be labeled with enzymes, DNA strands, or cell surfaces in order to monitor their complex dynamics and unveil the biochemical and biomechanical processes. Furthermore, we present how the orientation analysis of these nanoprobe can be applied to the microfluidic shear stress imaging [3] and the study of colloidal self-assemblies [4].

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0.3.79 Luminescent properties of the Yb-doped LaZr₂-xTi_xO₇ solid solution

Speaker: López-Pacheco Germán

Luminescent properties of the Yb-doped $\text{LaZr}_{2-x}\text{Ti}_x\text{O}_7$ solid solution.

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In this work, we present the photoluminescent properties of Yb^{3+} incorporated into the pyrochlore-type $\text{La}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$ (LZTO) solid solution. Samples were synthesized by the polymeric complex soft-chemical method and annealed at 1000°C for 1h. X-ray diffraction patterns reveal the crystalline structure evolution as a function of the Ti^{4+} amount in each compound, going from a cubic ($Fd-3m$) crystalline structure for Zr^{4+} -rich samples to a monoclinic ($P2_1$) crystalline structure for Ti^{4+} -rich samples. Absorption spectra of the samples show a notable shift to highest wavelength for Ti^{4+} -rich samples. This fact agrees with the reduction of the energy of the fundamental host transition for $\text{La}_2\text{Ti}_2\text{O}_7$ (LTO) as compared with the $\text{La}_2\text{Zr}_2\text{O}_7$ (LZO). Photoluminescence of the samples shows a broadening of the excitation spectra, compatible with the optical absorption results, when the Yb^{3+} emission is monitored at 976 nm in the Ti^{4+} -doped samples. For the LZO: Yb^{3+} sample, the excitation band is ascribed to a ligand-to-metal charge transfer (LMCT) $\text{O}^{2-} \rightarrow \text{Yb}^{3+/2+}$ state. In samples containing Ti^{4+} this band is associated with an LMCT $\text{O}^{2-} \rightarrow \text{Ti}^{4+/3+}$ state. Finally, a whole rational picture of all optical experimental observations using a vacuum referred binding energy diagram [1, 2] is presented, where relevant electronic levels of LZTO and Yb^{3+} are depicted.

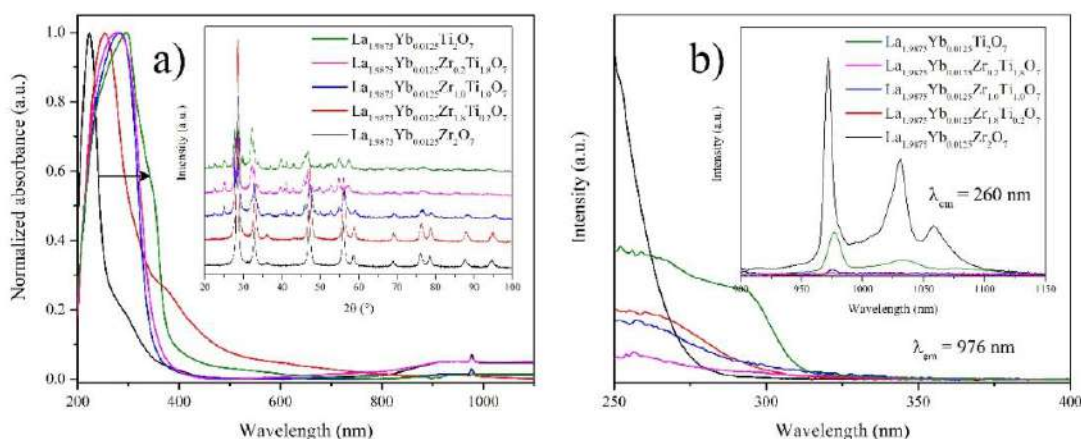


Fig. 1. a) Absorption and XRD patterns, and b) luminescence for LZTO: Yb^{3+} samples.

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0.3.80 Lumos Maxima Forcier: Remote Detection of Pico-Newton Forces by Photon-Avalanche

Speaker: Fardian-Melamed Natalie

Lumos Maxima Forcier:

Remote Detection of Pico-Newton Forces by Photon-Avalanche

Natalie Fardian-Melamed¹, Artiom Skripka^{2,3}, Changhwan Lee¹, Benedikt Ursprung¹, Tom P. Darlington¹, Maoji Wang⁴, Jordan M. Gerton⁴, Bruce Cohen², Emory Chan², P. James Schuck¹

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It has recently been shown that ensembles of lanthanide-doped upconverting nanoparticles (UCNPs) exhibit changes in their emission spectra due to applied forces in the nano-Newton regime and beyond [1-2]. Classical UCNPs appear promising for *in vivo*, sub-cellular, mechanical force sensing due to their nano-scale dimensions, their responsiveness to tissue-penetrating near-infrared (NIR), their non-binary optical readout, and their wide force-range mechano-sensitivity. However, the lowest forces detected by classical UCNPs are only in the nano-Newton regime [1], have so far been measured only on an ensemble level (due, in large part, to low single-particle brightness) [2], and while emitting non-biocompatible visible light.

Avalanching UCNPs (ANPs) [3], possessing steeply nonlinear optical responses, are ideally suited for sensing minute changes in their environments, as small perturbations are expected to usher large changes in signal. Because ANPs absorb and emit tissue-penetrating NIR light, they are uniquely positioned for sensing within biological cells and fluids. In order to characterize and understand the response of these ANPs to local stress and hence determine their functionality as mechano-sensors, it is important to study their mechano-opto-physics on a *single particle level*. Utilizing a custom designed combined AFM and inverted optical microscope system, we correlate *sub-nano-Newton*-range applied forces and observable changes in hyperspectral optical signals for isolated optimally-designed single ANPs, demonstrating their attractiveness as physiologically-relevant ultrasensitive local force sensors [4].

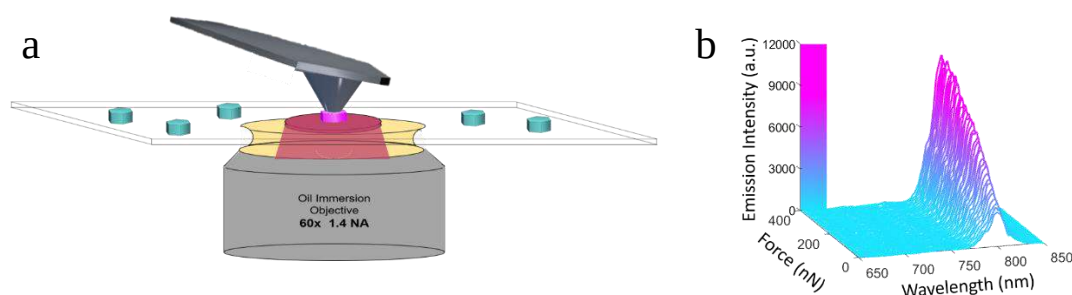


Fig. 1. **a.** Sub-nano-Newton force is applied to a single NP with an AFM tip while excited with NIR light from below. **b.** Force-dependent increasing intensity emission spectra, attained for a single NP while excited at 1064 nm

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0.3.81 Molecular logic breakthrough: photonic concatenation in upconverting nanocrystals

Speaker: Brites Carlos

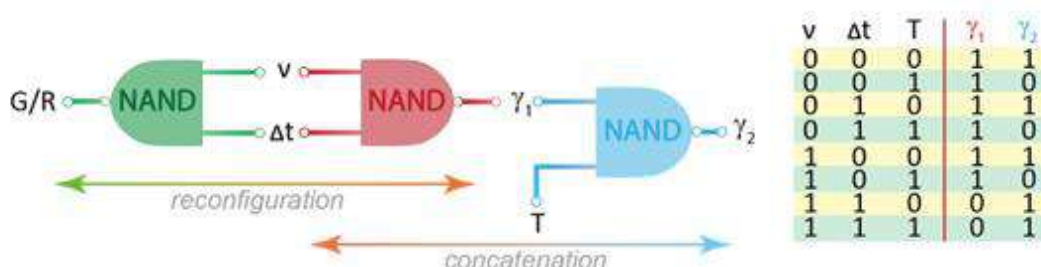
Molecular logic breakthrough: photonic concatenation in upconverting nanocrystals

Carlos D.S. Brites,^{1*} Sofia Zanella,¹ Miguel A. Hernández-Rodríguez,¹ Rute A.S. Ferreira¹ and Luís D. Carlos

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The current ubiquitous nature of Artificial Intelligence features that, in a few years, our society will probably be quite different from what we are used to and backed in very advanced computing systems that we still cannot imagine. However, further increases in digitalization will probably demand novel and innovative computing systems with higher processing speeds and low energy and capital costs. Even though silicon-based devices play a central role, it is now accepted that bottom-up technology may be decisive in improving the current state-of-the-art technology.^[2] In this oral communication, we present the first photonic concatenation of two molecular NAND logic gates that are not operating in solution and exploiting the unique photophysical properties of Yb³⁺/Er³⁺ core@shell Sr₂YF₇ nanocrystals activated by radiation and heat. Furthermore, the photoluminescent features of these nanocrystals allow the definition of combinatory logic gates and temperature-reconfigurable logic systems, defined for the first time for nanocrystals stimulated by physical inputs. Our results demonstrate that upconverting nanocrystals are enthralling nanoplatforms for the solid-state operation of molecular logic devices.^[3,4]



Reconfiguration and Concatenation of two NAND molecular logic gates based on the emission lines of Er³⁺. γ_1 denotes the intensity ratio $^4S_{3/2} \rightarrow ^4I_{15/2} / ^4F_{9/2} \rightarrow ^4I_{15/2}$ whereas γ_2 denotes the $^2H_{11/2} \rightarrow ^4I_{15/2} / ^4F_{9/2} \rightarrow ^4I_{15/2}$ one.

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0.3.82 Multimaterial and multicolour integration enabled by upconversion 3D printing and selective copper plating

Speaker: Marques-Hueso Jose

Multimaterial and multicolour integration enabled by upconversion 3D printing and selective copper plating

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Additive manufacturing has experienced important growth fostered by the innovation in materials and technology. However, there are challenges remaining, such as the integration of different materials in photopolymer platforms.

In this work, we present the 3D printing of multimaterial and multicolour samples using upconversion (UC) luminescence to drive the crosslinking of photopolymer in stereolithography. This has been achieved by overcoming the penetration depth of the photopolymer resins, which is usually below the mm-scale, but can be boosted more than one order of magnitude using UC[1]. Several photo-systems have been developed, including photoinitiators, activators, dyes for re-absorption and upconversion phosphors ($\text{NaYF}_4:\text{Yb}^{3+},\text{Tm}^{3+}$ and $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$). By using the invisibility windows, new structures can be printed through existing parts, which requires selective voxel crosslinking. Solid/flexible and multicoloured samples (acrylic/elastomer) have been 3D printed using this method [2]. Furthermore, the development of a selective copper plating technique provides a new tool for the inclusion of conductive metal parts, which enables the manufacturing of 3D circuitry [3].

The authors acknowledge the support of the UK Engineering and Physical Sciences Research Council, EPSRC, under grant EP/T013680/1.



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0.3.83 Nanoparticle composite complexes for near-infrared fluorescence and thermotherapy

Speaker: Gordel-Wójcik Marta

Nanoparticle composite complexes for near-infrared fluorescence and phototherapy

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The goal of this project is to design and develop a novel nanoagent that will synergistically incorporate multiple functionalities, including imaging and therapy, all within the same nanoprobe. This new, breakthrough paradigm is hence termed as “theranostic”, which simultaneously entails the incorporation of therapeutic and diagnostic moieties into a single nanoagent. The nanocomplex consists of a gold nanoshell encapsulated in a silica shell (Fig.1a,b), which is doped with near-IR fluorescent nanoparticles. In this study, we will propose the novel nanoagent, doped with Ag₂S QDs (Fig.1c) for nonlinear imaging techniques and three-dimensional optical imaging like light-field microscopy. We will emphasize the features of the nanoagent which are essential for it to become an efficient tool for the detection of tumors at the early stage and be used in phototherapy.

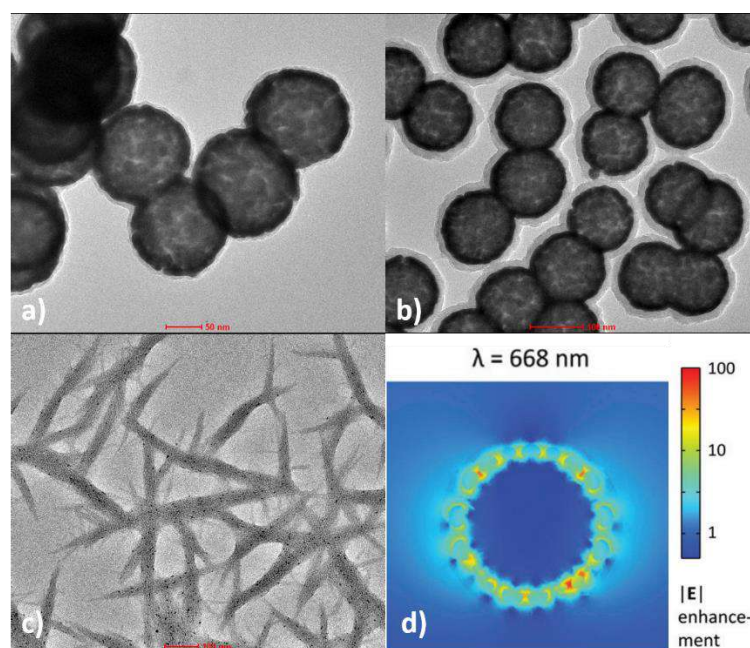


Fig. 1 Gold nanoshells with a silica shell equal 7 nm (a), 15 nm (b), self-assemble Ag₂S QDs (c), calculated electric field distributions near the resonance peaks of the nanoshell (d).

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Acknowledgements: This work was supported the project No. UMO-2021/43/D/ST5/02249, SONATA 17, funded by National Science Center Poland (NCN).

0.3.84 Nanophotonics tunes the emission properties of transparent thin films made of rare-earth nanocrystals

Speaker: Lozano Gabriel

Nanophotonics tunes the emission properties of transparent thin films made of rare-earth nanocrystals

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Rare earth (RE) emitters are central for applications related to the generation of light since these nanomaterials feature exceptional thermal and chemical stability. However, such stability entails an intrinsic complexity to alter their emission properties. Herein, we show that the integration of RE nanocrystals or nanophosphors in devised optical environments allows a fine control over the features of the emitted light, without modifying their chemical composition or compromising their efficiency. Key to the achievements herein reported is the careful analysis of the structural and optical properties of thin nanophosphor layers with the processing temperature to achieve bright, transparent and efficient light-emitting films that are suitable for the photonic integration.[1-3] In one of the examples we discuss, the integration of a thin nanophosphor film in the middle of a photonic multilayer renders an only-dielectric optical cavity. Following a precise computational design, the cavity resonances were devised to match selected emission peaks of the nanophosphors, hence tuning the spectral content of the emitted light.[4,5] Also, the nanoimprint of color-converting layers made of nanophosphors provide periodic surface textures, which enables brighter emission.[6] On another example, the integration of nanophosphors in the vicinity of the interface of a periodic multilayer and a metal film, which sustain optical Tamm Plasmons, enables the enhanced out-coupling of RE emission in well-defined directions.[7] Besides, we have demonstrated that the combination of nanophosphors and metallic nanoparticles, which behave as optical antennas and support localized or collective plasmon resonances, leads to enhanced emission.[8,9] From a different perspective, the incorporation of Mie resonators in a nanophosphor-based matrix allows increasing the fraction of light that is efficiently out-coupled in flexible materials.[10] The combination of nanophosphors and photonic architectures opens the door to develop versatile and cost-effective conversion layers, which connects with the growing interest of our society for the development of light sources with expanded functionalities.[11,12]

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0.3.85 Nd³⁺-doped SnO₂@TiO₂ for NIR-II fluorescence imaging and therapy.

Speaker: Felinto Maria

Nd³⁺-doped SnO₂@TiO₂ for NIR-II fluorescence imaging and therapy.

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In the last two decades, luminescence imaging has been one of the most rapidly advancing imaging technologies, allowing examination of structures of interest at the subcellular level. New luminescent materials that emit in the NIR region, from 700 to 2500 nm, are continuously sought for application, with great interest in the fields of biology and medicine. In fact, NIR light can penetrate biological tissues with minimal interference due to reduced absorption and scattering by tissues such as skin and blood in this wavelength range [1]. In this work, we synthesized a core-shell type mixed oxide SnO₂@TiO₂:xmol %Nd³⁺ via co-precipitation method, followed by hydrothermal treatment on the obtained precipitate, resulting in a very crystalline core-shell oxide. These materials were characterized by XRPD method, IR spectra, SEM, TEM, EDS, thermal analysis, diffuse reflectance spectroscopy and absorption and emission spectra. The results showed that the structure of these materials is cassiterite with a shift to larger 2θ values in all reflections, which are characteristic of the cassiterite structure of SnO₂. SEM images showed agglomerates of nanoparticles and TEM data showed nanoparticles lower than 5nm. The luminescence spectra show narrow emission bands assigned to the intraconfigurational Nd³⁺ transitions ⁴F_{3/2} → ⁴I_J (J = 13/2, and 11/2) in the NIR region of the spectra (Fig 1). Cell viability tests by the colorimetric method with MTS tetrazolium salt showed that nanoparticles were not able to cause significant biochemically damage to viable cells (murine fibroblasts NIH/3T3), showing the potential of the material for nanomedicine [2].

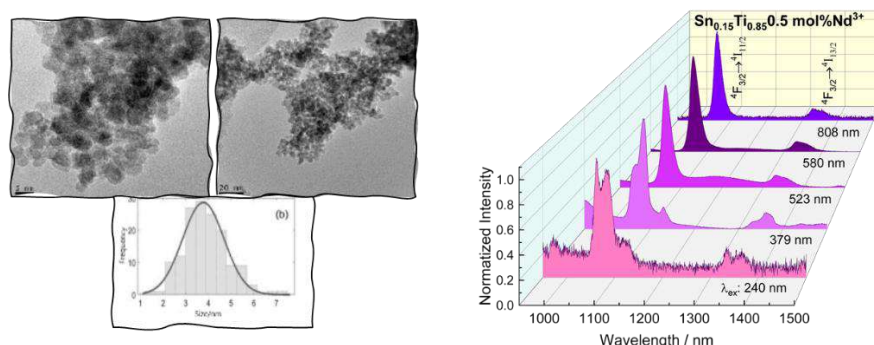


Figure 1 TEM micrographies of the SnO₂@TiO₂:0.5mol %Nd³⁺ (left) and Emission Spectra in the Near IR under various excitation wavelength.

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0.3.86 New Insights into Nd³⁺ to Yb³⁺ Energy Transfer: Implications for Luminescence Thermometry in Coordination Polymers

Speaker: Carneiro Albano

New Insights into Nd³⁺ to Yb³⁺ Energy Transfer: Implications for Luminescence Thermometry in Coordination Polymers

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Lanthanide-based materials have the potential for energy conversion due to tunable optical properties through factors such as doping, particle size, surface coating, and plasmonic coupling with metallic particles. [1,2]. Despite recent advancements in calculating Ln–Ln energy transfer rates [3], determining the distribution of Ln³⁺ ions within real-size nanomaterials remains challenging because a single nanoparticle may contain dozen thousands of Ln³⁺ ions interacting with each other. Once a distribution of Ln–Ln distances in a real-size system is obtained, the average Ln–Ln energy transfer rates $\langle W \rangle$ can be estimated and applied in a rate equation model that describes all interactions between the $|N\rangle$ states (Figure 1a). The rate equation solution gives the population of each level, including Nd³⁺ ⁴F_{3/2} and Yb³⁺ ²F_{5/2} levels for near-infrared emissions. The Nd–Yb energy transfer process was analyzed using theoretical calculations, which led to questions about the role of the Nd³⁺ ⁴F_{3/2} level in the energy transfer process. Additionally, simulations of thermometric parameters (Figure 1b) were conducted for different Yb³⁺ compositions in coordination polymers, and they agree with the experimental data (Figure 1c).

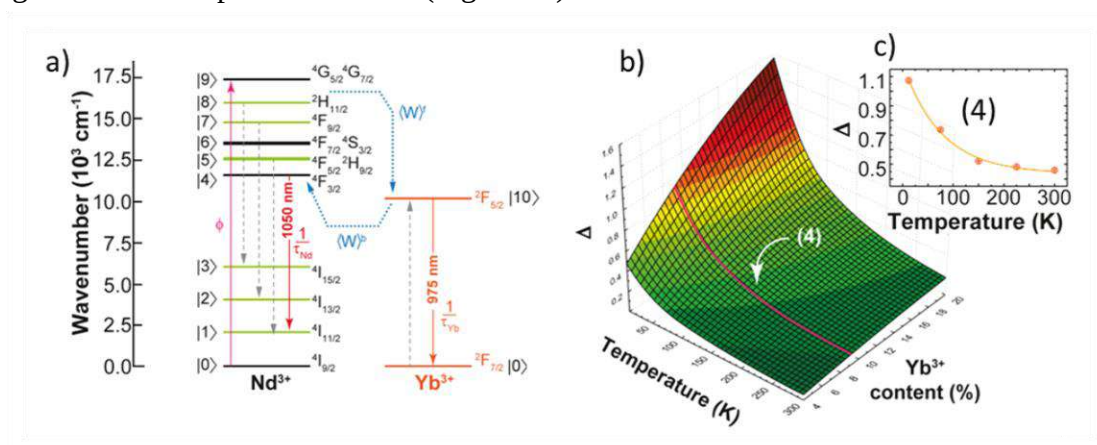


Figure 1. a) Simplified Jablonski energy level diagram illustrating the Nd³⁺–Yb³⁺ process. Solid and dashed arrows represent radiative absorption/emissions and transitions involved in the energy transfer, respectively. b) Simulated $\Delta = I_{Yb}/I_{Nd}$ parameters as a function of temperature and Yb³⁺ content. c) Experimental values of Δ for a selected Yb³⁺ composition.

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0.3.87 New strategies for lanthanide emission enhancement

Speaker: Qin Xian

New strategies for lanthanide emission enhancement

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Lanthanide-activated luminescent nanocrystals have emerged as an intriguing research field owing to their exceptional optical properties and diverse applications in photonics, sensing, and bioimaging^{1,2}. The inherent capability of lanthanide ions to facilitate upconversion and exhibit long-lived persistent luminescence renders them highly attractive for various technological advancements. Nonetheless, achieving efficient luminescence from these ions remains a formidable challenge, particularly when they are doped into nanocrystals of protein-like dimensions³.

While inactive shell passivation can effectively suppress surface-associated luminescence quenching, it unavoidably results in an enlargement of the particle size. Although energy loss can be compensated for using alternative approaches involving high-power excitation, the use of high-power irradiation poses the risk of tissue damage and necessitates complex instrumentation. In this presentation, we present a series of insights and recent advancements in enhancing lanthanide luminescence in small-sized nanocrystals. Contrary to intuitive understanding, our mechanistic studies have revealed the following:

1. The coordination environment of lanthanide ions can profoundly influence energy transfer between the lanthanides by modulating the energies of 4f^N excited states.
2. Slight variations in the coordination environment can induce marked substitution preference in lanthanide-doped fluoride lattices.

By manipulating lanthanide coordination through ligand coating or isovalent codoping, we have achieved emission enhancement in small-sized lanthanide-doped nanocrystals (Fig. 1). These findings challenge conventional notions and provide valuable insights into the intricate mechanisms governing lanthanide luminescence, paving the way for the development of highly efficient and compact nanocrystal-based systems.

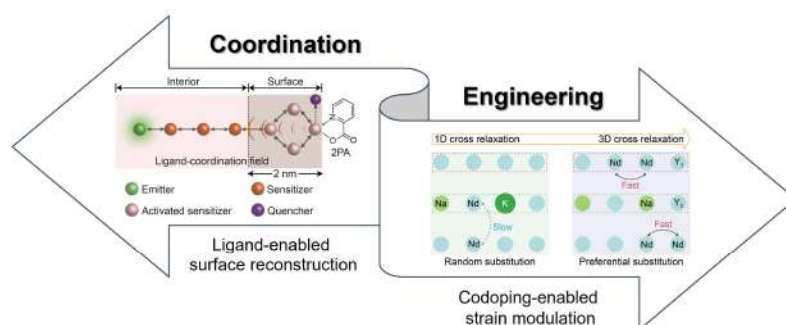


Figure 1 Schematics showing the modulation of lanthanide coordination environment.

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0.3.88 Non linear emission increase and giant absorption cross section of single CdSe/CdS nanocrystal within a plasmonic antenna

Speaker: Maitre Agnes

Non-linear emission increase and giant absorption cross-section of CdSe/CdS single nanocrystal within a plasmonic antenna

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Nanometric semi-conductor colloidal nanocrystals, like CdSe/CdS ones, are excellent single photon sources. Their emission is stable and bright, with a spectral bandwidth of the order of $\Delta\lambda=20\text{-}30\text{nm}$. In specific conditions of high excitation or high confinement, their emission is dramatically changed. They lose their single photon source quality, the dynamic of the emission is accelerated. The spectrum becomes very broad and can reach a few 100nm. Such condition can be achieved either by exciting at high power the emitters or by coupling them to antennas [1], increasing optical confinement.

By in situ optical lithography using high order Laguerre Gaussian mode, we deterministically positioned a single colloidal CdSe/CdS emitter [2] between a thick gold layer and thin gold patch. We achieve inside such plasmonic antennas a high interaction between the emitters and the confined field excited inside the antenna. We observe large modification of emission for quantum inside antennas illustrated by directive emission, high brightness and increased efficiency. By exciting the single CdSe/CdS nanocrystal antenna with increasing power we could evidence a emission which can be interpreted up to a certain excitation power as a 2-level system, letting us measuring the absorption cross section of the nanocrystal within antenna. We evidence a increase by 3 order of magnitude of absorption cross-section of emitters inside these antennas by comparison to the one single CdSe/CdS nanocrystal lying on glass. This dramatic increase is reminiscent of the interaction between single nanocrystal and antenna plasmons. At higher excitation, multi excitation recombination becomes radiative and the emission intensity becomes non linear.

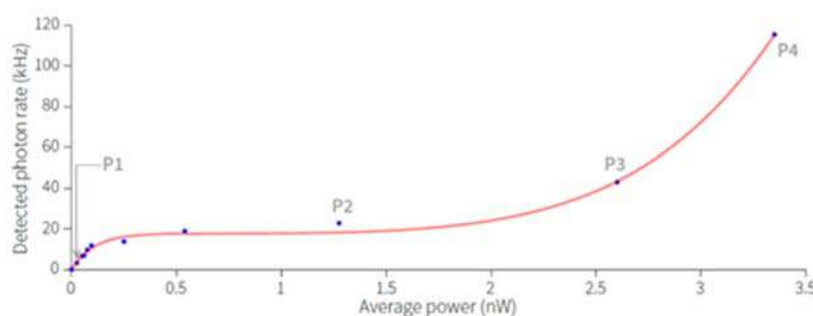


Figure 1: Emission of single CdSe/CdS nanocrystal within a patch antenna as a function of excitation power

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0.3.89 Novel highly luminescent diketofurofuran in crystal and liquid crystalline phases.
What is the difference?

Speaker: Duda Łukasz

Novel highly luminescent diketofurofuran in crystal and liquid crystalline phases. What is the difference?

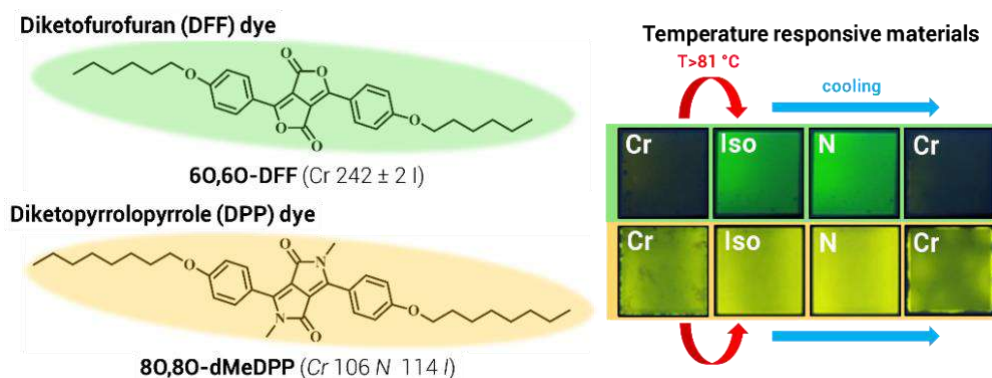
Ł. Duda,^{1,2*} M. Czajkowski,¹ S. Czarnocki,¹ M. Guzik,^{1,2} M. Skoreński,¹
B. Potaniec,¹ and J. Cybinska^{1,2}

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Luminescent dyes with high photoluminescence quantum yield (QY) are highly desirable in various applications such as light amplification and optical sensors. Such dyes incorporated into liquid crystal matrices may serve as thermofluorochromic and tunable light amplification systems. The number of dye classes studied in the liquid crystalline matrices is however limited to the most known pyromethanes, merocyanines, coumarins and rhodamines. However, dyes from less known chemical groups such as diketofurofurans may exhibit also high QY in solution and liquid crystal matrices [1].



Structures of the studied DFF and DPP dyes together with photographs of the obtained liquid crystalline temperature responsive (thermofluorochromic) materials.

Here we present the crystal structure and luminescent properties of novel diketofurofuran dye (DFF). Detailed studies of solubility in liquid crystals as well as determination of QY in crystal and liquid crystal matrices were performed. Spectroscopic properties of the synthesized dye were compared with the analogous dye from the diketopyrrolopyrrole family (DPP). For both dyes high values of QY in various (liquid and liquid crystalline) matrices were found (up to 95 %). On the other hand, lower values of QY and appearance of additional absorption band were observed for these dyes in solid matrices. This finding served as a base for preparation of a thermofluorochromic indicator. In the selected liquid crystalline matrix a visible change of the luminescent properties upon heating from crystalline (Cr) to nematic (N) or isotropic (Iso) phase was found for the DFF dye. Its performance was compared with the analogous DPP dye and other commercially available laser dyes. The DFF dye turned to be one of the best among the studied dyes.

[1] M. Czajkowski, Ł. Duda, S. Czarnocki, *et al. J. Mater. Chem. C* (2023), Accepted in February.

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0.3.90 Observation of multiple-quantum-well polaritons in organic-inorganic 2D perovskite films prepared by Langmuir Blodgett method

Speaker: Shimosako Naoki

Observation of multiple-quantum-well polaritons in organic-inorganic 2D perovskite films prepared by Langmuir–Blodgett method

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In two-dimensional (2D) materials, excitons formed in quantum wells can interact with neighboring quantum wells via light, if the energies of excitons in different wells are perfectly matched. This situation is called the formation of multiple-quantum-well (MQW) polaritons [1]. This causes the characteristic effects of MQW polaritons, such as energy splitting and the appearance of super-radiant modes. MQW polaritons have been studied using highly controlled GaAs systems and other materials [2]. On the other hand, organic-inorganic 2D perovskite materials have very large exciton binding energy [3] and uniform well width due to self-assembly. Therefore, the materials will enable us to observe the MQW polariton effect in fundamental optical spectra. In this study, the MQW polaritons have been observed using organic-inorganic 2D perovskite materials, in which the number of wells was controlled by the Langmuir-Blodgett (LB) method.

$[\text{CH}_3(\text{CH}_2)_{17}\text{NH}_3]_2\text{PbI}_4$ films were prepared on quartz glasses by the LB method [4]. Figure 1 shows the well number dependence of the differentiated reflection spectrum at 20 K. The reflection spectra were differentiated to observe the change of structure. For two quantum wells ($N = 2$), the reflection structure with the single excitonic peak was observed. The reflection structure changed with the increase in the number of quantum wells. This behavior corresponded to the theoretical calculation using the non-local susceptibility, indicating that the MQW polariton effect was observed in the organic-inorganic 2D perovskite material in the fundamental optical spectra.

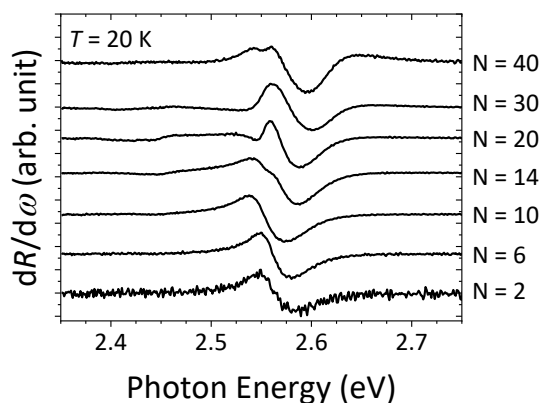


Fig. 1 Dependence of differentiated reflectance spectra on the number of quantum wells at 20 K.

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0.3.91 Optical environment determines radiative decay rate: the role of refractive index

Speaker: Romero Manuel

Optical environment determines radiative decay rate: the role of refractive index

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Luminescent nanomaterials are widely used in a variety of applications including bioimaging, signaling, anticounterfeiting or displays [1-2]. Typically, photonic crystals [3] and plasmonic [4] structures have been employed to enhance spontaneous emission in light-emitting materials by modifying the local density of optical states (LDOS). Although some work has already been carried out for nanoparticles in suspension [5], not much attention is paid to the role of refractive index in the modification of the spontaneous radiative decay rate in solid structures, despite of its direct impact in the luminescence quantum yield, and its importance to demonstrate coatings to be integrated in real materials and devices [6-7]. In this work, we use dipole sources in finite-difference time-domain (FDTD) simulations to study the effect of modifying the effective refractive index of thin films made of nanoparticles, finding discrepancies from analytical LDOS calculations in the effective medium approximation (EMA), and propose an empirical correction which accounts for the filling fraction of the films. We also present the first experimental study of the radiative decay rate in rare earth (RE)-doped nanocrystal thin films as a function of its effective refractive index, reporting 57% enhancement in the radiative rate with only 16% increase of the effective refractive index, which supports our theoretical description. In addition, a method to discriminate the non-radiative contribution of the measured photoluminescence decay spectra by using absolute quantum yield measurements is presented. In this way, our theoretical and experimental analysis spot the modification of the effective refractive index as a fundamental and direct approach to increase spontaneous decay rate and hence, photoluminescence quantum yield.

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0.3.92 Optimization of anisotropic LaPO₄:Eu³⁺ nanorods as polarized luminescence probes in fluid flow

Speaker: Zou Qilin

Optimization of anisotropic LaPO₄:Eu³⁺ nanorods as polarized luminescence probes in fluid flow

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Polarized luminescence in anisotropic particles is highly appealing for optical monitoring of the particle orientation induced by external stimuli such as electric or magnetic fields, as well as shear stresses in fluid flow.^[1] For such applications, Eu³⁺ doped LaPO₄ nanorods appear as excellent candidates as they present unique luminescence polarization features originating from the *f*-electron transitions in Eu³⁺ governed by the anisotropic symmetry of the host crystal structure. First results have been demonstrated for orientation analysis in microfluidic channels^[2,3] and further improvements of the technique now focus on higher degree of polarization (DOP) and adjustable size (mainly aspect ratio) of LaPO₄:Eu³⁺ nanorods in order to achieve a higher sensitivity of the orientation measurements.

For that purpose, we here report a strategy for synthesis of LaPO₄:Eu³⁺ nanorods with high luminescence efficiency, excellent colloidal stability and controlled aspect ratios through a microwave heating method. Ethylenediaminetetraacetic acid disodium salt (EDTA) is used as a surface complexing agent to coordinate with lanthanide ions for properly adjusting aspect ratio of the nanorods. When dispersed in ethylene glycol, these nanorods exhibit excellent colloidal stability as attested by their liquid crystalline behaviour. By applying an electric field to align the LaPO₄:Eu³⁺ nanorods, we can investigate the polarized luminescence properties as a function of their aspect ratio. The high DOPs of these nanorods allow an accurate orientation analysis in microfluidic channels. We demonstrate application of these nanorods as optical probes for local shear stress mapping with a largely extended sensitivity of the measurement thanks to the adjustable aspect ratio of the nanorods.

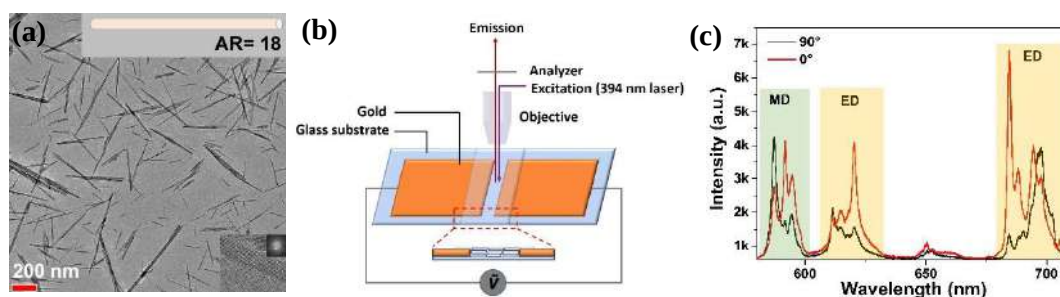


Figure 1. (a) TEM image of monazite LaPO₄:Eu³⁺ nanorods, (b) illustration of measuring polarization luminescence of aligned nanorods under electric field and (c) the acquired polarized luminescence spectra of LaPO₄:Eu³⁺ nanorods.

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0.3.93 Outstanding luminescent performance of monodisperse YVO₄:Eu³⁺ particles for ultrasensitive in vitro diagnosis

Speaker: Vieira Perrella Rafael

Outstanding luminescent performance of monodisperse $\text{YVO}_4\text{:Eu}^{3+}$ particles for ultrasensitive *in vitro* diagnosis

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Liquid-phase syntheses starting from homogeneous precursors have been applied to produce monodisperse inorganic oxides with well-controlled size distributions. However, the high surface area, poor crystallinity, and high defect density of the obtained nanoparticles are often detrimental in terms of luminescence.^{1,2} This challenge applies to rare-earth (RE) vanadates (REVO_4), a versatile class of luminescent materials. Here, we show that monodisperse 60 – 150 nm $\text{Y}_{1-x}\text{Eu}_x\text{VO}_4$ particles prepared by colloidal conversion of RE hydroxycarbonates in water/ethylene glycol (EG) suspensions display low emission quantum yields (2 – 12%), which demonstrates a poor luminescent performance (Figure 1a,b). To overcome this issue, we developed a facile, safe, and original protected annealing approach permitting thermal annealing at high temperatures (600 – 1000 °C) without particle aggregation or growth. The annealed solids are readily dispersed in water, leading to colloidal dispersions containing isolated highly crystalline particles (Figure 1c). By playing on the initial synthesis parameters (*e.g.*, water/EG ratio) and annealing temperature, we explored the possibilities these processes offer to control the size, microstructure, and crystalline quality of the final particles. Thus, we can produce suspensions of annealed particles exhibiting emission performances close to the bulk material, with emission quantum yields of around 50% (Figure 1d). Future work will be devoted to applying these highly bright particles as luminescent probes for ultrasensitive immunodetections of various analytes, like toxins and DNA (Figure 1e).

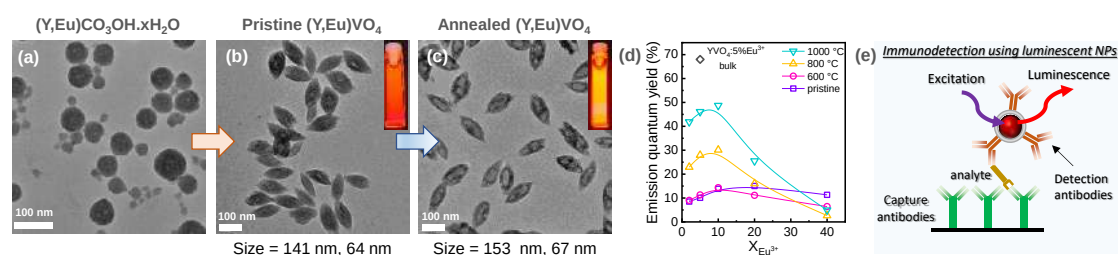


Figure 1. TEM images of (a) $(\text{Y,Eu})\text{CO}_3\text{OH}\cdot x\text{H}_2\text{O}$ and (b,c) $(\text{Y,Eu})\text{VO}_4$ particles before (b) and after the protected annealing at 1000 °C (c). Insets: photographs of the suspensions under UV light ($\lambda_{\text{exc}} = 312$ nm). (d) Evolution of the emission quantum yield as a function of Eu^{3+} concentration and annealing temperature. (e) Scheme representing a proposed immunodetection assay using luminescent nanoparticles.

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0.3.94 Persistent luminescence mesoporous nanoparticles as mediators for photodynamic therapy

Speaker: Bessiere Aurelie

Persistent luminescence mesoporous nanoparticles as mediators for photodynamic therapy

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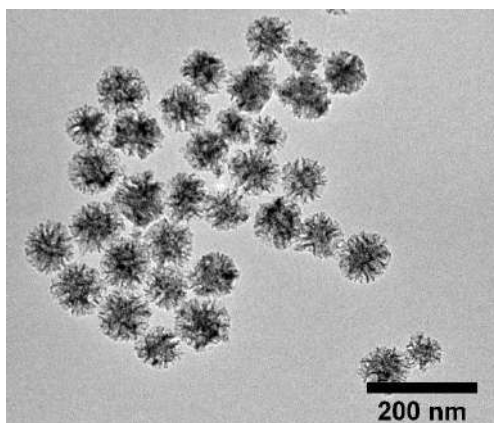
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Persistent luminescence (PERL) materials have the property to continue emitting light for a long period of time after excitation has ceased. When synthesized as nanoparticles, ZnGa₂O₄:Cr for instance [1], proved outstanding as *in vivo* small animal autofluorescence-free imaging probe [2]. In addition to imaging, those nanoparticles have recently revealed their potential as therapeutic agents to eradicate cancer tumours when coupled to organic photosensitizers, such as porphyrins or phthalocyanines [3]. The PERL nanoparticles constitute light-emitting nano-mediators to excite photosensitizers that produce cytotoxic ROS (Reactive Oxygen Species) and kill cancer cells by photodynamic therapy (PDT). For efficient action, the construction of nano-platforms that closely associate the PERL material with a chosen photosensitizer is essential. We have synthesized and studied various types of nano-composites PERL nanoparticles made of mesoporous silica nanoparticles filled with ZnGa₂O₄:Cr. The presentation will show the structural and optical characterization of the materials, their PERL intensity and decays and their ability to produce ROS for PDT activity.



TEM image of mesoporous silica nanoparticles filled with ZnGa₂O₄:Cr³⁺.

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0.3.95 Persistent luminescent and transparent composites as a tool to understand charge storage mechanisms

Speaker: Rodrigues Lucas

Persistent luminescent and transparent composites as a tool to understand charge storage mechanisms

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Persistent luminescent materials are usually optimized to obtain an as large as possible storage capacity. Due to insufficient knowledge about the trapping mechanism this is often done by a trial-and-error approach. Even if photo-redox processes in lanthanide (co)dopants are known to occur during the charging-discharging steps [1,2], their dynamics are not yet fully understood. To improve the knowledge about these dynamics, the characterization of the optical signature of the charge carriers being caught at and released from the traps is crucial. For these studies, minimally scattering samples are ideally required. Despite single crystals being an option, they do not allow large screening of their composition and are difficult to synthesize. In this work, we present persistent luminescent transparent composites as an alternative to low-scattering samples - glass or films containing persistent luminescence phosphors such as $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ (Figure) and $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},\text{Dy}^{3+}$. The use of nanofocused synchrotron radiation (XRF, XANES and XEOL) is important to clarify the properties of the persistent particles embedded in the composites and to study boundary effects between the phosphor and the matrix. The development of these materials opens new paths for detailed optical studies of trap states in charge storage materials. First, transient absorption spectroscopy allows to probe the fast dynamics in the charging and discharging process. Secondly, UV-vis-NIR absorption spectroscopy on transparent samples allows also to estimate the density of charge traps and the fraction of lanthanide ions participating in the charge trapping process.

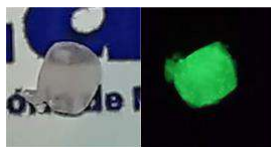


Figure. Photograph of glass composite containing $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ under visible light (left) and its persistent luminescence (right).

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0.3.96 Persistent Luminescent Nanoparticles: Elucidating the Luminescent Mechanism Using Various Synchrotron-based Spectroscopies

Speaker: Liu Lijia

Persistent Luminescent Nanoparticles: Elucidating the Luminescent Mechanism Using Various Synchrotron-based Spectroscopies

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Nanoparticles that emit persistent luminescence at the near-infrared wavelength region are of great potential as optical probes in a variety of biomedical applications. Although there have been many mechanistic studies on the persistent luminescence phenomena, most of the knowledge is obtained from the bulk phosphors (i.e. synthesized using a solid-state reaction). The properties of nanoparticles are highly dependent on their sizes, morphologies, and surface structure. A small adjustment in the synthesis condition could have a strong impact on the defect structure in the material, which further modifies the charge trapping kinetics. For nanoparticles, these changes are crucial, because they could alter the luminescence intensity and the persistence luminescence lifetime. In this talk, I will present several spectroscopy techniques based on synchrotron radiation in characterizing the electronic structure of persistent luminescent nanoparticles. These techniques, either focusing on the local chemical environment, such as X-ray absorption fine structure, and X-ray pair distribution function, or have a high spatial resolution (X-ray microscopy and X-ray excited luminescence mapping). Several representative nanoparticle system, such as Cr³⁺-doped ZnGa₂O₄, Mn²⁺-doped MgGeO₃ will be used as examples.

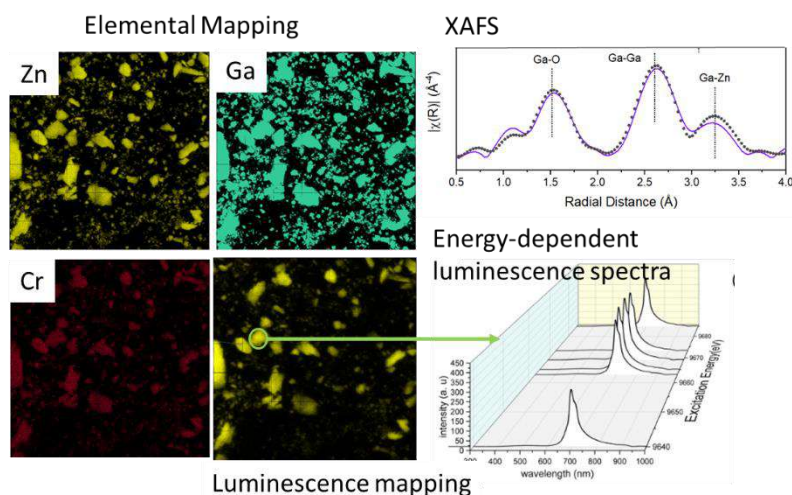


Figure 1. Spectroscopy and Microscopy Analysis on Cr³⁺-doped ZnGa₂O₄ nanoparticles: X-ray fluorescence microscopy, X-ray absorption fine structure, X-ray excited optical luminescence.

0.3.97 Persistent luminescent phosphor-in-glass composites

Speaker: Merizio Leonnarn Gotardo

Persistent luminescent phosphor-in-glass composites

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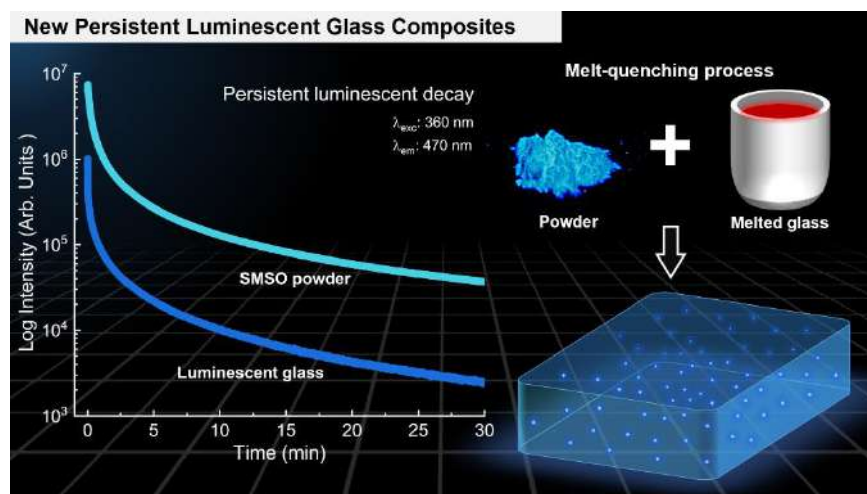
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Over the past few decades, global energy consumption has been on a continuous rise, largely attributed to technological advancements. To meet this growing demand, the development of efficient energy conversion and storage technologies has become crucial. Persistent luminescent (PL) materials have emerged as a promising solution due to their unique properties of emitting light for several hours after being exposed to an irradiation light source. One of the most promising PL materials is $\text{Sr}_2\text{MgSi}_2\text{O}_7\text{:Eu}^{2+},\text{Dy}^{3+}$ (SMSO), which emits blue light (λ_{em} : 460 nm) for more than 24 hours.[1] However, these crystalline compounds are typically obtained as powder samples, which limits their applications. One potential solution is to incorporate them into host systems such as polymers and glasses. Among these, glasses offer advantages such as UV-Vis transparency and chemical/thermal stability.[2] In this study, we propose the preparation of a host-guest system using the SMSO PL material and $\text{NaPO}_3\text{--Ga}_2\text{O}_3$ glass for potential applications in safety lights and luminescent markers.



Representation of SMSO – NaPGaO Glass composites

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0.3.98 Phase transition of gadolinium niobates doped with Eu^{3+} ions

Speaker: Cornet Louis

Phase transition of gadolinium niobates doped with Eu³⁺ ionsL. Cornet,^{1,2*} J.-M. Heintz,¹ R. Boulesteix,² A. Maitre,² and V. Jubera¹¹ Univ. Bordeaux, CNRS, Bordeaux INP, ICMCB, UMR 5026, 33600 Pessac, France² Univ. Limoges, CNRS, IRCer, UMR 7315, 87068 Limoges, France

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Rare-earth niobates compounds possess interesting properties such as ionic conductivity, thermal (barrier coating), magnetic or luminescent properties due to their chemical composition and crystal structure versatility [1,2]. They present a crystal structure depending on the rare-earth cations size and/or synthesis route. The niobates Gd₃NbO₇ and GdNbO₄ have been extensively studied [3]. Concerning Gd₃NbO₇, a weberite-like structure is reported under conventional solid state synthesis while a cubic lacunar fluorine (space group *Fm3m*) is observed when a liquid phase synthesis is used. In this later case, a phase transition toward weberite-like structure (space group *C2221*) occurs at high temperature [4]. GdNbO₄ crystallizes into two allotropic varieties. The low-temperature unit cell possesses monoclinic symmetry crystallising in the *C2/c* space group. A tetragonal unit cell (space group *I41/a*) is observed at higher temperature.

In this context, both Eu³⁺ doped GdNbO₄ and Gd₃NbO₇ have been synthesized by liquid phase synthesis. The chemical composition of the Weberite phase was tuned to follow its structural stability. Eu³⁺ ion, well-known for its use as structural probe (⁵D₀ → ⁷F_{0,1,2} energy levels), has enabled to characterize the evolution of crystalline structure of the prepared samples by photoluminescence coupled with XRD, Raman and FTIR spectroscopy. A comparison between the spectral distribution versus the local environment of Eu³⁺ ions will be discussed in both phases.

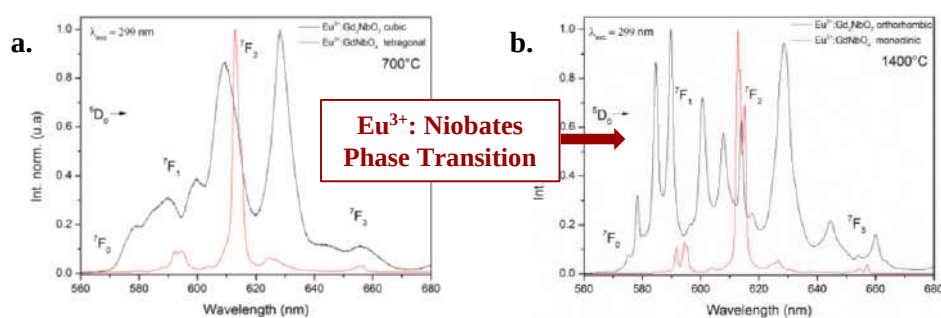


Figure : Eu³⁺ spectral distribution within Gd₃NbO₇, GdNbO₄ under 700°C (a) and 1400°C (b).

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0.3.99 Photoactive Cul-Cross-Linked Polyurethane Materials

Speaker: Perruchas Sandrine

Photoactive CuI-Cross-Linked Polyurethane Materials

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Photoluminescent materials displaying stimuli-responsive properties to various external factors are of increasing interest because of their potential applications in sensing.^[1] Copper(I) halide complexes present a wide range of photophysical properties due to the large panel of structural geometries they can adopt. An important feature of these complexes is the sensitivity of their luminescence properties in response to different external stimuli such as temperature, mechanical stress or solvent exposure, which can lead to the development of multifunctional materials.^[2-4]

Here, we present the synthesis of photoactive hybrid materials by incorporating copper iodide complexes by covalent grafting and serving as cross-linkers, within organic polymers (Figure 1). The structural and optical characterizations of these functional materials are presented. Evaluation of their luminescence responsiveness towards external stimuli such as temperature and solvent vapors is reported and the related mechanisms are discussed.^[5]

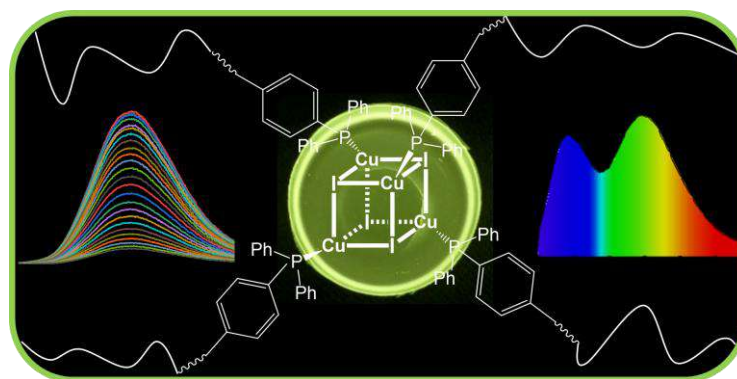


Figure 1. Photo of a sample (pellet) of the photoactive polyurethane materials under UV excitation, representation of the copper iodide complex grafted to the polymeric matrix and emission spectra recorded under different stimuli.

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0.3.100 Photoluminescence and exciton-phonon coupling in single CsPbCl₃ nanocrystals

Speaker: Guilloux Victor

Photoluminescence and exciton-phonon coupling in single CsPbCl₃ nanocrystals

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Over the last years organic and inorganic lead halide perovskites nanocrystals have come to light as a new generation of promising semiconductor materials for a large variety of optoelectronic technologies such as LEDs, lasers and photo-detectors but also for more advanced applications in quantum optics or spintronics [1,2]. Among these materials CsPbCl₃ has the largest energy band gap showing an absorption threshold and photoluminescence (PL) in the blue spectral range. Excitons are at the center of all the optical and electronic properties of CsPbCl₃ nanocrystals and are characterized by the smallest Bohr radius, 1.7 nm, amongst all of the lead halide perovskites materials [3]. In this work, we use a high-spatial resolution photoluminescence (PL) set-up and measure the PL of single NCs with a mean size of ~ 8 nm. The emission is characterized by the presence of a doublet associated to the bright exciton. We correlate the results with calculations of the exciton fine structure taking into account the interplay between the e-h exchange interaction and the crystal field, the dielectric environment and the effect of the slight shape anisotropy observed experimentally [4]. In a second time, we took advantage of the emission polarization properties to track the energy and the linewidth broadening of individual peaks with increasing temperature [5]. Two regimes exist in the broadening of emission peaks, at low and high temperature, dominated respectively by acoustic or longitudinal optical phonons couplings. We deduce the respective strengths of the interactions.

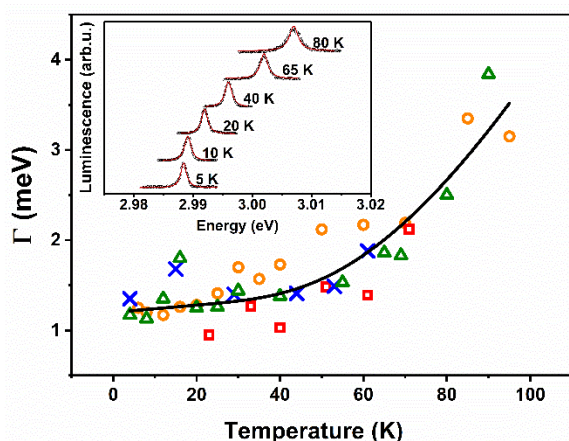


Figure caption: Evolution with temperature of the linewidth of four lines corresponding to four different NCs. The inset shows the temperature evolution of one of the selected lines.

Our results indicate the decisive role of either intrinsic or environmental parameters on the response of individual perovskite nanoparticles.

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0.3.101 Photoluminescence emission enhancement in the $\text{LiSrVO}_4\text{:Eu}^{3+}$ vanadate phosphor by partial substitution of alkali metal ions ($\text{Li}^+/\text{Na}^+/\text{K}^+$) and optical transition probabilities using Judd-Ofelt analysis

Speaker: Kennedy S Masilla Moses

Photoluminescence emission enhancement in the $\text{LiSrVO}_4\text{:Eu}^{3+}$ vanadate phosphor by partial substitution of alkali metal ions ($\text{Li}^+/\text{Na}^+/\text{K}^+$) and optical transition probabilities using Judd-Ofelt analysis

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The phosphor converted WLEDs gain crucial attention in solid state lighting (SSL) for the generation of illumination. The Eu^{3+} activated LiSrVO_4 phosphors were synthesized via solid state reaction technique. Powder XRD of the $\text{LiSrVO}_4\text{:xEu}^{3+}$ (0-15 mol% in steps of 3) samples revealed a monoclinic crystal structure belonging to the $\text{P2}_1/\text{m}$ space group. Scanning electron microscopy results showed that the particle size of the $\text{LiSrVO}_4\text{:9mol\% Eu}^{3+}$ phosphor was in the micrometer range with an irregular spherical shape. The optical diffuse reflectance spectrum (DRS) consisted broad band absorption in the ultraviolet (UV) region (260-370 nm) which was due to the charge transfer between the ligand-metal in the VO_4 tetrahedral group and the sharp absorption bands in the visible region were ascribed to the characteristics of the Eu^{3+} ions. From the DRS, the band-gap and the refractive index values were calculated. The $\text{LiSrVO}_4\text{:Eu}^{3+}$ phosphor was found to absorb strongly at 396 nm (NUV light) and 464 nm (blue light). They exhibited the strongest photoluminescence (PL) intensity at 618 nm for the samples under the excitation of 396 nm. The emission intensity of the phosphors were improved by co-doping with the alkali metal ions ($\text{Li}^+/\text{Na}^+/\text{K}^+$). The optical transition probabilities of the $\text{LiSrVO}_4\text{:9mol\% Eu}^{3+}$ phosphor were also analyzed using Judd-Ofelt theory. The optimized phosphor showed an excellent thermal stability. The PL lifetime values were found to be in the microsecond range. The values of absolute and relative sensitivities were calculated from the temperature dependent lifetime measurements. The $\text{LiSrVO}_4\text{:9mol\% Eu}^{3+}$ phosphor yielded CIE coordinates(x , y) of (0.5987, 0.4005), a low correlated color temperature (CCT) of 1468K, and a high color purity of 99.9%. These results indicated the tremendous potential of the LiSrVO_4 based phosphors for the WLEDs application.

0.3.102 Polychromatism of all light waves as a new tool for the analysis of fluorescence

Speaker: Niewiadomska-Kaplar Justyna

Polychromatism of all light waves as a new tool for the analysis of fluorescence

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Light is one of the diagnostic tools in chemistry. Research on light vision mechanisms in biosystems and on the mechanisms of formation of deficits in color discrimination[1] reveals that not only white light is polychromatic but all light waves are. The spectrum of white light is composed of aggregations of 4 monochromatic waves: *magenta UV* 384 nm, cyan 432 nm, yellow 576 nm and *magenta IR* 768 nm, grouped in 5 **bi-chromatic** waves: cinnabar red (*magenta IR* + yellow), green (yellow + cyan), indigo (cyan + *magenta UV*) and also two *semi-bright* bi-chromatic waves - *porphyry IR* (semi-infrared wave composed of the magenta IR 768 nm wave and the colorless infrared wave 864 nm) and *porphyry UV* (semi-ultraviolet wave composed of the magenta UV 384 nm wave and the colorless ultraviolet wave 288 nm). The light waves thus composed create the following light sensations due to the mechanism of additive synthesis:

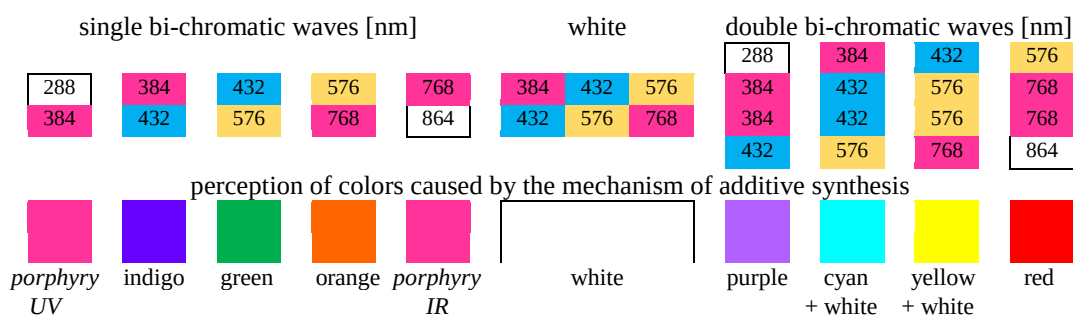


Figure 1. Polychromatism of the light waves and the mechanism of additive synthesis create the colour sensations

If the excitation light of the fluorophores has different chromatic components, the chromatic difference between the excitation light and the light emitted by the fluorophores may not be caused by the phenomenon of fluorescence but by the mechanism of selective absorption, in which a part of the components of the incident polychromatic light are absorbed by the fluorophores and the remaining components are reflected, as shown in the table below:

fluorophore	incident light ≈ 360 nm	reflected light ≈ 435 nm	absorbed light ≈ 336 nm
DyLight 350			

Figure 2. Interpretation of the emission of light 432 nm by fluorophore DyLight 350 as a mechanism of selective absorption.

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0.3.103 Polymer nanocomposites of cesium lead halide nanocrystals for fast timing in radiation detection

Speaker: Král Jan

Polymer nanocomposites of cesium lead halide nanocrystals for fast timing in radiation detection

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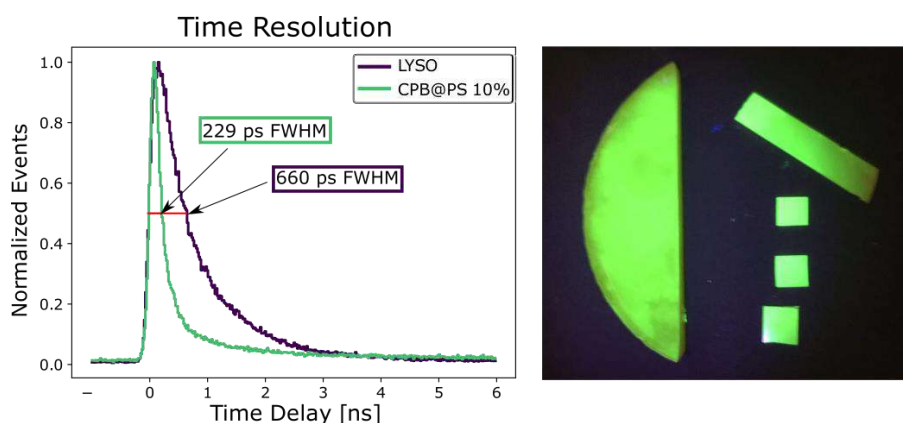
² Institute of Physics of Czech Academy of Sciences, Prague, 162 00, Czech Republic

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In the field of radiation detection, fast timing is of high importance and the search for new materials with ultrafast emission to satisfy requirements for the *Time-of-Flight* measurements in PET, CT or high energy physics is ongoing. One of the promising candidates are luminescent nanocrystals with ultrafast decay times, such as cesium lead halide nanocrystals. To fully exploit their favourable properties in detector design, their poor chemical stability and low stopping power for ionizing radiation have to be tackled. Embedding nanocrystals in a polymer matrix improves their stability and a combination of highly loaded polymer nanocomposites with scintillating bulk crystals following the heterostructure design enhances a deposition of ionizing radiation energy in nanocrystals [1]. In this work we report the preparation, characterization and timing properties of CsPbBr₃ and CsPb(Br/Cl)₃ nanocrystals embedded in polymer matrices with high filling factors. To preserve luminescent properties of nanocrystals and limit agglomeration during preparation of nanocomposites, advanced polymerization techniques and copolymerizable ligands were used. Luminescence and timing properties of these materials were characterized including the time resolution measurement using a novel setup coupled to analog silicon photomultipliers and low energy pulsed X-ray excitation [2]. When comparing with the state of the art inorganic (LYSO:Ce) crystal, more than twofold time resolution improvement was obtained.



Comparison of measured time delay distribution for CsPbBr₃ polystyrene (CPB@PS) nanopomposite with the 10% filling factor and the state-of-the-art inorganic crystal LYSO:Ce

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0.3.104 Precisely tailoring upconversion luminescence dynamics of rare earth based nanophosphors

Speaker: Zhang Hong

Precisely tailoring upconversion luminescence dynamics of rare earth based nanophosphors

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With the advancement of nanosynthetic chemistry in the past two decades, we have witnessed the rapid progress of rare earth-based nano-nonlinear luminescence (mainly upconversion luminescence), demonstrating many desirable application prospects. Making these visions a reality still requires painstaking efforts to achieve efficient luminescence and specific modulation of the spectrum, which requires in-depth and quantitative understanding and control of the microscopic energy migration and conversion process.

Here we introduce some very interesting results obtained recently in our group in several key aspects of these upconversion nanophosphors, including mainly establishment and experimental confirmation of (i) quantitative theoretical model of energy migration in upconversion dynamics, (ii) quantitative relationship between upconversion dynamics and detrimental charged impurities, and (iii) the essential role of phonons in cross relaxation. Based on these updated comprehension we have successfully realized tailoring precisely the upconversion dynamics in large time range from nanostructure, and significantly lifting upconversion luminescence intensity with two orders of magnitude simply through minimizing phonon assistance in cross-relaxation processes. These important results help us to thoroughly understand luminescence dynamics of rare earth based nanophosphors and shall facilitate the practical applications.

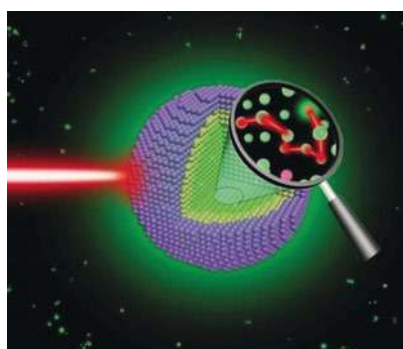


Figure 1 Microscopic picture of energy migration in rare earth based nanophosphors.

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0.3.105 Predicting spectroscopic properties via machine learning

Speaker: Sójka Małgorzata

Predicting spectroscopic properties *via* machine learning

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Developing new efficient phosphor materials is a long-standing quest in the field of solid-state lighting. Ce³⁺-substituted phosphors, in particular, are widely explored materials due to their broad interconfigurational 5*d*→4*f* luminescence giving rise to efficient emission. However, to observe 5*d*→4*f* luminescence in the visible part of the electromagnetic spectrum, a few requirements have to be fulfilled. The position of the excited 5*d* levels is greatly affected by the surrounding environment and can be effectively tuned through host structure interactions.¹ Therefore, designing new efficient phosphors requires *a priori* knowledge about the redshift. Nowadays, the conventional method of identifying new phosphors involves chemical intuition or trial-and-error synthesis. Here, a tree-based ensemble learning algorithm employing extreme gradient boosting is trained to predict the redshift and magnitude of a crystal field splitting (E_{cfs}) by analyzing the optical properties of over 200 Ce³⁺ substituted inorganic phosphors. The experimentally measured redshift and E_{cfs} of these compounds were featured using the materials' centroid shift, the rare-earth coordination environment, and the chemical descriptors provided by the Materials Project. The resulting ensemble model can reliably estimate redshift and E_{cfs} , providing an effective tool for predicting the optical properties of Ce³⁺-activated inorganic phosphors.

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0.3.106 Probing Ion Migration by Luminescence in YPO₄:Tb³⁺

Speaker: Zhang Shuai

Probing Ion Migration by Luminescence in YPO₄:Tb³⁺

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Defects are common in inorganic materials and strongly affect physical and chemical properties. Understanding the role of defects is one of the remaining big challenges in the field of luminescent materials. The formation and annihilation of defects are closely linked to the migration of ions in the solid. Temperature and time are parameters that control the diffusion of ions in solid but also particle size, atmosphere and ionic radius affect ion migration. Slow migration of defects and/or ions occurs during solid-state annealing but has not been well-studied.

Here YPO₄:Tb³⁺ is chosen as a model system to optically probe ion migration through the change in the blue/green emission ratio and luminescence decay curves. In Tb³⁺ doped phosphors, the Tb³⁺ ion exhibits dominant blue emission from the ⁵D₃ level for low doping levels. Cross-relaxation with a nearby Tb³⁺ ion results in the Tb³⁺ ion being in the ⁵D₄ excited state giving green emission. The blue/green emission intensity ratio provides information on the ion distribution. The resulting variation of the time- and spectrally-resolved luminescence are used to quantify thermally activated Tb³⁺ ion migration. This research not only provides fundamental insight in ion migration in solids but also enables a new class of materials for thermal history sensing.

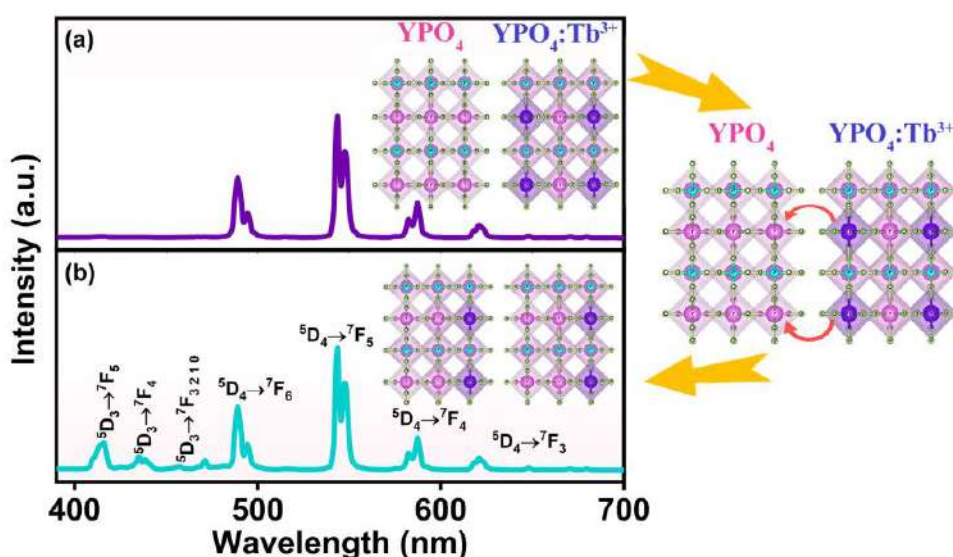


Figure 1 (a) Emission spectra of a pressed tablet of thoroughly mixed YPO₄ and YPO₄:10%Tb³⁺ with a ratio of 6:1 (b) The emission spectra of the tablet (a) after annealing at 1200°C.

0.3.107 Progress of the investigations on fluoride crystals as viable solid-state UV laser media

Speaker: Sarukura Nobuhiko

Progress of the investigations on fluoride crystals as viable solid-state UV laser media

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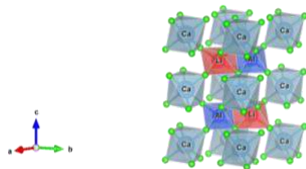
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We present the progress of our investigations on fluoride crystals as viable solid-state ultraviolet (UV) laser media. Fluoride crystals, particularly LiCaAlF₆ (LiCAF), LuLiF₄ (LuLiF), CaF₂, and LaF₃, are candidate laser host materials due to their wide band gaps which make them transparent down to the vacuum UV (VUV) region (~ 100 nm). These crystals have also been successfully doped with rare earth ions such as cerium (Ce³⁺), praseodymium (Pr³⁺), and neodymium (Nd³⁺) whose interconfigurational transitions result in broad UV fluorescence bandwidths. Although some of the fluoride crystals are less susceptible to excited-state absorption and solarization, their laser performance can significantly drop with pump and probe polarization and their anisotropic nature. Therefore, we have performed numerical and spectroscopic investigations on the structural origin of the fluoride crystal properties. For instance, for LiCAF, a series of first-principles calculations based on the density functional theory (DFT) demonstrate monotonical increase in band gap with applied uniform pressure. Moreover, x-ray absorption near-edge spectroscopy (XANES) results along the Ce K-edge reveal that Ce ions in a Ce-doped LiCAF crystal solely exhibit an oxidation state of 3+. In contrast, XANES analysis along the Ce L3-edge confirms the dominance of Ce³⁺ ions in the same crystal, but the crystal also exhibit features similar to the CeO₂ (Ce⁴⁺) reference. With this comparison of results, the features observed from the crystal's Ce L3-edge XANES spectra should be interpreted differently instead of the presence of Ce⁴⁺ ions. As additional investigations are currently underway to further understand our results and the structural and optical properties of the fluoride crystals, we will share some insights and outlooks toward the fluoride crystals' development as potential solid-state UV laser media.



Schematic representation of the LiCaAlF₆ crystal structure

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0.3.108 Pump-induced refractive index changes in Tb³⁺ doped materials

Speaker: Catunda Tomaz

Pump-induced refractive index changes in Tb³⁺ doped materials

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Pump-induced refractive index changes (RIC) have been reported in several important laser materials [1,2], such as doped with Cr³⁺, Ni²⁺, Nd³⁺, Yb³⁺ and more recently, Tb³⁺. In all these cases the RIC change is attributed to the metastable excited state population, actually to the difference between the ion polarizability ($\Delta\alpha_p$) in excited and ground states. In this presentation we focus on the case of Tb³⁺ doped RIC observed different hosts: CaF₂ crystal, zinc phosphate glasses (PZABP and CAP) and aluminosilicate glasses (CAS and LSCAS).

Time-resolved Z-scan measurements were performed using a cw laser in order unequivocally discriminated thermal and electronic contributions to RIC. The 488nm wavelength was chosen due to the resonance absorption of ⁷F₆→⁵D₄ transition, where ⁷F₆ is the ground state and ⁵D₄ is the first metastable state of Tb³⁺ (lifetime ~ 2 ms). In case of PZABP (phosphate glasses) the electronic component of the RIC was shown to increase linearly with the Tb³⁺ concentration indicating concentration independent value, $\Delta\alpha_p = (2.4 \pm 0.2) \cdot 10^{-26} \text{cm}^3$. In the case of alumino silicate glasses, the behavior of RIC depends critically on the silica content of the host glasses. $\Delta\alpha_p$ decrease by one order of magnitude ($7 - 0.8 \cdot 10^{-25} \text{cm}^3$) with the increase of silica and consequent increase in bandgap from 4.6 to 5.0 eV. Actually, the lowest value we found, $\Delta\alpha_p = 6.6 \cdot 10^{-27} \text{cm}^3$, was determined in CaF₂, a fluoride crystal with ~10 eV band gap.

A strongly nonlinear dependence of the amplitude of the Z-scan signal (ΔT_{pv}) with incident intensity (I) was observed in low silica aluminosilicates glasses (LSCAS). In this case, the RIC should be expressed by $\Delta n = n_2 \cdot I + n_4 \cdot I^2$, where the real part of n_2 is proportional to $\Delta\alpha_p$ and n_4 is related to second excited state (⁵D₃) with $\Delta\alpha_p^* \sim 7 \cdot 10^{-24} \text{cm}^3$.

It was previously observed in Nd³⁺ and Yb³⁺ doped materials, that $\Delta\alpha_p$ varies by ~1 order of magnitude with the host character, increasing in the following order: fluorides, phosphates, silicates and oxides [1,2]. This behavior indicates that $\Delta\alpha_p$ is mainly affected by the ion 4f → 5d transitions, which are known to present a great deal of host dependence and their energy increase with the host bandgap. In this paper, an even greater host dependence was observed (~2 orders of magnitude) which can be attributed to the exceptionally low energy position of the 4f⁷5d¹ levels of Tb³⁺.

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0.3.109 Random Laser and Replica Symmetry Breaking in Nd³⁺-doped lead-germanate glass and glass-ceramic powders

Speaker: Da Silva Davinson

Random Laser and Replica Symmetry Breaking in Nd³⁺-doped lead-germanate glass and glass-ceramic powders

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Random Lasers (RLs) operating in the near-infrared are reported for powders of Nd³⁺ doped zinc-tellurite glass (TZO), alumina lead-germanate glass (GPA), magnesium lead-germanate glass (GPM), and glass-ceramics (GPM-GC). The glass samples were fabricated by conventional melt-quenching technique. GPM-GCs samples were obtained by devitrifying the GPM glass at 830 °C for different time intervals. Powders with average grain size between 1 and 2 µm were prepared by grinding each sample. Photoluminescence (PL) characterization was achieved by exciting the powders at 808 nm. The input-output curves showed that only the samples doped with high concentrations of Nd³⁺ (> 5%wt.) presented RL emission at 1068 nm, despite the occurrence of luminescence concentration quenching (LCQ). This was possible since the RL dynamics is much faster than the spontaneous emission [1-3]. A fast pulse, in the range of ns, was observed for all samples, above the RL threshold, which is characteristic of the laser emission. It was also observed a slower signal, superimposed to the fast pulse, attributed to the spontaneous emission and amplification of the spontaneous emission (ASE). The RL feedback mechanism was the multiple scattering of light by the micrometric particles, which acted simultaneously as gain medium and scatterers. For GPM-GC, we observed that the PL intensity was enhanced, and the RL threshold was minimized for the samples with higher degrees of crystallization. The enhanced performance is attributed to the growth of the residence-time of photons inside the GCs samples and to the higher quantum efficiency of Nd³⁺ incorporated within the microcrystals [2]. Additionally, the phenomenon of Replica Symmetry Breaking (RSB), characteristic of a photonic-phase-transition [4], was identified for both GPM and GPM-GCs samples, by measuring the PL intensity fluctuations below and above the RL threshold. Reduction of the PL linewidth above the RL threshold was not observed; this is attributed to the inhomogeneous broadening that occurs in glass matrices, since the local field in the vicinity of doped ions varies significantly from site to site, when compared to crystalline hosts. This was the first time, for the best of our knowledge, that RL operation and RSB were reported for a glass-ceramics system. In summary, the results herein reported showed that the employment of glasses and GCs as RL hosts may be very promising for developing improved coherent light sources based on disordered media.

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0.3.110 Rare earth imbedded polymer nanoparticles for extracellular singlet oxygen sensing in bacteria

Speaker: Dinga Kehbidla Daniel

Rare earth imbedded polymer nanoparticles for extracellular singlet oxygen sensing in bacteria

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The increasing microbial resistance to antibiotics severely threatens global health and calls for the extension of the antimicrobial toolbox^[1]. To this effect, the use of singlet oxygen ($^1\text{O}_2$) in this fight has picked up steam in the recent decades. However, its facile detection in biological media remains a challenge. Luminescent lanthanide complexes (LLC) have increasingly become a centre of attraction in materials chemistry due to several unique optical advantages over conventional fluorescent dyes. Their remarkably long lifetimes, large “ligand-induced” Stokes shifts (Richardson shift), and narrow emission make these dyes unparalleled in biological applications, as these enable easy discrimination against biological background autofluorescence^[2]. Though typically acting as external sensitization of the central rare earth ion, the coordinating organic ligands can be exploited as chemical traps for certain analytes in the medium. Reaction of $^1\text{O}_2$ with the antennae of some such LLCs leads to switching ON of the luminescence of the Ln^{3+} emission, hence signalling the presence of $^1\text{O}_2$ in the medium^[3].

Here we describe a straightforward method for the incorporation of rare earth $^1\text{O}_2$ probes in polymer nanoparticles (NP's) for the detection of $^1\text{O}_2$ in aqueous dispersion and on bacteria cell walls. These NP's form stable colloids and can detect $^1\text{O}_2$ in both acidic and basic media. The exceptionally long decay times of the resulting species of up to 850 μs allow for an even easier discrimination against biological background autofluorescence compared to the pristine Eu-complex. The high positive zeta potential of these particles readily allows for their adsorption on the negative cell walls of both Gram + and – bacteria. Here, the particles are able to detect any $^1\text{O}_2$ generated extracellularly or in the bacteria cell walls, leading to brightly red marked bacteria cells for easy discrimination.

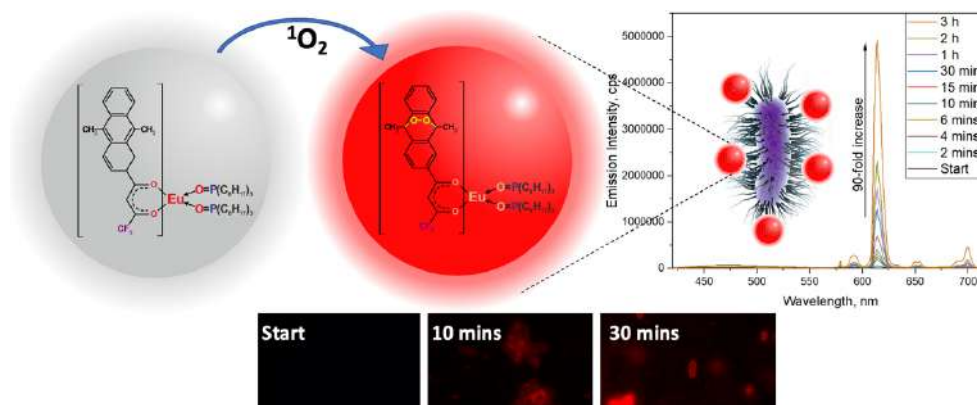


Figure 1: Eu-complex $^1\text{O}_2$ probe imbedded in polymer NP's adsorbed on bacteria surface, reacting with $^1\text{O}_2$ generated by an external photosensitizer – Rose Bengal – to give red-luminescence; (Top-left) Illustration, (Bottom) Microscopic images of *E. coli* with up to 30 min exposure. (Top-right) Emission spectrum showing increasing Eu^{3+} intensity with exposure time to $^1\text{O}_2$.

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0.3.111 Rare earth ion activated GdPO₄ and related phosphor materials for solid state lighting applications

Speaker: C Shivakumara

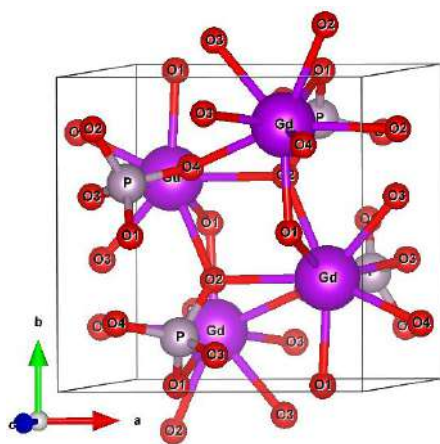
Rare earth ion activated GdPO₄ and related phosphor materials for solid state lighting applications

C. Shivakumara

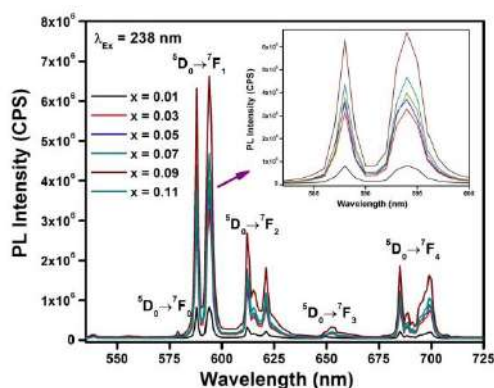
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From past few decades, rare earth ions activated gadolinium orthophosphate (GdPO₄) phosphors generated great attention as multimodal agents mainly for optoelectronic and biomedical applications. Due to their excellent ability of hosting activator and sensitizer ions in their lattice, higher quantum yields, lower photo-bleaching potential, high chemical and thermal stability, importantly low toxicity and bio-compatibility nature. On doping with suitable rare earth ions, the GdPO₄ host lattice turned to be a bi-functional magnetic and luminescent material. Compared to other lanthanide ions, Eu³⁺ ion is the most attractive and an extensively used luminescent activator ion due to its broad excitation band, excellent red emission and high thermal stability. Eu³⁺ activated GdPO₄ crystallizes in the hexagonal structure at low temperature and monoclinic structure at high temperature.



Crystal structure of GdPO₄



PL spectrum of Gd_{1-x}Eu_xPO₄ phosphors

Among these phases, monoclinic phase is playing important role in the energy transfer between Gd³⁺ and Eu³⁺ in GdPO₄ phosphor and it was clear that, the monoclinic phase exhibits an enhanced luminescent properties as compared to the hexagonal structure. Further, luminescence efficiency can be amplified by modifying the phosphor compositions by co-doping with suitable sensitizer ions. Such as, monovalent alkali metal ions (Li⁺, Na⁺ and K⁺) are widely used as sensitizers due to their ionic radius and ionic charges which are different from those of the host (Gd³⁺) ion, the distortion of crystal lattice is introduced as well as a break of the local site symmetry which can lead to a better color purity for optoelectronic and enhanced luminescent intensity for LEDs applications. In this presentation, I will discuss the synthesis, structure and luminescent properties of Eu³⁺/Sm³⁺ doped GdPO₄ and LaPO₄ phosphors, further effects on luminescent properties on co-doped with monovalent, divalent and trivalent ions as a sensitizer's in the doped GdPO₄ matrix.

0.3.112 Rare-earth complex as a self-calibrated photoluminescent sensor for low-range pressure measurement

Speaker: Zhou Yujiao

Rare-earth complex as a self-calibrated photoluminescent sensor for low-range pressure measurement

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Photoluminescent rare-earth-based composites have been studied for years in pressure-sensing applications. The advantages such as diverse functionality, low cost, and high optical efficiency make them one of the most important families in the study of photoluminescent sensors. The high-range pressure sensing property of Yb³⁺/Er³⁺ doped upconversion nanoparticles has been recently discovered. The reduction in interionic distances caused by the compression of the structure leads to a change in Ln-Ln energy transfer, which results in changes in the lifetime, intensity ratio, and brightness of the Ln³⁺ emitter under applied pressure up to 5 GPa.[1,2] In this study, we focus on low-range (< 1 GPa) pressure-sensing photoluminescent materials for application in tribological pressure measurement. The Ln-based complex provides a softer structure than the pure inorganic matrix in order to optimize the low-range pressure sensitivity. The energy transfer between two Ln³⁺ varies with pressure, so the relative intensity changes with pressure. The high sensitivity, reversibility and reproducibility show significant interest in using this material as a self-calibrated sensor in pressure sensing.

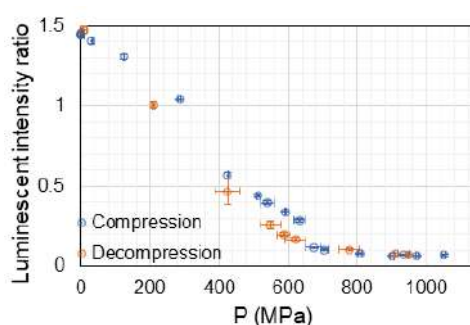


Figure: Luminescent intensity ratio as a function of applied hydrostatic pressure (up to 1 GPa)

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0.3.113 Realizing High-Performance UVB-LEDs Through Substrate-Dominated Strain-Modulation

Speaker: Li Tai

Realizing High-Performance UVB-LEDs Through Substrate-Dominated Strain-Modulation

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AlGaIn-based ultraviolet-B light-emitting diodes (UVB-LEDs) can be applied in many fields, such as phototherapy, vitamin D3 synthesis promotion, and plant growth regulation.^[1] In general, they are mainly grown on AlN templates which are prepared on sapphire substrates. Unfortunately, owing to the large lattice mismatch with AlN templates, the multiple quantum wells (MQWs) of UVB-LEDs usually suffer from excess compressive strain. The obstinate excess of compressive strain severely undermines the performances and hinders the applications of AlGaIn-based UVB-LEDs.

In this work, a substrate-dominated strain-modulation strategy is proposed and used to achieve high-performance UVB-LEDs.^[2] The compressive strain in Al_{0.55}Ga_{0.45}N underlayer and Al_{0.28}Ga_{0.72}N/Al_{0.45}Ga_{0.55}N MQWs is efficiently suppressed through introducing manageable tensile strain in the AlN template. Benefiting from this, the 20×20 mil² UVB-LED chip with an emission peak at 303.6 nm showed a wall-plug efficiency (WPE) of 3.27% under a forward current of 20 mA. A high light output power (LOP) of 57.6 mW was demonstrated with an extremely low voltage of 5.87 V under a forward current of 800 mA. In addition, it is impressive that the light output power degraded only 17% after 1000 h operation under a forward current density of 75 A/cm². Our UVB-LED demonstrates both a high level of WPE and long lifetime, which will promote the utilization of AlGaIn-based UVB-LEDs to a large extent.

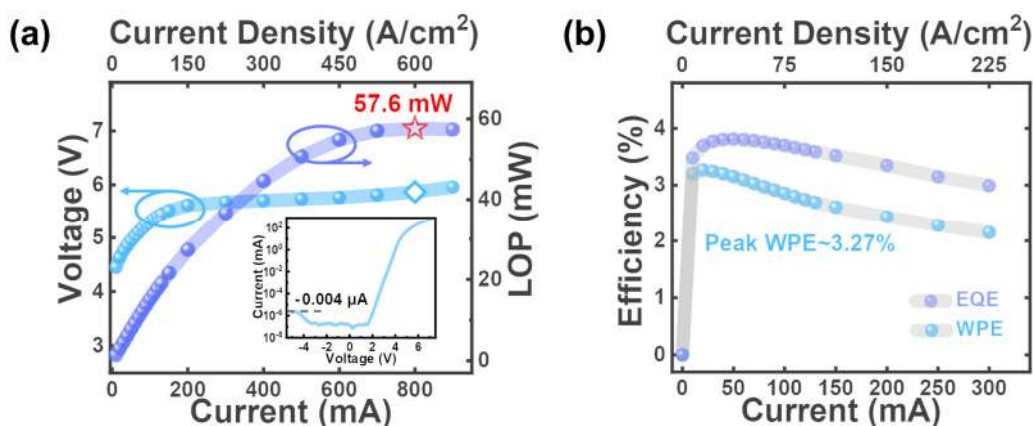


Figure 1. (a) Room-temperature forward I-V characteristics and current-dependent LOP of the UVB-LED chip. The inset displays the I-V characteristics in a semi-log scale. (b) Integrating sphere measurements of the current-dependent EQEs and WPEs of the UVB-LED chip.

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0.3.114 Recent progress in the development of LaVO₄-based nanoparticles with enhanced luminescent efficiency

Speaker: Chukova Oksana

Recent progress in the development of LaVO₄-based nanoparticles with enhanced luminescent efficiency

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Vanadate matrices are well known hosts for luminescent rare earth (RE) ions since middle of 20th century, when YVO₄:Eu³⁺ crystalline compositions became into mass usage as red phosphor for luminescent lamps, cathodoluminescent tubes and oscillograms [1]. The main reasons for application of vanadates for these purposes are their high radiation hardness and high efficiency of RE³⁺ luminescence in vanadate matrix. Nowadays, traditional applications of phosphors are currently extended to wide technical areas used in various color imaging, lightening systems and renewable energy production. The new applications require development of new compositions with special enhanced luminescence characteristics. Thus, the search of new promising luminescent vanadate compositions was extended in the last decades on the LaVO₄ matrix which is also could be quite effective host for the luminescent RE ions.

The LaVO₄ matrix is characterized by a feature unique for the orthovanadate compounds: this is a dimorphism of the LaVO₄ crystal structure [2]. Dimorphism of LaVO₄ can be an essential advantage in the search of compositions with certain spectroscopy characteristics needed for one of the mentioned purposes: luminescent properties of the RE³⁺ ions are known to be depended on the symmetry of the crystal surrounding. In some ranges of concentrations, it is possible to synthesize two-phase La_{1-x}RE_xVO₄ nanoparticles and to get advantages of the both crystal structures in the same sample. It is expected that interaction and excitation energy transfer between two crystal phases (monoclinic and tetragonal) in synthesized two-phase crystalline nanoparticles will increase their luminescence efficiency. We have investigated the La_{1-x}RE_xVO₄ nanoparticles synthesized by various methods (solid-state, co-precipitation, sol-gel, hydrothermal) with various RE activators (Eu, Er, Sm, Dy, Yb). For all the investigated RE ions, increasing of their concentrations lead to transformation of crystal structure of the La_{1-x}RE_xVO₄ nanoparticles from monoclinic to tetragonal. Phase transformation effects on morphology and luminescence properties of the studied compositions. It was found that the RE³⁺ ions form two types of emission centers in the samples under study related with the abovenoted two crystal phases. Different types of centers are characterized by different rates of excitation energy harvesting and transfer to the emission centers as well as by different emission efficiency. The assumption is made that two-phase nanoparticles can combine advantages of the both phases in the same sample.

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0.3.115 Recording the birth of a Agregation Induced Emission crystal

Speaker: Pansu Robert

Recording the birth of a AIE crystal

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90% of the chemicals are purified by precipitation. But the nucleation mechanism is unknown and “crystal growth and design” remains a domain of recipes and know how. To discover the mechanism of the nucleation, we use the possibility to induce, by a laser shot, the nucleation of crystals (NPLIN).^[1] With NPLIN, we know when (ns) and where (μm) the crystal will be produced. AIE crystals are fluorescent solids formed from non-fluorescent solutions. This allows to detect and characterize the smallest fluorescent aggregate. From the fluorescence signal, we can identify the polymorphs, measure the nucleation rate, the growth rate, the density of defects in the crystals. We use microfluidic channels under a microscope. The flow allows a constant renewal of the solution for the collection of nucleation events with a high statistic. With microfluidic we can prepare flows with controlled metastable supersaturations by the mixing of a solvent and an antisolvent.^[2]

Two examples will be presented. The NPLIN nucleation of DBDCS, an organic AIE molecule, is performed during an anti-solvent precipitation. We show that the spontaneous nucleation and the NPLIN produce the same distribution of polymorphs. Thus, NPLIN trigs the nucleation but does not change the mechanism. We also show that the polymorph dominant at the nucleation spot is not the one that escapes and grows. The mechanism of NPLIN is not known but optical tweezer effects can be observed when focusing the laser in solvent flows. In contrast the NPLIN nucleation of MAPbBr₃ - a hybrid lead halide perovskite - occurs even below the saturation.^[3] MAPbBr₃ presents a retrograde solubility in DMF and crystalizes at high temperature. We see a thermal lensing effect during the nucleation. Thus, NPLIN could be due in the case of MAPbBr₃ to a heating of the solution by the laser.

In both cases, we observe that the nucleation is preceded by the formation of the super-cooled liquid phase of the solute. This nucleation mechanism has been called two steps nucleation.^[4] We shall discuss this mechanism in the frame of the thermodynamic of solutions.

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0.3.116 Reexamination of the luminescent properties of Pr³⁺, Er³⁺, Tm³⁺ and Ho³⁺ doped Bi₄Ge₃O₁₂ single crystals for the visible and mid-infrared laser applications

Speaker: Guyot Yannick

Reexamination of the luminescent properties of Pr³⁺, Er³⁺, Tm³⁺ and Ho³⁺ doped Bi₄Ge₃O₁₂ single crystals for the visible and mid-infrared laser applications

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Undoped BGO is a well-known scintillating material. Doped with transition metal ions (Cr ions more particularly), it exhibits interesting photorefractive properties which can be used in the realization of photo-induced holographic gratings. Doped with trivalent rare-earth ions, it shows promising luminescent properties which can be used advantageously for the lighting, temperature sensing and laser applications. Concerning the latter, however, only the spectroscopic properties of Nd³⁺ have been carefully enough studied and Nd³⁺ doped BGO crystals lased efficiently [1-3]. Therefore, the aim of the present communication is to address the case of the other most important ions for laser application, i.e. Pr³⁺, Er³⁺, Tm³⁺ and Ho³⁺. For that purpose, high quality BGO (Bi₄Ge₃O₁₂) crystals doped with various amounts of ions were grown as 2 mm diameter and 50 mm long rod-type crystal fibers by using the micro-pulling down technique. Samples 2 mm long were then cut and polished to perform a very detailed spectroscopic study consisting of (i) revisiting and completing the absorption spectra already available in the literature [4-6], in order to derive the most reliable radiative lifetimes and branching ratios of the most important emitting levels and associated emission transitions, (ii) recording the corresponding emission spectra and fluorescence lifetimes, in order to re-examine the non-radiative multi-phonon relaxation parameters which were proposed in the past, and to finally show, via stimulated emission and gain cross section spectra, the interest of Pr³⁺, Er³⁺, Tm³⁺ and Ho³⁺-doped BGO crystals as visible and mid-infrared laser materials for tunable and/or short-pulse laser operation. Doing so, a special attention was dedicated to the question of the electron-phonon coupling and multi-phonon relaxation mechanisms affecting the emission lifetimes and quantum yields of the excited emitting levels in these materials, a question that still suffers from some ambiguity [4-6].

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0.3.117 Relaxation processes in wide gap solids leading to ultrafast cross - and intraband luminescence

Speaker: Kirm Marco

Relaxation processes in wide gap solids leading to ultrafast cross - and intraband luminescence

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Cross-luminescence (CL) and intraband luminescence (IBL) are ultrafast intrinsic emissions due to radiative recombination of electrons from the valence band with holes in the outermost core band [1] and electron or hole transitions within the conduction or valence band [2], respectively. As shown for BaF₂ in Fig. 1, the lifetime of CL is in the sub-ns time domain, whereas IBL is even faster, possessing the lifetime of a few picoseconds due to competing phonon relaxation. Such excellent timing properties are of interest for scintillator applications [3], although the light yields of these emissions are very low in comparison to widely used rare earth doped wide gap scintillators. In recent years we have developed luminescence setups for time-resolved spectroscopy studies of ultrafast relaxation processes, whereas at the FemtoMAX beamline of MAX IV Lab (Lund, Sweden), the time resolution achieved is as high as 30 ps (IRF) [4].

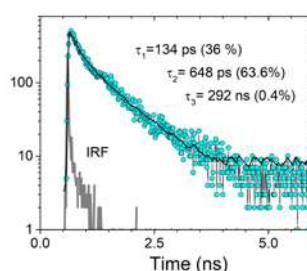


Fig. 1. A CL decay curve recorded through a 216 nm interference filter for a BaF₂ crystal excited by 10 keV X-ray pulses at the FemtoMAX beamline (MAX IV Lab) at 300 K [4].

We investigated the dynamics of intrinsic electronic excitations in classical binary cross-luminescence crystals (BaF₂, CsCl) and ternary hexafluorides (BaGeF₆ and Na₂GeF₆ powders and K₂GeF₆ single crystal). The latter materials possess both CL and IBL appearing due to the hybridized Ge states enriching the valence sub-band structure [5]. The gaps between valence sub-bands prolong the IBL decay time to tens of picoseconds favorable for applications. The branching of relaxation processes leading to different emissions will be analyzed taking into account electronic band structure calculations and our VUV spectroscopy results. Application prospects of novel ternary hexafluoride single crystals as ultrafast scintillators will be considered.

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0.3.118 Scintillation Properties and Mechanisms of (PEA)₂PbBr₄ down to 10K

Speaker: Van Blaaderen Jasper

Scintillation Properties and Mechanisms of (PEA)₂PbBr₄ down to 10K

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Last decade organic-inorganic perovskites have gained significant attention for their optoelectronic properties. Their small band gap and low temperature solution based synthesis makes them very interesting candidates for scintillation application [1].

Especially the 2D perovskites phenethylammonium lead bromide ((PEA)₂PbBr₄) and buthylammonium lead bromide ((BA)₂PbBr₄) have shown to be promising compounds for scintillator applications due to their temperature stable exciton luminescence [1,2]. Most publications focus on the room temperature scintillation properties. We will report on optical and scintillation properties of (PEA)₂PbBr₄ and benzylammonium lead bromide ((BZA)₂PbBr₄) down to 10K [3]. At low temperatures the total spectral intensity of PEA₂PbBr₄ shows negative thermal quenching. This can be linked to the combined effect of free exciton luminescence and the temperature dependent formation of self-trapped excitons. Additionally, a second sub nanosecond decay component was discovered at 10K, next to the 150 ns decay component. Similar behavior is observed for (BZA)₂PbBr₄.

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0.3.119 Scintillation properties of composite scintillators based on doped orthosilicate compounds

Speaker: Witkiewicz-Lukaszek Sandra

Scintillation properties of composite scintillators based on doped orthosilicate compounds

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The single crystals (SC) of Ce³⁺ doped A₂SiO₅ (A = Lu, Y) orthosilicates have been developed as promising scintillators for positron emission tomography (PET) due to their desirable properties such as high density, fast decay time and high light output [1]. Meanwhile, apart from their applications in crystal form, these orthosilicates also attract attention regarding the development of single crystalline film (SCF) scintillating screens for microtomography using the liquid phase epitaxy (LPE) method [2].

Recently, we developed various types of the doubly- and three-layered composite scintillators (CS), based on the SCFs of Ce³⁺ and Pr³⁺ doped (Y, Lu)AG simple garnets and Ce³⁺ doped (Y,Lu,Tb,Gd)₃(Al,Ga)₅O₁₂ mixed garnets, grown using the LPE method onto heavy LuAG:R (R=Pr,Ce,Sc) and GAGG:Ce substrates [3, 4]. The results of our current researches show that the epitaxial structures of orthosilicates can be also considered as promising composite scintillators for simultaneous detection of α -, β -particles and γ -rays.

In this work, two different sets of CSs based on the YSO:Ce SCF/LYSO:Ce SC and (Y_{0.75}Lu_{0.25})SO:Bi SCF/LYSO:Ce SC epitaxial structures were grown by the LPE method. For the characterization of the luminescent and scintillation properties of SCF and bulk crystal parts of composite scintillators, the absorption and CL spectra as well as pulse height spectra scintillation decay kinetics under α - and β - particle and γ - quantum excitation were applied. Furthermore, we show the possibility of the simultaneous registration of these types of ionization radiation by the way of separation of the scintillation decay kinetics of SCF and SC parts of composite scintillators (Fig.1a). Namely, the (Y_{0.75}Lu_{0.25})SO:Bi SCF/ LYSO:Ce SC type of composite scintillator are characterised by high LY of their film and bulk crystal parts and suitable Figure of Merit (FOM) ratios $FOM_{\alpha\beta} = t_{\alpha} - t_{\beta}/t_{\alpha} + t_{\beta}$, $FOM_{\alpha\gamma} = t_{\alpha} - t_{\gamma}/t_{\alpha} + t_{\gamma}$ and $FOM_{\beta\gamma} = t_{\beta} - t_{\gamma}/t_{\beta} + t_{\gamma}$ under simultaneous registration of mentioned types of radiation (Fig.1b).

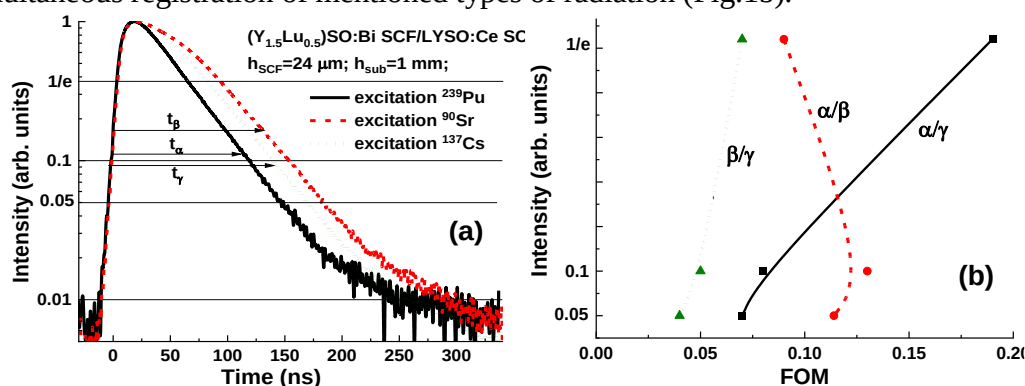


Fig.1. (a) - separation of the scintillation decay curves of (Y_{0.75}Lu_{0.25})SO:Bi SCF/LYSO:Ce SC composite scintillators under excitation by α - (²⁴¹Am) and β - (⁹⁰Sr) particles and γ -quanta (¹³⁷Cs). (b) -scintillation intensity decay and FOM values of this composite under registration of the mentioned types of radiation.

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0.3.120 Scintillation properties of Na₂O-ZnO-SiO₂ glass system: Potentially interesting distributed sensor of harmful radiation

Speaker: Jary Vitezslav

Scintillation properties of Na₂O-ZnO-SiO₂ glass system: Potentially interesting distributed sensor of harmful radiation

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Common rare-earth (RE)-doped silica optical fibers are usually used for a construction of distributed radioluminescent sensors [1]. However, low solubility of RE ions inside glass matrix reduce the overall fiber response toward the radiation [2]. The radioluminescence properties of the fiber can be improved by nano-structuralizing of the fiber core by creating an inorganic nanocomposite of radioluminescent nanoparticles distributed inside the glass matrix [3]. The final luminescence properties of nano-structuralized optical fiber are given by the properties of the incorporated nanoparticles. Therefore, the successful preparation of inorganic nanocomposites consisting of radioluminescent nanoparticles distributed inside host glass matrix represent the challenging task for current material research.

In presented work we introduce the basic study of the Er³⁺, Yb³⁺-doped Na₂O-ZnO-SiO₂ glass system prepared using controlled crystallization of precursor glass by annealing in the 700 – 900 °C range which contains scintillating nanoparticles of various forms, such as Na₂ZnSiO₄, α-Zn₂SiO₄, Zn₂SiO₄. Their structural and morphological characteristics are investigated by the X-ray diffraction and transmission electron microscopy analysis. Their scintillation and optical properties are afterwards studied by the methods of time-resolved luminescence spectroscopy and by the setup for a fast scintillation decay measurement with time resolution below 100 ps. The intense UV emission under the X-ray excitation peaking at around 330 – 360 nm reaching 500% of the intensity of the standard Bi₄Ge₃O₁₂ scintillation material, with corresponding fast scintillation decay time in the orders of few units of nanosecond, make these materials worth of further investigation in the field of distributed radiation detectors.

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Acknowledgment

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0.3.121 Selective laser spectroscopy of $\text{La}_{1-x-y}\text{Y}_x\text{Nd}_y\text{F}_3$ mixed nanocrystals

Speaker: Dolgov Leonid

Selective laser spectroscopy of $\text{La}_{1-x-y}\text{Y}_x\text{Nd}_y\text{F}_3$ mixed nanocrystals

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Large inhomogeneous broadening of rare earth luminescence spectra, inherent to mixed crystals (solid solutions) such as $\text{La}_{1-x-y}\text{Y}_x\text{Nd}_y\text{F}_3$ makes it possible for selective excitation of certain subsets of Nd^{3+} ions prospective for quantum information processing. Two interacting rare earth ions can model the two-qubit control-NOT quantum gate operation [1]. The practical implementation of this idea requires, at first stage, the synthesis of monodisperse crystalline nanopowders and site-selective time-resolved laser spectroscopy at low temperatures.

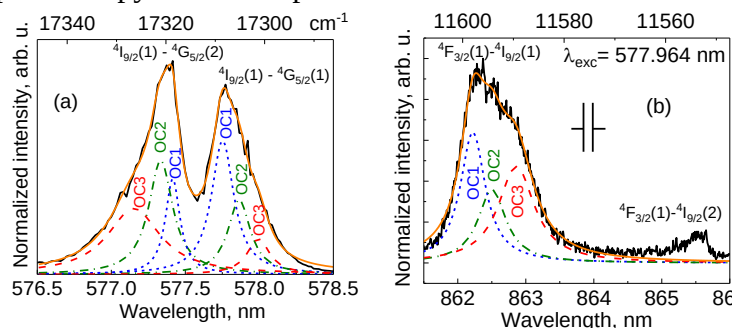


Fig. 1. $\text{La}_{0.89}\text{Y}_{0.1}\text{Nd}_{0.01}\text{F}_3$, $T = 4.2$ K: (a) luminescence excitation spectrum at the $^4\text{I}_{9/2}(1) \rightarrow ^4\text{G}_{5/2}(1,2)$ transition of Nd^{3+} ion detected at the $^4\text{F}_{3/2}(1) \rightarrow ^4\text{I}_{9/2}(1, 2)$ transitions; (b) luminescence spectrum in the range of $^4\text{F}_{3/2}(1) \rightarrow ^4\text{I}_{9/2}(1,2)$ transitions for $\lambda_{\text{exc}} = 577.964$ nm. Dashed lines show decomposition of spectral bands on Lorentzian components of optical centers OC1-OC3.

It was demonstrated that low-temperature luminescence excitation spectra of $\text{La}_{1-x-y}\text{Y}_x\text{Nd}_y\text{F}_3$ nanopowders include two inhomogeneously broadened bands with maxima at about 577.7 and 577.3 nm, which correlate with $^4\text{I}_{9/2}(1) \rightarrow ^4\text{G}_{5/2}(1)$ and $^4\text{I}_{9/2}(1) \rightarrow ^4\text{G}_{5/2}(2)$ transitions of the Nd^{3+} ion, respectively (Fig. 1a). The luminescence band with maximum at ~ 862.5 nm, corresponding to the $^4\text{F}_{3/2}(1) \rightarrow ^4\text{I}_{9/2}(1)$ transition, includes the luminescence of three groups of optical centers (OC1 - OC3) (Fig. 1b). Their luminescence spectral lines were selected by tuning the laser excitation wavelength with spectral resolution of 0.0065 nm. The inhomogeneous broadening of the $^4\text{G}_{5/2}(1)$ and $^4\text{G}_{5/2}(2)$ states and the energy difference between $^4\text{G}_{5/2}(1)$ and $^4\text{G}_{5/2}(2)$ states increase with increasing yttrium concentration in the solid solution from 10 to 30 %. Density functional calculations revealed three possible local positions of molecular OH groups replacing fluorine ions in the mixed subsystem $\text{La}_{1-x-y}\text{Y}_x\text{Nd}_y\text{F}_3$ during its synthesis. It has been suggested that the revealed difference in the luminescence quenching kinetics of the OC1 - OC3 centers, detected at the initial stage of ordered static quenching, may be due to different positions of local OH groups and their different local concentrations in the coordination spheres closest to Nd^{3+} ions.

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0.3.122 Significant Enhancement of the Upconversion Emission of Nanoparticles at Cryogenic Temperatures

Speaker: Wu Kefan

Significant Enhancement of the Upconversion Emission of Nanoparticles at Cryogenic Temperatures

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Lanthanide-doped upconversion nanomaterials (UCNP) capable of converting effectively low-energy photons to high-energy emissions have broad and important applications. Recent nanostructure designs have realized unprecedented high-level-doping UCNPs. This otherwise very promising strategy for upconversion emission enhancement, however, suffers from the accompanied side effect – intensified detrimental cross-relaxation (CR). We have discovered the crucial role of phonons in these CR processes and validated that effective suppression of the phonon effect via cryogenic temperature can significantly limit the CR and greatly lift the upconversion emission of two orders of magnitude. From theoretical simulations and temperature-dependent UC spectra, the phonon role in CR is quantitatively elucidated. Based on this, we also realized the tuning of CR processes simply through control of the excitation power density. Our work not only unraveled the CR mechanisms in UC nanophosphors but also provided a promising strategy for cryogenic applications of UCNPs, including broad temperature sensing.

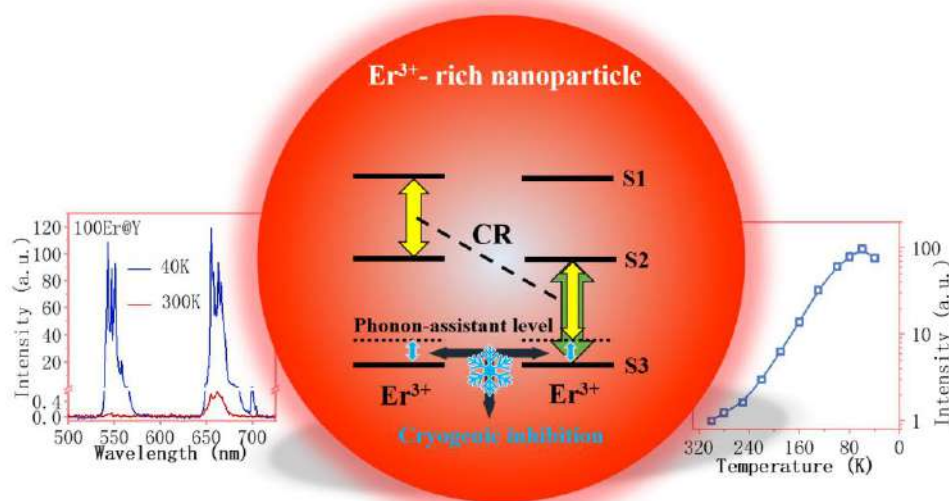


Figure 1. By introducing a cryogenic environment to suppress the harmful cross-relaxation, the upconversion intensity of Er^{3+} -rich UCNPs is significantly improved over 100-fold.

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0.3.123 Spatial distribution of PL intensity of NV^- and NV^0 centers in relation to optically stimulated charge transfer

Speaker: Akimoto Ikuko

Spatial distribution of PL intensity of NV⁻ and NV⁰ centers in relation to optically stimulated charge transfer

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Negatively charged nitrogen-vacancy centers (NV⁻) in diamond are red-light emitters that provide optically detectable spin states for quantum applications. Therefore, stability of NV⁻ centers under light is very important. It has been known that some part of NV⁻ centers are turned into neutral NV⁰ centers by transferring electrons under intensive photoexcitation [1]. Tunneling transfer has been pointed out as the charge transfer mechanism, but the details are unknown. In this study, we investigated the charge transfer mechanism between NV⁻ and NV⁰ centers in a Ib-diamond crystal by photoluminescence (PL) and electron paramagnetic resonance (EPR) measurements.

By measuring PL spectrum from the (110) plane under photoexcitation on the (100) plane at wavelength of 532 nm (10 mW) at 88 K, we confirmed that PL intensity of NV⁰ center increases but that of NV⁻ decreases by irradiation of additional light at wavelength of 415 nm (120 mW). The PL intensity ratio of NV⁰/NV⁻ increases in a few minutes after lighting and decreases in several tens of minutes after lighting off. This time evolution was coincident with that of EPR intensities in other localized states; increase of neutral substitutional nitrogen center (N_s⁰) and decrease of negatively charged substitutional nickel center (Ni_s⁻) after lighting, and those recovery after lighting off. Based on wavelength dependence of the stimulation light, we conclude that electrons are excited from Ni_s⁻ and NV⁻ to the conduction band and transferred to the site of N_s⁺, then the charge shifts from NV⁻ to NV⁰, from Ni_s⁻ to Ni_s⁰, and from N_s⁺ to N_s⁰ cause the observed signal changes under the stimulation light.

The presence of the N_s⁺ centers as electron acceptors is key to the charge state instability of NV⁻ centers under light. We measured microscopic spatial distribution of PL intensity of NV⁻ and NV⁰ centers within the same crystal at a corner near the (111) plane by the excitation at wavelength of 532 nm at 5.8 K. Figure 1 shows a spatial map of the zero-phonon-line (ZPL) intensity ratio of NV⁰/NV⁻, indicating that the PL intensity of NV⁰ appears at the edge of crystal habit and inside kinks but not at the largest plane of (001). That is, the NV⁰ centers are not uniformly distributed next to the NV⁻ centers. This map probably reflects the skewed distribution of N_s⁺ centers. Based on the experimental data, the charge transfer mechanisms will also be discussed, including recovery process in the dark.

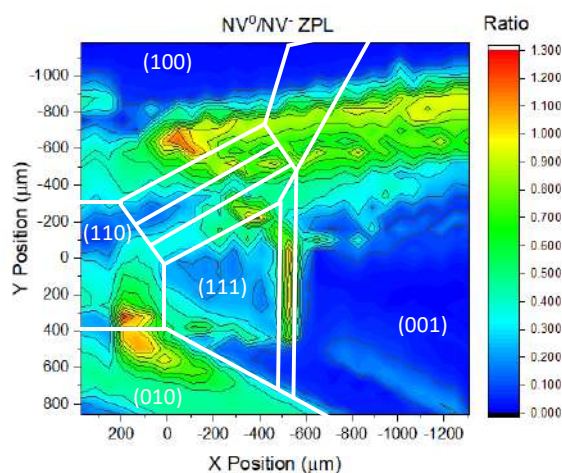


Figure 1 A contour map of PL intensity ratio of zero-phonon line of NV⁰ to that of NV⁻ excited at wavelength of 532 nm at 5.8 K. White lines indicate crystal habits.

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0.3.124 Spectral broadening of single spherical nanocrystal CdSe/CdS under high excitation power

Speaker: Simonot Damien

Spectral broadening of single spherical nanocrystal CdSe/CdS under high excitation power

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CdSe/CdS core/shell nanocrystal are excellent bright nano-emitters both at the individual and collective scale. At room temperature, they behave as high quantum efficiency single photon sources thanks to the electronic confinement and efficient Auger processes. Single photon emission can be described by the recombination of a single exciton within a simple two-level system. Under low excitation power at room temperature, the emission linewidth is approximately $\Delta\lambda \approx 20$ nm. However, by increasing the excitation power, we lose the single photon character and we observe a spectral broadening which can exceed $\Delta\lambda \approx 150$ nm.

Moreover, the emission intensity grows non-linearly with increasing excitation power [1][2]. The two-levels system paradigm fails for interpreting those features. We have developed a more general model based on the radiative recombination of multiple excitonic levels within a single nanocrystal. This model relies on the determination of the excitonic energy levels of a single quantum dot, on the statistical description of the electron and hole populations, n_e and n_h , in a quasi-equilibrium and on their recombination.

The Fermi-Dirac distribution $n(E)$ for electrons and holes involves two unknown parameters: the chemical potential of radiation $\Delta\mu$ [3] and the electronic temperature T . The photoluminescence spectrum P for a single quantum dot can be expressed as

$$P(E) = E \sum_i \sum_j g_i^e g_j^h n_i^e(E_i^e) n_j^h(E_j^h) f_{ij}^{exc} \frac{1}{\sqrt{2\pi}\Gamma_{ij}} e^{-\frac{(E-E_{ij}^{exc})^2}{2\Gamma_{ij}^2}}$$

where the energy E_{ij}^{exc} , the degeneracy factor $g_{i,j}$, the oscillator strength f_{ij} and the width Γ_{ij} refer to the excitonic transition ij and are computed within a two-band description for electrons and holes in CdSe/CdS heterostructures. This model allows for the determination of the chemical potential of radiation and the temperature in accordance with the evolution of experimental photoluminescence spectra and intensity. The large broadening of the spectrum is associated to a strong increase of the chemical potential of radiation and temperature.

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0.3.125 Spectral Evolution in an Organic Laser Diode

Speaker: Lenstra Daan

Spectral Evolution in an Organic Laser Diode

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Experimental results of stimulated emission in organic devices under electric pumping are still under debate [1]. We present simulations of spectral dynamics of light emission unveiling sharp peak emission of organic laser diodes well below laser threshold, indicating that narrow-peak emission is not necessarily a signature of lasing.

Simulations of time-resolved output spectra of electrically pumped organic laser diodes are confronted with experimental measurements (under optical pumping). In cases of large triplet-induced gain quenching (e.g. in Alq3 or DCM), lasing occurs during the first few nanoseconds at most after the onset of electrical excitation [2,3]. In cases with less triplet quenching (e.g., BsB-Cz [1]), cw lasing is possible. This has consequences for the form of the observed LV and output spectrum characteristics.

Simulated time-resolved output-power spectra will be presented from below to above the threshold for (pulsed or cw) lasing, as well as time-averaged output spectra. In Fig 1(a) the laser-pulse duration is much shorter than the integration time of the spectral measurement, leading to a rather “smeared out” laser threshold compared to case (b), where the material BsB-Cz leads to cw lasing and a sharper threshold. Well-below threshold, a cavity-induced narrow peak on top of the spontaneous-emission shoulder may be visible in the output spectrum. In (c) measured spectra with DCM under optical pumping are shown.

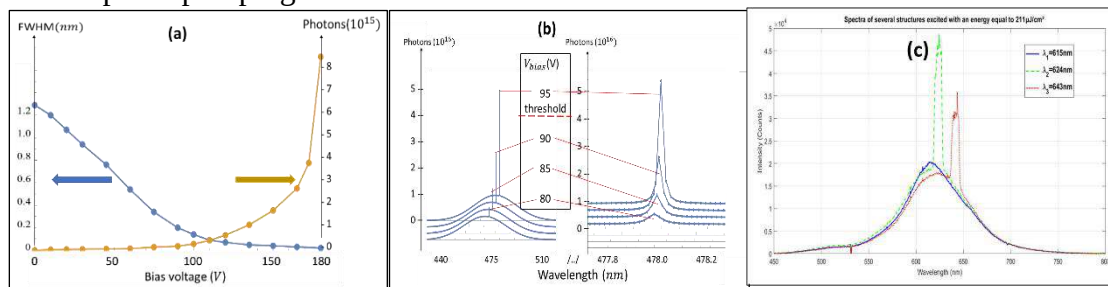


Figure 1: (a) Simulated emitted photon number (right scale) and FWHM linewidth of the peak in the optical spectrum (left scale) vs. bias voltage. The material is DCM (2%), with the cavity tuned at the top of the emission spectrum ($\lambda_{\text{CAV}} = 610\text{nm}$, $Q=600$), the bias pulse applied during 12ns and the spectrum averaged over 50ns; the threshold for (short-pulse) lasing is around 110V. (b) Emission spectra for BsB-Cz, the cavity tuned 3nm right from the top of the emission spectrum ($\lambda_{\text{CAV}} = 478\text{nm}$, $Q = 600$), bias voltage applied over 100ns and averaging time 100ns. The threshold for (cw) lasing is $\approx 92.5\text{V}$. (c) Observed spectra under optical pump excitation in DCM ($Q \approx 600$).

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0.3.126 Spectroscopic investigation of Praseodymium and Neodymium doped fluoride crystals for mid infrared applications

Speaker: Gennari Fulvia

Spectroscopic investigation of Praseodymium and Neodymium doped fluoride crystals for mid infrared applications.

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Although materials for solid state lasers are largely available in the visible and near infrared regions, the same does not remain true if we step into the mid-infrared one. Moreover, 3-6 μm emitters can potentially be of fundamental importance for applications, such as deep tissue imaging, molecular spectroscopy, food-quality assessment, anti-counterfeiting and more [1].

In this work, we present a thorough investigation of the spectroscopic properties of both the low-energy $^3\text{F}_{2,3,4}$ and the $^3\text{H}_{5,6}$ Pr^{3+} upper levels, in Yb:Pr co-doped LiYF_4 (YLF), GdYF_4 (GLF) and KYF_4 (KYF) single crystals, and the $^4\text{F}_{3/2}$ level in Nd doped YLF crystal at room temperature.

Praseodymium presents some promising fluorescence around 3 μm , and in the 4-6 μm and 6-8 μm bands [2]. Neodymium presents a very interesting emission around 2 μm that is far less studied than its other emissions. Fluorides have relatively low phonon energies, resulting in a higher quantum efficiency in the infrared, while still possessing good optical and thermo-mechanical properties.

The polarized absorption and emission spectra of 10%Yb,1%Pr:YLF, 10%Yb,1%Pr:KLF, and 10%Yb,1%Pr:GLF, have been acquired with a Fourier-Transform Infrared Spectrometer (FTIR) from 8000 to 1000 cm^{-1} after pumping the Yb^{3+} ions at 980 nm. The same study has been applied to Nd:YLF, pumped with a 808 nm laser. The Pr results will show intense emission bands that extend from 8000 to 7000 cm^{-1} (corresponding to about 1.2-1.4 μm) and from 6000 to 4500 cm^{-1} (corresponding to about 1.6-2.2 μm), and weaker signals at around 2700-3000 cm^{-1} (about 3.3-3.7 μm) and around 1800-1500 cm^{-1} (about 5.5-6.6 μm). The Nd^{3+} $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{3/2}$ emission cross section has been calculated. This investigation is useful both to increase the knowledge of the less-investigated infrared energy levels of rare earth ions, and for assessing their potentialities as possible laser emitters.

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0.3.127 Spectroscopic studies of rare-earth free hybrids derived from thianthrene–phosphonic acid

Speaker: Ganesan Parameshwari

Spectroscopic studies of rare-earth free hybrids derived from thianthrene-phosphonic acid

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The development of rare earth-free luminescent materials is a very important and inevitable topic for the future, due to the severe supply shortage of rare earth elements and their lack of recyclability. With this in mind, we synthesize organic-inorganic (hybrid) crystalline luminescent materials based on rare-earth free metallophosphonate whereas, the organic part provides a rigid platform that can be easily modified by adding different functional groups. The metallophosphonate materials differ by the nature of the molecules and their positions and interactions in the crystal structure, and also by the nature and size of the cations. In consequence, we explore structure-dependent properties such as rigidity, thermal stability, and luminescent properties, e.g. additional luminescence bands, aggregation-induced or enhanced emission (AIE/AEE), or Excimer-like emission [1, 2].

Here, we present different metallophosphonates (hybrid) that are synthesized by hydrothermal route from thianthrene phosphonic acid (organic ligand) with different alkaline earth elements with increasing atomic radius (Mg, Ca, Sr, Ba) and transition elements (Mn, Co, Cu, Zn). Due to the chemical and structural differences, the synthesized hybrid materials exhibit optical spectroscopic properties that differ from organic ligands and from each other. In particular, the photoluminescence of the thianthrene-based hybrids exhibits properties such as fluorescence in the far UV region and room temperature phosphorescence (RTP) in the visible region, hypsochromic shift (blue shift), and additional red luminescence bands observed in the presence of specifically selected cations (Mg, Sr).

We will therefore present in detail the spectroscopic properties obtained from different alkaline earth/transition elements incorporated in metallophosphonate materials and their relationship with structural properties, highlighting aggregation-induced emission phenomena.

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0.3.128 Strong absorbing sputtered luminescent thin films for luminescent solar concentrator applications

Speaker: Derksen Max

Strong absorbing sputtered luminescent thin films for luminescent solar concentrator applications

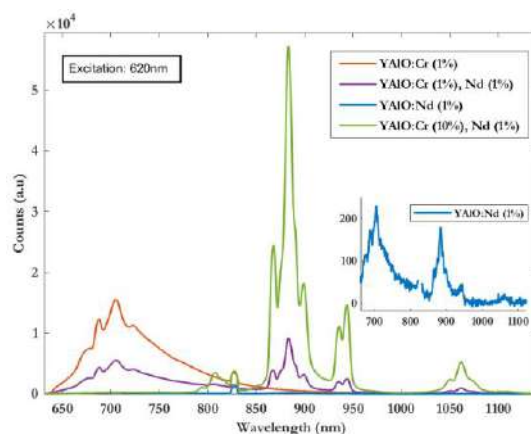
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Luminescent solar concentrators (LSCs) combined with photovoltaic cells can generate electricity and have the potential to be used as photovoltaic windows, that is an LSC-PV-window. To efficiently and quickly apply this technology on a large scale, sputtering is an accessible and scalable technique already used by glass industry. However, complying with maximum sputtering times is a critical cost requirement for industry, which limits the thickness of the films to just a few 100 nm. For maximum PV-window power output, such thicknesses pose a real challenge to absorb a significant part of the ultraviolet and visible solar spectrum.

In this work, we investigate whether highly concentrated Cr^{3+} thin films doped with Nd^{3+} , can be used as LSC material with strong and broad absorption. Cr^{3+} absorbs across the visible spectrum and can transfer energy to Nd^{3+} . However, in single-doped Cr^{3+} materials, high concentrations of Cr^{3+} lead to quenched emission due to $\text{Cr} \rightarrow \text{Cr}$ transfer, where energy is eventually lost to defects. Our study examines whether the energy migration among Cr^{3+} ions can facilitate energy transfer to Nd^{3+} . To explore this systematically, we sputter 4 metallic targets at right angles from one another, Y^{3+} , Al^{3+} , Cr^{3+} and Nd^{3+} in a mixed argon/oxygen atmosphere. By not rotating the substrate a compositional gradient is formed. Using a custom built set-up, position dependent emission, excitation, transmission and lifetime measurements are semi-automatized and mapped against the elemental composition for a rapid optimization of the luminescence. We will show that energy transfer takes place between Cr^{3+} and Nd^{3+} despite Cr^{3+} luminescence being quenched in the equivalent single doped Cr^{3+} films. Furthermore we will demonstrate our unique technique of analyzing a range of materials on a single substrate.



Emission spectra of various yttrium aluminate thin films doped with: chromium (1%), chromium & neodymium (1%), neodymium (1%) and chromium (10%) & neodymium (1%).

0.3.129 Structural and luminescent properties of gold based double perovskites semiconductors

Speaker: Delport Géraud

Structural and luminescent properties of gold based double perovskites semiconductors

Over the past years the family of halide perovskites crystals have been vastly investigated to design thin film based optoelectronics devices for applications such as solar cells, lights emitting diodes... One major advantage of halide perovskite with respect to conventional semiconductors is their chemical versatility that allows us to finely tune many of their optoelectronic properties. However conventional lead based perovskites suffer from many drawbacks, including toxicity and poor stability.

In this context, double perovskite and in particular gold based double perovskite $\text{Cs}_2\text{Au}_2\text{X}_6$ stand out as promising alternatives. In this presentation, I will detail our recent advances on the preparation in terms of powders and thin films, that allowed us to produced materials much more stable than conventional lead halide perovskites. I will also detail the characterization of the structural and luminescent properties of such materials.

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0.3.130 Structural and Optical Properties of Ni²⁺-Doped Double Perovskite-Type Phosphors

Speaker: Kitagawa Yuuki

Structural and Optical Properties of Ni²⁺-Doped Double Perovskite-Type Phosphors

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The wide-band near-infrared (NIR) phosphors have been widely studied for various applications, such as bio-imaging, sensing, and photovoltaic cells. Ni²⁺ ions with the 3d⁸ configuration are the promising NIR luminescence and absorption center due to the spin-forbidden ³T₂-³A₂ transition with an energy difference of 6000–10000 cm⁻¹. In this study, the optical properties of Ni²⁺ ions in the octahedral sites of the cubic and monoclinic double perovskites, AELaMgTaO₆ (AE = Ba, Sr, and Ca), are investigated based on the structural analysis, spectroscopy, and *ab initio* calculation.

Fig. 1 shows the diffuse reflectance spectra of the Ni²⁺-doped double perovskite samples. The phase transition from the cubic BaLaMgTaO₆ (BLMT) to the monoclinic SrLaMgTaO₆ (SLMT) and CaLaMgTaO₆ (CLMT) caused blue-shift of the ³T₁ and ³T₂ absorption bands. The energy levels of Ni²⁺ at the Mg²⁺ site in the AELMT hosts were calculated by the *ab initio* calculation with the *n*-electron valence state perturbation theory (NEVPT2) method [1], suggesting that the shortest averaged Ni–O bond lengths in the SLMT host lead to a larger crystal field splitting than the distorted octahedral site in the CLMT host. **Fig. 2** shows the photoluminescence (PL) spectra of the samples with the Ca²⁺ or Sr²⁺ substitution in the Ba²⁺ sites. The AE²⁺ substitution brings the tunable NIR emission band with a peak of 1450–1500 nm. The results are expected to promote research on developing NIR phosphors with local environmental design.

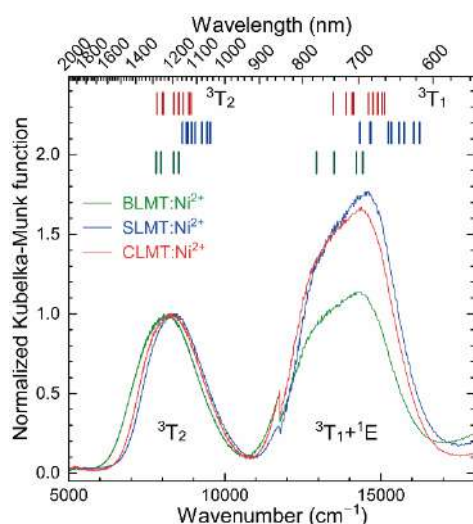


Fig. 1 Diffuse reflectance spectra of the Ni²⁺-doped AELMT samples. The tick marks represent the calculated energy levels of Ni²⁺ ions (3d⁸ configuration).

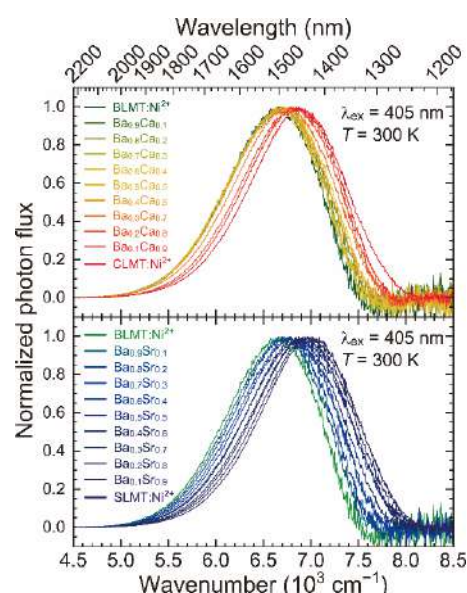


Fig. 2 PL spectra of the Ni²⁺-doped double perovskite samples at 300 K.

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0.3.131 Structural changes with chromium charge transformation in Cr,Ca;YAG transparent ceramics

Speaker: Boiko Vitalii

Structural changes with chromium charge transformation in Cr,Ca;YAG transparent ceramics

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Yttrium aluminium garnet (YAG, $\text{Y}_3\text{Al}_5\text{O}_{12}$) is known as one of the most used oxide crystals widely used as the active medium in solid-state lasers and phosphors. However, their efficiency may be limited by the presence of various defects, such as structural defects and oxygen vacancies, which can lead to heat dissipation and consequently to the intensification of undesired non-radiative processes. Structural point defects in the ceramic can be a source of traps for both electrons and holes. At the same time, understanding the nature of electron capture with subsequent recombination is interesting for ceramics with long-term emission or optical memory. The effect of the addition of dopants and their concentration on the structural properties can be determined with high sensitivity from specific changes in the vibrational spectrum of the host material. [1]. And the number of traps and their parameters can be determined by thermoluminescence (TL) analysis [2].

In the current work, a correlation between the change in chromium valence and the consequent structural changes of YAG was analyzed by Raman and TL spectroscopy. Raman spectroscopy allowed, in this case in general, to identify the deformation of the YAG crystal lattice with a change in the oxidation state of the chromium ion. On the other hand, TL analysis, carried out after pre-irradiation with X-rays at different doses and heating rates, allowed to distinguish the nature of the traps in the host material. Based on the results, a possible mechanism of energy transfer between the traps and luminescence centres in the YAG host is proposed and discussed.

This work was supported by Polish National Science Centre, grant OPUS 23 Nr. UMO-2022/45/B/ST5/01487.

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0.3.132 Study of diamond surfaces functionalization to stabilize negatively charged NV centres

Speaker: Ngandeu Ngambou Midrel Wilfried

Study of diamond surfaces functionalization to stabilize negatively charged NV centres

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The negatively charged nitrogen-vacancy centre (NV⁻ centre) is one of the most promising systems for applications in quantum technologies. In recent decades, it has shown numerous interesting properties notably the possibility to optically manipulate and read out its spin state at room temperature. These specific properties have paved the way to ultra-sensitive, high-performance and innovative quantum sensors which could open up perspectives in investigating properties that would remain inaccessible by conventional devices. Nevertheless, integration of NV centres in sensing and quantum applications relies on their tailored fabrication in an ultra-pure host material.

Very high crystalline quality diamond films are indeed required for the development of these applications, in which the density, environment, orientation of the introduced colour centres must be perfectly controlled which is now possible thanks to microwave Plasma-Assisted Chemical Vapour Deposition (PACVD)¹. However, obtaining high densities of shallow NV centres (few nm from the surface) remains very challenging. A widely used technique for creating NV centres at precisely controlled locations in depth is nitrogen ion implantation at low energy followed by annealing. For this purpose, we developed a versatile implantation system allowing both introducing nitrogen using N₂⁺ or creating vacancies with He⁺ ions bombardment in diamond to create high density of NV centres near the surface².

Nevertheless, it is known that the close proximity of the surface tends to favour and stabilize the less useful neutral form of NV defects, the NV⁰ centres. In addition, the presence of impurities either on the surface or in the bulk of the crystal induces fast decoherence and strongly limits the performance of the foreseen devices. In this work, we study the effect of impurities such as H, and the effect of surface terminations on NV centres charge stability, as well as more generally on NVs' spin properties.

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0.3.133 Synthesis of luminescent donor-acceptor molecules comprising 2,2'-bipyrimidine

Speaker: Wang Shenming

Synthesis of luminescent donor-acceptor molecules comprising 2,2'-bipyrimidine

Shenming WANG,¹ Gaël Zucchi^{1,*}

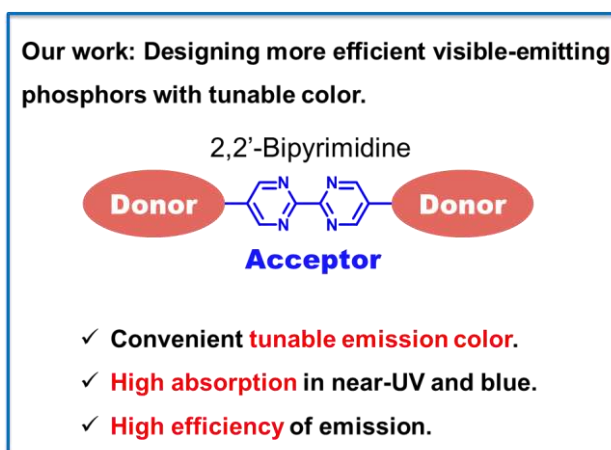
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Commercial white light emitting diodes (LEDs) are made up of a blue emitter covered with an inorganic yellow phosphor, typically YAG:Ce [1]. The white light is not of perfect quality, as it lacks some red component [2]. Also, the excess of blue light due to the low absorbance of the phosphor is harmful to the eyes.

In order to improve the performance of the existing devices, we propose to design organic emissive molecules that could further be used to design phosphors for that purpose as they combine a convenient tunability of emission color by modification of their chemical structure with high absorption coefficient.

We will present the synthesis of original new molecules where an electron-rich unit is bound to an electron-poor moiety. This strategy has been well developed to lower the bandgap of conjugated systems [3], and then design molecular materials with both red-shifted absorption and emission. In particular, compounds with 2,2'-bipyrimidine as an electron-acceptor will be described, as it was recently shown in our lab that it could red-shift the emission of conjugated donor-acceptor polymers [4].



Several visible-emitting molecules have been obtained, and their photophysical properties will be presented, including quantum efficiencies. The structure-emission relationship will also be presented in order to get a better understanding on the behaviours of these compounds.

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0.3.134 **Synthesis of luminescent nanoparticles for application in Light-emitting electrochemical cells (LECs)**

Speaker: Roselli Baptiste

Synthesis of luminescent nanoparticles for application in Light-emitting electrochemical cells (LECs)

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Semi-conducting nanoparticles are interesting materials in many applications. Focusing on luminescence, some of them show great benefits like emission tunability, high quantum yield, accessible surface modification etc...¹ One of the possible applications is in light-emitting electrochemical cell (LEC), a device comparable to organic light-emitting diode (OLEDs) however including solid electrolyte in a polymer matrix.² When a potential is applied, ions and counter-ions from the electrolyte will migrate to the anode and cathode, creating 3 layers: n doped region, p doped region and the junction region.³ It allows injected charges (holes and electrons) to move through the device and recombine to produce light emission (figure 1a). Here, 2 types of nanoparticles are used as luminescent material i.e., lead halide perovskite nanocrystals (LHP NCs) and silver indium sulfide-zinc sulfide (AgInS-ZnS) core-shell nanoparticles, in order to obtain luminescence in blue, green and red. Since 2015 and Kovalenko's team work on LHP NCs⁴, plenty of work are reported in literature mainly because emission has a tunable wavelength, a narrow band and a quantum yield up to 99%.⁵ On the other hand, AgInS/ZnS core-shell nanoparticles have a large emission wavelength which can be beneficial for white emitting devices. This study includes the method of synthesis of these two materials, the optimization of the synthesis parameters for better control of the emission wavelength, stability etc..., and structural, electrochemical and optical characterizations. Furthermore, latest progress in device elaboration and electrochemical characterization of deposition will also be discussed.

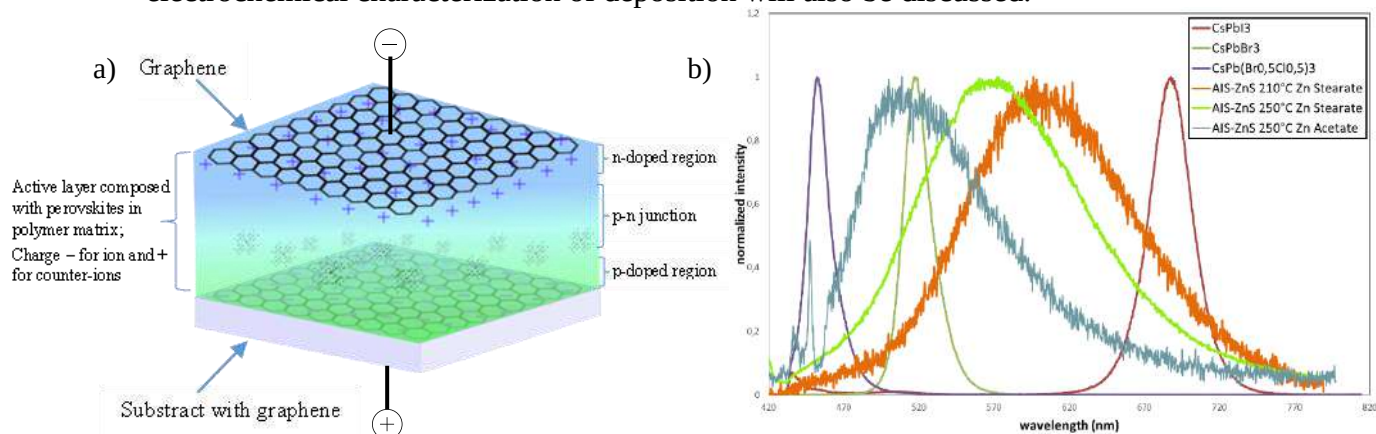


Figure 1: a) LEC device; b) photoluminescence spectra of AgInS-ZnS (AIS-ZnS) and LHP NCs (excitation 405 nm)

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0.3.135 Tailored Patterning of Single Luminescent Nanoparticles

Speaker: Zhang Heyou

Tailored Patterning of Single Luminescent Nanoparticles

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Luminescent nanoparticles offer great potential for many applications including QLED display, biolabeling and sensing, optical modulation, and photovoltaics, because quantum size effects can be exploited to tune their photophysical properties. Typically, such particles are prepared using well-established wet chemistry approaches. For practical applications, however, it remains challenging to transfer the synthesized particles onto solid substrates. Thereby it is a particular concern to prevent aggregation. Preferentially, the single particles can be arranged on an array to allow for designing optoelectronic devices.

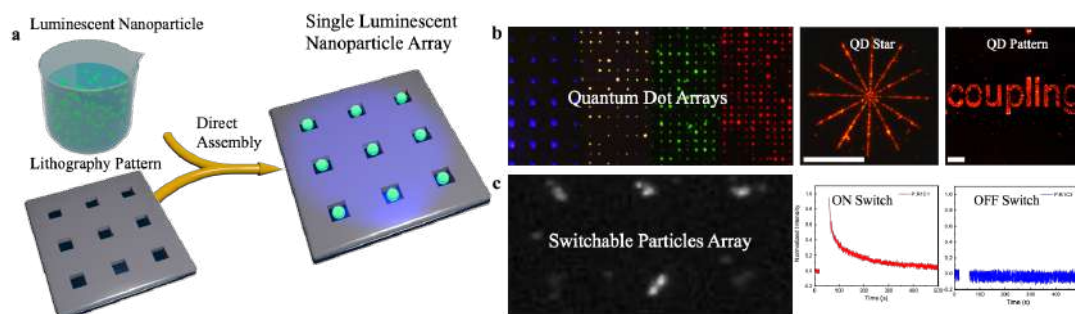


Figure 1: (a) Schematic presentation of the route for assembling an array of luminescent nanoparticle. (b) Examples of quantum dot arrays. (c) Example of an optically switchable particle array.

Here we introduce a bottom-up method that enables the direct transfer of nanoparticles from the solution onto a solid-state substrate, resulting in a well-ordered single particle array. The method has been developed for the direct assembly of colloidal gold nanoparticles into single particle arrays. We have extended this approach to accomplish patterns of fluorescent quantum dots, and fluorescent polymer beads that accommodate photochromic molecules.

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0.3.136 Tailoring RE-luminescence in nanocrystals via inter-particle energy transfer

Speaker: Khanin Vasili

Tailoring RE-luminescence in nanocrystals via inter-particle energy transfer

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The emission and excitation characteristics of a phosphor are set by the host material and active ion species. Co-doping different ions in the same host material opens up more possibilities to tune the optical properties via resonant energy transfer processes, but is often limited by metal-to-metal charge transfer (CT) interactions that lead to quenching [1]. Mixing nanocrystals with different dopant ion species enables inter-particle Förster resonant energy transfer (IFRET) [2]. This circumvents the CT quenching by the gained freedom to tune the particle-to-particle distances, while it also allows for choosing suitable host materials for both donor and acceptor ions independently. Subsequently, IFRET allows for almost independent tuning of the excitation and emission properties, paving the road for improved and new applications in lighting, displays, and beyond.

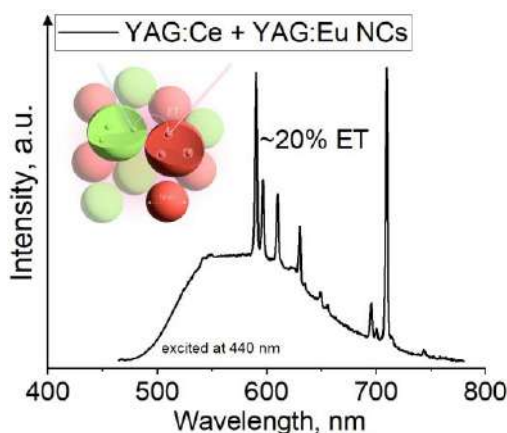


Figure 1. Photoluminescence emission spectrum of (YAG:Ce + YAG:Eu) composite of nanoparticles. Both $\text{Ce}^{3+} {}^2\text{D}_{3/2} \rightarrow {}^2\text{F}_J$ and $\text{Eu}^{3+} {}^7\text{D}_0 \rightarrow {}^7\text{F}_J$ transitions are visible under 440 nm excitation into Ce^{3+} .

Here, we demonstrate efficient IFRET between different types of oxide nanocrystals doped with RE ions. We describe optimized methods to grow the individual materials in solution, yielding +95% quantum yield materials, as well as how to effectively control the IFRET efficiency in the range of 10-90% by varying the spacing between the particles. Particular focus is given to Ce^{3+} and Eu^{3+} -doped garnets (Figure 1), as blue-excitable Eu^{3+} -doped materials are of specific interest as downconverter material for white LEDs.

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0.3.137 Taking advantage of Cr³⁺ ions in luminescence thermometry based on hybrid organic-inorganic formates

Speaker: Stefańska Dagmara

Taking advantage of Cr³⁺ ions in luminescence thermometry based on hybrid organic-inorganic formates

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Recently, a lot of attention has been focused on hybrid organic-inorganic compounds crystallizing in a three-dimensional (3D) perovskite-type architecture. The general formula of ABX₃ perovskite compounds (A = alkali metal or organic cation; B = divalent metal cation; X = halide, HCOO[−], N₃[−], CN[−], N(CN)₂[−] and H₂PO₂[−]) consist of corner-sharing BX₆ (X = Cl, Br, I, O, and N) octahedral units. Metal ions and linkers create a three-dimensional framework, while the organic cations are accommodated inside the created voids. Hybrid organic-inorganic perovskite (HOIP) are often called multifunctional materials because they exhibit several physical phenomena at the same time. In consequence, HOIPs offer a wide range of potential applications for catalysis, gas storage, drug delivery, nonlinear optics, solid-state lightening, luminescent sensors, temperature sensors, biomedical photonics, and many more.

One of the interesting group is perovskite with formate linkers. During the presentation, the structural and optical properties of formate hybrid perovskites containing Cr³⁺ ions will be discussed. Attention will be focused on the effect of the organic cation A⁺ on the luminescent properties and temperature sensing ability of [A]B(HCOO)₃:Cr³⁺ compounds. What is more, the influence of metal B substitution on structure, bond lengths, distortions of CrO₆ octahedra, crystal field strength around Cr³⁺ ions, and consequently on the luminescence properties and temperature detection will be presented.

This work was funded by the National Science Centre (Narodowe Centrum Nauki) in Poland under the project SONATA 16 no. 2020/39/D/ST5/01289.

0.3.138 The Bright Side of Lanthanide Single-Molecule Magnets: A New Class of Magneto-Optical Materials

Speaker: Long Jérôme

The Bright Side of Lanthanide Single-Molecule Magnets: A New Class of Magneto-Optical Materials

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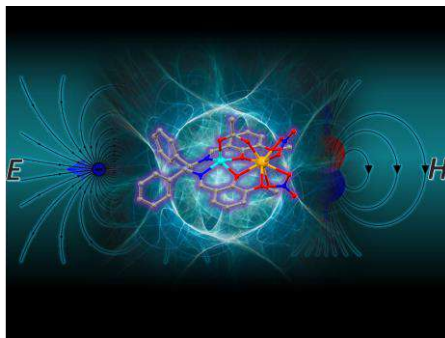
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Coordination chemistry allows the tailored design of multifunctional molecule-based materials where the properties are gathered into a single molecular system.

Single-molecule Magnets (SMM) belong to a specific class of magnetic materials affording a magnetic bistability at the molecular scale. By using specific molecular building blocks, we show that these systems could also exhibit additional properties such as luminescence, optical activity and ferroelectricity. Remarkably, we demonstrate that such molecular systems could go beyond the simple superposition of the properties and exhibit cross-coupling effects that could be used in potential applications related to data storage.[1]

We will focus on the cross-coupling between luminescence and magnetic field to design dual sensors affording the dual and synchronous detection of the temperature and magnetic field in large ranges.[2]



Molecular structure of a multifunctional molecular complex

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0.3.139 The brightest stars burn the fastest: about optical detrapping induced by afterglow emission

Speaker: Van Der Heggen David

The brightest stars burn the fastest: about optical detrapping induced by afterglow emission

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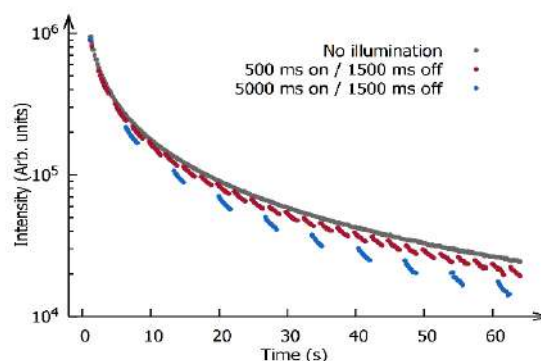
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Persistent phosphors are materials that continue to emit light long after the excitation source has been removed.^[1] They are commonly used in safety signs and gadgets, but their potential applications are much broader, including pressure and light sensing, as well as bio-imaging. To achieve persistent luminescence, a phosphor must contain specific defects that can serve as charge trapping centers. When a persistent phosphor is excited, the charge trapping alters the material's absorption spectrum, which can have a significant impact on the phosphor's performance. For example, if the absorption of the filled traps coincides with the activator's excitation spectrum, optically stimulated detrapping can occur, leading to additional losses when filling the traps in the phosphor which was demonstrated to occur in the green-emitting $\text{SrAl}_2\text{O}_4:\text{Eu,Dy}$.^[2]

Recently, we discovered that some of the shallower trapping centers in $\text{SrAl}_2\text{O}_4:\text{Eu,Dy}$ induce an absorption band covering nearly the complete visible spectrum. Using green stimulation light, these traps can be efficiently emptied, as shown in the figure below and this reduces the persistent luminescence. However, the phosphor's afterglow emission is also reabsorbed by filled traps, which accelerates the afterglow and decreases the integrated emission intensity. This process is particularly significant in large transparent samples, such as single crystals, ceramics or glasses, where the chances for reabsorption are significantly increased compared to powder samples.



The effect of stimulation with a pulsed green laser on the afterglow decay curve of a $\text{SrAl}_2\text{O}_4:\text{Eu,Dy}$ single crystal previously exposed to blue light for 5 minutes. The afterglow was only recorded while laser was switched off.

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0.3.140 The energy gap law at work: Emission yield and rate fluctuations of single NIR emitters

Speaker: Basché Thomas

The energy gap law at work: Emission yield and rate fluctuations of single NIR emitters

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Internal conversion (IC) often is the dominating relaxation pathway in NIR emitters, limiting their fluorescence quantum yield. In this context, we have investigated Dibenzoterrylene (DBT) by bulk and single molecule spectroscopy. In stark contrast to Terrylene, DBT – an unsubstituted aromatic hydrocarbon – shows an unexpectedly strong fluorescence solvatochromism. With increasing solvent polarity, the S_1 - S_0 energy gap decreases leading to a decrease of the fluorescence quantum yield and an increase of the IC rate in full accordance with the energy gap law.¹ Making use of the fluorescence solvatochromism of DBT, the validity of the energy gap law was also demonstrated at the single molecule level. By controlling the fluorescence lifetime and quantum yield of single DBT molecules, the S_1 - S_0 energy gap dictates how these quantities develop during spectral fluctuations (Figure 1).

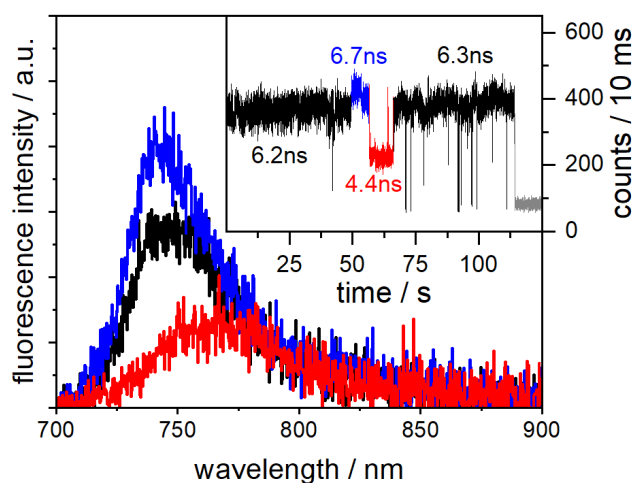


Figure 1: Fluorescence spectra and intensity time trace (inset) of a single DBT molecule as a function of time. Fluorescence lifetimes during the different phases are given in the inset.

Our results open new avenues into unexplored single molecule photophysics. Along these lines, we will discuss first attempts to improve the fluorescence quantum yield of DBT to obtain a bright single quantum emitter in the NIR.

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0.3.141 The impact of energy migration between Ln³⁺ ions, on the efficiency of upconversion resonant nonradiative energy transfer (UC-FRET)

Speaker: Kotulska Agata

The impact of energy migration between Ln³⁺ ions, on the efficiency of upconversion resonant nonradiative energy transfer (UC-FRET)

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Efficiency of resonant non-radiative FRET energy transfer from lanthanide doped nanocrystals to an organic energy acceptor, could be influenced with composition and chemical architecture of nanosized core-shell phosphors doped with Er³⁺ and Yb³⁺ lanthanide ions (Ln³⁺).

The distribution and concentration of Ln³⁺ ions in core-shell nanocrystals, indicate the distance between donor (D) ions and acceptor (A) organic dyes. Probability of energy migration depends on distance between neighbors. In a single nanocrystal there are hundreds or even thousands of Ln³⁺ dopant ions, that's why rate equation model could not give the full answer about energy output to the surface. Total distance traveled by absorbed energy, resulting from energy migration between Ln³⁺, could therefore result in different resonant energy transfer efficiency to the A at the surface. Aiming to understanding experimental behavior of UC-FRET, we adopt and Monte Carlo modeling (fig. 1).

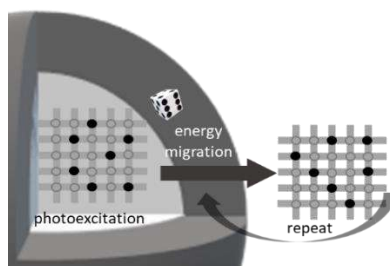


Figure 1: Schematic representation of energy migration considered in Monte Carlo calculations.

The main objective of our studies is to understand how energy migration between lanthanide ions affect the efficiency of Förster energy transfer between multiple donor ions doped upconverting core-shell nanoparticle donors and multiple organic acceptors on the surface.

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0.3.142 The influence of Eu and Al doping on the energy transfer from high- to low-energy Eu centers in SiO₂

Speaker: Cho Chun-Ting

The influence of Eu and Al doping on the energy transfer from high- to low-energy Eu centers in SiO₂

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Lanthanide ions have low solubility in amorphous SiO₂ due to size and charge mismatch causing clustering and, therefore, low luminescence quantum yield, often preventing application in photonics. Nogami et al. proved that codoping Al³⁺ in SiO₂ can enhance the luminescent intensity of Eu²⁺ [1]. Previous research has investigated the optimum codoping concentration of Mg²⁺ for maximum Eu emission intensity [2] and optimum codoping ratio of Al³⁺ to Nd³⁺ [3]. However, only a few works study the ratio of Al³⁺ to Eu²⁺ in SiO₂ and the corresponding influence on luminescent properties. In this work, we show that by co-doping SiO₂ with Al, the Eu²⁺ luminescence quantum yield can be enhanced by more than a factor of 10. Specifically, we found that for 1 mol% Eu, a minimum of 3 to 4% aluminum was required to avoid concentration quenching, while for 3 % Eu it was 12% Al. We, therefore, conclude that the Al/Eu ratio in SiO₂ phosphors must be above 4. To understand this behavior, three amorphous nano-phosphors series were synthesized via a base-catalyzed Sol-Gel approach and investigated by luminescence decay time, excitation, emission, absorption, and quantum efficiency measurements. With increasing Eu%, at fixed Al%, the decay time and quantum yield decrease while the emission shifts to the red (Fig. 1a). This can be explained by resonance energy transfer from Eu²⁺ centers with higher energy states to Eu²⁺ centers with lower energy. The transfer is confirmed by a rise time in the low energy emission and a drop in the decay time of the high energy centers. When increasing the Al% at fixed Eu%, the decay time and quantum yield increase, and the red-shift is reduced (Fig. 1b). This confirms earlier observed enhanced Eu solubility and reduced Eu clustering by Al co-doping,

causing the onset of concentration quenching to shift to higher Eu%.

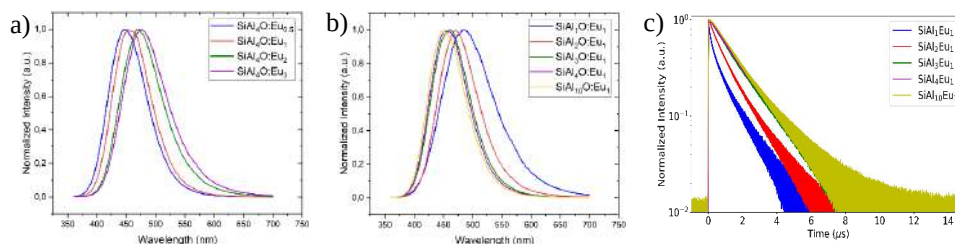


Figure 1: Samples are presented in form of SiAl_xO:Eu_y, where x and y represent the mol% of Al and Eu, respectively, to all cations (Si + Al + Eu). a) emission spectra of fixed-Al and varying-Eu

samples. b) emission spectra of fixed-Eu and varying-Al samples. c) decay signals of fixed-Eu and varying-Al samples.

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0.3.143 The influence of imidazolium counterions on the luminescence properties of (Cn-mim)(Eu(tta)₄) tetrakis complexes in solid-state and ionic liquid solutions

Speaker: Brito Hermi

The influence of imidazolium counterions on the luminescence properties of $[\text{C}_n\text{mim}][\text{Eu}(\text{tta})_4]$ tetrakis complexes in solid-state and ionic liquid solutions

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A series of lanthanide tetrakis complexes $[\text{C}_n\text{mim}][\text{Ln}(\text{tta})_4]$ where Ln^{3+} : Eu^{3+} and Gd^{3+} , C_nmim : imidazolium-based counterions (n from 3 to 8) and tta : thenoyltrifluoroacetate were synthesized by a one-pot method. The $[\text{C}_n\text{mim}][\text{Ln}(\text{tta})_4]$ complexes are thermostable up to 210 °C and present an isomorph-like character for the complexes with $n = 5, 6$, and 7. The phosphorescence spectral profile of the $[\text{C}_n\text{mim}][\text{Gd}(\text{tta})_4]$ complexes showed intense emission broadbands, in which the barycenters are slightly shifted to energies from the 18950 to 18450 cm^{-1} range. The $[\text{C}_n\text{mim}][\text{Eu}(\text{tta})_4]$ complexes in solutions of the corresponding $[\text{C}_n\text{mim}]\text{Br}$ ionic liquids show similar emission spectral profiles as their corresponding in the solid state, indicating that the coordination polyhedron does not undergo a significant variation when the chemical environment is changed. Relatively high values of the intensity parameter Ω_2 in both media are presented. The Ω_4 values of the complexes in solutions of ionic liquids are also similar, reinforcing that there are small changes in the polyhedral coordination from the solid state to the ionic liquid solution. The series presents high intrinsic emission quantum efficiencies, $90\% \geq Q_{\text{Eu}}^{\text{Eu}} \geq 53\%$. In addition, theoretical calculations on the intramolecular energy transfer (IET) reveal the participation of the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$ and ${}^7\text{F}_1 \rightarrow {}^5\text{G}_2$ transitions for the IET via S_1 while the IET via T_1 state is dominated by the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$ and ${}^7\text{F}_1 \rightarrow {}^5\text{D}_0$ transitions. Therefore, due to their high luminescent features, these Eu^{3+} tetrakis complexes are potential candidates to be applied as optical markers in the solid-state or even in ionic liquid solutions.

Acknowledgments: This work was supported by FAPESP / N° 2021/08111-2

0.3.144 The material science and engineering of anti-Stokes fluorescence cooling in silica optical fibres

Speaker: Ballato John

The material science and engineering of anti-Stokes fluorescence cooling in silica optical fibres

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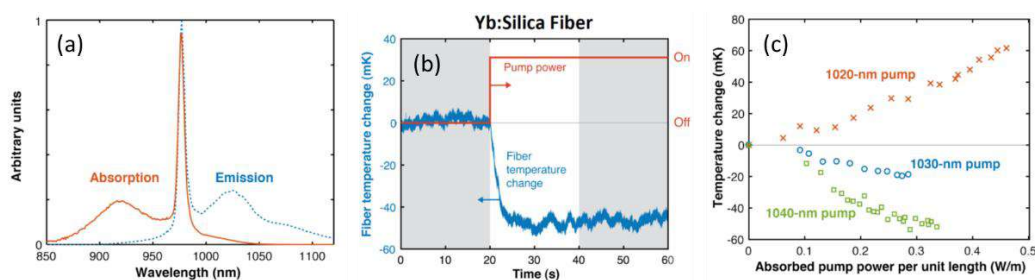
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The optical cooling of solids via anti-Stokes fluorescence (ASF) has enjoyed steady attention since it was first realized experimentally in 1995. However, until recently, ASF cooling had only been observed in select rare-earth-doped crystals and more exotic glasses, such as fluorides. A major advance in this field was made in 2020 when ASF cooling was enabled in silica-based optical fibres [2-4], opening to door to large scale investigation and implementation.



(a) Relative absorption and emission spectrum for Yb:silica fiber, (b) temperature change as a function of time with and without pump verifying ASF cooling, and (c) ASF cooling with pump wavelength and power.

This talk will focus on the underlying materials science and engineering that permitted the realization of ASF cooling in silica fibres. This includes insights into the role of glass composition and process parameters on the Yb spectroscopy, internal quantum efficiency, and fibre attenuation. The inclusion of rare-earth-doped nanoparticles and their evolution during the fibre fabrication process will also be discussed as it relates to their luminescent properties and ASF cooling [5].

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0.3.145 The spectroscopic properties of Cr³⁺ ions and (Cr³⁺-Ca²⁺) couples

Speaker: Chaika Mykhailo

The spectroscopic properties of Cr³⁺ ions and [Cr³⁺-Ca²⁺] couples

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The recent progress in the automatic motor vehicle increase demands for compact LIDAR systems. The most popular 1 μm Q-switched lasers consist of the active element (Nd³⁺:YAG) with the Cr⁴⁺:YAG saturable absorber layer. Cr⁴⁺ ions formation in YAG lattice requires co-doping with divalent impurities. Chromium charge transformation process occurs during air annealing, when Ca²⁺ ions recharge Cr³⁺ ions in tetravalent state. The current understanding of Cr³⁺ $\rightarrow$ Cr⁴⁺ ions valence transformation should be revised due to the recent result related to Ca²⁺ ions distribution in YAG ceramics. The fact that the diffusion activation energy of Ca²⁺ and Cr³⁺ ions is at least twice of that calculated for Cr⁴⁺ ions formation indicate that at least part of Cr³⁺ and Ca²⁺ ions are occupied nearby cation positions. The most probably that the part of Ca²⁺ and Cr³⁺ ions forms charge neutral Cr³⁺/[Ca_C' ... V_O[•]] couple, destroying which the Cr³⁺ $\rightarrow$ Cr⁴⁺ ions valence transformation occurs. The one of the possible way for confirmation of presence Cr³⁺/[Ca_C' ... V_O[•]] couple in YAG ceramics is monitoring influence of near located Ca²⁺ ions on Cr³⁺ emission.

In this work the difference between the spectroscopic properties of single Cr³⁺ ion and the Cr³⁺/[Ca_C' ... V_O[•]] couples were detected by optical spectroscopy. For this purpose, Cr,Ca:YAG transparent ceramics were made by solid-state reaction sintering, the concentration of Cr³⁺/[Ca_C' ... V_O[•]] couples was controlled by means of annealing in oxidized/reduced atmosphere.

During the air annealing, the oxygen from air ambient dissolve into the sample and destroy the Cr³⁺/[Ca_C' ... V_O[•]] couples, as in result the Cr⁴⁺ ions appears. As in result, the fully reduced sample and fully oxidized sample have different concentration of Cr³⁺/[Ca_C' ... V_O[•]] couples. To confirm this hypothesis, it was investigated the difference in spectroscopic properties of fully reduced and fully oxidized samples. This is possible due to the nephelauxetic effect based on the deformations of (CrO₆)⁹⁻ active cluster by means of substitution of next-nearest-neighbors Y³⁺ ions by larger cations such as Ca²⁺ ion. This substitution leads to Cr–O covalency changes due to shorter/higher Cr–O distances. It was shown that the substitution of Y³⁺ ion from NNN by larger Ca²⁺ ions leads to red shift of the R-lines. Also, it's lead to increase the Cr³⁺/[Ca_C' ... V_O[•]] couples leads to decrease in the transition probabilities between ²E_g and ⁴T_{2g} states of Cr³⁺ ions which in result to decrease in relatively intensity of ⁴T_{2g} $\rightarrow$ ⁴A_{2g} transition.

This work was supported by Polish National Science Centre, grant: OPUS 23 Nr UMO-2022/45/B/ST5/01487.

0.3.146 The spectroscopic properties of (GUA)Mg(HCOO)₃: Cr³⁺ for application in luminescence thermometry

Speaker: Adaszyński Marek

The spectroscopic properties of [GUA]Mg(HCOO)₃: Cr³⁺ for application in luminescence thermometry

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One of the most crucial, fundamental physical parameter in both scientific investigations and technological development is temperature. This leads to the fact that thermometry present around 80% of the global sensor market [1, 2]. Various construction can be used to build the thermometer. The most common used are the contact thermometer with thermocouples, which are not suitable for measuring fast moving objects or on a submicron scale [1]. These limitations provided the development of a new class of noninvasive luminescent based thermometers, which basically can implement as an example a change in spectral shift of a given transition or a change in emission intensity of a single or more transitions in comparison to the temperature of the sample [2]. Multiple luminescent materials can be applied for this use such as metal-organic frameworks, lanthanide-doped phosphors, quantum dots, and organic dyes [1].

Among numerous materials, organic-inorganic hybrid perovskites stand out, due to unique structural tunability and spectroscopic properties [3]. In this work, the perovskite type-hybrid material [GUA]Mg(HCOO)₃: xCr³⁺ with three different Cr³⁺ concentrations (x = 0.01, 0.03, 0.05) will be presented. The structure, which has the general perovskite-type formula ABX₃ [3], is based on organic guanidine (GUA) cation and formate anions. As a metal cation, magnesium derivative will be extensively examined. The doping Cr³⁺ ion provides temperature-dependent narrow emission band at around 685 nm, which comes from spin-forbidden ²E_g → ⁴A_{2g} transition. Another broad band emission at around 775 nm is attributed to spin-allowed ⁴T_{2g} → ⁴A₂ transition. Moreover, the weak band at around 535 nm appears in around 120 K, which is coming from a GUA⁺ cation.

Apart from luminescence properties, synthesis, and structural properties will be presented. Based on the measurements the crystal field and energy bandgap parameters will be calculated. Finally, the possibility for the application in luminescence thermometry will be extensively analyzed.

This work was funded by the National Science Centre (Narodowe Centrum Nauki) in Poland under the project SONATA 16 no. 2020/39/D/ST5/01289.

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0.3.147 The versatility of MOFs as a powerful tool to design luminescent thermometers

Speaker: Serier-Brault Hélène

The versatility of MOFs as a powerful tool to design luminescent thermometers

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The temperature is a basic physical parameter that is essential in both science and industry areas. One of most promising non-invasive technique to measure the temperature relies on ratiometric luminescent thermometers where the absolute temperature is optically determined *via* the measurements of the intensities of two transitions of distinct emitting centers. If the first studies on luminescence thermometry refer to inorganic compounds such as oxides, fluorides or sulfides, metal-organic frameworks (MOFs) recently appeared as promising candidates. In the last decades, MOF materials have been investigated as various sensors due to their multiple luminescent centers and tunable luminescence properties. Indeed, compared with organic dyes or inorganic luminescent materials, the luminescence of MOFs is more diverse because the metal nodes, organic linkers, ligand-metal charge transfer, and guest species within framework can potentially generate emissions. Consequently, many combinations are possible to elaborate ratiometric MOF luminescent thermometers. Here, we will propose a small overview of the state-of-the-art about the use of MOFs in this hot topic together with a presentation of our recent results.

0.3.148 Time-Resolved and polarimetry cathodoluminescence to probe crystal phase, carrier lifetime and diffusion length in single GaAs nanowires

Speaker: Collin Stéphane

Time-Resolved and polarimetry cathodoluminescence to probe crystal phase, carrier lifetime and diffusion length in single GaAs nanowires

Thomas Bidaud,¹ Hung-Ling Chen,¹ Romaric De Lépinau,^{1,2} Andrea Scaccabarozzi,^{1,2} Fabrice Oehler,¹ Jean-Christophe Harmand,¹ Andrea Cattoni,¹ and Stéphane Collin^{1, 2}

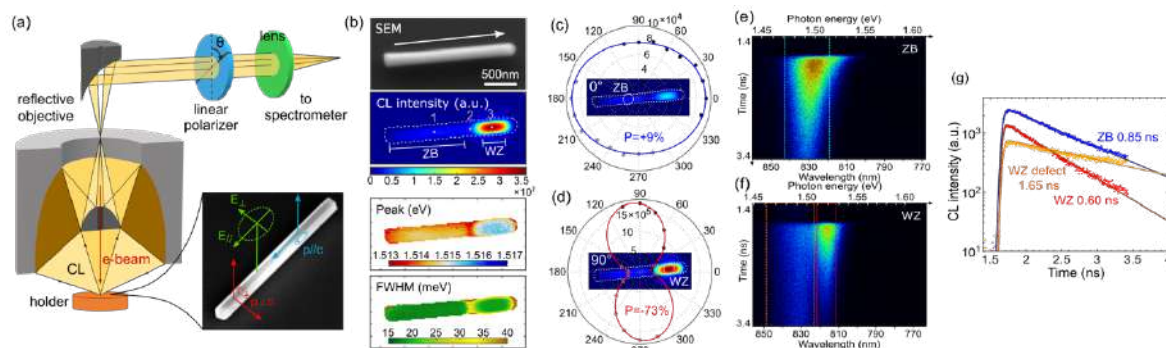
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Semiconductor nanowires (NWs) have attracted a great attention in fundamental research and devices such as LED and solar cells. GaAs NWs are prominent for novel optoelectronics and the crystal structure can be switched from bulk cubic zinc-blende (ZB) to hexagonal wurtzite (WZ) phase, but it is still challenging to characterize their transport and optoelectronic properties at the nanoscale.

In this contribution, we use polarimetric cathodoluminescence to distinguish zincblende (ZB) and wurtzite (WZ) segments in single core/shell GaAs/AlGaAs nanowires (Figure, a-d). Then, we perform time-resolved cathodoluminescence (TRCL) to probe locally the recombination dynamics in both ZB and WZ phases of the same nanowire (Figure, e-g). Then we use high-resolution CL mapping to measure the diffusion length of minority carriers (not shown). Overall, we show that high-resolution CL mapping with polarimetry and time-resolved capabilities constitute a powerful tool to characterize of crystal phase, local defect, transport and recombination mechanism at the nanoscale.



CL polarimetry and TRCL measurements of an undoped GaAs NW. (a) Schematics of CL polarimetry measurement. (b) SEM and CL maps (integrated CL intensity, CL peak position and FWHM) of an undoped GaAs NW. Arrow indicates the NW growth direction. (c,d) Polar plot of the CL intensity extracted from: (c) pure ZB and (d) pure WZ region of the NW as a function of the polarizer angle. Insets show the CL intensity maps acquired under 0° and 90° polarizer. (e,f,g) **Time-resolved CL measurement.** (a,b) Streak images of the luminescence decay acquired when the pulsed electron beam excites: (e) the ZB and (f) the WZ part of the NW. (g) Time decay of the luminescence integrated over the different spectral ranges: (blue) ZB 819–843 nm, (red) WZ 812–822 nm, (orange) WZ 823–849 nm.

References

Our previous work on the quantitative assessment of doping in single GaAs nanowires:

<https://sunlit-team.eu/publications/articles/>

0.3.149 Transparent persistent phosphor films allow optical environment design: beyond limits set by composition

Speaker: Castaing Victor

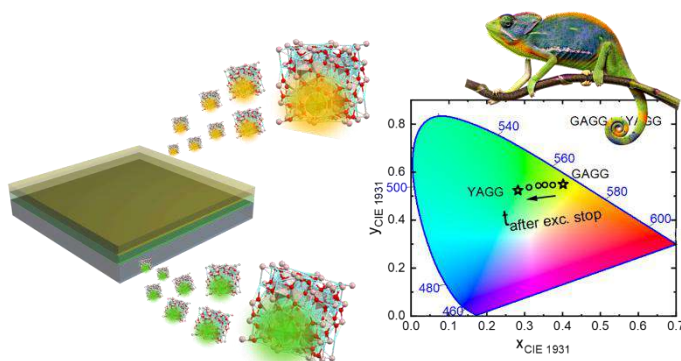
Transparent persistent phosphor films allow optical environment design: beyond limits set by composition

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Persistent phosphors feature unique long-lasting luminescence arising from a temporary charge storage at defects. Apart from their current commercial use as bulk powders dispersed in resins for design and night signalization, persistent phosphors rise increasing interest for emerging nanotechnologies.[1] However, their relatively low storage capacity combined to the difficulty to finely tune their properties hurdle their development. In this regard, playing with transparent luminescent materials optical environment allows both enhancement and modifications of their properties without altering their composition, an opportunity yet to be explored with persistent phosphors. In this context, transparent persistent phosphor films were prepared following direct deposition of precursor gels and wet deposition of colloiddally stable persistent nanoparticles.[2],[3] Syntheses and thin film processing methods were optimized not only to render homogeneous and transparent coatings but also to maximize afterglow emission. Thanks to deposition method flexibility as well as layer transparency, optical environment of persistent phosphor films have been tuned in a controlled manner, allowing us to obtain coatings with remarkable time-dependent chromaticity, enhanced number of collected afterglow photons as well as energy storage speed-up. Our transversal approach offers promising opportunities towards the conception of persistent nanophosphors with intense and original properties.



Schematics of persistent phosphor building block with time-dependent chromaticity.

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0.3.150 Tunable 3D luminescence patterns in glass with femtosecond laser

Speaker: Fouad Alassani

Tunable 3D luminescence patterns in glass with femtosecond laser

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Monitoring local luminescence properties in 3D multi-scale architecture having sub-wavelength dimensions is attractive for multiple potential applications for sensors, optical data storage, integrated light source, or data communication. For such a challenge, Femtosecond (fs) Direct Laser Writing (DLW) stands out as a unique technique to imprint in transparent dielectric materials complex structures. In the last decade, we have demonstrated the capability to induce multi-scale photonic architecture using fs DLW in glass by promoting local redox and ionic migration [1]. In silver-containing glass, the local formation of silver clusters exhibiting an intense luminescence in the visible range has been achieved. We have recently demonstrated that the co-doping of silver ions and Bi³⁺ or Yb³⁺ ions in phosphate glass allows extending the 3D fluorescence structure from the visible to the near IR (Figure 1) [2]. The tunable luminescence arises from the fs laser triggering both the photochemistry of silver ions forming silver clusters (visible emitter) and the photo redox reaction of Bi³⁺ forming low valence Bismuth ions (Bi²⁺ red emitter and Bi⁺ near IR emitter). The energy transfer mechanism from the silver cluster to bismuth or rare earth ions has been demonstrated. The DLW process can also lead to co-localized local refractive index change which allows combining waveguiding, diffraction, and local luminescence properties for complex Photonic Integrated Circuit engineering (PIC).

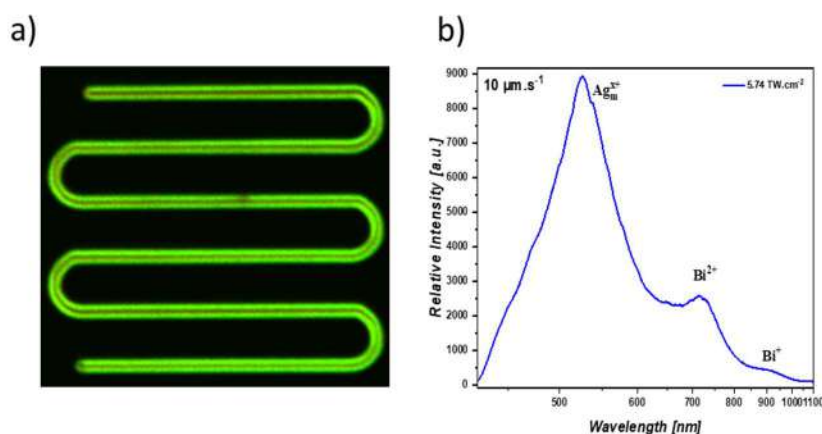


Figure 1: Fluorescent of DLW pattern, b) Emission spectra of Dlw pattern for 405 nm excitation

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0.3.151 Un-expected dominant substitution of Ba²⁺ site instead of La³⁺ one in cubic Nd³⁺-doped BaLaLiWO₆ perovskites - a new host lattice for transparent ceramics

Speaker: Prokop Kacper Albin

Un-expected dominant substitution of Ba²⁺ site instead of La³⁺ one in cubic Nd³⁺-doped BaLaLiWO₆ perovskites - a new host lattice for transparent ceramics

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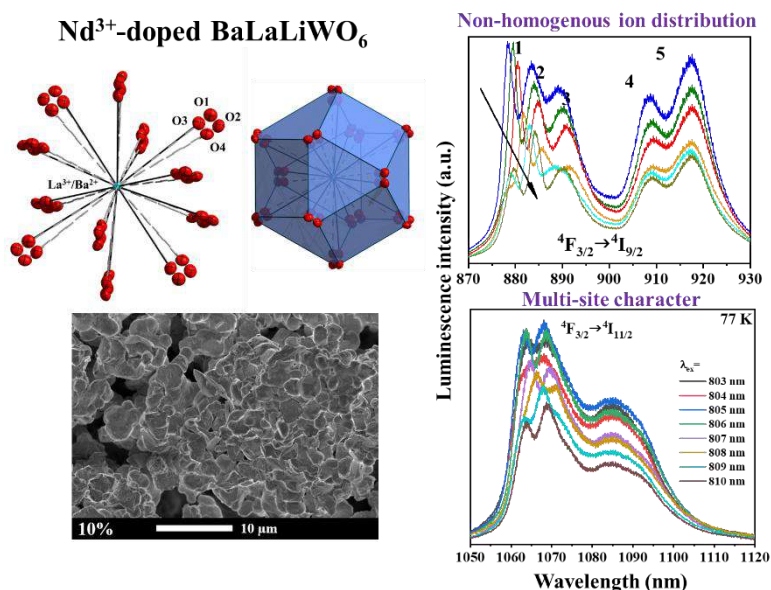
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Searching new compounds which could be useful for fabrication of new optical transparent ceramics we considered AA'BB'O₆ perovskites. BaLaLiWO₆ with a cubic structure (s.g. *Fm* $\bar{3}$ *m*, No. 225) seems to be a good candidate to realize this very difficult task. A series of micro-crystalline samples activated by Nd³⁺ ion (0-20 mol%) was synthesized via a high-temperature solid-state reaction method. The Nd³⁺ dopant was chosen as laser dopant and structural probe. Crystal structure of BaLaLiWO₆ (see below) solved basing on the small single crystal was reported for the first time.



Coordination of La³⁺/Ba²⁺ cations by the O²⁻ anions in BaLaLiWO₆, SEM micrograph and Nd³⁺ ion luminescence at 77 K under site selective excitation.

The originality of this research results from un-expected substitution of divalent Ba²⁺ ions by trivalent Nd³⁺ ones till 7 mol% and then of both Ba²⁺ and La³⁺ sites, which has also consequences in the spectroscopic properties. A few Nd³⁺ non-equivalent symmetry sites and inhomogeneous Nd³⁺ ion distribution in the lattice, detected by site-selective laser spectroscopy at 77K, have been pointed out in accordance with the crystallographic analysis. The thermal studies such as HT-XRD and DT-TGA were useful to optimize the sintering conditions enabled to fabricate via Spark Plasma Sintering (SPS) method a first translucent micro-ceramics of quite high density.

0.3.152 Unusual Photoluminescence Temperature Dependence in Ag₂S Nanocrystals

Speaker: De Wit Jur

Unusual Photoluminescence Temperature dependence in Ag₂S Nanocrystals

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Ag₂S nanocrystals (NCs) have attracted significant attention because of their bright emission bands in the near infrared (NIR). The non-toxicity and temperature-dependent emission make it a promising candidate for future *in-vivo* imaging and thermometry applications.^[1] The emission wavelength can be tuned between 900 and 1200 nm by changing the size, which falls within with the second biological NIR window and makes Ag₂S NCs suitable for imaging and sensing applications.^[2]

Up to now, there has been no detailed investigation of the emission mechanism in Ag₂S NCs below room temperature. To understand the strong temperature dependence of the luminescence, we have performed emission and time-resolved emission spectroscopy on Ag₂S NCs down to 4 K. Upon cooling, initially the luminescence intensity and decay time increase, consistent with the previously observed quenching and faster decay above room temperature. An upper limit for the RT quantum yield of ~15 % could be determined based on emission intensity and decay measurements. Unexpectedly, below 200 K, a decrease in the average decay lifetime is observed while the emission intensity remains roughly the same. Based on these results and similarities between CuInS₂ and Ag₂S NCs, we propose an emission mechanism for Ag₂S NCs.

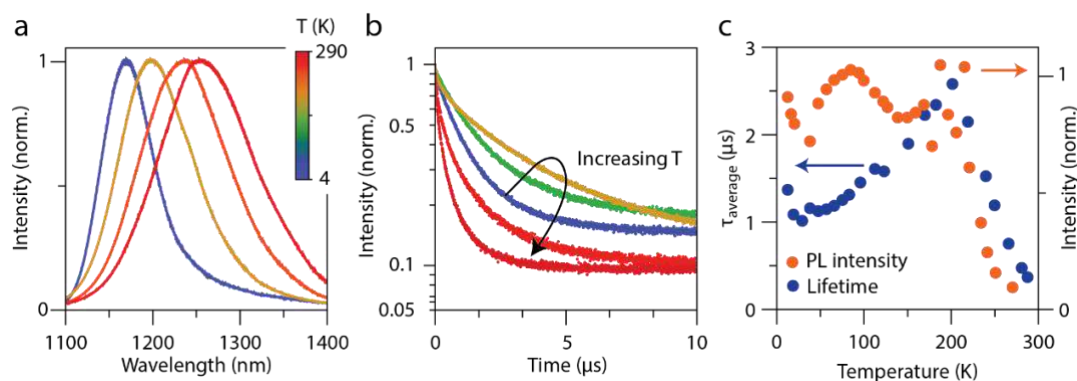


Figure 1 | Temperature-dependent optical properties of Ag₂S QDs. (a) Emission spectra at variable temperatures between 4–290K. A strong blueshift of the emission band is observed with decreasing temperature. (b) Temperature-dependent luminescence decay curves. (c) Emission intensity and lifetime as a function of temperature. The blue dots represent the weighted average lifetime as determined from a three-exponential fit. The orange dots show the normalized integrated emission intensity.

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0.3.153 Up-conversion luminescence at the nanoscale: benefits and difficulties

Speaker: Piatkowski Dawid

Up-conversion luminescence at the nanoscale: benefits and difficulties

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Up-conversion nanocrystals activated by rare-earth ions opened a new chapter in the field of anti-Stokes luminescence processes. Due to their nanoscopic dimensions, comparable with the range of electrostatic interactions, they can easily couple to the surroundings forming more complex systems. Such multi-component nanostructures usually offer new functionality and show additional, desired, or unwanted physical effects. This talk presents our latest results, illustrating the benefits and fundamental problems of applying up-conversion materials at the nanoscale.

In the last years, much attention has been paid to developing hybrid nanostructures comprising nanocrystals and various metallic nanoparticles. Interaction between such objects often modifies the up-conversion processes. We show that gold nanospheres, for instance, due to their relatively narrow resonance, may act very selectively, e.g., enhancing the red emission of Er^{3+} and, at the same time, quenching the green one. On the other hand, elongated metallic nanoparticles like silver nanowires, featuring spectrally broad plasmonic resonance, can enhance all Er^{3+} emission lines and significantly improve absorption. Moreover, silver nanowires can support surface plasmon polaritons, transporting the energy along the nanowire. Our recent results show that energy transfer up-conversion ($\text{Er}^{3+}/\text{Yb}^{3+}$) and photon avalanche up-conversion (Tm^{3+}) processes can be activated exclusively by propagating plasmon polaritons without the participation of photons.

We also discuss some problems and complications associated with implementing the up-conversion materials at the nanoscale. We demonstrate that even a little uncontrolled interaction with surfactants can disturb the up-conversion mechanisms and reduce their efficiency. Moreover, we show that local temperature fluctuations initiated by an operating laser can intensify nonradiative relaxation channels. We show how the latter affects the up-conversion luminescence thermometry. Eventually, we demonstrate the temperature readout from a single nanocrystal monitoring a warm single nanowire and point out parasitic processes disrupting such a measurement.

This research was financed from Project no. 2017/26/E/ST3/00209 founded by the National Science Centre, Poland.

0.3.154 Up-converting nanocrystals coupled to a single silver nanowire as a source of surface plasmon polaritons for direct measurement of propagation losses

Speaker: Cwierzona Maciej

Up-converting nanocrystals coupled to a single silver nanowire as a source of surface plasmon polaritons for direct measurement of propagation losses

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In this work, we discuss a prototype hybrid nanostructure consisting of Er³⁺/Yb³⁺ co-doped up-conversion nanocrystals (NCs) and a single silver nanowire (NW). In this experiment, nanocrystals serve as a very efficient, multi-band source of surface plasmon polaritons (SPPs) propagating through the nanowire. Based on efficient infrared excitation, large anti-Stokes shift, and optical cutting technique, we developed a new experimental approach for direct measurements of SPPs propagation losses.

Examined nanostructure consists of silver nanowires dispersed on the surface of the microscope coverslip. A good quality nanowire, about 15 µm long, was chosen for the experiment. Next, a few-femtoliter droplet of nanocrystals was deposited on one end of the nanowire, forming NCs-NW coupled system. We show that luminescence activated at one NW end can be transported to the opposite end by SPPs.

The experiment is realized using a scanning confocal microscope optimized for the anti-Stokes emission and equipped with two (top and bottom) coaxial objectives. An infrared laser operating at 980 nm is focused by the top objective directly on the NCs droplet. Usually, excited nanocrystals emit to free space, but some can launch SPPs propagating toward to opposite nanowire end. We use intensities of the up-converted emission collected from the free end of the nanowire by the bottom objective to estimate SPPs propagation losses. Significantly, the length of the NW is gradually reduced during the experiment using a precise laser cutting technique. Also, the dimension of the NW is controlled optically by analyzing the complex character of the interaction between the NW and modes of tightly focused Gaussian beam. This approach shows great potential for precise and cheap characterization of metallic nanostructures for nanophotonic applications.

This research was financed from Project no. 2017/26/E/ST3/00209 founded by the National Science Centre, Poland.

0.3.155 Upconversion nanoparticles- based portable biosensor to monitor kidney health

Speaker: Arai Marylyn

Upconversion nanoparticles- based portable biosensor to monitor kidney health

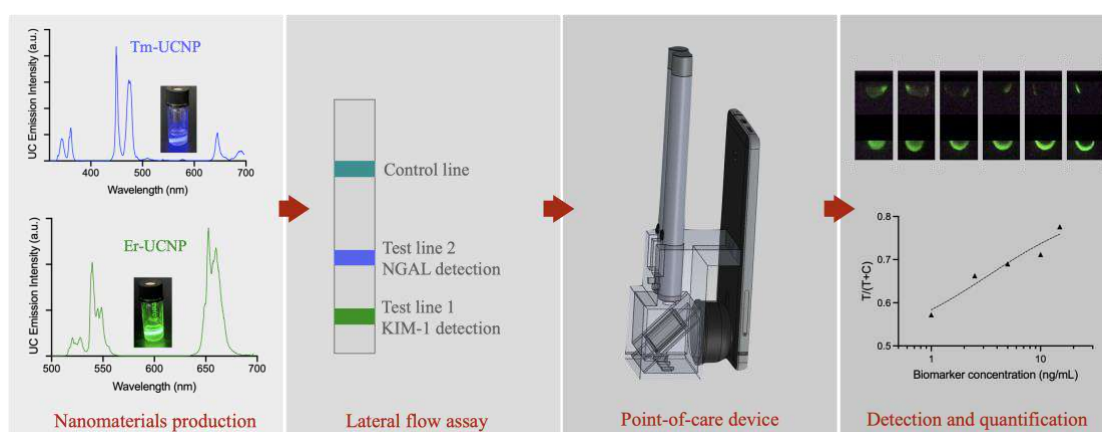
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Acute kidney injury (AKI) is a severe renal disease comprising an abrupt decrease in kidney function within 7 days or less. It has an enormous impact at an alarming rate, leading to the death of ~2 million people annually across the globe. The incidence rate of as much as one in five hospitalized patients accounts for more than 13 million individuals every year, making AKI one of the primary concerns in public health. Despite enormous developments in the diagnostic field, there is still an urgent need for generic, accurate, and point-of-care platforms capable of enabling the rapid and precocious diagnostics of AKI to allow faster and more adequate treatment.¹ Considering these problems, we developed a portable lateral flow assay (LFA) biosensor based on luminescent upconversion nanoparticles (UCNPs) for the detection of two AKI-related biomarkers: kidney injury molecule-1 (KIM-1) and neutrophil gelatinase-associated lipocalin (NGAL). In this LFA, novel and highly emissive Er³⁺- and Tm³⁺-doped UCNPs (NaYF₄:Yb³⁺/Er³⁺, Tm³⁺@NaYF₄@mSiO₂@Au)² conjugated to specific antibodies were used to detect the presence of KIM-1 and NGAL in urine samples and monitor kidney health by diagnosing the development of AKI in patients. Besides the UCNPs-based LFA, we also developed a portable device for luminescent signal acquisition and processing using a smartphone, as schematically shown in the figure below. With our sensor, the biomarkers can be detected and quantified in the range of 0.1 to 15 ng/mL and the results are obtained in less than 15 min, showing the system's potential to be used in POC applications.



Schematic representation of the main steps for UCNPs-based sensor development.

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0.3.156 UV-A emitting persistent luminescence nanoparticles as triggers for bioorthogonal photoclick reactions

Speaker: Ganigal Paul

UV-A emitting persistent luminescence nanoparticles as triggers for bioorthogonal photoclick reactions

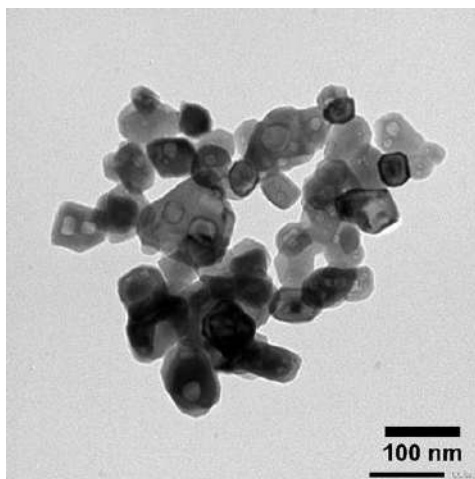
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Persistent luminescence (PERL) materials have the property to continue emitting light for a long period of time after excitation has ceased. When synthesized as nanoparticles, ZnGa₂O₄:Cr for instance [1], proved outstanding as *in vivo* small animal autofluorescence-free imaging probe [2] emitting in the NIR around 700 nm, i.e. in the first biological optical window. Our present goal is to design PERL nanoparticles emitting in the UV-A to trigger a bioorthogonal photoclick reaction *in vivo*. Bioorthogonal and click chemistry have been awarded 2022 Nobel prize in chemistry (Bertozzi, Meldal and Sharpless) as they constitute wonderful tools to probe living systems. Click reactions are specifically designed to bind small molecules together with high efficiency, versatility, irreversibility and selectivity, therefore without perturbing the chemical environment of a cell. The presentation will show the synthesis, structural and optical characterizations of YPO₄:Ce,Ho nanoparticles emitting persistent luminescence in the UV-A as well as their ability to trigger a bioorthogonal photoclick reaction. Radioluminescence, thermoluminescence, PERL intensity and decay profile of the nanoparticles are compared to YPO₄:Ce,Ho bulk phosphors.



TEM image of YPO₄:Ce,Ho nanoparticles presenting UV-A emitting PERL.

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0.3.157 Valence state conversion of Mn ions in Li₂O-ZnO-GeO₂ glass-ceramics

Speaker: Babkina Anastasiia

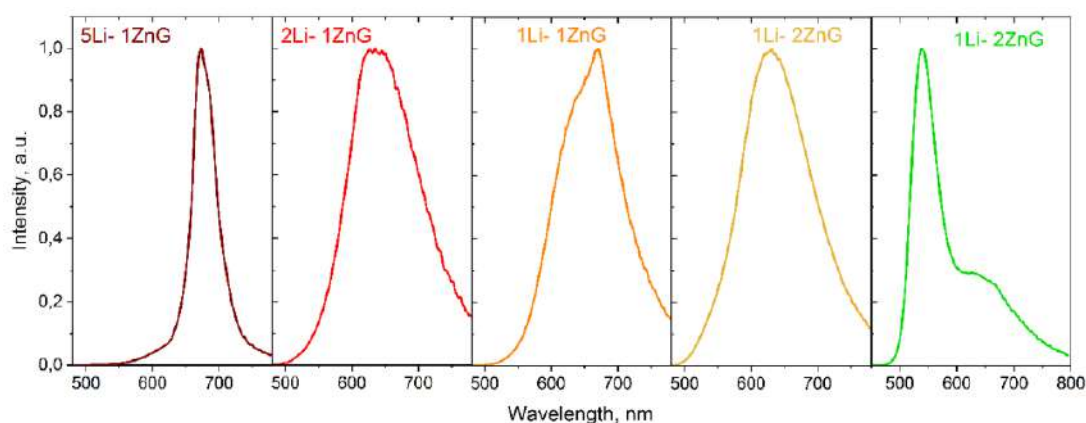
Valence state conversion of Mn ions in Li₂O-ZnO-GeO₂ glass-ceramics

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Manganese ions are attracted by the fact that under the redox conditions of material synthesis, different coordination and the crystal field strength, they are able to tune their luminescence maximum from the blue to the red region [1]. Lithium zinc germanate glass-ceramics with manganese studied in this work were obtained by isothermal treatment of glasses with the composition of 0.1 MnO₂ - (30 - x) Li₂O - x ZnO - 69.9 GeO₂, where x = 5, 7.5, 10, 15, 20, 22.5 mol.%. Glass with high Li₂O content demonstrated narrow luminescence near 670 nm, corresponding to the ²T_{1g}, ²E_g(G) → ⁴A_{2g}(F) transitions in Mn⁴⁺ ions. Glass with low content of Li₂O possessed broad luminescence near 540 nm corresponding to Mn²⁺ ions. Glass with Li₂O/ZnO ratio close to 1 showed wide luminescence at about 650 nm, also corresponded to Mn²⁺ ions. After isothermal treatment at 560-640°C, crystals were nucleated in the glass matrix: Li₂Ge₄O₉ at high Li₂O content, Li₂Ge₇O₁₅ in intermediate compounds, and GeO₂ in low Li₂O glass. In the luminescence spectra of glass-ceramics obtained at 560°C, the band at 670 nm of Mn⁴⁺ predominated. In the spectra of glass-ceramics obtained at 640°C, there was a decrease in the red luminescence intensity and an increase in green one.



Luminescence spectra of glasses activated with Mn with different Li₂O/ZnO ratios

This research was supported by Russian Science Foundation (Agreement #19-72-10036).

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0.3.158 Versatile magnetic field and temperature luminescence probes of hierarchically structured lanthanide-doped NaREF₄ nanoparticles and their interaction with surface acoustic waves

Speaker: Sigoli Fernando A

Versatile magnetic field and temperature luminescence probes of hierarchically structured lanthanide-doped NaREF₄ nanoparticles and their interaction with surface acoustic waves

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The engineering of core@multishell nanoparticles containing heterogeneous crystalline phases in different layers constitutes an important strategy for obtaining optical probes. The possibility of obtaining an opto-magnetic core@multishell nanoparticle capable of emitting in the visible and near-infrared ranges by upconversion and downshifting processes is highly desirable, especially when its optical responses are dependent on temperature and magnetic field variations. Up to date, the interaction of Ln-UCNPs with surface acoustic waves (SAWs) remain mostly unrevealed. SAWs are mechanical waves confined on the solids surface and with well-defined velocities. Our research group has great knowledge for synthesizing hierarchically structured core@multishell nanoparticles of heterogeneous crystalline phases. The synthesis strategy was efficient in obtaining spheroidal nanoparticles of approximately 13 nm of heterogeneous crystalline phases, formed by a core of cubic phase and shells with hexagonal phase or a core@shell nanoparticles with hexagonal phase, confirmed by XRD, TEM, and luminescence measurements. The structural and compositional hierarchies were confirmed by EDS mapping and HAADF images, optimizing and arrange the optical and magnetic properties of interest in different regions of the nanoparticle. Optically active shells, in the hexagonal phase, emit in the visible region and the NIR range after excitation at 980, 808, and 1550 nm, covering two different biological windows. The nanoparticle emissions are affected by temperature, where the emissions of Er^{III} emissions in 528 and 540nm can be taken to propose a temperature probe based on upconversion emissions in a temperature range of 77 to 427K. Emissions in the NIR cover higher temperatures ranging from 427 to 633K. The core@multishell nanoparticle can also have its luminescence modulated by the application of an external magnetic field, where at 15K the intensity increase of the applied magnetic field improves the emission intensities and promotes the splitting of Zeeman's doublets, for the transition ⁴S_{3/2} of the Er^{III} ion. However, at 150K the increase of magnetic field decreases the intensities of the upconversion emission. Concerning the SAW applications on a piezoelectric LiNbO₃ substrate, it is well-known that high SAW powers can induce temperature changes. Therefore, we probed photoluminescence emission as a function of time and power of SAW at 5, 215 and 300 K. For high SAW power regimes applied at low temperatures, the upconversion emission spectrum and the resulting LIR using Stark levels, indicates a considerable local temperature increase. We also identified the population mechanisms between the multiplets energy states. The magneto-optical properties of nanoparticle reveal its versatile nature and its applicability in magnetic field, optical temperature probes for future SAW-based circuits containing nanostructures.

0.3.159 Yb³⁺ concentration influence on NIR and upconversion emission and temperature sensing properties of Er³⁺/Yb³⁺ co-doped Ta₂O₅ nanoparticles

Speaker: Borges Fernanda

Yb³⁺ concentration influence on NIR and upconversion emission and temperature sensing properties of Er³⁺/Yb³⁺ co-doped Ta₂O₅ nanoparticles

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Tantalum oxide (Ta₂O₅) has become a versatile material with applications in different domains such as optoelectronics, capacitors, and photocatalysis. Regarding biological applications, due its anti-bacterial activity, high corrosion resistance, low toxicity, and high biocompatibility, Ta₂O₅ has been used as a coating material for clinical instruments, tissue regeneration, and implants [1]. To combine the great advantages on biological applications that Ta₂O₅ can provide with luminescent properties (by doping the material with Ln³⁺ ions) in order to develop a multifunctional platform for theranostics applications, it is crucial to obtain control over the morphology and size of the desired material. Er³⁺ and Yb³⁺ co-doped Ta₂O₅ nanoparticles have been synthesized by a facile method through the formation of tantalum glycolates poured in acetone, which gives spherical shape particles, with morphology and size well controlled. In this work we investigated the influence of the annealing temperature as well as the Yb³⁺ concentration (0-30 mol %) on the structural and luminescence properties. Particles sizes ranging from 141 to 260 nm were observed by TEM for the samples annealed at 800 °C. XRD analysis affords the orthorhombic L-Ta₂O₅ crystalline structure. FTIR spectroscopic studies showed that OH and CH groups were eliminated after the annealing treatment. Intense and broad emission bands centered around 1530 nm were observed, due to the different symmetry sites that RE³⁺ ions can occupy within the Ta₂O₅ structure. UC luminescence with intense green and red emission intensity under 980 nm and 1550 nm excitation, respectively, were measured and the mechanisms involved at both excitation wavelengths could be elucidated by the number of photons. The performance of 0.5 mol % Er³⁺/1.5 mol % Yb³⁺ co-doped Ta₂O₅ sample as a primary thermometer was investigated, by predicting the absolute temperature through the Boltzmann distribution law, from the ratio of ²H_{11/2} → ⁴I_{15/2} and ⁴S_{3/2} → ⁴I_{15/2} transitions of Er³⁺ ions [2]. The maximum relative thermal sensitivity of 0.996 ± 0.004 % K⁻¹ at 298 K and a minimum δT of 2.08 K were obtained. The calculated repeatability was above 95 %. These results clearly show that a promising multifunctional platform for Biophotonics applications based on Ta₂O₅ with size and morphological control can be designed.

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0.4 Posters

0.4.1 Advanced superstructures of nanoparticles in liquid crystal topological defects

Speaker: Essaoui Lamya

Advanced superstructures of nanoparticles in liquid crystal topological defects

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It is still a challenge to obtain a well-assembled network of nanoparticles (Nps) which is similar everywhere and most importantly, oriented along a unique direction. Confining fluorescent Nps into the topological defects^{1,2} of smectic liquid crystals may allow to tackle this issue and ultimately may lead to the emergence of new optical properties. For example, when fluorescent nanorods are concerned, a fixed orientation of the nanorods allows for the control of the polarization of NP emitted light³.

By using optical microscopy, fluorescence microscopy and synchrotron-based grazing incidence X-ray scattering (GISAXS) we study the coupling between smectic liquid crystals defects and fluorescent nanorods. We try to understand whether the assembly of Nps arrange itself in one-dimensional -1D (dislocations) or two-dimensional – 2D (grain boundaries) defects depending on Np concentration. We demonstrate that in both kinds of defects the average orientation of the nanorods is fixed, leading to a unique emitted light polarization all over the sample³. We observe the effect of the temperature on the Np organization and thus on the Nps optical properties, in relation with the evolution of the defect structure close to the smectic phase transition.

Our findings open up a route for collective behaviors between NPs that could emerge in relation to the well-ordered close packing of Nps confined within the smectic liquid crystal defects.

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0.4.2 Advancing on New Luminescent Material: CYTOP Fiber Empowered using Femtosecond Laser Direct Writing

Speaker: Que Ruyue

Advancing on New Luminescent Material: CYTOP Fiber Empowered using Femtosecond Laser Direct Writing

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Compared to conventional silica based optical fibers, polymer optical fibers (POFs), such as a perfluorinated polymer CYTOP (cyclic transparent optical polymer), have many advantages such as bending flexibility, biocompatibility, making it suitable for biomedical applications. For example studies on CYTOP fiber based Bragg grating sensing have been carried out [1]. However, luminescence sensing with CYTOP is new. To introduce luminescent properties in a fiber, fluorescent dyes or molecules, Carbon Dots, or a piece of rare-earth ion-doped fiber, are embedded in the optical fiber or coated on the surface. These sensors can be used for concentration sensing of oxygen [2], Ferric ions [3], detection of Hg(II) [4], pH sensing, or even for monitoring human physiological function [5]. Here, an easy method to create luminescent materials in situ by femtosecond laser direct writing (FLDW) is proposed. An ellipsoidal luminescent volume can be formed in CYTOP fiber core at the focal point of a femtosecond laser beam. Emission and excitation spectra and lifetimes are characterized. Results indicate that when more laser energy applied, the luminescent brightness increases significantly with the laser-induced luminescent materials increasing and they are distributed at the periphery. In the meantime, a species that excites at longer wavelengths appears. These results share similarities with the results in a cyclic olefin polymer [6].

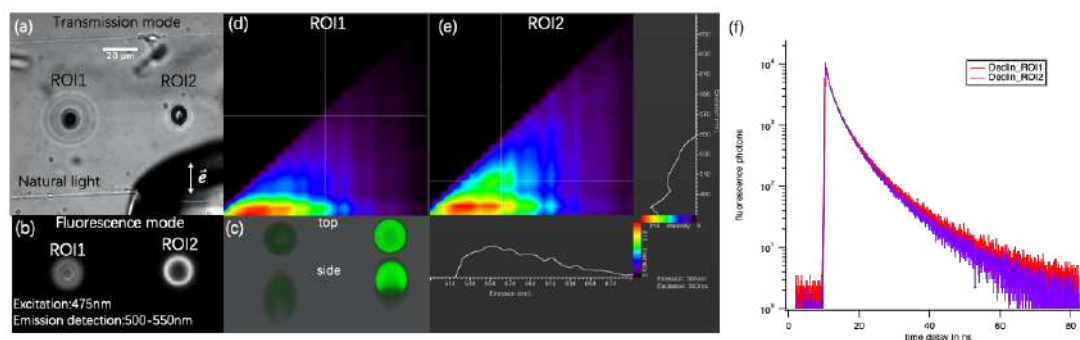


Figure.1 (a) transmission image of 2 laser irradiated regions (ROI). Parameters of ROI1: 1030nm, 165fs, 10MHz, 55.5 mW, polarization as shown in (a), exposure time of 4s; ROI2: same as ROI1 except 2 times of extra exposure of 100ms under power 18.5mW. (b) fluorescence image of ROI1 and 2.(c) screenshots of 3D model of ROIs on top view and side view. (d)-(e) the excitation-emission matrix of ROIs. (f) lifetime decays of ROIs excited at 515nm, detection 520nm-600nm

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0.4.3 AlN – persistent luminescence

Speaker: Berzina Baiba

AlN – persistent luminescence material

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Long-lasting persistent luminescence (PersL) of AlN materials, nominally pure or doped with Eu or Mn ions, was systematically studied, using various spectral methods. The PersL emission spectra, caused by the pre-irradiation of samples with UV light of different wavelengths or X-rays, were examined and compared with the corresponding characteristics measured under the direct sample excitation. The PersL excitation spectra characterizing UV light pre-irradiation and PersL kinetics under UV light and X-ray pre-irradiation were studied. In order to reveal the PersL mechanisms, the thermoluminescence spectra and glow curves were also examined.

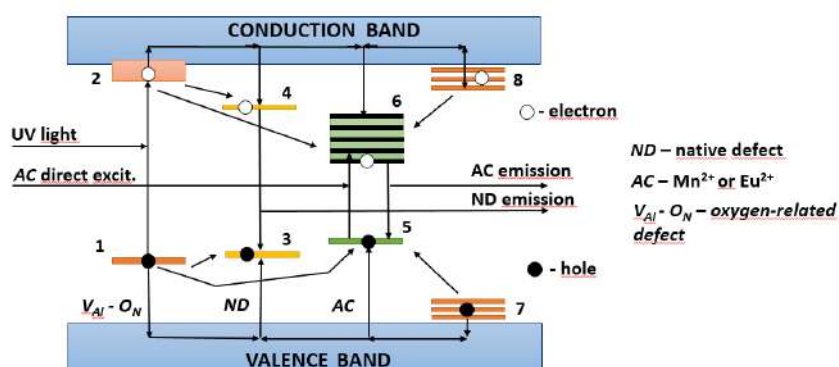


Fig. 1. An energy level scheme of doped AlN illustrating the luminescence processes and mechanisms.

Analysis of the results obtained allows finding out the processes in irradiated material resulting in PersL as well as revealing of the luminescence mechanisms schematically depicted in Fig. 1. The main conclusions are the following: 1. The native defects in AlN host are the key in formation of the PersL determining its properties, while the dopants and other luminescent defects serve as PersL emitters. 2. In order to cause the PersL emission, the coordinated action of the electron and hole processes is necessary.

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0.4.4 Aluminium nitride based luminescent materials for biomedical applications

Speaker: Ruska Rihards

Aluminium nitride based luminescent materials for biomedical applications

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Over the past few decades, persistent luminescent materials have gained attention for their use in biomedicine. To be deemed suitable for biomedical applications, luminescent materials must meet certain criteria. They must be nanosized, emit light within biological windows, excite with X-rays or other transmissible light, contain trap centers of optimal depth and, most importantly, be non-toxic. Various oxide and fluoride nanomaterials have long been studied, but these materials usually contain heavy elements or are hard to remove from organism due to their high stability and low solubility. Nitrides might be a good alternative as they are less stable and can be degraded in organism. One of the promising nitride matrices with previously mentioned favourable properties is AlN.

In this study, we investigated the luminescence characteristics and stability of top-down and bottom-up made AlN:Mn and AlN:Cr nanomaterials. XRD, photoluminescence, its excitation spectra and kinetics were measured. All materials exhibited characteristic dopant ion luminescence (600 nm for Mn²⁺ and 694 nm for Cr³⁺ ions (Fig.1.)). Co-doping and several other methods were employed to enhance the luminescence intensity.

Our findings indicate that AlN has the potential to be a suitable luminescent matrix for biomedical applications. Further research will be conducted to develop and test AlN nanomaterials based on our results. Overall, this study provides insights into the use of AlN as a material for biomedical applications.

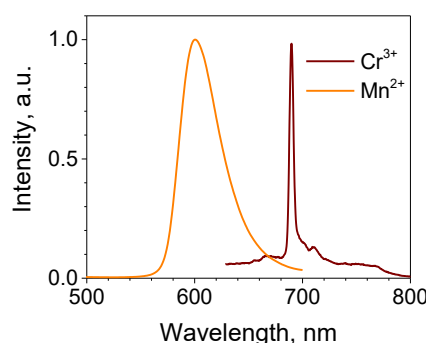


Fig.1. Characteristic luminescence bands of Mn²⁺ and Cr³⁺ ions in AlN matrix

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0.4.5 An insight into the luminescent properties and Judd-Ofelt analysis of the Sm³⁺ doped Ca₂LiMg₂V₃O₁₂ phosphors

Speaker: Kennedy S Masilla Moses

An insight into the luminescent properties and Judd-Ofelt analysis of the Sm³⁺ doped Ca₂LiMg₂V₃O₁₂ phosphors

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Abstract

In this study, undoped and the Sm³⁺ doped garnet type vanadate Ca₂LiMg₂V₃O₁₂ (CLMV) with varying Sm³⁺ concentration (0.01-0.09 mol %) were synthesized via the solid-state reaction method. The phase formation of the samples was confirmed using powder XRD, while SEM and EDAX were employed to investigate the morphological properties and elements present in the samples. The band gap energy values of both the CLMV and the CLMV:0.07Sm³⁺ were determined using DRS measurements. The photoluminescence properties of the pure CLMV and the CLMV:xSm³⁺ (x=0.00-0.09 mol %) were studied under the excitation at 346 nm and the emission at 617 nm, with an additional study of the dominant characteristic emission peak of the Sm³⁺ under the excitation at 405nm. The lifetime decay analysis and the CIE color coordinates were also reported. Judd-Ofelt intensity parameters were calculated using the excitation spectra, and it was employed to predict various radiative properties such as branching ratio (β_r), total transition probability (A_T), and radiative life time (τ_{calc}). The study concludes that the phosphor is suitable for solid-state lighting applications.

0.4.6 Anisotropic luminescence of β -LiGaO₂

Speaker: Trinkler Laima

Anisotropic luminescence of β -LiGaO₂

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Beta LiGaO₂ (β -LGO) is a wide band gap crystal ($E_g \approx 6$ eV) potentially promising for practical application. β -LGO has a non-centrosymmetric wurtzite-derived crystalline structure, determining anisotropic physical properties such as birefringence, polarized luminescence, piezoelectricity, pyroelectric luminescence. The comprehensive spectral study of β -LGO single crystal has been done including methods of photoluminescence (PL), polarised luminescence and pyroluminescence in temperature region 10-300 K.

Luminescence spectrum of the crystal contains emission bands at 4.43, 3.76, 2.38 and 1.77 eV. Exciton bands at 6.043, 6.085 and 5.980 eV, corresponding to three crystallographic axes, have been found in the PL excitation spectrum under the synchrotron irradiation, whose relative contribution depends on crystal orientation (Fig.1). Study of polarized luminescence 4.43 eV under the excitation with ArF laser (193 nm, 6.42 eV) with varied intensity in the 10-300 K temperature range has demonstrated that the excitation-induced and temperature-induced band's energy and intensity behaviour depends on the orientation of the crystal in relation to the incident light. Coexistence of two radiative processes is proposed for the explanation of the PL in β -LiGaO₂ crystal: the tunnel recombination of donor-acceptor pairs (DAP) and the recombination of a free electron with an acceptor center (e-A). Besides, in β -LGO crystal pyroelectric luminescence has been observed. The obtained spectral and kinetic characteristics and temporal structure of pyroelectric luminescence signal allows proposing of the luminescence mechanism as radiative recombination of electrons with positively charged intrinsic luminescence centres inside the crystal.

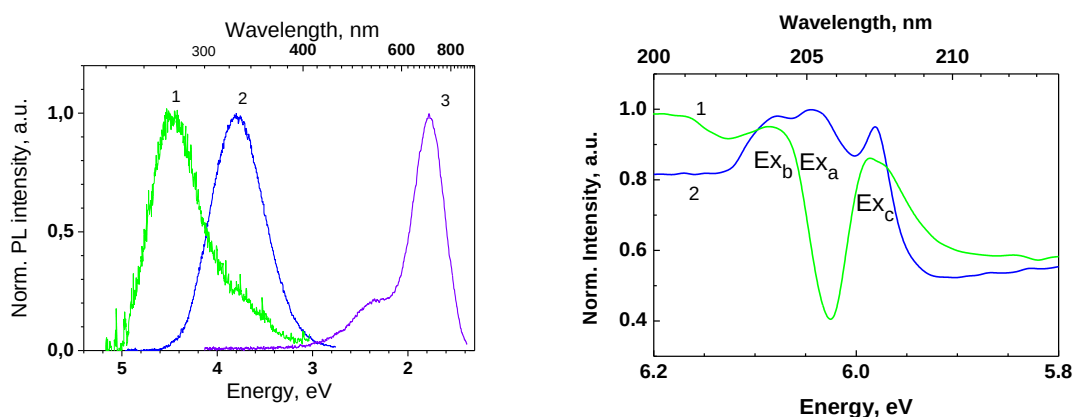


Figure 1. Photoluminescence spectrum of LiGaO₂ under deuterium lamp excitation 6.42 eV (1), 5.85 eV (2), 4.96 eV (3) and PL excitation spectrum (for λ_{lum} 4.27 eV) under synchrotron irradiation at 10 K: (1) – horizontal, (2) – vertical orientation of crystal.

0.4.7 Applications of tunable AIE-dyes based on furan derivatives

Speaker: Łupińska Kamila

Applications of tunable AIE-dyes based on furan derivatives

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The Donor- π -Acceptor molecules are an interesting class of easily synthesizable compounds that have unique spectroscopic properties. [1] The molecular design of the D- π -A compound allows the occurrence of the Intramolecular Charge Transfer (ICT) effect, which is beneficial for applications in nonlinear optics, laser light generation, and sensing. [2] Furthermore, some of the molecules represented by the furan family show Aggregation Induced/Enhanced Emission (AIE/AIEE), [3] a very promising phenomenon for bio-imaging purposes. [4]

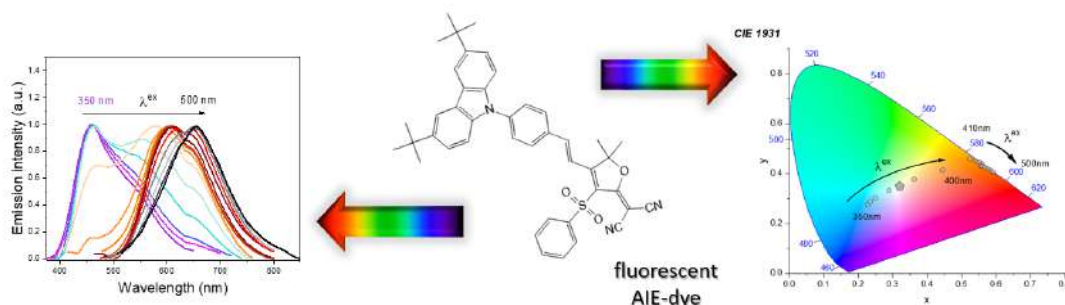


Fig. 1. The tunability of fluorescence spectra of tBuCBzSO₂Ph with respect to pumping wavelength and corresponding CIE 1931 graph.

The presentation will contain the results of aggregation and excitation wavelength influence on the fluorescence of selected furan derivatives. Moreover, the ability to generate laser light and obtain the Organic Light-Emitting Diode (OLED) will be discussed.

Acknowledgement: The work was supported by National Science, Poland (2020/39/O/ST5/01865)

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0.4.8 Bayesian statistics for multimodal problems applied to emission spectra broadening of a single core/shell CdSe/CdS nanocrystal.

Speaker: Simonot Damien

Bayesian statistics for multimodal problems applied to emission spectra broadening of a single core/shell CdSe/CdS nanocrystal.

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In the fields of probabilistic inference and data analysis, multiple dimensional and multimodal probability distributions are often encountered. Standard maximisation algorithms tend to be effective in finding single local maxima of the likelihood function of a statistical model but may have difficulties in finding global maxima when the function is complex and multidimensional.

For CdSe/CdS core/shell quantum dots, under low power of excitation, an emission line with a width of $\Delta\lambda \approx 20$ nm is observed, while under high excitation power, the spectral broadening can exceed $\Delta\lambda \approx 150$ nm [1]. To understand this broadening, a theoretical model has been developed assuming a quasi-equilibrium Fermi-Dirac distribution for electrons and holes. Numerous unknown and sometimes correlated parameters are involved. To find the parameters of this multimodal problem, we adapted a Bayesian method, widely used in the cosmology community. Using a series of quasi-random samples, Nested Sampling (NS) is a specific type of Markov Chain Monte Carlo algorithm [2] that is especially useful for the analysis of complex and high-dimensional data. It allows the reduction to one-dimensional sampling by the use of a dynamical ensemble of sampling points that evolves during the different steps of the algorithm. As output, the full probability distribution of the parameters are provided. As an example of typical output, we present the distribution probability of respectively the temperature and chemical potential of electrons of the quasi-equilibrium Fermi-Dirac distribution. Even when those parameters are correlated, the algorithm allows us to find their most probable value with a limited computational effort. In conclusion, the Nested Sampling with Bayesian Inference method is well suited to determine parameters for multimodal distributions, even with noisy data, making it a very efficient practical tool for determining physical parameters.

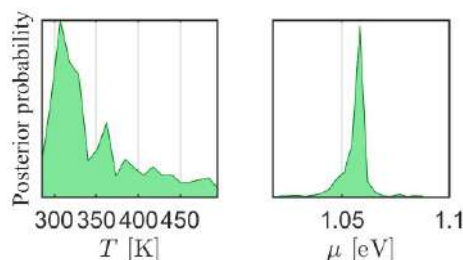


Figure 1: From Markov Chain Monte Carlo nested sampling, the probability distributions of a) the electronic temperature and b) the chemical potential of the electron are calculated.

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0.4.9 Bidirectional, Indefinite Near Infrared Nanocrystal Photoswitching

Speaker: Schuck James

Bidirectional, Indefinite Near Infrared Nanocrystal Photoswitching

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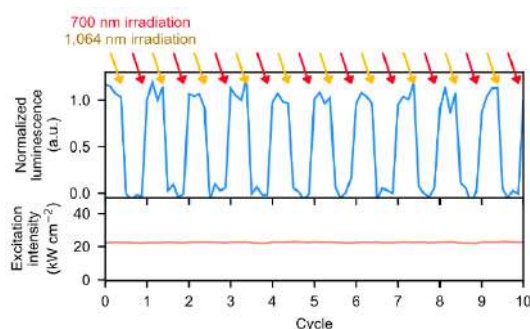
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Materials whose luminescence can be switched by optical stimulation drive technologies ranging from superresolution imaging, nanophotonics, and optical data storage, to targeted pharmacology, optogenetics, and chemical reactivity. Here, we present 2-way, NIR photoswitching of avalanching nanoparticles (ANPs) [1], showing full optical control of upconverted emission using phototriggers in the NIR-I and NIR-II spectral regions useful for subsurface imaging. Employing single-step photodarkening and photobrightening, we demonstrate indefinite photoswitching of individual nanoparticles (>1000 cycles over 7 h) in ambient or aqueous conditions without measurable photodegradation. Critical steps of the photoswitching mechanism are elucidated by modeling and by measuring the photon avalanche properties of single ANPs in both bright and dark states. Unlimited, reversible photoswitching of ANPs enables indefinitely rewritable 2D and 3D multi-level optical patterning of ANPs, as well as optical nanoscopy with sub-Å localization superresolution that allows us to distinguish individual ANPs within tightly packed clusters.



Perfectly stable NIR photoswitching of a single ANP

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0.4.10 Blue-to-UV upconversion of the Pr^{3+} - Gd^{3+} couple in inorganic compounds

Speaker: Förster Tom

Blue-to-UV upconversion of the Pr³⁺-Gd³⁺ couple in inorganic compounds

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The COVID-19 pandemic has increased the focus on applications in the field of disinfection using ultraviolet (UV) light [1]. However, only UVB (280 – 320 nm) and UVC light (200 – 280 nm) can be used for this due to the range of absorption of microorganisms [2]. Commercially available UVC light sources typically rely on electric discharge of Hg, having multiple downsides such as short lifetimes, large heat generation and safety hazards. Narrow-band UV light emitting micro- or nanocrystalline phosphors can be a more promising option for antimicrobial lamps. The trivalent lanthanide Gd³⁺ (4f⁷) could be used for this purpose due to its high quantum yield and very narrow line emission in the UVB range (~ 310 nm) [3]. Because of the inefficient absorption of Gd³⁺ [4], expensive and intense UV light sources are required for direct excitation. An alternative, sustainable approach is indirect excitation via Pr³⁺ (4f²). The electronic structure of Pr³⁺ allows upconversion to the states of the excited 4f¹5d¹ configuration states upon irradiation with intense blue light (~ 450 nm) [5]. From these, energy transfer to the Gd³⁺ ion is available [6]. In contrast to the energy levels from the shielded 4fⁿ configuration, the energy of the 4fⁿ⁻¹5d¹ configuration of trivalent lanthanides can be controlled by the chemical nature of the surrounding host compound [7]. In addition, the excited state dynamics of the blue-absorbing ³P_J (J = 0, 1, 2) levels of Pr³⁺ is strongly affected by the vibrational energies of the host. Thus, a fundamental understanding of the upconversion mechanism is crucial for an appropriate choice of the host compound for highest possible efficiency and matching of the excited 4f¹5d¹ states of Pr³⁺ with both the resonance condition for upconversion and the excited 4f⁷ levels of Gd³⁺. For that purpose, Pr³⁺ and Gd³⁺ are doped in selected halidoelpasolites, garnets, silicates and borates to understand the influence of phonon energy and crystal field splitting and analyzed by time-resolved and temperature-dependent luminescence spectroscopy.

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0.4.11 Catalase-like decomposition of Hydrogen Peroxide by Gadolinium Orthovanadate Nanocrystals

Speaker: Hubenko Kateryna

Catalase-like decomposition of Hydrogen Peroxide by Gadolinium Orthovanadate Nanocrystals

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Oxidative stress caused by an overproduction of reactive oxygen species (ROS) is the key factor in developing a variety of pathological conditions. Recently, various nanomaterials have attracted growing interest as nano-antioxidants with ROS-regulating ability. This work showed the high antioxidant behavior of luminescent GdVO₄:Eu³⁺ nanoparticles revealed by spectroscopic methods and using ROS sensor and propose the mechanism describing their ROS scavenging action.

It was revealed that luminescent GdVO₄:Eu³⁺ nanoparticles effectively scavenge hydrogen peroxide (H₂O₂). The investigation of absorption spectra of colloidal solutions of nanoparticles and XPS studies have shown that the decomposition of hydrogen peroxide is mainly carried out by electron capture by pentavalent vanadium ions, with their reduction to a 4+ and 3+ states. However, it cannot be ruled out that the decomposition of hydrogen peroxide occurs through a reaction in which it acts as an oxidant, oxidizing trivalent and tetravalent vanadium to a 5+ state.

The catalase-like mechanism of hydrogen peroxide decomposition (without the formation of toxic hydroxyl radicals) as well as the effective neutralization of other types of ROS makes luminescent GdVO₄:Eu³⁺ nanoparticles a promising material for the development of novel theranostic agents with strong antioxidant properties.

Funding: This research was supported by the Philipp Schwartz-Initiative of the Alexander von Humboldt-Stiftung.

0.4.12 Characterization and modification of UV emitting $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Pr}^{3+}$ material

Speaker: Nilova Dace

Characterization and modification of UV emitting $\text{Ca}_2\text{Al}_2\text{SiO}_7\text{:Pr}^{3+}$ material

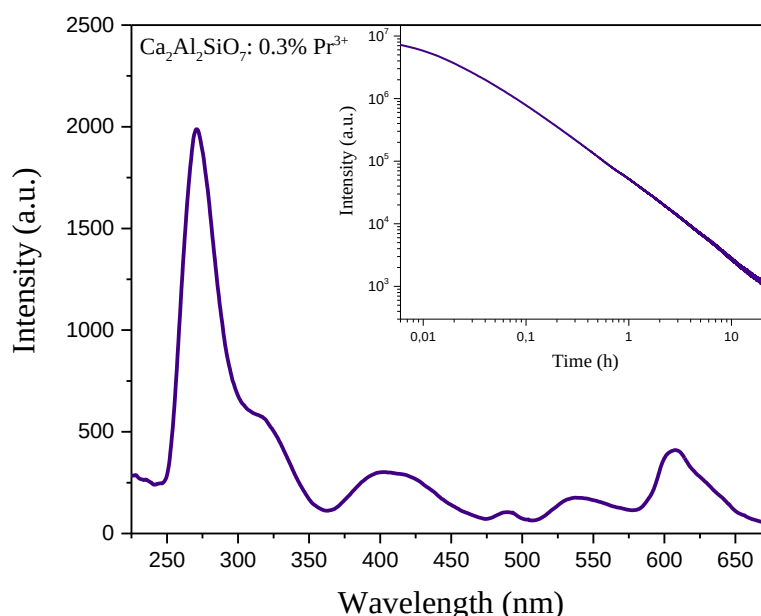
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Nowadays, persistent luminescence (PersL) is widely studied and used in everyday life. Research and improvement of persistent phosphors for existing and new applications are in demand. In recent years, great attention has been paid to materials exhibiting PersL in the UV range. Still, often the structure and PersL mechanisms of such materials have been characterized insufficiently.

This report provides results for UV-C emitting persistent phosphor $\text{Ca}_2\text{Al}_2\text{SiO}_7\text{:Pr}^{3+}$. Using a variety of spectroscopic methods incorporation of Pr^{3+} ions in the matrix is analyzed and the material is characterized by optical and structural properties. Additionally, results for modifying the PersL properties by adding the coactivators and changing the synthesis parameters will be discussed.



Persistent luminescence spectrum of the $\text{Ca}_2\text{Al}_2\text{SiO}_7\text{:0.3\% Pr}^{3+}$; inset: corresponding persistent luminescence decay curve of UV bands after irradiation for 10 min with X-rays.

This work has been funded by the ESF in the framework of project "Strengthening the doctoral capacity of the University of Latvia within the framework of the new doctoral model" No. 8.2.2.0/20/1/006.

0.4.13 Chiral tetranuclear Eu_2Ir_2 molecules as tunable ratiometric luminescent thermometers

Speaker: Rzepiela Jan

Chiral tetranuclear {Eu₂Ir₂} molecules as tunable ratiometric luminescent thermometers

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A new trend has emerged from the field of luminescent materials in which strong temperature dependence of luminescence is generated and such property is utilized to construct contactless and reliable optical thermometers for application in chemical reactors and biological studies.^{1,2} Lanthanide(III) complexes are known for their strong emission with high-temperature dependence which makes them good candidates for the construction of such devices.³ On the other hand, molecular materials based on cyanido metal complexes are exploited due to the extraordinary magnetic and optical properties, including chirality-related effects, e.g., magneto-chiral dichroism or magnetization-induced second harmonic generation.^{4,5} Finally, cyclometalated Ir(III) complexes are effective molecular building blocks for the construction of novel optical materials due to their strong and tunable charge transfer emission in the visible to NIR regions.⁶ In these regards, we decided to focus on the combination of cyanide chemistry with an organometallic approach to obtain a novel class of chiral luminescent dicyanido-iridate(III) complexes, further bonded with strongly emissive Eu(III) centers. We present an organic salt of (TBA)₂{[Eu^{III}(NO₃)₃(H₂O)]₂[Ir^{III}(CN)₂(*R,R*-pinppy)₂]₂} **1** and its fluorinated analogue **2** (Figure 1). Both obtained molecular materials consist of four metal centers, two Ir(III) and two Eu(III) ones. They exhibit a strong temperature variation of the emission pattern which leads to the ratiometric luminescent thermometry effect based on the Ir(III)- and Eu(III)-based emission peaks with the tuning of optical characteristics by the fluorination of the applied ligand. The further potential of these materials for non-linear optical properties is also discussed.

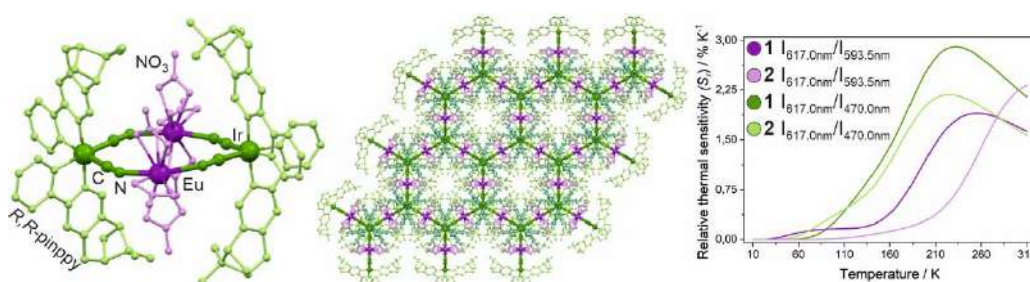


Figure 1. The crystal structure of the {Eu₂Ir₂} molecules (**1**) and the representative characteristics of the luminescent thermometry for **1** and the fluorinated analogue **2**.

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0.4.14 Comparative studies of structural and spectroscopic properties of cubic Nd³⁺-doped M₃Y(PO₄)₃ (M = Sr²⁺ or Ba²⁺) from eulytite family

Speaker: Prokop Kacper Albin

Comparative studies of structural and spectroscopic properties of cubic Nd³⁺-doped M₃Y(PO₄)₃ (M = Sr²⁺ or Ba²⁺) from eulytite family

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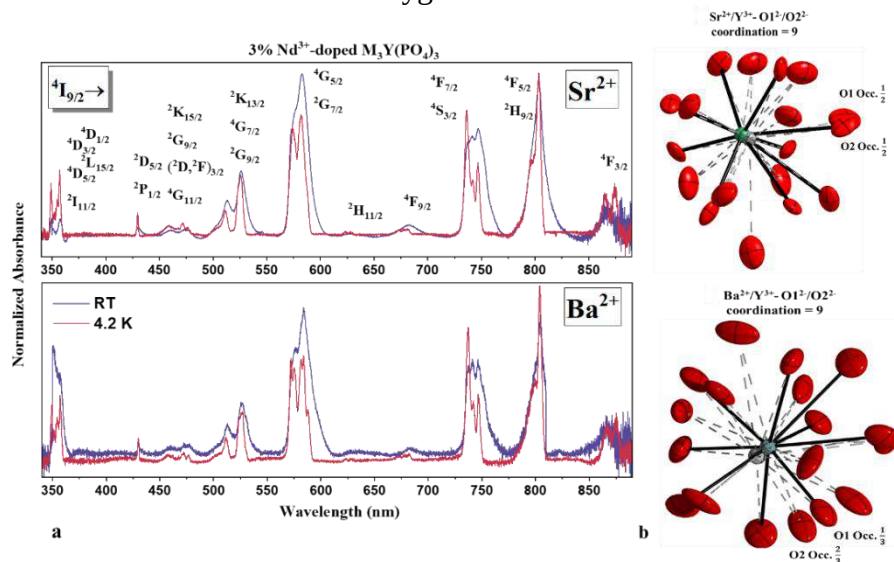
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Two series of eulytite-type Nd^{3+} -doped $\text{Ba}_3\text{Y}(\text{PO}_4)_3$ and $\text{Sr}_3\text{Y}(\text{PO}_4)_3$ micro-crystalline powders were investigated in terms of further use of these matrices to achieve the difficult task of fabricating transparent ceramics. The relationship between structure and the spectroscopic properties as well as an effect of size of divalent $\text{Sr}^{2+}/\text{Ba}^{2+}$ cation creating a network was investigated. XRD method confirmed that all the obtained materials are single-phase and crystallize in the cubic system (space group $I\bar{4}3d$, No. 220). The crystal structures of $\text{Ba}_3\text{Y}(\text{PO}_4)_3$ and $\text{Sr}_3\text{Y}(\text{PO}_4)_3$ were solved based on the small single crystals selected from micro-crystalline powders. The diffraction patterns were also refined by the Rietveld method. $\text{M}^{2+}/\text{Y}^{3+}$ are randomly disordered in C_3 point symmetry cationic site. The Nd^{3+} ions mainly reside at the Y^{3+} symmetry site but partial substitution of Ba^{2+} or Sr^{2+} sites cannot be excluded. These phosphates show not only cation disorder but also disorder in the oxygen sublattice.



Absorption spectra of Nd^{3+} -doped $\text{M}_3\text{Y}(\text{PO}_4)_3$ ($\text{M}=\text{Sr}^{2+}$, Ba^{2+}) recorded at RT and 77 K (a).
with of $\text{Y}^{3+}/\text{Ba}^{2+}$ and $\text{Y}^{3+}/\text{Sr}^{2+}$ cations by possible O^{2-} anions (b).

High resolution measurements such as absorption at 4.2K and laser excited site-selective emission at 77K were used to determine the multisite character of Nd^{3+} ions. Inhomogeneous distribution was also clearly visible in the excited state dynamics of $^4\text{F}_{3/2}$ doublet studies. Both types of samples activated up to 20 mol% shown weak concentration quenching. As presents Figure above, the greater disorder is observed for strontium host lattice.

0.4.15 Comparative study of scintillation properties of $(C_6H_5C_2H_4NH_3)_2Pb_{0.9}M_{0.1}Br_4$ (M = Fe, Co, Ni, Cu, Zn, Cd, Hg, Sn) single crystals

Speaker: Yanagida Takayuki

Comparative study of scintillation properties of (C₆H₅C₂H₄NH₃)₂Pb_{0.9}M_{0.1}Br₄ (M = Fe, Co, Ni, Cu, Zn, Cd, Hg, Sn) single crystals

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Scintillators are one of the phosphors which can convert the absorbed energy of ionizing radiations to low energy photons (UV~NIR) immediately [1]. The spectrum of the applications is quite wide, including medical, security, well-logging, environmental monitoring, high energy physics and so on [2]. Up to now, many kinds of scintillators have been investigated in both inorganic and organic materials, and recently, organic-inorganic perovskite materials have attracted much attention for scintillator uses. Historically, studies of organic-inorganic perovskite for scintillator applications started at ~20 years ago [3], and at that time, scintillation light yield was low although a fast speed was ideal. After some continuous investigations, several years ago, the weak point of low scintillation light yield was solved by our group [4]. Based on such a background, in this study, we focus on (C₆H₅C₂H₄NH₃)₂Pb_{0.9}M_{0.1}Br₄ (M = Fe, Co, Ni, Cu, Zn, Cd, Hg, Sn) single crystals, as series of continuous works from above commented investigations [3,4].

These single crystals were synthesized by the poor solvent diffusion method. After the synthesis, powder X-ray diffraction (XRD) patterns were observed. Then, photophysical properties such as photoluminescence (PL) excitation and emission spectra, quantum yield, and decay time were investigated. Finally, scintillation properties including X-ray induced radioluminescence spectrum, decay time, and gamma-ray induced pulse height spectrum to determine the absolute scintillation light yield were evaluated.

By the poor solvent diffusion method, typically 5 × 5 × 0.5 mm³ bulk single crystals were successfully grown, and from XRD, generation of 2-dimensional quantum well structure was confirmed. In PL, emissions from free and trapped excitons were observed at 410 and 440 nm, respectively. Similar spectral features were also observed in radioluminescence spectra. When 662 keV gamma-rays from ¹³⁷Cs were irradiated to these samples, (C₆H₅C₂H₄NH₃)₂Pb_{0.9}Zn_{0.1}Br₄ showed the best scintillation light yield of 18000 ph/MeV with a fast decay time of 11 ns.

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0.4.16 Concentration quenching of the red emission ascribed to the $1D_2$ - $3H_4$ transition in $\text{CaYAl}_3\text{O}_7\text{:Pr}$

Speaker: Hernandez Zamudio Ruben Alfredo

Concentration quenching of the red emission ascribed to the $^1D_2$ - $^3H_4$ transition in $\text{CaYAl}_3\text{O}_7:\text{Pr}$

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Luminescence in Pr-doped compounds has been investigated profusely. In this regard, one of the topics worth investigating is the quenching of the red luminescence associated with the $^1D_2$ - $^3H_4$ transition. Concentration quenching of this red emission has been reported in $\text{YPO}_4:\text{Pr}^{3+}$ [1,2]. In this work similar results are presented, but for $\text{CaYAl}_3\text{O}_7:\text{Pr}^{3+}$. The CaYAl_3O_7 and $\text{CaY}_{1-x}\text{Pr}_x\text{Al}_3\text{O}_7$ ($x=0.001$ - 0.024) samples were synthesized by the polymerizable complex method. X-ray diffraction patterns confirmed the formation of the CaYAl_3O_7 tetragonal crystalline structure for all the samples. The optical properties of the compounds were characterized by diffuse reflectance and photoluminescence spectroscopies. The emission spectra, whether exciting through the f - d or f - f states, show the continuous ratio reduction of the integrated intensity red emission, ascribed to the $^1D_2$ - $^3H_4$, and the integrated intensity greenish-blue emission ($^3P_0$ - $^3H_4$). As in $\text{YPO}_4:\text{Pr}^{3+}$, the mechanism invoked to explain the observed luminescence quenching is a cross-relaxation energy transfer process between Pr^{3+} .

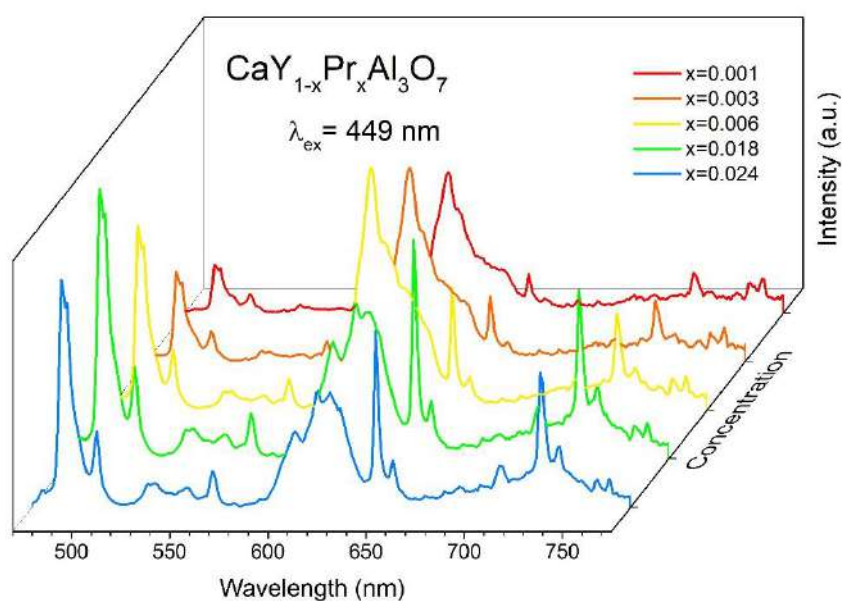


Fig 1. Emission spectra of $\text{CaYAlO}:\text{Pr}^{3+}$ as a function of the Pr concentration.

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0.4.17 Core@shell strategy to enhance green up conversion emission of LaAlO₃:Er^{III},Yb^{III} nanoparticles

Speaker: Pires Ana Maria

Core@shell strategy to enhance green up conversion emission of LaAlO₃:Er^{III},Yb^{III} nanoparticles

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Upconverter nanoparticles are currently of particular interest due to their potential application in nanobiomedicine, since lower energy photons, with greater penetrability into biological tissue, are converted into higher energy electromagnetic radiation [1]. Seeking to intensify the luminescence of these nanoparticles, one of the strategies involves their suitable coating, resulting in core@shell systems [1]. Thus, upconverter particles of LAO:Er^{III}_{0.01}, Yb^{III}_{0.01}, (LAO = LaAlO₃)^[2], average diameter of 30 nm, were obtained via modified Pechini method using citric acid and sorbitol as precursors, they were then pre-calcined at 350°C/2h and calcined at 950°C /3h, and then coated with LAO:Nd^{III} *x* at% (*x* = 10 or 30); LAO:Nd^{III} *x* at%,Yb^{III} *y* at%(*x*, *y* = 30, 2 or 30, 20). Therefore, the samples labelled as LAO:Er_{0.01},Yb_{0.01}@LAO:Nd_{0.10} or 0.30; LAO:Er_{0.01},Yb_{0.01}@ LAO:Nd_{0.30},Yb_{0.03} or 0.20 were characterized by SEM, XRD, FTIR, diffuse reflectance and photoluminescence. Focusing on the optical data, and monitoring the Er^{III} ²H_{11/2}, ⁴S_{3/2} → ⁴I_{15/2} transition in the green, emission spectra under 808 nm (500 mW) laser, that excites both Er^{III} and Nb^{III}, Fig. 1a, indicate that the samples with shell containing Yb^{III} (3 or 20 at%) induces luminescence enhancement. When a laser at 980 nm (500 mW) is used to excite directly Yb^{III}, Fig. 1b, the samples with shells containing Yb^{III} also exhibit the highest relative intensity. Kinetic measurements setting the excitation and emission windows at 980 nm and 542.5 nm, respectively, resulted in values between 56 and 68 μs of Er^{III} excited state decay, Fig. 1c. The shell, in all cases, leads to increased lifetime, although the sample with 30% of Yb^{III} exhibited a value close to the non-coated one, probably due to concentration effect. Anyway, both the presence of Nd^{III} and its combination with Yb^{III} in the shell yield to an enhancement of green emission when compared to the uncoated core. Therefore, the core@shell strategy was successful in intensifying the emission in the green, qualifying the systems produced here for biological application, especially in nanothermometry.

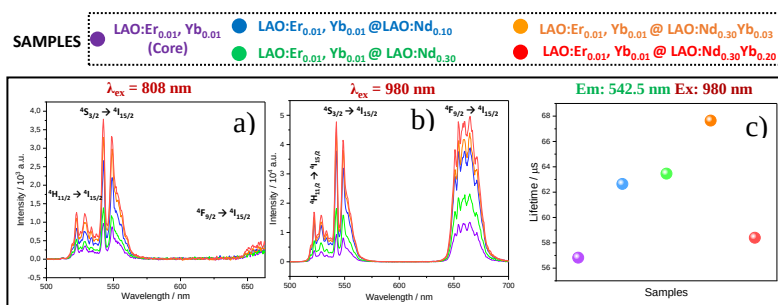


Figure 1. Emission with excitation 808 nm a) and 980 nm; transition lifetime with excitation set at 980 nm

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0.4.18 Correlation between the synthesis route and spectroscopic properties in nano and micro-crystalline Yb³⁺-doped LuPO₄

Speaker: Prokop Kacper Albin

Correlation between the synthesis route and spectroscopic properties in nano and micro-crystalline Yb³⁺-doped LuPO₄

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Rare earth-doped orthophosphates establish a considerable family of compounds characterized by different physico-chemical properties. Their high thermal stability, high insolubility, relatively cheap synthesis, and the fact that they are good host lattices for RE³⁺ ions make them a new promising matrix for inorganic luminescent materials. Among the lanthanides ions, Yb³⁺ is an optically active ion for laser applications but also very often is used as sinister in transfer energy processes. In addition, the possibility to obtain effective luminescence in the NIR region makes it attractive also from the bio-imaging point of view. So far only few papers devoted to the RE³⁺-doped MPO₄ compounds reported basic research on influence of synthesis route on structural and spectroscopic properties of obtained materials. However, that type of research is very important to full-understanding of the spectroscopic properties and modeling new efficient optical materials with potential applications.

So, taking advantage of Yb³⁺ ion as a structural probe, here we present a detailed analysis of both structural characterization and high-resolution spectroscopic properties of Yb³⁺-doped LuPO₄ in the form of nano/micro-crystalline powders crystallizing in a zircon-type tetragonal system. A series of nano-crystalline samples (0.5 – 5 mol%) was obtained by microwave-assisted synthesis. Here, the RE³⁺ nitrates and a task-specific ionic liquid (TSIL) *i.e.* choline dihydrogen phosphate (as the reactant), and an in-situ nanoparticle templating agent was employed. This protocol allowed to fabrication of fine nano-size powders exhibiting desired well-crystallized single-phase phosphate nano-materials. To comparative study, a series of micro-material obtained using the high-temperature-solid-state reaction was used. The comparison of nano and micro-crystalline materials revealed un-expected properties. Two non-equivalent symmetry sites of Yb³⁺ in LuPO₄ host were confirmed. The results were correlated to LuPO₄ activated by Nd³⁺ reported by us previously [1-3].

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Acknowledgments

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0.4.19 Correlative characterization of nanocrystals by hard X-ray nanoprobe: local chemical composition and optical dynamics

Speaker: Bonino Valentina

Correlative characterization of nanocrystals by hard X-ray nanoprobe: local chemical composition and optical dynamics

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The successful development of devices with efficient carrier dynamics in confined systems are strongly related to the local environment of the carriers. Indeed, relaxation times and recombination processes are intimately connected to undesired compositional heterogeneities, impurities and defects. This topic is addressed in two types of nanocrystals: color centers in Co-doped ZnO nanowires (NWs) and in core/shell multi-quantum wells (MQWs) of InGaN/GaN NWs with polar and non-polar facets. A multimodal approach, based on X-ray fluorescence, X-ray excited optical luminescence (XEOL) and time-resolved XEOL (TR-XEOL), is carried out to locally correlate the optical emission and the recombination dynamics with the chemical composition of the systems.

For the characterization, a hard X-ray nanoprobe with a nominal size of 50 x 50 nm² and a photon flux up to 10¹² ph/s was used at the ID16B synchrotron beamline. TR-XEOL was detected using a streak camera, with an instrument response function of 85 ps, which allows capturing the relaxation dynamics of the carrier and the related spectral emission in a single 2D image. The unique character of intense X-rays as an exciting source for optical luminescence is the excitation of both valence and core-shell electrons, yielding new relaxation paths not reachable with traditional optical sources. Moreover, intense X-rays probes, having superior chemical detection limits and the capability to resonantly excite specific atoms, provide correlative measurements between the optical emission and the local chemical composition and environment.

In Co-doped ZnO NWs, the Co-implanted profile inside the host ZnO matrix correlated well with the spatial distribution of the Co emission. A new fast radiative path, with a relaxation time of about 1.7 ns, was observed for the first time, and associated to the direct excitation of the core electrons of Co atoms by X-rays [1]. In core/shell MQWs of InGaN/GaN NWs the optical dynamics of the wells were resolved in space by scanning the NW along its length and width. From a preliminary analysis of the data, two relaxation times are observed in both polar and non-polar planes which suggest that both well thickness variations and In homogeneities may contribute to the relaxation behavior[2].

These studies highlight the potential of multimodal characterization of nanosized optical material with multiple radiative dynamics via synchrotron radiation.

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0.4.20 Crossover thermometry – The relative of classic Boltzmann thermometry

Speaker: Bendel Benedikt

Crossover thermometry – The relative of classic Boltzmann thermometry

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Luminescence thermometry has become attractive as a method for remote and non-invasive temperature sensing. Different kinds of luminescence thermometers can be used, depending on the nature of the observed optical signal [1] such as the decay time [2], the emission band position or bandwidth of the optical center [3]. A commonly used readout is the luminescence intensity ratio (LIR) of two thermally coupled excited states. Suitable phosphors for this method are based on the $4f^n-4f^n$ luminescence of the trivalent lanthanide ions in inorganic host compounds because of the narrow emission lines and high quenching temperatures. The ratio of the emission intensities arising from the excited thermally coupled levels follows Boltzmann's law, but the optimum temperature range depends on mutual intrinsic non-radiative coupling as well as the energy difference between the two excited states. This defines the dynamic working range of the luminescent thermometer [4]. The non-radiative transitions between the excited states in trivalent lanthanide ions are intraconfigurational $4f^n-4f^n$ transitions, which barely affect the equilibrium bond lengths upon excitation and emission. Many activators are, however, instead also characterized by excited states with different equilibrium configurational coordinates, which necessarily needs to a crossing point. and makes a non-radiative crossover between two thermally coupled excited states possible. Often, the intrinsic crossover transition rate is much higher than the radiative decay rate of the two states. This enables a detectable emission from the energetical higher excited state at unexpectedly low temperatures thereby increasing the both the signal-to-noise ratio and relative sensitivity [5]. It turns out that also these thermometers follow Boltzmann's law but the underlying coupling kinetics governing the dynamic working range of crossover thermometers differ from the conventional case of multi-phonon transitions. In this work, an overview over the similarities and differences of crossover thermometers compared to conventional Boltzmann-type luminescent thermometers will be presented and benefits and challenges are discussed [6].

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0.4.21 CVD Er:Y₂O₃ thin films for on-chip quantum technologies

Speaker: Anna Blin

CVD Er:Y₂O₃ thin films for on-chip quantum technologies

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Oxide crystals doped with rare-earth ions (such as Eu:Y₂SiO₅) are promising materials for quantum technologies, due to their narrow optical and spin transitions. In a context of device miniaturization, nanomaterials such as thin films and nanoparticles are advantageous alternatives to the use of bulk crystals [1]. However, their optical coherence properties are strongly influenced by defects or impurities. Controlling the crystalline quality of these layers is therefore a major challenge.

The objective of this work is to develop films with the best possible crystalline quality, or even epitaxial. For this purpose, Er:Y₂O₃ (0.067 % Er) thin films were deposited on different substrates: silicon, quartz, sapphire and yttria-stabilized zirconia (YSZ); and their impact on morphology and optical properties were assessed. The technique used is direct liquid injection chemical vapor deposition (DLI-CVD) with deposition conditions that had been optimized in a previous work [2, 3].

According to SEM images (Fig. 1 a and b) and XRD measurements, the films are polycrystalline. However, the film deposited on YSZ exhibits texturing along the [400] direction and has aligned and square-shaped grains (Fig. 1 a), whereas for the other substrates, the film grows predominantly along the [222] direction and have randomly oriented grains (Fig. 1 b). Regarding optical properties, the emission spectra at 10 K of the ⁴S_{3/2} → ⁴I_{15/2} transition (around 560 nm), as shown in Fig. 1 c), and ⁴I_{13/2} → ⁴I_{15/2} transition (around 1.5 μm) are similar for all samples, as well as the lifetimes of the excited levels ⁴S_{3/2} (564 nm) and ⁴I_{13/2} (1536 nm).

Thus, although all the samples show comparable results in terms of morphology and optical properties, YSZ appears to be the most promising substrate due to the strong texturing, and grain orientation.

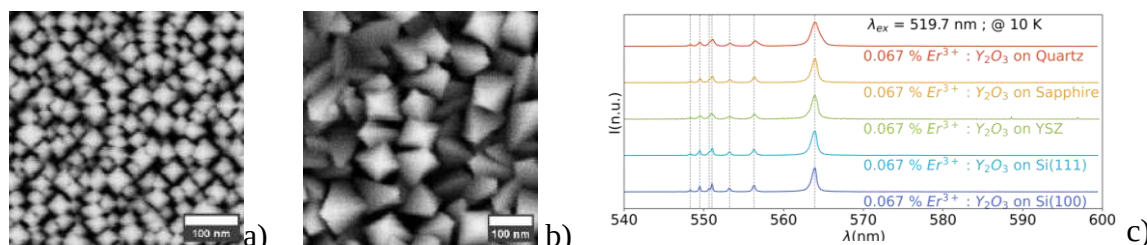


Fig. 1 SEM micro-photographs of Er:Y₂O₃ thin films on Si(100) a) and YSZ substrates b) and photoluminescence spectra of thin films deposited on several substrates c).

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0.4.22 Detection of Glucose in Homogeneous Solution and Cells Based on Quantum Dot-to-Fluorescent Protein FRET

Speaker: Fayad Nour

Detection of Glucose in Homogeneous Solution and Cells Based on Quantum Dot-to-Fluorescent Protein FRET

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Förster energy transfer (FRET) is a distance-dependent process, in which energy is transferred non-radiatively between two suitable chromophores within a 10 nm range. This mechanism has been used in a variety of genetically encoded biosensors that consist of two fluorescent proteins coupled by a sensory domain that can adjust their distance and therefore the FRET efficiency. The most common genetically encoded FRET pair consists of CFP (cyan fluorescent protein) and YFP (yellow fluorescent protein) due to the significant overlap between the emission spectrum of CFP and the absorption spectrum of YFP. On the other hand, FPs have some disadvantages, such as low brightness, photobleaching, broad emission spectra, and sample autofluorescence. Here, we demonstrate the self-assembly of the CFP-YFP FRET biosensor around CdSe/ZnS core/shell QDs. The advantages of using semiconductor quantum dots (QDs) in FRET are due to the size-tunable absorption and emission, narrow emission spectra and broad excitation spectra, high signal intensity, and good biocompatibility. Here, we study the FRET interaction between QDs and two FPs. Furthermore, we show that the QD-FRET biosensor system can be used for glucose sensing. In addition, we illustrate the intracellular conjugation of QDs and FPs, which has promising applications in biosensing and live-cell imaging.

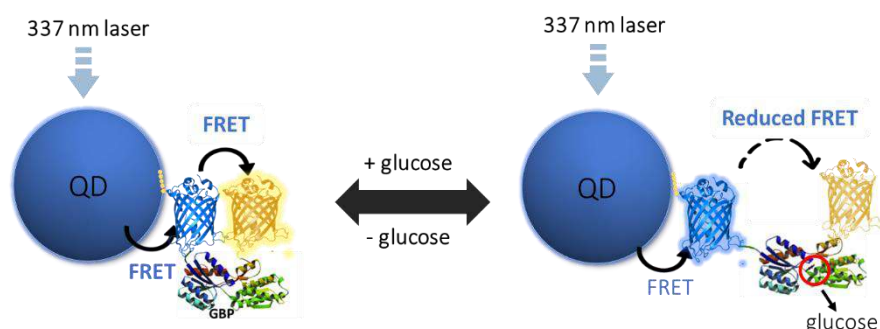


Figure. FRET interaction between QD and Fluorescent Proteins.

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0.4.23 Determination of the band alignment between CdSe and CdS from the collective absorption spectrum of core/shell CdSe/CdS nanocrystal

Speaker: Simonot Damien

Determination of the band alignment between CdSe and CdS from the collective absorption spectrum of core/shell CdSe/CdS nanocrystal

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CdSe/CdS core/shell nanocrystals are excellent nano-emitters working at room temperature with high quantum efficiency. At the individual scale, they are bright single photon sources. These quantum dots can be used as bricks in nanophotonics and quantum technology, for laser sources, or as biomarkers. The study and understanding of the luminescence mechanisms in these structures is therefore crucial. These mechanisms are dominated by the exciton wave function, the oscillator strength of the transition and its corresponding energy.

In order to determine the wave function and energy of an exciton, we theoretically solve the coupled Schrödinger equations of the electron and the hole in a spherical core/shell structure. Our model considers the diameter of the core, the thickness of the shell, the pressure effects due to the difference in lattice parameter between CdSe and CdS, the ligands surrounding the nanocrystals, the alignment of the bands between CdSe and CdS, also called offset. This parameter, crucial for determining the emission characteristics of nanocrystals, remains undetermined in the literature, its value being estimated to be between -0.3 and 0.4 eV [1]. We determine here the value of this offset by two complementary experimental methods: Our photoabsorption measurements and the XPS spectroscopy performed at the SOLEIL synchrotron give a value of the offset between the CdSe and CdS close to 0.2 eV, thus answering an important question for predicting the emission properties of these nanocrystals.

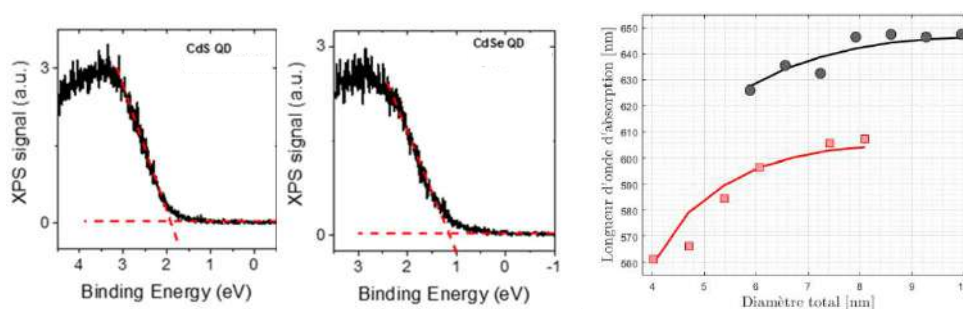


Figure 1: a) and b) Photoemission signal relative to the valence band for large core CdS and CdSe nanocrystals c) Experimental and numerical wavelength of the fundamental transition of core/shell nanocrystal. From different CdSe core of 4nm and 6 nm, 1 to 6 monolayers of CdS are added.

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0.4.24 Development of disilicate-based persistent luminescent thin films

Speaker: Bonturim Everton

Development of disilicate-based persistent luminescent thin films

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Luminescent materials have a strong impact on the new technologies related to photonics and their worldwide applications. Considering the role of thin films in the industry as the higher area of uniform monolithic and dense materials (Fig.1a), it's important to develop new routes to produce persistent luminescence (PersL) systems, one of the most important photonic materials on energy storage, signaling, and solar cells fields.[1] In this work, the $\text{Sr}_2\text{MgSi}_2\text{O}_7\text{:Eu}^{2+},\text{Dy}^{3+}$ (SMSO) was synthesized *via* the co-precipitation method followed by thermal annealing using the microwave-assisted solid-state method (MASS), aiming to obtain a purest and most efficient PersL powder material (Fig.1b).[2] The particulate was dispersed in a media of ethylcellulose/terpineol to prepare a homogeneous and stable suspension that was used to do the deposition of the thin film via spin-coating. The thin films were heated at 400 °C for 3 h to eliminate the organic phase from the final sample. The interface between the substrate and PersL thin film with around 240 μm thick shows a significant adhesion when observed by SEM cross-sectional fracture profile (Fig.1c). The luminescence spectrum of the thin film shows a high emission broadband, centered at 480 nm, assigned to the transition of Eu^{2+} (Fig.1d). Thus, we have demonstrated the viability to produce ceramic thin films that shows emission in a blue region with persistent luminescence.

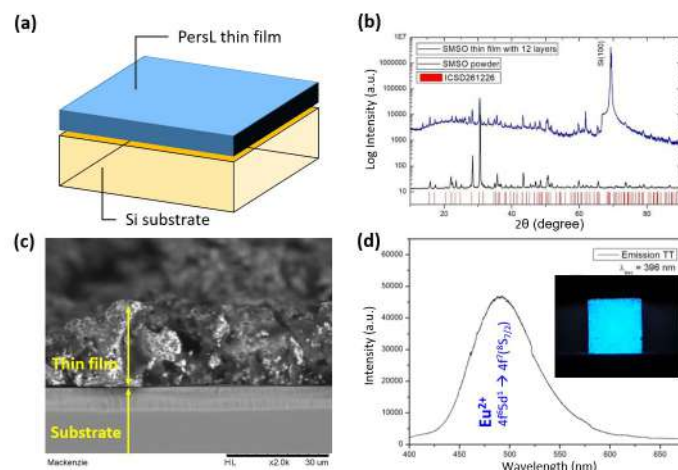


Figure 1 – Schematic of (a) persistent luminescent (PersL) thin film deposited on Si substrate, (b) crystallographic phase analysis by XRD of $\text{Sr}_2\text{MgSi}_2\text{O}_7\text{:Eu}^{2+},\text{Dy}^{3+}$ powder and its thin film form, (c) cross-section SEM analysis of the sample and (d) the photoluminescence emission spectrum and the photography insert of the thin film after heating-treatment.

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0.4.25 Development of luminescent K₂O-P₂O₅-WO₃-V₂O₅-Eu₂O₃ glasses and glass-ceramics

Speaker: Chornii Vitalii

Development of luminescent $\text{K}_2\text{O-P}_2\text{O}_5\text{-WO}_3\text{-V}_2\text{O}_5\text{-Eu}_2\text{O}_3$ glasses and glass-ceramics

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Glass-ceramics (GCs) are composite materials consisting of crystals located in a vitreous host. Some useful physical properties of such composites can be obtained due to a presence of interphases between a glass and crystal grains (interphase region). It can be assumed the size of interphase region and its properties are highly dependent on chemical composition of glass and crystals, synthesis procedure and further treatment (e.g. annealing). Phosphate-based glasses are known to be transparent in visible spectral range and can be considered as a good host for elaboration of optical GCs. Currently, co-sintering, sol-gel and glass crystallization methods are the most popular approaches for obtaining of glass-ceramics [1]. The main advantage of glass crystallization technique is related with close composition of glass and crystalline components that results in decreasing of a light scattering in material. The low light scattering is crucial for development of high-quality optical glass-ceramics.

In this work the glasses and glass-ceramics of $\text{K}_2\text{O-P}_2\text{O}_5\text{-WO}_3\text{-V}_2\text{O}_5\text{-Eu}_2\text{O}_3$ compositions have been prepared by conventional melt quenching and glass crystallization techniques, respectively. The samples of glass and GC have been characterized via powder X-ray powder diffraction, thermogravimetric analysis (DTA), scanning electron microscopy, energy dispersive X-ray analysis, IR, optical absorption, and photoluminescence spectroscopy.

It was found that the samples of glass-ceramics consist of $\text{K}_2\text{O-P}_2\text{O}_5\text{-WO}_3\text{-V}_2\text{O}_5$ glass host and embedded $\text{K}_2\text{Eu}(\text{PO}_4)(\text{WO}_4)$ particles of sizes about few micrometers. According to thermogravimetric analysis some small hygroscopicity is inherent for the samples studied. The glass transition temperature was found to be near 370 °C for all the samples. The IR spectra have shown the presence of PO_4^{3-} , $\text{P}_2\text{O}_7^{4-}$, WO_4^{2-} , WO_6^{6-} and VO_4^{3-} molecular groups both in the glass and GC. The Eu^{3+} - containing samples of glass and GC reveal intensive red luminescence under excitation at 365, 405, and 473 nm at room temperature. The photoluminescence is related with $f-f$ radiation transitions in the Eu^{3+} ions. The widths of some spectral lines in the GC emission spectra are comparable with ones for $\text{K}_2\text{Eu}(\text{PO}_4)(\text{WO}_4)$ crystals [2], while other lines are somewhat widened. The developed glass-ceramics can be considered as promising luminescent materials for creating light-transforming coatings for white LEDs.

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0.4.26 Development of persistent luminescence glassy composites by viscous flow sintering

Speaker: Gomes Fernandes Roger

Development of persistent luminescence glassy composites by viscous flow sintering

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Given the accelerated technological expansion, there are a growing interest in basic and applied research in physics, chemistry, and materials engineering focused on the study of new multifunctional materials and technologies for advanced applications. In this work, we studied the incorporation of persistent luminescence particles (PeL) in oxide glasses through viscous flow sintering process to obtain transparent glassy composite materials containing PeL. Furthermore, we are evaluating whether PeL dissolves into the glass matrix that can act as an impurity, which promote glass crystallization and lose materials' physical and chemical properties. Specifically, the PeL were characterized before and after its incorporation into the glasses for comparison of form parameters (size and shape), particle distribution, and their optical properties. Finally, a controlled study of X-ray damage on the PeL will be conducted at the CARNAUBA beamline of the Brazilian Synchrotron Light Laboratory (Sirius) to understand whether high X-ray flux will affect the PeL and how to control and prevent this damage to maintain the PeL properties.

0.4.27 Dysprosium(III)–Dicyanidoplatinate(II) Chains for Linking Luminescent Thermometry and Molecular Nanomagnetism

Speaker: Bonarek Paweł

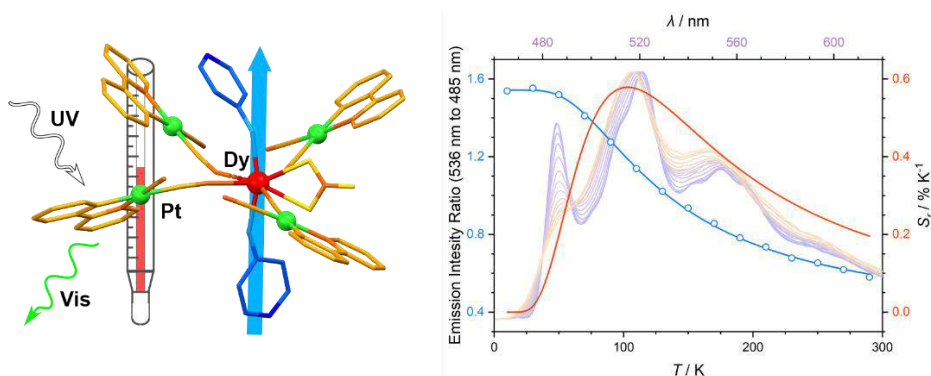
Dysprosium(III)–Dicyanidoplatinate(II) Chains for Linking Luminescent Thermometry and Molecular Nanomagnetism

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Multifunctional molecular materials are gaining attention in materials science due to their ability to combine multiple physical properties in a single-phase system, which may simplify future devices and enable currently unattainable technologies. Single-Molecule Magnets (SMMs) have the potential as ultra-dense information storage media, but require low temperatures for proper functioning.^[1] The material additionally exhibiting thermosensitive photoluminescence would allow for crucial temperature control without contact but with high sensitivity and resolution.^[2] We found that emissive polycyanidometallates of transition metals can serve as efficient metalloligands for variously functionalized luminescent lanthanide-based SMMs.^[3,4] In this study, we synthesized a family of 1-D hetero-bimetallic d-f coordination assemblies that incorporate Dy^{III} centers and [Pt^{II}(CN)₂(ppy)][−] metalloligands with the formula of {[Dy^{III}(L)₂(NO₃)] [Pt^{II}(CN)₂(ppy)]₂} · n(solvent) (L = MeOH, 4-pyridone, 4-pyridazone, 1-methylpyridin-4(1H)-one; ppy = 2-phenylpyridinato). They exhibit bright green luminescence originating from the Pt^{II}-ppy metal-to-ligand charge transfer, which is thermosensitive and suitable for use in ratiometric luminescent thermometers. The SMM effect attributable to the incorporated Dy^{III} centers was achieved by inserting additional O-donor organic ligands at the axial positions. The presented systems are unique examples of molecular luminescent thermometers linked through cyanido bridges to the lanthanide molecular nanomagnets.



The molecular fragment of the selected Dy^{III}(4-pyridone)–Pt^{II} coordination chains and their representative normalized luminescence spectra in 10–290 K (background), measured and fitted emission intensity ratios in those temperatures (blue) and corresponding sensitivity curve (red).

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0.4.28 Effect of thermal exposure on the luminescence of lanthanide doped titanium dioxide

Speaker: Alonso Nicolas

Effect of thermal exposure on the luminescence of lanthanide doped titanium dioxide

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The dependence of the luminescence of certain phosphors on the temperature and the duration of exposure during a past thermal event is a key property for off-line temperature (i.e. thermal history) mapping on engine components [1]. The present work investigated the potential of trivalent lanthanide ions-doped titanium dioxide nanophosphors for thermal history sensing. The influence of rare earth doping level and phosphor preparation method on the material structure and microstructure was studied to understand the thermosensitive photoluminescent response of the phosphor. In particular, the effects of dopant nature (Eu^{3+} , Dy^{3+} , Er^{3+} , Tm^{3+} and Yt^{3+}) and concentration (1 to 10 at. %) on the evolution of the photoluminescence signal after a short time exposure in the range 600°C-750°C was investigated. Titanium dioxide particles were synthesized by a sol-gel route. Dopant concentration was shown to significantly impact the luminescence behavior of these thermosensitive phosphors, as illustrated in Figure 1 (a) with $\text{TiO}_2:\text{Eu}^{3+}$. The relative importance of the amorphous to crystalline ratio, of the anatase to rutile phase transition, and of the crystallite growth on the evolution of the photoluminescence intensity and decay time with exposure temperature was then discussed. The structural characterization by XRD was completed by Raman spectroscopy for minor phases detection. The relative quantities of titania phases (Figure 1 (b)) and the presence of minor phases were shown to play an important role on the variation of luminescence properties.

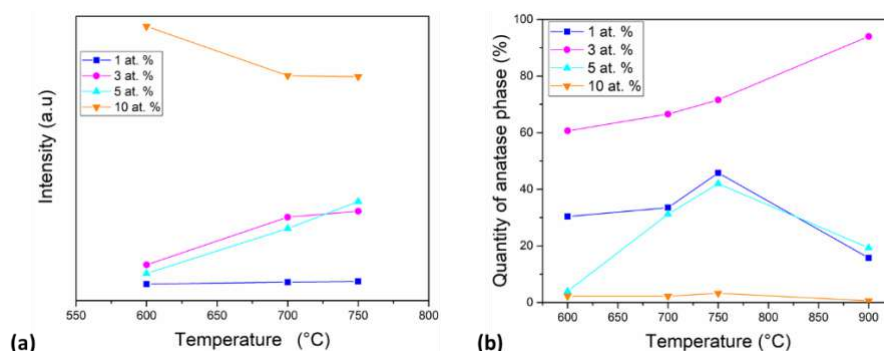


Figure 1: (a) Evolution of $\text{TiO}_2:\text{Eu}^{3+}$ luminescence intensity as a function of heat treatment temperature and (b) anatase phase

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0.4.29 Electric field-driven change in structure and luminescent properties of Eu³⁺ doped (1-x)(Na_{0.5}Bi_{0.5})TiO₃-xBaTiO₃

Speaker: Han Jaeho

Electric field-driven change in structure and luminescent properties of Eu³⁺ doped (1-x)(Na_{0.5}Bi_{0.5})TiO₃-xBaTiO₃

Presenting J. H. Han,¹ S. W. Wi,¹ E. Y. Kim², S. Y. Cho², S. D. Bu² and Y. S. Lee^{1,*}

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Recently, the idea of creating multifunctional materials that combine luminescence with electronic properties has attracted great interest. Inspired by this, we investigated the luminescent properties of Eu³⁺-doped (1-x)(Na_{0.5}Bi_{0.5})TiO₃-xBaTiO₃ (NBT-BT:Eu) relaxor ferroelectrics for x = 0.00–0.08. We found that the introduction of Eu³⁺ generated good emission properties in the samples without weakening their piezoelectric properties. Rietveld refinement structural analysis revealed that the structural phase of NBT-BT:Eu was a mixture of rhombohedral and monoclinic phases with a significant x-dependence. We observed that NBT-BT:Eu underwent a structural phase transformation upon the application of an electric field. Interestingly, the structural changes caused by poling led to a reduction in the emission of Eu³⁺. The poling-driven emission quenching behavior resulted from the increase in the local structural symmetry around Eu³⁺ in the poled samples. This correlation between the structural and luminescent properties suggests that NBT-BT:Eu has a high possibility of being used as a multifunctional optical-electric material.

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0.4.30 Elucidation of Energy Transfer and Luminescence Quenching In Eu³⁺ Doped In₂O₃ Thin Film Composition Libraries

Speaker: Zom Jeffrey

Elucidation of Energy Transfer and Luminescence Quenching In Eu^{3+} Doped In_2O_3 Thin Film Composition Libraries

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Highly efficient downshifting phosphors that can convert ultraviolet to visible light can be applied for lighting, increasing the efficiency of solar cells, and improving crop yield in greenhouses. In_2O_3 has been reported to have transfer efficiencies to doped Eu^{3+} as high as 90% [1], making it an interesting candidate phosphor. Most research proposes a Förster-type energy transfer mechanism, in which the energy of exciton trapped by oxygen vacancies is resonantly transferred to the Eu^{3+} -dopant [2]. In this work we used magnetron sputtering to create thin films of $\text{In}_2\text{O}_3:\text{Eu}^{3+}$ with a gradient thickness and doping concentration. We characterised the concentration dependent luminescent properties such as the (temperature) dependent excitation and emission spectra, emission intensity, and excited-state lifetime, to investigate the energy transfer and quenching mechanism from In_2O_3 to Eu^{3+} . We have found evidence for an energy transfer mechanism in which the divalent state of Eu^{3+} lying below the conduction band can act as an electron trap which can lead to energy transfer but is also likely the origin of the low quenching temperature.

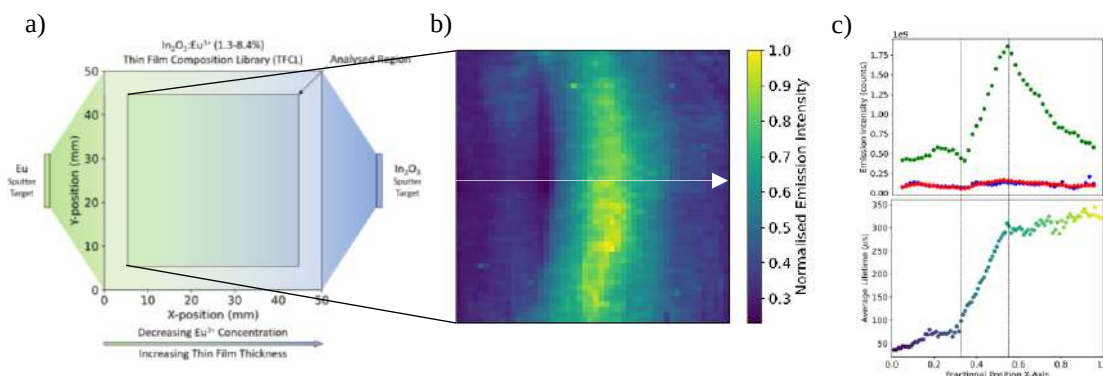


Figure 1: a) Schematic picture of the $\text{In}_2\text{O}_3:\text{Eu}^{3+}$ thin film with gradient composition. b) Normalised emission intensity of the Eu^{3+} emission as function of position. c) Emission intensity and excited-state lifetime as function of Eu^{3+} concentration (x-position dependent) showing a concentration dependent quenching and energy transfer efficiency.

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0.4.31 Enhancing red upconversion through Ce³⁺ co-doping in ultrafast synthesis of NaBiF₄:Yb, Ho(Er)

Speaker: Giordano Luidgi

Enhancing red upconversion through Ce³⁺ co-doping in ultrafast synthesis of NaBiF₄:Yb,Ho(Er)

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The study aimed to investigate the effect of Ce³⁺ ions on the upconversion (UC) luminescence properties of NaBiF₄ phosphors co-doped with Yb³⁺, Ho³⁺ (Er³⁺), Ce³⁺. The samples were synthesized through an ultrafast coprecipitation reaction technique at room temperature based on the work from Lei *et al.* [1] XRD analysis confirmed the formation of NaBiF₄ and the possible introduction of Yb³⁺, Ho³⁺ (Er³⁺), and Ce³⁺ dopants in the host materials. Under 980 nm excitation, NaBiF₄:Yb³⁺, Ho³⁺ (Er³⁺), Ce³⁺ showed the characteristic emissions of the activator cations.

Introduction of Ce³⁺ did not change the visible emission in the green and red ranges, but only their relative intensities. Furthermore, addition of Ce³⁺ cations led to a significant decrease in the average lifetimes of all monitored emissions (for Ho³⁺ and Er³⁺). This decrease was due to energy losses in non-radiative pathways after the introduction of Ce³⁺. The Ce³⁺ effect, enhancement the red UC emission versus green UC emission, is due to the good energy overlap between the activators manifolds and the ²F_{7/2} manifold of Ce³⁺, favoring the red emission. Mechanisms and interaction parameters are fully described. Overall, this study showed that the introduction of Ce³⁺ in NaBiF₄ phosphors co-doped with Yb³⁺/Ho³⁺ (Er³⁺)/Ce³⁺ did not significantly affect the emission features but their relative intensities and average lifetimes, increasing the red to green ratio. The green to yellow color emission change was in deep explored in NaBiF₄: Yb³⁺, Ho³⁺, Ce³⁺, presenting the most promising interest and a novel application in two-level anti-counterfeiting was proposed. [2]

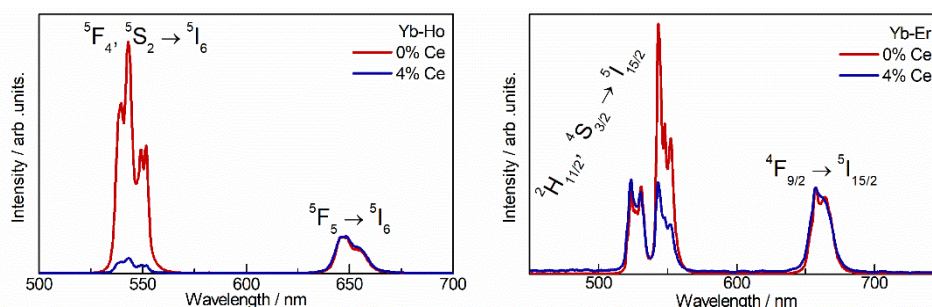


Figure. Upconversion spectra of NaBiF₄:Yb, Ho (Er), Ce, with two different Ce concentrations.

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0.4.32 **Eu³⁺-doped Li₂ZnSn₃O₈ and Li_{1.6}Zn_{1.6}Sn_{2.8}O₈ stannate materials prepared via Solid-state methods for luminescent temperature sensors**

Speaker: S. N. Saula Matheus

Eu³⁺- doped Li₂ZnSn₃O₈ and Li_{1.6}Zn_{1.6}Sn_{2.8}O₈ stannate materials prepared via Solid-state methods for luminescent temperature sensors

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The development of new europium-doped inorganic luminescent materials is more than ever a reality, allowing the emergence of innovative and improved solid-state lasers, biological and forensic markers, thermal sensors, and other several products in photonic technology areas. More also, there is a growing interest in the deployment of significant energy and time-saving heating methods to obtain these materials. In this sense, the Microwave-Assisted Solid-state Synthesis (MASS) method has been highlighted by its efficient punctual heating process, generating high-purity materials, besides being able to be performed by the use of domestic microwaves^[1]. Therefore, in this work, stannate-based host matrices' properties such as their easy production, inexpensiveness, thermal stability, and favorable band gap to allow persistent luminescence phenomenon was exploited aiming their application in new photonic technologies^[2]. Luminescent materials, Li₂ZnSn₃O₈:Eu³⁺ and Li_{1.6}Zn_{1.6}Sn_{2.8}O₈:Eu³⁺ (with varied activating dopant ions concentration), were synthesized by ceramic and domestic microwave-assisted solid-state methods after gridding Li₂CO₃, ZnO, SnO₂, Eu₂O₃ precursor oxides. The materials were characterized by thermal analysis, powder X-ray diffraction, scan electron microscopy, FTIR and Raman spectroscopy. The PXRD patterns indicate the formation of the desired Li₂ZnSn₃O₈ and Li_{1.6}Zn_{1.6}Sn_{2.8}O₈ matrices phases, showing a high crystallinity. The photoluminescence properties of the materials were determined based on the excitation and emission spectra, presenting intense emission colors that vary from white to red depending on the host matrices and Eu³⁺ ion activator contribution to luminescence materials at a given temperature. The emission spectra show narrow emission bands characteristic of ⁵D₀ → ⁷F₀₋₄ Eu³⁺ transitions and a broad emission band from the host

matrix covering the 500 to 720 nm spectral range (Fig 1.a,b). In both cases, upon temperature lowering from 298 to 77 K, the intensity ratio of Eu³⁺ ions transitions - host matrix defects emission decreases, which confirms the change in the emission color of the materials at different temperatures. These optical features may be explored for applications as luminescent thermal sensors.

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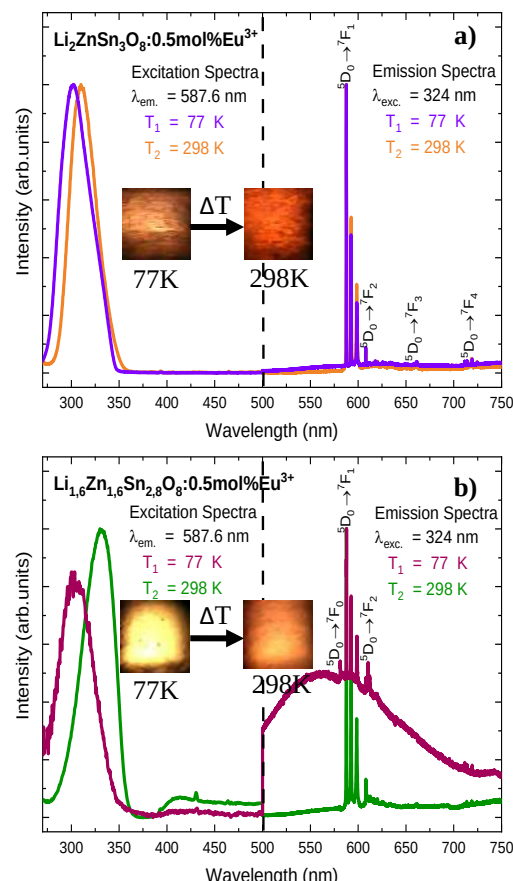


Fig 1. Excitation (left) and emission (right) spectra of Eu³⁺-doped a) Li₂ZnSn₃O₈ and b) Li_{1.6}Zn_{1.6}Sn_{2.8}O₈. The respective luminescence materials emission color at 77 and 298 K are also shown.

0.4.33 Exciton-like formations in the field of local lattice deformation by sodium impurity ions in a KCl:Na crystal

Speaker: Shunkeyev Kuanyshbek

Exciton-like formations in the field of local lattice deformation by sodium impurity ions in a KCl:Na crystal

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The mechanisms of creation and further radiative relaxation of exciton-like formations (bound excitons) in a field of local deformations of a KCl crystal matrix have been studied by the methods of optical absorption, luminescence and thermoactivation spectroscopy. Local deformation of the lattice was achieved by a targeted doping of KCl with different concentrations of Na⁺ impurity ions (0.68 Å), the ionic radius of which is noticeably smaller than that of a matrix cation (1.33 Å).

As a result, a unique effect [1, 2] of the enhancement of exciton-like luminescence bands peaked at 2.8 eV and 3.1 eV has been revealed in KCl:Na crystals. These bands are even more intense than a typical emission in classical CsI and CsI:Na scintillators, which appeared via radiative decay of excitons in regular lattice sites or due to the energy transfer from a matrix to impurities (see Fig. 1).

As a working hypothesis, it could be assumed that the X-ray luminescence bands at 2.8 eV and 3.1 eV, which significantly increase with impurity concentration in KCl:Na crystals, are associated with the exciton-like formations created at room temperature via the recombination of conduction electrons with mobile holes that undergo relaxation in the region of a local deformation of the crystal lattice by Na⁺ ions. In KCl at 80 K, the mean free path of unrelaxed holes ($90a$, a is the lattice constant) considerably exceeds the corresponding values for free excitons ($2a$).

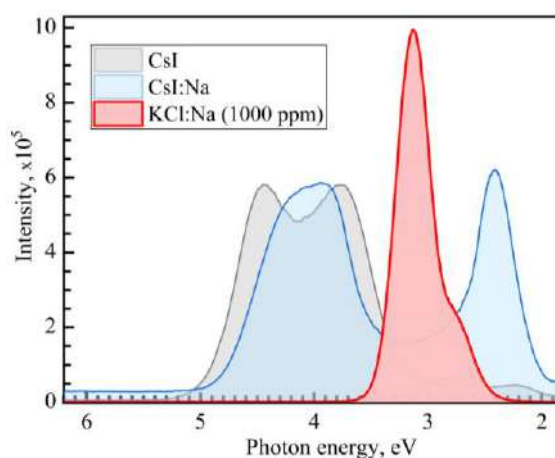


Figure 1. X-ray luminescence spectra of CsI, CsI:Na and KCl:Na scintillation crystals at 300 K.

The behavior of photoluminescence excited in the VUV spectral region by photons which directly form free anion excitons or generate electron-hole pairs in a KCl:Na crystal have been considered as well.

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0.4.34 Exploring Stretched-Exponential Decay in LuAG:Pr,Sc single-crystalline films

Speaker: Lalinsky Ondrej

Exploring Stretched-Exponential Decay in LuAG:Pr,Sc single-crystalline films

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This study presents a novel approach to modeling the cathodoluminescence (CL) decay of garnet single-crystalline structures, specifically the single-crystalline films of lutetium aluminum garnet, co-doped with praseodymium and scandium $\text{Lu}_3(\text{AlSc})_5\text{O}_{12}:\text{Pr}$ (LuAG:Pr,Sc), at high temperatures (400–490 K). The authors found that the commonly used sum of (five) exponentials was inadequate and instead used a sum of one exponential and one stretched-exponential function

$$I(t) = I(\infty) + A_0 \exp\left[-(t/\tau_0)^\delta\right] + A_1 \exp(-t/\tau_1), \quad (1)$$

considerably reducing the number of fitting parameters from eleven to six. The use of a stretched-exponential function is rare in bulk single-crystals and SCFs and has not been previously reported in garnet single-crystalline structures. The authors suggest that the stretched-exponential decay is caused by electron retrapping [1], which is stronger than radiative recombination, and may occur on predicted Sc-related traps [2]. The relative contribution of the stretched-exponential increases with increasing temperature. Using a more concise fit model not only leads to better quality fits (Figure 1) but also highlights the issue of interpreting multi-exponential fits. This work contributes to a deeper understanding of luminescence decay in garnet single-crystalline structures and has implications for future research in this area.

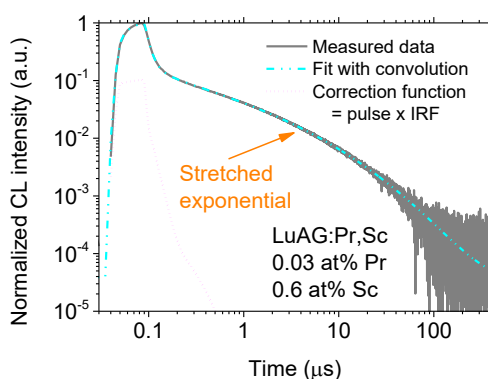


Figure 1: The CL decay of the LuAG:Pr,Sc with 0.03 at% Pr and 0.6 at% Sc at 490 K. Correction function for 50 ns and fit with convolution are also shown. The sum of one exponential and one stretched-exponential function, Equation (1) was used for the fit model.

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0.4.35 Fluorescent Nanodiamonds as Quantum Biosensors

Speaker: Su Jia

Fluorescent Nanodiamonds as Quantum Biosensors

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The development of novel quantum biosensing systems will improve the extension of measurement to the nanoscale. It helps the observation of the intracellular metabolic processes. Diamonds containing nitrogen-vacancy centers have received increasing interest. They are used in an expanding number of sensing of biophysical quantities, such as heat, magnetism, and free radicals in living organisms, due to their high biocompatibility, unique optical properties, and spin properties. However, with limitation of the intrinsic properties of nanodiamonds and the wide field optical microscope technology, detection of spontaneous process in living cell are still facing challenges by multiple correlated nanodiamonds. This work aims to expand the intracellular quantum sensing technology of nanodiamonds. We improved the coherence properties of internal defects in nanodiamonds and cooperate with surface biochemical modification. We developed a novel three-dimensional optically detected magnetic resonance technology, which helps subcellular investigation by multiple correlated nanodiamond quantum sensors. It will provide the basis for further detection of biochemical substances and micro environmental factors at the nanoscale in cells and will help explore the metabolic characteristics and related mechanisms of a series of diseases.

0.4.36 From glow to no-go: Uncovering the true thermal quenching profiles of (persistent) phosphors

Speaker: Fritz Verena

From glow to no-go: Uncovering the true thermal quenching profiles of (persistent) phosphors

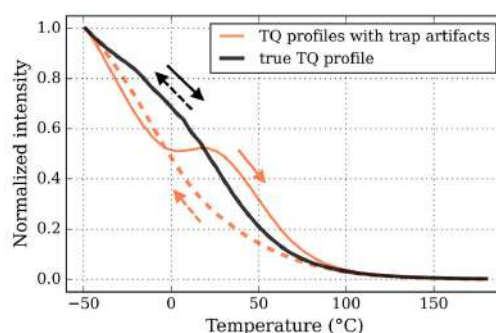
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Thermal quenching (TQ) refers to the gradual loss of quantum efficiency in luminescent materials as temperature increases. This phenomenon arises due to the thermal activation of non-radiative pathways, and poses a significant limitation to the application potential of luminescent materials [1,2]. Achieving high efficiency at elevated temperatures remains a challenging trade-off. Although numerous host-dopant combinations have been investigated over the past decades, most fail to achieve the desired thermal stability without sacrificing other desirable properties such as high absorption, short decay times, high quantum efficiency, and the desired spectral properties [3]. Accurately quantifying the TQ behavior is a crucial first step towards optimizing phosphors and overcoming these trade-offs. However, this task is complicated by the presence of traps within the material, which can introduce artifacts into the TQ profiles.

In this study, we investigate the impact of charge trapping and detrapping on TQ profiles and propose methods to remove these artifacts and uncover the true underlying TQ curves. Our findings demonstrate the need for careful consideration of trapping and detrapping processes. For the extreme case of persistent phosphors, which of course have lots of traps, we show how, once an accurate TQ profile has been established, one can straightforwardly determine the degree of non-radiative losses in the material. The proposed method offers a more robust approach to quantifying TQ behavior in luminescent materials and therefore paves the way for the rational design of luminescent materials with improved thermal stability and performance.



TQ measurements on a persistent phosphor: Trap artifacts become apparent due to the vast difference between TQ profiles during cooling (dashed line) and heating (solid line).

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0.4.37 Full control of the electric and magnetic light-matter interactions through a plasmonic mirror on a near-field tip

Speaker: Reynier Benoît

Full control of the electric and magnetic light-matter interactions through a plasmonic mirror on a near-field tip

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Light-matter interactions are often considered to be mediated by the optical electric field only, discarding the optical magnetic field. Although interactions between light and magnetic dipole (MD) transitions are very weak, they can be studied in a certain class of materials. For instance, it was demonstrated that MD-emission in Eu³⁺ could be manipulated by tuning the local magnetic quantum environment using dielectric or plasmonic nano-structures [1,2]. As well, it is possible to manipulate the excitation of the ED and MD by controlling the electric and magnetic fields' spatial distribution[3].

Here, by manipulating the spatial distributions of the electric & magnetic optical fields and their local density of states, we report the selective excitation and emission control of ED and MD transitions.

Using a scanning near-field optical microscope (SNOM), a plasmonic nanomirror at the end of an optical fiber tip is placed on top of a Eu³⁺ doped Y₂O₃ nanoparticle (Figure 1). The 3D scanning properties of the SNOM allow to couple, in space, the electric and magnetic nodes and anti-nodes of the standing wave to the electric or magnetic transitions of the Eu³⁺ ions. By collecting luminescence, we imaged both electric and magnetic nodes and anti-nodes of a standing wave (Figure 2) with their associated local density of states and demonstrated an increase in the collected luminescence by magnetic excitation with respect to a far-field excitation.

Finally, we demonstrated that we could also control the luminescence emission by manipulating the quantum environment solely through magnetic or electric excitation.

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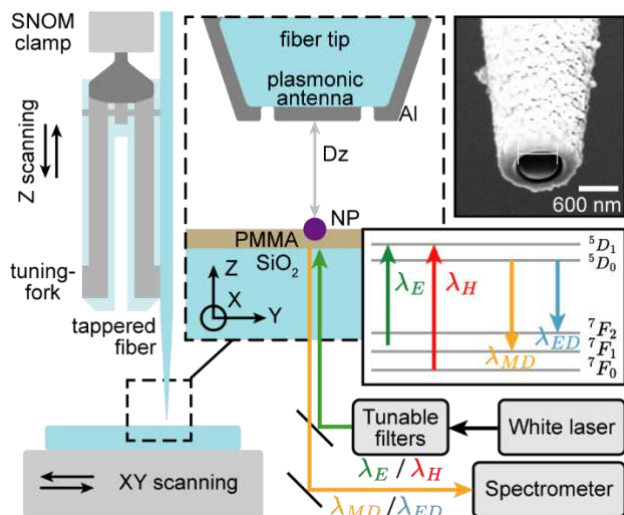


Figure 1 : Schematic of the experimental set-up. A plasmonic-mirror antenna at the end of a fiber tip is approached in close proximity to a $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ doped nanoparticle using a SNOM, which allows us to position the antenna at the nanoscale with respect to the nanoparticle. Selective electric or magnetic excitation is controlled by tunable filters. The luminescence is collected and analyzed by a spectrometer for each antenna-particle position.

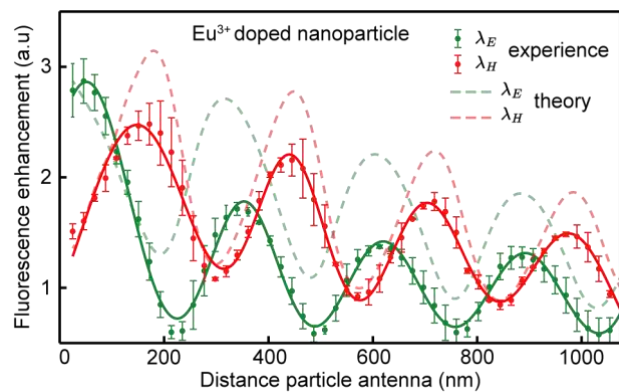


Figure 2 : Luminescence enhancement of a nanoparticle excited at either λ_E or λ_H , in function of the particle-antenna distance. The electric and magnetic nodes and anti-nodes of the standing wave are imaged.

0.4.38 Growth of GGAG:Ce,Mg in oxygen overpressure by laser-diode floating zone method

Speaker: Zajíc František

Growth of GGAG:Ce,Mg in oxygen overpressure by laser-diode floating zone method

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Oxide-based scintillators from garnet family $\text{Gd}_3(\text{Al,Ga})_5\text{O}_{12}$ (GGAG) doped by Ce^{3+} [1] exhibit a high density ($>6 \text{ g/cm}^3$), Ce^{3+} fast $5d \rightarrow 4f$ emission with a light yield approaching 60,000 ph/MeV and the fast component of scintillating decay of $\sim 60\text{ns}$ and energy resolution below 5%@662keV where all these parameters depend on Ga/Al ratio [2]. Very expensive commercial production of GGAG is carried out by the Czochralski method using costly iridium crucibles and ZrO_2 thermal shield due to the high melting point of 1800°C [3]. Due to the reactivity of the gallium oxide and cheaper Mo or W crucibles around the melting point, their use is excluded [3].

The main problem of Czochralski growth of GGAG is evaporating of volatile Ga_2O_3 from the melt [4]. This is handled by adding Ga_2O_3 to the precursor mixture above stoichiometric amounts and growth in the atmosphere containing a few percent of O_2 [5-8]. Gallium evaporation creates cation vacancies which inevitably leads to the formation of anionic vacancies and trapping centers [8]. The use of an oxygen-poor growth atmosphere leads to oxygen vacancies, which act as shallow traps [9], thus contributing to longer scintillation response [7].

We will present detailed results of first-ever use of the crucible-free Laser-Diode Floating Zone Method grown single crystals of GGAG including one codoped with Mg^{2+} . Methods was already developed and optimized by the growth of Nd:YAG [10]. LFZM has the potential to become the method of the first choice for cheap growth of single crystal scintillator and laser materials in the oxidizing environment generally unattainable by the crucible-based Czochralski and micro-pulling down methods.

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0.4.39 Heterometallic coordination frameworks based on dicyanidoaurates exhibiting rich luminescent response to temperature variation

Speaker: Boidachenko Kseniia

Heterometallic coordination frameworks based on dicyanidoaurates exhibiting rich luminescent response to temperature variation

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Metal complexes that emit light are of great interest for their use in various applications, such as optical sensors, light-emitting devices, and bioimaging.^[1,2] One advantage of using metal complexes is the ability to tune their optical properties by modifying structural parameters. In this regard, gold(I) dicyanido complexes, $[\text{Au}^{\text{I}}(\text{CN})_2]^-$, have attracted considerable attention as their strong visible photoluminescence can be modified by changing the $\text{Au}\cdots\text{Au}$ interatomic distances.^[3]

The goal of this work was to construct photoluminescent s-d bimetallic cyanido-bridged coordination systems containing aurophilic interactions generating photoluminescence tunable by external stimuli, including temperature variation. To achieve this, we combined dicyanidoaurate(I) ions with selected alkaline earth metal ions (Ca^{2+} , Sr^{2+} , Ba^{2+}) and organic ligands, 1,10-phenanthroline (phen) and 4-methyl-1,10-phenanthroline (4-Mephen). We obtained a series of six 0-D or 1-D cyanido-bridged coordination skeletons decorated with organic molecules (Figure 1). They exhibit strong photoluminescence which is strongly modulated with temperature, usually from yellow-greenish emission at 30 K to white-blue emission at 300 K, which can be utilized in optical thermometry. The rich luminescent response of obtained materials to temperature variation is demonstrated and discussed.

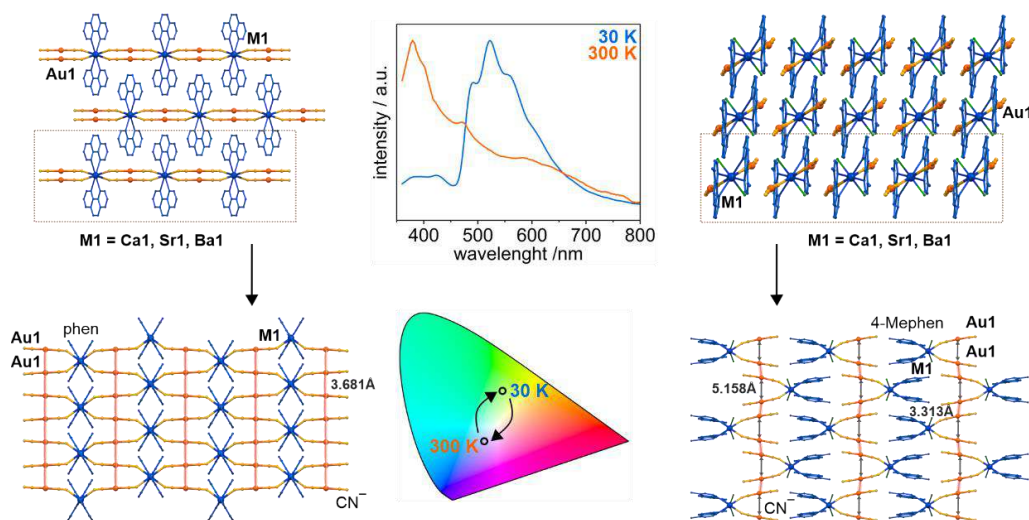


Figure 1. Crystal structures of obtained heterometallic dicyanidoaurate(I)-based coordination frameworks and the examples of representative temperature-dependent luminescent characteristics.

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0.4.40 Highly luminescent $\text{Gd}_2\text{O}_2\text{S}:\text{Er}^{3+},\text{Yb}^{3+}$ upconversion microcrystals obtained by a time- and energy-saving microwave-assisted solid-state synthesis

Speaker: Machado Ian

Highly luminescent Gd₂O₂S:Er³⁺,Yb³⁺ upconversion microcrystals obtained by a time- and energy-saving microwave-assisted solid-state synthesis

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Er³⁺- and Er³⁺,Yb³⁺-doped Gd₂O₂S are one of the most efficient upconversion (UC) systems available to date¹. However, synthesizing such materials can be challenging as several hours of heating at >1000 °C in high power furnaces (>5 kWh) are necessary². Here, the microwave-assisted solid-state (MASS) synthesis was explored as an alternative to prepare these materials, using two different precursors – lanthanide oxides Ln₂O₃ and hydroxycarbonates Ln(OH)CO₃ (Ln: Gd, Er, Yb). All UC materials were quickly obtained in 50 minutes starting from a mixture of Ln₂O₃ (or Ln(OH)CO₃), elemental sulfur, and Na₂CO₃. The Gd₂O₂S crystal structure was achieved with high purity for all materials despite the short microwave processing time. Several Er³⁺,Yb³⁺ concentrations were investigated, and the Er_(1%),Yb_(10%) combination was showed to give the most intense UC emission (Figure 1). Such UC intensity was observed to be only 3 times less bright compared to a similar commercial material with same dopant concentration.

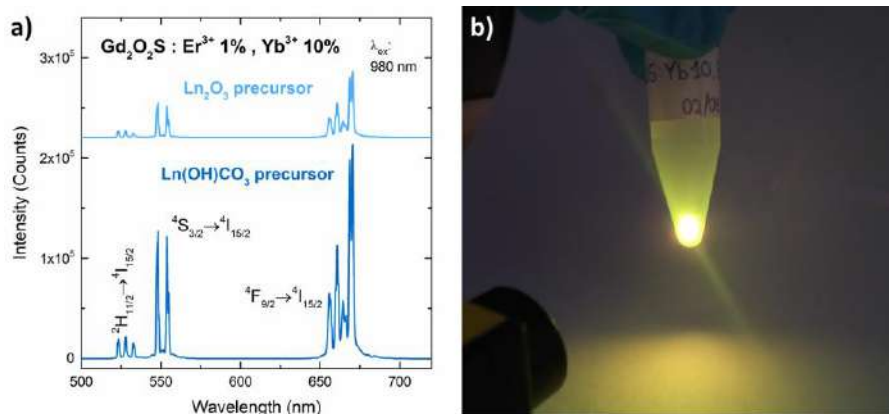


Fig. 1 (a) UC emission spectra of Gd₂O₂S:Er³⁺_(1%),Yb³⁺_(10%) materials prepared by the MASS synthesis using two different lanthanide precursors, Ln₂O₃ and Ln(OH)CO₃, where Ln: Gd, Er, Yb. (b) UC emission of the same material (Ln(OH)CO₃ precursor) under 980 nm laser excitation.

The use of Ln(OH)CO₃ as starting materials instead of Ln₂O₃ aided Er³⁺ and Yb³⁺ diffusion through the Gd₂O₂S lattice, improving doping homogeneity and enhancing UC efficiency (Fig. 1). In summary, high-quality UC materials were rapidly (50 min) obtained by a simple method using a low-power domestic microwave oven (1 kWh). This represents a 79% decrease in processing time and 93% decrease in energy consumption, without significant losses on optical properties. The MASS method was proven as a promising alternative synthesis for high performance UC materials.

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0.4.41 Imidazole based Thermally Activated Delayed Fluorescence emitters: correlating photophysical and electrochemical properties with electrochemiluminescence performances.

Speaker: Alberoni Chiara

Imidazole based Thermally Activated Delayed Fluorescence emitters: correlating photophysical and electrochemical properties with electrochemiluminescence performances.

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Thermally Activated Delayed Fluorescence (TADF) emitters represent a metal-free alternative to phosphorescent transition metal complexes in different yields, from organic light emitting diodes (OLEDs) to photocatalysis, biomedicine and, more recently, electrochemiluminescence (ECL).¹ In this contribution, new TADF emitters, showing an imidazole-based acceptor moiety and different donors, were studied, structurally characterized and tested in electrochemiluminescence using benzoyl peroxide (BPO) as coreactant. efficiency in ECL increases dramatically with increasing electrochemical reversibility of redox processes rather than with increasing quantum yield in photoluminescence. Some compounds exceed the ECL efficiency of the [Ru(bpy)₃]Cl₂ standard in the same set of reaction conditions up to 28 times.²

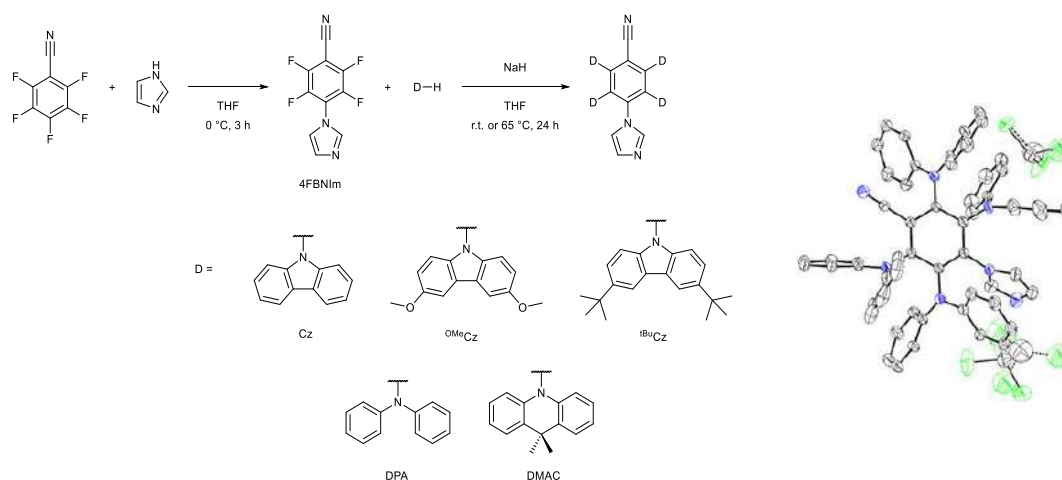


Figure. Synthetic procedures to mono-imidazole precursor and final TADF compounds and ellipsoid representation of one of them.

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Acknowledgements

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0.4.42 Importance of High Gas Barrier Layer on Self-Recovery of Photodegraded CsPbBr₃ Perovskite Nanocrystals

Speaker: Iso Yoshiki

Importance of High Gas Barrier Layer on Self-Recovery of Photodegraded CsPbBr₃ Perovskite Nanocrystals

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In our previous work, self-recovery of photodegraded CsPbBr₃ nanocrystals (NCs) was reported [1]. This phenomenon was explained by re-adsorption of surface ligands which was desorbed by excitation light. However, the ambient air prevented the phenomenon due to irreversible change in surface chemical state of the NCs by oxidation. In this work, importance of high gas barrier layer on self-recovery of photodegraded NCs was investigated [2].

CsPbBr₃ NCs were prepared by the hot-injection method using oleic acid and oleylamine. Resulting NCs were centrifuged and vacuum-dried to obtain solid samples [1]. NCs film samples were prepared as illustrated in Fig. 1. The glass plate and copolymer films of ethylene vinyl alcohol (EVOH) and ethylene vinyl acetate (EVA) were used as the sealing layer for the NCs. Reference sample exposure to the ambient air was also prepared. The film samples were irradiated by a 468 nm blue LED for 72 h, followed by dark storage for 168 h.

As exhibited in Fig. 2, glass-NCs and EVOH-NCs was blackened by the irradiation, which was attributed to generated surface defects due to the photoinduced desorption of surface ligands. Their color returned to the initial yellow, indicating re-adsorption of the surface ligands. In contrast, EVA-NCs did not show the blackening under the irradiation and self-recovery of photoluminescence. This result was similar to that of the reference sample. EVA has lower gas barrier properties compared to EVOH; therefore, oxidation of the NCs was not prevented by EVA. These verified importance of high gas barrier layer on self-recovery of photodegraded NCs.

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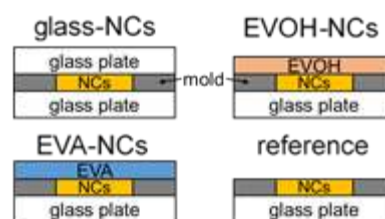


Fig. 1 Schematic structures of prepared NCs film samples.

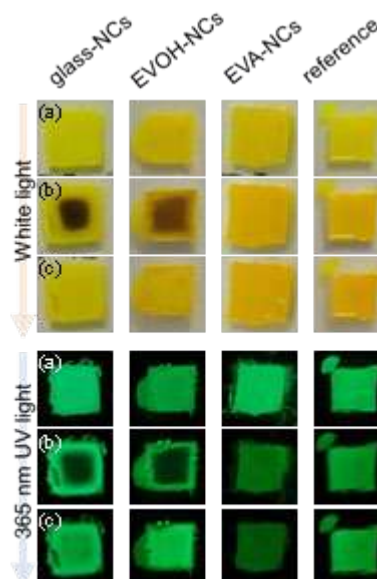


Fig. 2 Photographs of NCs film samples (a) before and (b) after 72 h LED irradiation, and (c) after following 168 h dark storage.

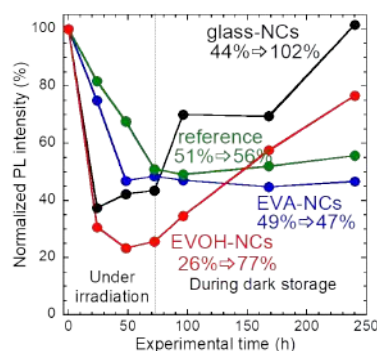


Fig. 3 Changes in normalized PL peak intensities of the NCs film samples.

0.4.43 Improved emission properties of Methylammonium Lead Bromide Perovskite films by Bathocuproine Additive for LED devices

Speaker: Coya Carmen

Improved emission properties of Methylammonium Lead Bromide Perovskite films by Bathocuproine Additive for LED devices

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Hybrid organic-inorganic metal halide perovskites (PVKs) have emerged in recent years as revolutionary semiconductor materials for lighting and photovoltaic applications, among others. Focusing on emissive applications, they are especially convenient because they present an efficient luminescence band, whose color is easily adjusted by halide selection, reaching quantum efficiencies > 20%. Besides, they are fabricated by cost-effective and low-temperature methods. However, many challenges still need to be solved, such as low operational stability. In this work, the additive engineering strategy is used, taking advantage of its solution processing capability, seeking to improve the final morphology and passivating defects between grain boundaries.[3,4] Bathocuproine (BCP) is introduced in the antisolvent step of the synthesis of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ thin films, focusing on the effect of the polar/antipolar character of the antisolvents (chloroform/toluene), and the mixture with BCP on final morphological, structural and optical properties. The introduction of BCP does not alter the crystalline structure and induces more oriented films (XRD). AFM images shows denser films with reduced grain sizes, both aspects reduce non-radiative recombination and are thus beneficial for light-emission. This is corroborated by the increase of the photoluminescence (PL) intensity upon BCP addition. Moreover, the short component of the PL decay curves (A_1 in fitting expression, $A_1e^{-(cte/t1)} + A_2e^{-(cte/t1)}$), which is related to the the presence of traps at grain boundaries, is reduced with BCP in toluene demonstrating that traps associated to defect states, are effectively reduced. BCP also increases the stability of the films maintaining almost unchanged the decay curves after 130 days while decay times are significantly decreased without the additive.

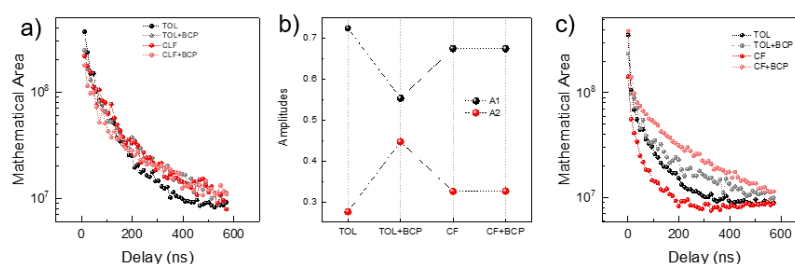


Figure 1. PL decays of MAPbBr_3 thin films trasient (5 ns, 10 Hz pulse, 290 nm excitation wavelength) for a) fresh samples, b) exponentials weights and c) PL decays after 130 days.

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0.4.44 In situ shear flow monitoring using luminescent nanorods for the characterization of ion sweeping on capacitive electrodes

Speaker: Magermans Lilian

In situ shear flow monitoring using luminescent nanorods for the characterization of ion sweeping on capacitive electrodes

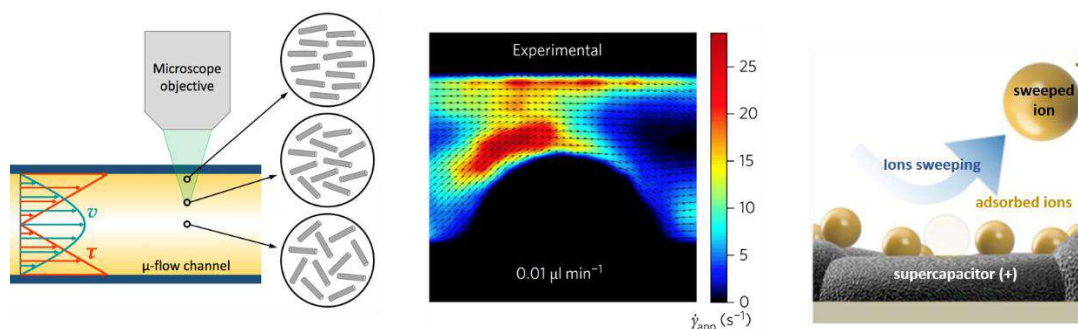
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Recently, we demonstrated an electrochemical kinetic energy harvesting system based on selective ion sweeping effect [1]. When electrolyte flows over a capacitive electrode, ions adsorbed on the electrode surface are swept away due to the interfacial shear stress. If this ion sweeping occurs at only one electrode of a circuit, it induces potential bias and can thus generate electric current. To optimize the energy harvesting efficiency, it is imperative to understand how the hydrodynamic parameters quantitatively influence on the electrochemical response of the cell. This requires shear stress measurements close to the electrode surface during the ion sweeping process.



Local photoluminescence measurements allow for flow shear monitoring in microfluidic channels which are used to characterize ion sweeping on capacitive electrodes

In this work we demonstrate *in situ* flow shear measurements using luminescent probes as a tool to characterize the ion sweeping phenomenon. We use europium doped LaPO₄ nanorods which emit strongly polarized luminescence due to their anisotropic crystal structure. By distinguishing between emission peaks originating from magnetic and electric dipole transitions, we can measure the three-dimensional orientation of the nanorods through spectroscopic measurements of their polarized luminescence [2]. When the nanorods are added to the electrolyte flowing over the electrode in the ion sweeping cell, they will collectively align due to the flow shear. Using a confocal microscope to collect the polarized luminescence of the rods, we can locally determine their collective orientation which provides a direct measure of the shear stress [3]. This allows us to characterize the ion sweeping phenomenon by making simultaneous measurements of the electrochemical response and the shear stress close to the electrode surface.

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0.4.45 Incorporation of a Flavin Derivative into Al-based Metal-Organic Frameworks for the Sensing of Nitro-containing Compounds

Speaker: Vollrath Annette

Incorporation of a Flavin Derivative into Al-based Metal-Organic Frameworks for the Sensing of Nitro-containing Compounds

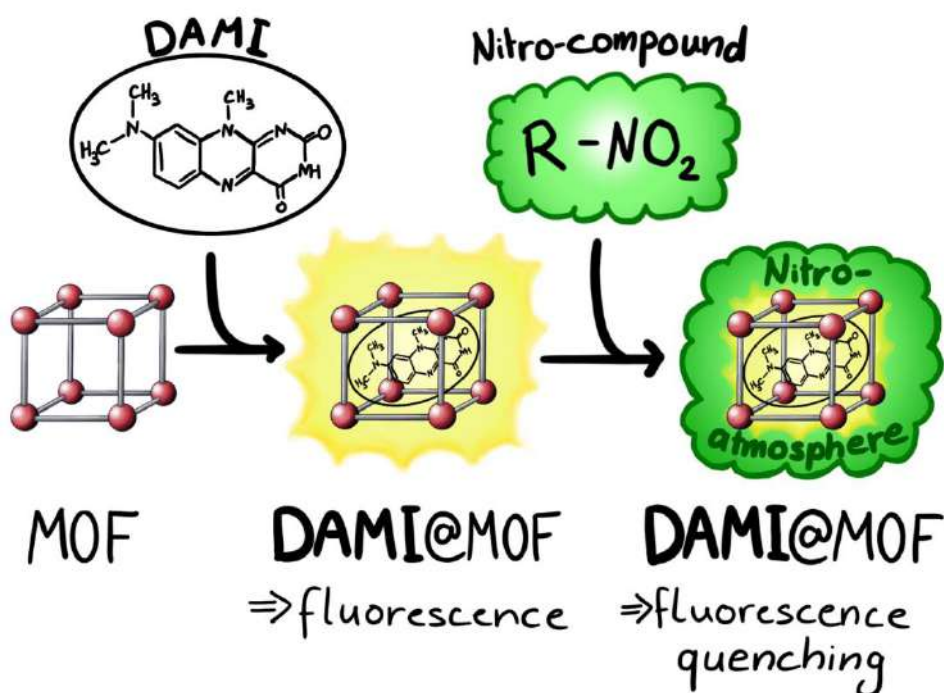
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The incorporation of the flavin derivative 8-(dimethylamino)-10-methylisoalloxazine (**DAMI**) into Al-based metal-organic frameworks (MOFs), namely DUT-4, DUT-5 and MIL-53, by a post-synthetic method was investigated. **DAMI** shows no fluorescence in the pure solid state, only in solution. In addition to the two phases of the dye as a pure solid and a liquid solution, the “solid solution” was investigated as a third phase using the dye@MOF compounds as an example. By incorporating the flavin derivative into the defined porous metal-organic frameworks, altered photophysical properties of the dye were observed. Thus, the fluorescence of the dye was affected by the rigid MOF environment. After testing different chemicals, only nitro-containing compounds could quench the fluorescence intensity of the composites. This leads to a possible application of the dye@MOF composites as sensors for nitro-containing compounds.



0.4.46 Influence of co-dopants on the persistent luminescence of $\text{CaYGaO}_4\text{:Eu}^{2+}$

Speaker: Kaaroud Khadija

Influence of co-dopants on the persistent luminescence of CaYGaO₄:Eu²⁺

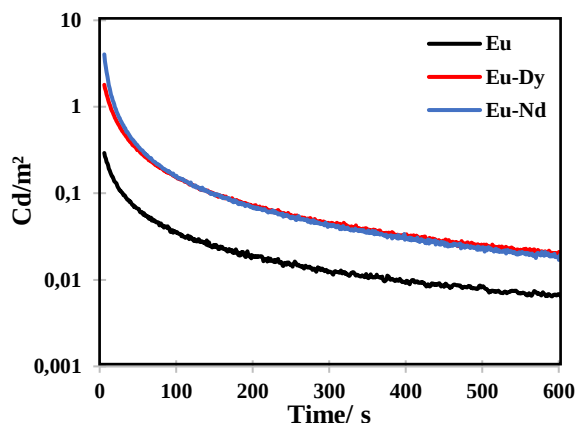
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Persistent luminescence refers to the long-lasting luminescence of phosphors after exposure to visible light, ultraviolet (UV) or ionizing radiation [1]. During this excitation, traps are being filled, which are then slowly thermally emptied. Persistent luminescent materials, which can demonstrate an afterglow with a duration from seconds to hours, [2], are widely used in different fields as emergency signs, photocatalysis and bioimaging.[3-4]

In this study, a systematic investigation was carried out on the Eu²⁺ doped CaYGaO₄ phosphors, especially the influence of Eu²⁺, Dy³⁺, and Nd³⁺ in persistent luminescence were discussed. The CaYGaO₄:Eu²⁺, CaYGaO₄:Eu²⁺, Dy³⁺ and CaYGaO₄:Eu²⁺, Nd³⁺ phosphors were synthesized by a solid-state reaction process under reducing CO atmosphere [5]. Compared with other reducing atmosphere methods, the process using activated carbon allows a much larger reduction of Eu³⁺ to Eu²⁺. Our findings demonstrate that the CaYGaO₄ phosphor doped with Eu²⁺ shows an efficient red emission at 650 nm, as a result of transitions from the Eu²⁺ 4f⁶ 5d¹ electronic state. Doping with appropriate amounts of Dy³⁺ and Nd³⁺ significantly improves the afterglow properties of the phosphors, where the red emission spectra are observed, which is assigned to the Eu²⁺ ions transition. The doping of Nd³⁺ and Dy³⁺ changes the trap density. The trap depth varied slightly with different dopants, thus offering a way to improve the afterglow behaviour. The thermoluminescence analysis (TL) glow curves will be reported, as well as the influence of the excitation wavelength on the trapping.



Afterglow decay curves on CaYGaO₄:Eu²⁺ persistent phosphors with different co-dopants.

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0.4.47 Influence of triplet-triplet annihilation in ^6Li -loaded liquid scintillators

Speaker: Watanabe Akito

Influence of triplet–triplet annihilation in ⁶Li-loaded liquid scintillators

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In certain organic scintillators, neutron and γ -ray events are differentiated by pulse shape discrimination (PSD) based on the difference in their scintillation lifetimes. Because neutron events are strongly affected by the delayed emission via triplet–triplet annihilation (TTA), control of the contribution of the TTA process plays a crucial role in attaining superior PSD capability. In typical binary organic scintillators, the TTA process is activated by adding a high concentration of phosphor.¹ However, concerning PSD capabilities, all that has been done so far is no more than an insufficient discussion on a PSD capability for discriminating the signals of fast neutrons and γ -ray, and therefore, the measurement for thermal neutrons, which can be efficiently detected by a neutron capture reaction with ⁶Li, should be elucidated. Herein, we investigated the PSD capability for detecting thermal neutron events in a ⁶Li-loaded multicomponent liquid scintillator.

For the PSD experiments, we used a scintillation liquid, composed of toluene, methanol, lithium-6 salicylate, DPO, and POPOP. Here, DPO concentrations, added as a primary solute, of 5, 30, 50, and 100 g/L were investigated, and the scintillation pulse caused by the irradiation using a ²⁵²Cf neutron source was recorded under the condition wherein the neutrons were decelerated by a polyethylene block. Subsequently, two-dimensional histograms of the pulse height were generated by placing the prompt and delayed signals of the pulse on the horizontal and vertical axes, respectively.

Fig. 1 shows the two-dimensional histograms. One aligned set derived from γ -ray events was observed for all samples. By increasing the DPO concentration to 30 g/L, another spot ascribed to thermal neutron events appeared above the γ -ray signals. This spot is further separated from the γ -ray signals by increasing the DPO concentration to 100 g/L. The higher DPO concentration increases the physical collision possibility of DPO; neutron and γ -ray events were distinguishable in the high-concentrated DPO samples. This result indicates that the control of TTA is effective in obtaining efficient PSD capability even for thermal neutron events.

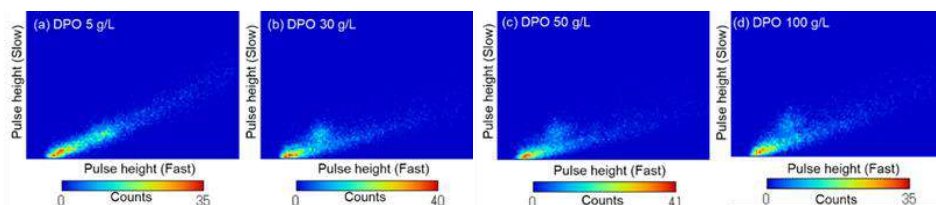


Figure 1. Two-dimensional histograms of pulse height: (a) 5, (b) 30, (c) 50, and (d) 100 g/L DPO.

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0.4.48 Interdependence of structural and compositional parameters on up-converting hafnia nanoparticles

Speaker: Guichard Xavier

Interdependence of structural and compositional parameters on up-converting hafnia nanoparticles

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NIR-Vis up-conversion (UC) plays a key role in many emerging applications such as theranostics, solar energy harvesting, sensing and others.^[1] While rare earth (RE) up-conversion luminescence in fluoride nanoparticles is extensively studied,^[2] fewer reports are available on RE-doped metal oxide-based UC nanoparticles, despite their higher chemical stability. In particular, HfO₂ nanocrystals seem to be a promising alternative because of their high stability and biocompatibility.^[3] Nevertheless, the polymorphism observed in hafnia when high RE doping levels are used, prevents a clear understanding of the parameters relevant for controlled and improved UC. Therefore, a finer control over doping levels and crystal structure is necessary to optimize the optical performance.

In this work, we studied the influence of structural and compositional modifications on the up-conversion luminescence (UCL) recorded in Er/Yb co-doped hafnia nanocrystals obtained by a colloidal solvothermal synthesis. The up-conversion characteristics of the materials were monitored in dependence of structural parameters such as crystal size and lattice symmetry, determined by means of X-ray diffraction and transmission electron microscopy (TEM), and originating from the multifunctional doping.^[4] We report that the cubic polymorph of hafnia expresses much higher up-conversion efficiency with respect to monoclinic nanoparticles. On the other hand, the elemental analysis carried out by TEM energy dispersive X-ray spectroscopy (EDS) allowed us to correlate the composition of Er/Yb/Lu:HfO₂ with the main UC features like efficiency and the ratio between green and red emission deriving from radiative recombination on Er³⁺ centres. Moreover, the experimental platform described here allowed us to possibly explain the inhomogeneity of doping in mixed polymorphs by analysing UCL profiles as probes of the local rare earth environment. These results give useful insights about the phenomena responsible for UCL alteration in hafnia nanocrystals, allowing their employment in various fields, thanks to improved UC intensities and control over the emission profile.

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0.4.49 Intimate phosphors mixing: can energy transfers tune persistent luminescence?

Speaker: Bondi Roberto

Intimate phosphors mixing: can energy transfers tune persistent luminescence?

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Persistent luminescence (PersL) refers to long-lasting photon emission, from seconds to hours, arising from charge storage and release. PersL mechanism typically involves host, emitters (rare-earths or transition metals) and traps (lattice/intrinsic defects or intentionally introduced co-dopants), being both PersL spectral features and decay kinetics ruled by phosphor composition and structure.^[1] Indeed, under excitation, charge carriers are created and subsequently trapped. Trapped charge carriers can be released from traps by external physical stimulations, and further recombine to generate luminescence. After excitation ceases, photons emitted following thermal charge carriers recombination (at RT) leads to so-called PersL. Since PersL covers a multitude of applications, to meet practical demand, different strategies like tune-depth or conduction band engineering have been employed to tune phosphors PersL emission, excitation and decay kinetics.^[2] In this work, instead of using these generic strategies, SrAl₂O₄:Eu²⁺, Dy³⁺ commercial PersL phosphor were intimately mixed with nanoparticles featuring intense fast decaying luminescence (ZnS prepared by hydrothermal method, Fig.1) or persistent luminescence (CaS:Eu²⁺, Dy³⁺, prepared by high temperature co-precipitation method) in different spectral regions, to investigate on energy transfers effect on PersL properties.

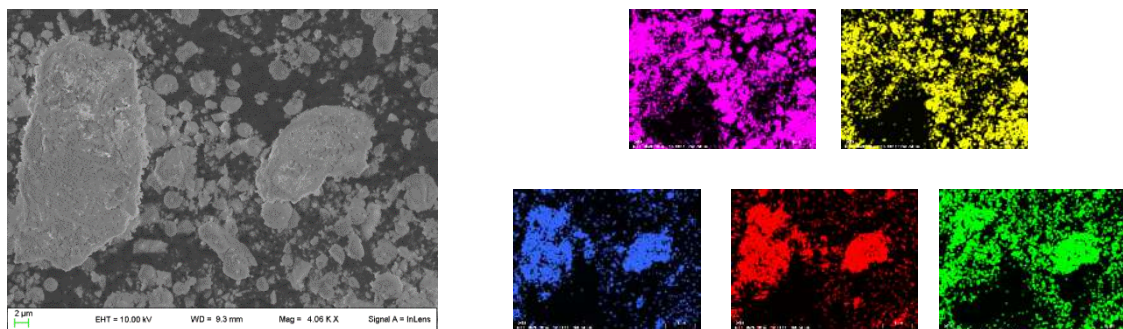


Figure 1: SEM Images of ZnS particles (spherical shape) into the SrAl₂O₄:Eu²⁺, Dy³⁺ crystals. Elements are highlighted with different colours: Zn (purple), S (yellow), Sr (blue), Al (red) and O (green).

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0.4.50 Investigating the role of particle aggregation state in phosphor emission brightness

Speaker: Fond Benoît

Investigating the role of particle aggregation state in phosphor emission brightness

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Luminescent thermometers based on lanthanide or transition metal doped inorganic phosphor particles are proven to be promising materials for contactless temperature detection. In many applications, such as in biomedical imaging or flow imaging, low particle concentrations are used forming an optically thin system. In those systems, particle brightness plays a crucial role in measurement performance. Regardless of the application, emission signal levels of phosphors are often reported in bulk powder state. Nevertheless, a previous research study showed that comparing the brightness of two different phosphors, such as ZnO and (Ba,Mg)Al₁₀O₁₇:Eu²⁺, can yield very different results when probed in dilution and bulk powder [1]. In this work, we explore further the extent and the reasons for those differences. First, we investigate whether such effect can also bias the determination of optimum concentration for a single host using luminescent particles based on Nd³⁺/Er³⁺ lanthanide ions sensitized with various doping concentration of Cr³⁺ transition metal ion. As shown in Fig. 1, the luminescence intensity continues to increase with dopant concentration in the liquid dispersion while it reaches a maximum at 10% Cr³⁺ in bulk powder form. The optimum dopant concentration is therefore dependent on the probed state. To explain this phenomenon, we also performed quantum efficiency and absorption cross section measurements. We devised an absorption measurement method based on determining light attenuation in liquid dispersion at two different wavelengths to separate the contribution of Mie scattering and absorption to the extinction. The results showed that the quantum efficiency has a maximum at 10% Cr³⁺ while the absorption cross section increases linearly with concentration. Therefore, we can conclude that the brightness in the dispersed state is directly related to the product of particle absorption cross section and quantum efficiency, while in bulk powder, the dependence on the absorption cross section is sublinear, due to the

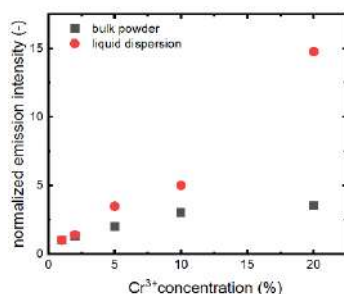


Fig.1 Luminescence intensity in bulk powder and liquid dispersion for Y₃Al₅O₁₂: high optical

thickness of the state.

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0.4.51 Investigation of the Sm^{2+} site occupation in the perovskite type system MCaCl_3 ($\text{M} = \text{K}, \text{Rb}, \text{Cs}$)

Speaker: Fischer Pia

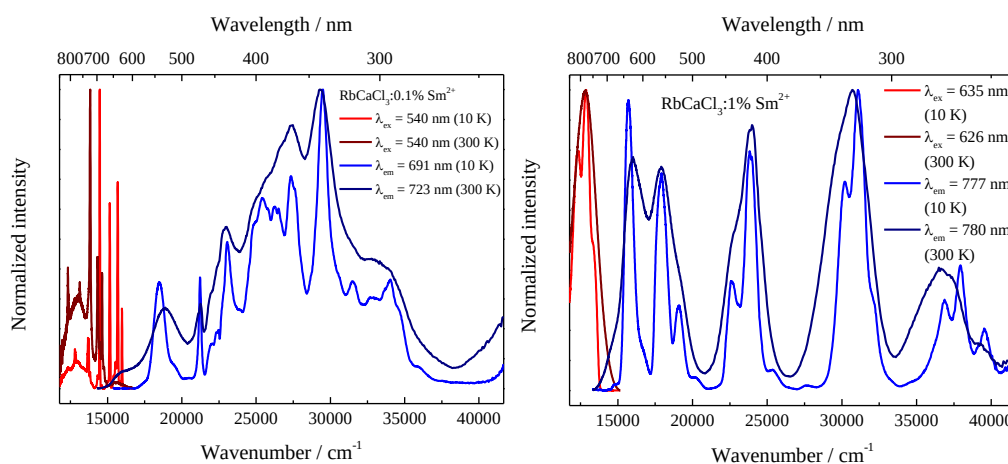
Investigation of the Sm²⁺ site occupation in the perovskite type system MCaCl₃ (M = K, Rb, Cs)

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Even if the luminescence properties of divalent lanthanides are of great interest in the recent research, the focus is on Eu²⁺ in most studies.^[1] Nevertheless, Sm²⁺ shows very interesting properties which help to investigate structure property relationships.^[2,3] Regarding similar or identical structures, the influence of different factors on the luminescence of Sm²⁺ can directly be observed. Here, the luminescence properties of the perovskite type compounds MCaCl₃:Sm²⁺ (M = K, Rb, Cs) are presented for the first time focussing on the influence of the doping concentration on the crystallographic site occupied by Sm²⁺. Despite there is only one crystallographic Ca²⁺ site in the crystal systems emission from two independent sites was detected. Therefore both, alkaline and alkaline earth cationic sites are occupied by Sm²⁺ which leads to 4f⁶→4f⁶ and 4f⁵5d¹→4f⁶ emission features. The preference for a site depends on the size of the alkaline cation but also on the doping concentration. Regarding the low temperature excitation spectra together with the site symmetries helps to unambiguously assign the transitions to the respective crystallographic position.



Excitation and emission spectra of RbCaCl₃:0.1%Sm²⁺ (left) and RbCaCl₃:1%Sm²⁺ (right). 4f⁶→4f⁶ as well as 4f⁵5d¹→4f⁶ emission bands originating from two different sites are detected.

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0.4.52 Luminescence and scintillation properties of GSAG:Ce garnet films

Speaker: Kucera Miroslav

Luminescence and scintillation properties of GSAG:Ce garnet films

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Scintillation materials with short decay time and low afterglow are crucial for applications requiring fast response, such as high-rate imaging techniques, medical applications, or electron-beam inspection systems [1]. Here, scintillation, luminescence, and optical properties of Ce³⁺ activated multicomponent gadolinium scandium garnet, Gd₃Sc_xAl_{5-x}O₁₂:Ce with variable Ce and Sc contents, $x=1.7-2.1$ and Ce=0.04–3% were studied, Fig. 1. The single crystalline films were grown by liquid phase epitaxy from the BaO flux [2]. Substitution of Sc for Al resulted in the narrowing of the optical band gap due to the mixing of 4s scandium states at the bottom of the conduction band. This in turn led to the reduction of the thermal quenching temperature. The combined effect of Sc and Gd substitution increases the crystal field resulting in a red emission shift to 555 nm. The co-doping with divalent Mg²⁺ ions significantly accelerated the decay kinetics from 58 to 3 ns, Fig. 2, reduced the afterglow signal, and decreased the light yield.



Fig. 1. GSAG:Ce samples with various Ce content from 0 to 1%

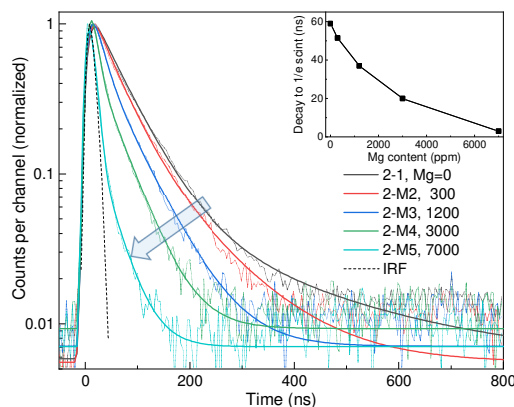


Fig. 2. Scintillation decays of GSAG:Ce,Mg with various Mg²⁺ co-doping. The inset shows decay time as a function of Mg content.

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0.4.53 Luminescence based Circular Dichroism

Speaker: Markovic Obren

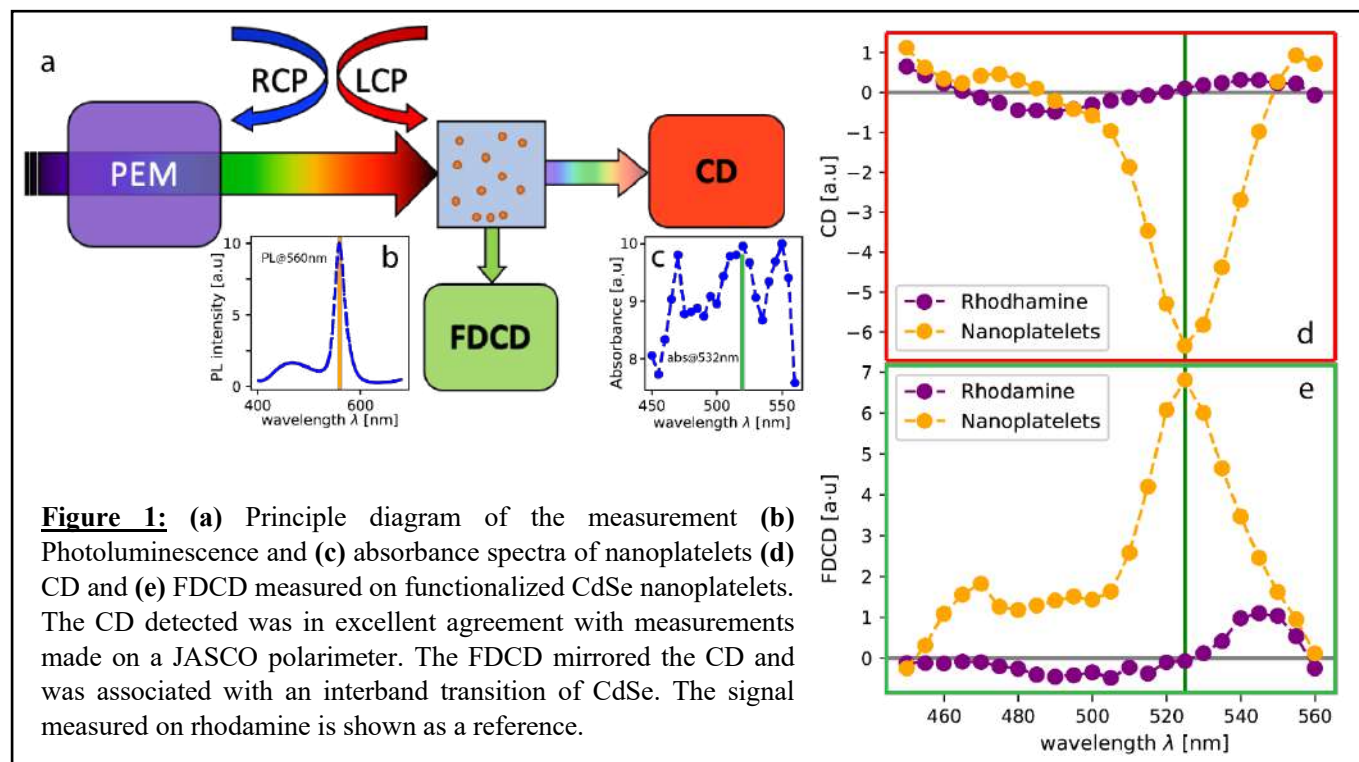
Luminescence based Circular Dichroism

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Sensitive and enantiomer-selective detection of chiral molecules is an important issue for many fields, including biology, chemistry, and the pharmaceutical industry. Indeed, chirality is a common property for both natural and synthetic molecules, leading to potentially very different effects depending on the enantiomer. Most of the current detection methods are based on circular dichroism (CD) spectroscopy – the quantification of the differential absorption of left and right-handed circularly polarized light – and consist in measuring the transmission of an incident beam through the chiral medium. However, this approach requires large volumes of solution and is intrinsically limited in sensitivity. Here, we propose a method to measure CD based on detecting the photoluminescence of chiral fluorescent emitters instead of absorption. Indeed, for low excitation powers, the differential emission of the two enantiomers is equal to their differential absorption, and therefore their CD spectroscopy can be performed on the luminescence signal. In this case, photoluminescence can be collected on very small volumes involving very small amounts of chiral objects, and consequently, very high sensitivity can be achieved. As an example, we show in **Figure 1**, the CD signals recorded in absorption, (c) and (d), and emission, (b) and (e), for fluorescent chiral nanoplatelets (1D confinement quantum dots) and compare them to the case of an achiral molecule, the rhodamine.

This circular dichroism detected by fluorescence can find applications in monitoring the grafting dynamics of chiral molecules, even at the single-molecule level. Moreover, it can be applied to molecules in their natural environment, such as living cells. Coupled with nanophotonics techniques to generate superchiral light, this new approach will also allow detecting CD in zeptoliter volumes [1]



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0.4.54 Luminescence Concentration Quenching in Nitrogen-doped Graphene quantum dots

Speaker: Da Silva Davinson

Luminescence Concentration Quenching in Nitrogen-doped Graphene quantum dots

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The investigation of the luminescence mechanisms originated from carbon-based quantum dots has been a fruitful research subject in recent years [1]. However, even though the synthesis processes to obtain highly efficient graphene quantum dots (GQDs) with redshifted photoluminescence (PL) have been improved, few works have exploited the occurrence of luminescence concentration quenching (LCQ) in suspensions based in GQDs. The aim of this work is to investigate the occurrence of LCQ of graphene quantum dots doped with nitrogen (GQDN), synthesized from sucrose, and dispersed in different solvents. The synthesis of graphene quantum dots doped with nitrogen (GQDN) was started with the carbonization of sucrose, obtained from refined sugar. Initially, an aqueous solution of sucrose (1g/mL) was prepared. Sulfuric acid was added to the solution in a 2:1 ratio. Approximately, 4 g of the carbonaceous material from the reaction was subjected to a reflux in 20 mL of nitric acid for 4 hours, in order to promote the formation of GQDN. Then, the nitric acid was evaporated and the resulting nanoparticles were dispersed in 3 different solvents: dimethylformamide (DMF), dimethylsulfoxide (DMSO) and isopropyl alcohol (C₃H₈O). The PL of the samples was investigated using a CaryEclipse / Varian spectrofluorometer. The results showed that GQDN dispersions in polar protic solvents (H₂O and C₃H₈O) present PL in the blue region (480 nm), when excited in the UV region, between 340 and 360 nm. On the other hand, GQDN dispersed in polar aprotic solvents (DMF and DMSO), showed a broad emission band, which extended from 450 to 600 nm, approximately, when excited between 400 and 550 nm. LCQ of GQDN suspensions was evaluated for the first time. The study showed that in suspensions prepared with DMF and DMSO, LCQ occurred when GQDN concentrations exceeded 1.12 g/L and 2.65 g/L, respectively. In samples prepared in H₂O and C₃H₈O, PL did not exhibit LCQ within the range of investigated concentrations. The occurrence of LCQ is commonly attributed to energy transfer mechanisms between the fluorophores. In high concentrations, the luminescence may be quenched due to the rise of nonradiative relaxation. Results of GQDN incorporated to SiO₂ powders obtained from sol-gel synthesis will also be shown. Recent results of the group have shown that the occurrence of LCQ may be interesting for random lasers [2, 3]. We also believe that the results presented herein may be employed for the optimization of graphene quantum dots suspensions for several applications, such as sensors, WLEDs, and lasers.

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0.4.55 Luminescence of organic compounds for the detection of nerve agents and its simulants

Speaker: Bureau Valentin

Luminescence of organic compounds for the detection of nerve agents and its simulants

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Chemical warfare agents represent a threat to army and civilians. Nerve agents are a deadly type of chemical agents. They inhibit the acetylcholinesterase enzyme (AChE) and induce death by asphyxia. G-series agents such as sarin, tabun or soman can be used in vapor phase as in the Tokyo subway sarin attack[1]. It is mandatory to be able to detect those compounds "on site". Unfortunately, precise detection usually requires complex and bulky detection devices, difficult to transport on field. On site detection is achieved using colorimetric paper as PDF1/M8 or photoelectric flame photometer as AP4C, that present drawbacks such as false positives or limited informations. Luminescence is a way to achieve selective, rapid and precise on site detection using portable spectrofluorometers. Organic chemistry can be used to provide luminescent molecules for detection of nerve agents and simulants[2]. Thus, luminescence for detection of nerve agents gas and its simulants will be discussed. A scope of molecules combining a fluorophore moiety and a nerve agent sensor moiety has been studied. In a first step the emission and excitation features of the molecules in liquid phase before and after exposition to different concentrations of diethyl chlorophosphate (DCP), a simulant of the nerve agent sarin will be presented. In a second step, to address a practical application, the sensor molecules were included in a solid substrate and their luminescence features before and after exposition to DCP in liquid and vapour phase will be presented.

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0.4.56 Luminescence properties of Cu₂O single crystals and epitaxial Cu₂O thin films electrodeposited on metallic substrates

Speaker: Trinkler Laima

Luminescence properties of Cu₂O single crystals and epitaxial Cu₂O thin films electrodeposited on metallic substrates

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Luminescent properties of epitaxial Cu₂O thin films were studied in 10-300 K temperature range and compared with luminescent properties of Cu₂O single crystals. Cu₂O thin films were deposited epitaxially by the electrodeposition method on either Cu or Ag substrates using varying processing parameters, which determined the epitaxial orientation and encapsulated surface. Cu₂O (100) and (111) single crystal samples were cut from a crystal rod grown by the floating zone method. Luminescence spectra of thin films contain the same emission bands as single crystals around 720, 810 and 910 nm, characterizing v_O^{2+} , v_O^+ and v_{Cu} defects, correspondingly. Additional emission bands, whose origin is under discussion, are observed around 650-680 nm, while the exciton features are negligibly small, Fig.1. The relative mutual contribution of the emission bands varies depending on the particular thin film sample. Existence of the domains of crystallites with different orientation determines the polarization of luminescence. PL of both Cu₂O thin films and single crystals is characterized with negative thermal quenching in the low temperature region, the reason of this phenomenon is discussed.

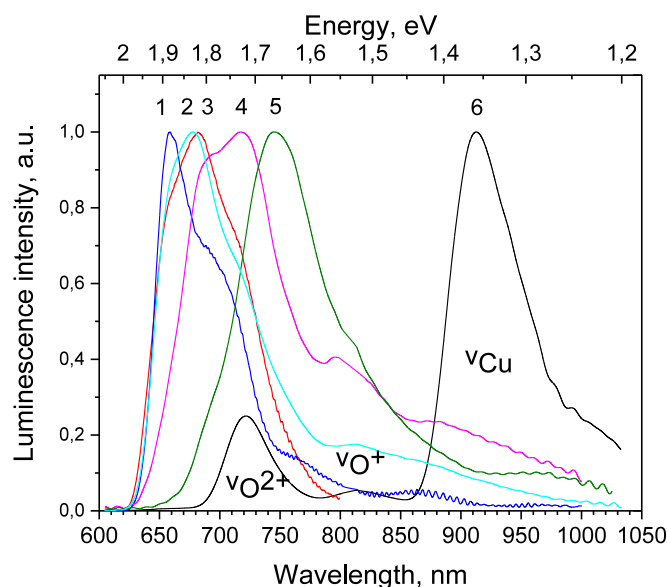


Fig. 1. Normalized photoluminescence spectra of Cu₂O samples under 532 nm at 10 K: (1-5) thin films and (6) single crystal (100) .

0.4.57 Luminescence properties of non-doped and RE-doped LiF/CaF₂ (RE = Tb, Dy, and Tm) eutectics

Speaker: Kawaguchi Noriaki

Luminescence properties of non-doped and RE-doped LiF/CaF₂ (RE = Tb, Dy, and Tm) eutectics

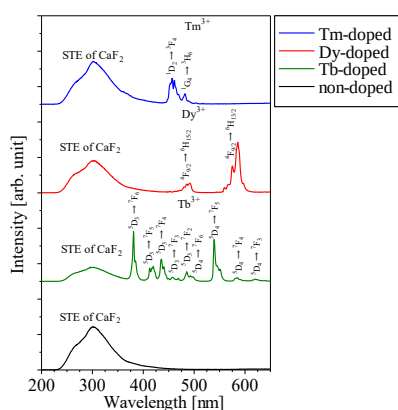
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Radiation dosimetry is one of the applications of luminescent materials. If thermoluminescence, optically-stimulated luminescence, or radiophotoluminescence intensities of the luminescent materials monotonically increase with increase in radiation dose, such luminescent materials can be utilized for radiation dosimetry. Crashed single crystals (Al₂O₃:C), glasses (Ag-doped phosphate glasses), and ceramics (Mg₂SiO₄:Tb, CaF₂:Dy, CaSO₄:Tm, and others) are used for dosimetry applications [1]. In this study, non-doped and RE-doped LiF/CaF₂ (RE = Tb, Dy, and Tm) eutectics have been investigated as the dosimetric materials. Eutectics are phase separated composites which are formed by solidification of melt having multiple phases. Since eutectics generally have lower melting points than the materials with similar composition, they have the advantage on production cost. Figure 1 shows X-ray excited luminescence spectra of non-doped and RE-doped LiF/CaF₂ (RE = Tb, Dy, and Tm) eutectics. Emission peaks due to both the self-trapped exciton (STE) of CaF₂ and 4f-4f transitions of RE³⁺ ions are observed. Figure 2 shows The thermoluminescence spectrum of the Dy-doped LiF/CaF₂ eutectic. Only the intensity of the STE emission decreases in the higher temperature range. The STE emission of CaF₂ can highly quench [2] due to thermal dissociation of the excitons. Therefore, RE-ions can increase thermoluminescence intensities of LiF/CaF₂ eutectics. Monotonic increase of thermoluminescence intensities of all the samples against X-ray doses were observed with different dose ranges. The most sensitive sample to X-rays was the Tb-doped LiF/CaF₂ which showed the monotonic increase in the range from 0.01 to 10 mGy.



0.4.58 Luminescence quenching in photonic resins for personal printable devices to monitor skin production of vitamin D3

Speaker: Vaz Elaine

Luminescence quenching in photonic resins for personal printable devices to monitor skin production of vitamin D₃

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In this work we present a printable photonic device based on luminescence quenching monitoring for personal dosimetry of vitamin D₃ production in the skin, catalyzed by solar UVB radiation, which can provide more than 90% of the daily dose needed by the human body and may be the best option to reduce this oral vitamin supplementation. The active part of the device is a 3D printable molecular dosimeter [1] in which we establish a relationship between the luminescence quenching of the $^5D_0 \rightarrow ^7F_2$ Eu³⁺ emission in a printable Eu(btfa)₃·bipy@resin composite and the UVB cumulated dose, and then with the cutaneous vitamin D₃ production catalyzed by this radiation. The conversions are performed in a cell phone that reads the Eu³⁺ transition peaked at 612 nm, under a LED excitation UVA short pulse. Figure 1A shows the $^5D_0 \rightarrow ^7F_2$ luminescence during a UVA pulse before and after 1,2 J/cm² UVB dose exposition and this quenching is converted in UVB dose as a function of UVB relative dose exposure [2] and then in the skin vitamin D₃ production [3]. The correlation with skin production of vitamin D₃ is performed by taking the printed dosimeter photonic signal as the input for calculations in a software developed here to run on a smartphone (Figure 1B). The smartphone App we developed receives the data from the printable photonic composite and takes information from users, including the proportion of exposed skin, providing the percentage achieved to reach the medically prescribed vitamin D dose level.

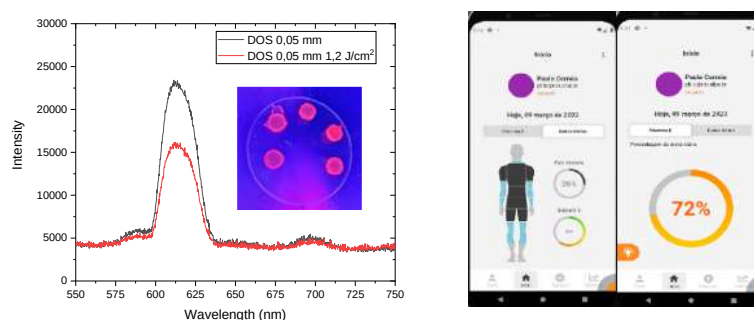


Figure 1: A) Partial quenching of luminescence from five discs printed with the photonic resin before (black line) and after (red line) exposure to a UVB dose of 1.2 J/cm²; B) Screenshot of the App that reads this luminescence through a cell phone interface and converts the luminescence suppression into skin production of vitamin D₃ for personal monitoring.

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0.4.59 Luminescent behavior of unusual Tb³⁺ tetrakis carboxylate complexes: high green emission under UVA, UVB and UVC

Speaker: Assunção Israel

Luminescent behavior of unusual Tb³⁺ tetrakis carboxylate complexes: high green emission under UVA, UVB and UVC

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Recent studies revealed that tris Tb³⁺ complexes with the carboxylate-based flufenamate anion (fluf), exhibit high intensity luminescence and has received particular attention as tris compounds ¹. To date, no flufenamate-based tetrakis Ln³⁺ complexes were reported so far. In this work, two novel tetrakis compounds with general formula Q[Tb(fluf)₄], where Q: 1-ethyl-3-ethylimidazolium (C₂mim) and benzimidazolium (Bzim) counterions were successfully synthesized and characterized by elemental and thermal analyses, ESI-MS spectrometry, FTIR spectroscopy and XPD diffraction. In addition, their photophysical properties revealed a wide range excitation comprising the UVA, UVB and UVC irradiation and characteristic narrow emission peaks centered on the Tb³⁺ ion assigned to the intraconfigurational ⁵D₄ → ⁷F₆₋₀ transitions, respectively at 489, 544, 585, 621, 646, 667 and 679 nm when excited at 254, 310 and 405 nm, as shown in Figure 1 (left) for the Bzim[Tb(fluf)₄] complex, while Figure 1 (right) shows digital photographs of the tetrakis complex under ambient light and irradiation at UVA, UVB and UVC and its green emission mainly due to the most intense ⁵D₄ → ⁷F₅ transition.

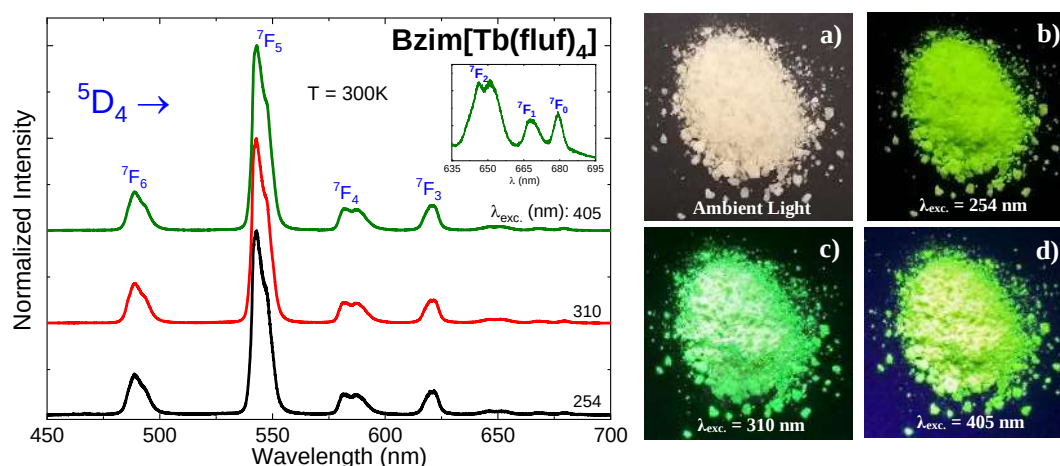


Figure 1. Emission spectra of the Bzim[Tb(fluf)₄] complex, recorded at 300 K under excitation at 254 (UVC), 310 (UVB) and 405 nm (UVA) (left) and digital photographs of the complex under ambient light (a) and excitation at UVC (b), UVB (c) and UVA (d) on the right.

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0.4.60 Luminescent properties of Ba₂MgWO₆ doped with Dy³⁺

Speaker: Vu Thi Hong Quan

Luminescent properties of Ba₂MgWO₆ doped with Dy³⁺

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This work reports the luminescent properties and the temperature sensitivity of Ba₂MgWO₆ (BMW) double perovskite doped with Dy³⁺. A series of samples doped with 0.1%-7% Dy³⁺ ions was synthesized by the co-precipitation method[1]. The unit cell volume of BMW:Dy³⁺ increased when the content of Dy³⁺ increased, which proved that Dy³⁺ ions replaced Mg²⁺ sites in the structure. Due to the structure's high symmetry site of the Dy³⁺ ions, the domination of the $^4F_{9/2} \rightarrow ^6H_{15/2}$ magnetic dipole over the electric-dipole transitions in the emission spectra was observed (Fig. 1). In addition, the energy transfer efficiency between the host and the Dy³⁺ ions increased from 54.6% to 92.3% when the Dy³⁺ concentration increased from 0.1% to 7%. All samples' 300 K chromaticity coordinates were presented on the CIE 1931 chromaticity diagram. Besides, the temperature-dependent emission spectra of the sample doped with 2%Dy³⁺ were measured from 80 K up to 300 K. The temperature sensing performance of BMW:2%Dy³⁺ was investigated based on the fluorescence intensity ratio of the host, and the $^4F_{9/2} \rightarrow ^6H_{15/2}$. The maximum relative sensitivity was found to be 2.26%K⁻¹ at 193 K. The temperature uncertainty was found below 0.2 K. The results indicated the potential application of the studied phosphor BMW:Dy³⁺ for low-temperature sensing.

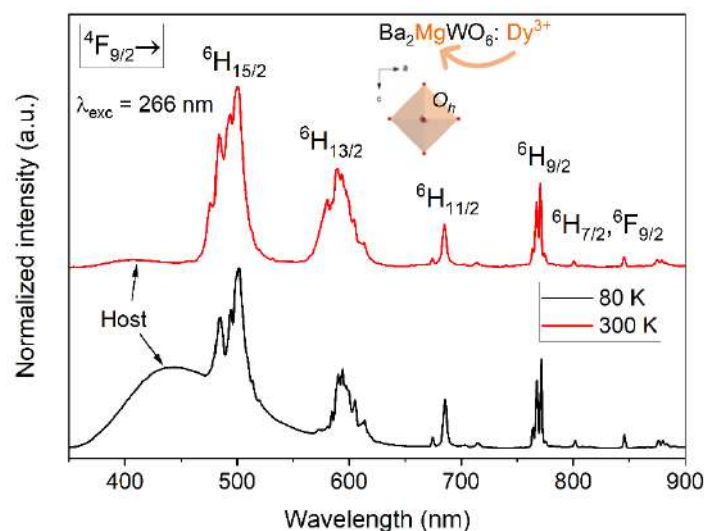


Figure 1: Emission spectra of Ba₂MgWO₆: 2%Dy³⁺ at 80 K and 300 K

Acknowledgment

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0.4.61 Luminescent reversed rib waveguides – a hybrid photonic platform based on sol-gel technology and polymers

Speaker: Duda Łukasz

Luminescent reversed rib waveguides – a hybrid photonic platform based on sol-gel technology and polymers

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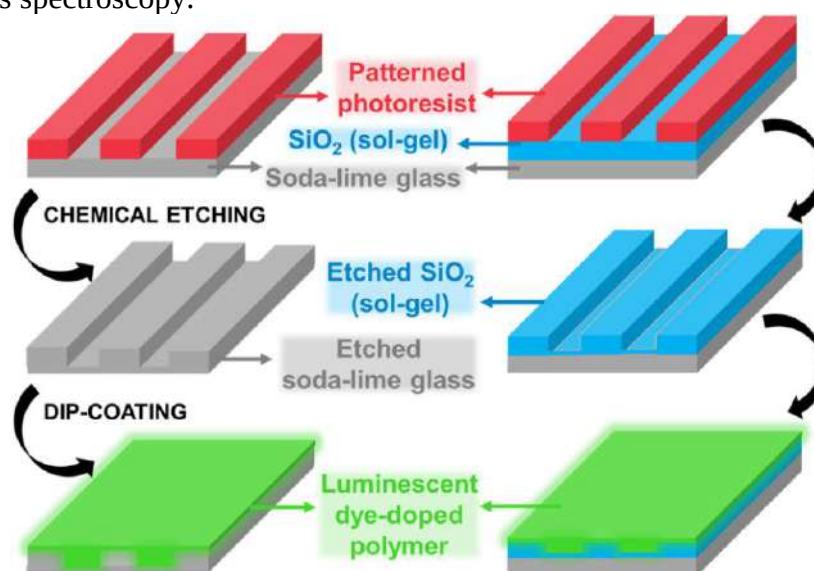
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The most common methods for fabrication of waveguide structures in photonic integrated circuits (PICs) are wet chemical etching and inductively coupled plasma reactive ion etching (ICP-RIE). An advantage of the chemical etching over the second technique is its simplicity and cost effectiveness. Additionally, a deposition of an active material *e.g.* dye-doped polymers into fabricated photonic structures may be used for construction of integrated photonic devices such as solid-state lasers [1].

In this work we present a comparison of the wet-chemical etching of soda-lime glass substrates and SiO₂ layers, which were deposited on the substrates using the sol-gel process and dip-coating method. The etching rate and quality of the etching for both type of samples was compared. In the fabricated grooves, a dye-doped polymer with refractive index higher than the refractive index of the substrate was deposited using the dip-coating method as presented in Figure below. Modal characteristics of the fabricated waveguides were obtained using numerical calculations. Moreover, the luminescent properties of the fabricated structures were investigated using the UV-Vis spectroscopy.



Process of fabrication of reversed rib waveguides using dye-doped polymers on wet-etched soda-lime glass or SiO₂ on soda-lime glass.

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0.4.62 Luminescent thermometers based on SHG-active magnetic cyanido-bridged frameworks exploring UV-vis light absorption of Nd³⁺ ions

Speaker: Zakrzewski Jakub

Luminescent thermometers based on SHG-active magnetic cyanido-bridged frameworks exploring UV-vis light absorption of Nd³⁺ ions

Jakub J. Zakrzewski,^{1,*} Junhao Wang,^{2,3} Robert Jankowski,¹ Hiroko Tokoro,² Shin-ichi Ohkoshi,³ and Szymon Chorazy¹

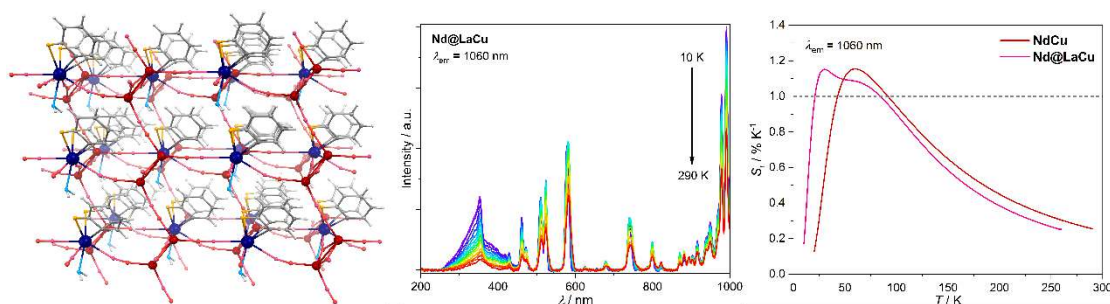
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Functional molecule-based materials employing d- and f-block metals are broadly investigated from the viewpoint of various optical, magnetic, and electrical phenomena, as well as their conjunction, being the result of the molecular origin of the employed building blocks.^[1–3] Among them, recent advances in optical thermometry, investigated as a potential pathway for temperature sensing in novel electronic devices, medical diagnostics, or chemical reactors, direct scientific attention towards the employment of non-standard spectroscopic characteristics as the source of the output, temperature-variable optical signal.^[4] Due to their versatile intrinsic properties, lanthanide(3+) ions are often used, and apart from the temperature-sensitivity of emission intensity ratio between two luminophores,^[5] lately single-centered luminescent thermometers have been recognized to potentially offer high thermal sensitivity.^[6] In this context, we aimed to find a route towards molecule-based materials employing Nd³⁺ emission for sensitive optical thermometry and focused on systems built with polycyanidocuprate(I) units that additionally offer efficient generation of the second harmonic light. As the result, we present optical thermometry based on the *T*-variable excitation spectra and the multi-functional nature of the obtained materials related to magnetic and NLO properties.



Structural view and temperature-variable optical properties of Nd³⁺-based polar coordination frameworks incorporating polycyanidocuprate(I) metalloligands.

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0.4.63 LumStimAge project: Application of thermally and optically stimulated luminescence imaging in dating and characterisation of heritage objects.

Speaker: Zink Antoine

LumStimAge project: Application of thermally and optically stimulated luminescence imaging in dating and characterisation of heritage objects.

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The Centre de Recherche et de Restauration des Musées de France (C2RMF) has acquired, with funding from Île de France region, a system of thermally stimulated luminescence (TL) and optically stimulated luminescence (OSL) imaging of heritage materials. It will lead to expand our knowledge of the mechanisms implemented in dating and of the properties of archaeomaterials: control of the homogeneity of the grains within a sample; distribution of radioactivity – microdosimetry, identification of hot spots; emission characterization (reproducibility, stability over time, sensitivity); research on hybrid materials, identification of phosphors and their dosimetric and luminescent characteristics; evolution of the luminescence according to the degrees of heating; study of the kinetics of luminescence. We plan to do by developing the potential of TL / OSL imaging to achieve sufficient sensitivity to quantify light intensity of each grain, even for young samples. The use of TL/OSL imaging is challenging due to the low light intensity and the fast kinetics of the observed phenomena, but also because of optical aberration phenomena due to the proximity between luminescent grains [1,2]. The project includes the physical optimization of the detection, calibration, signal-to-noise measurement system, but also the development or the adaptation of image processing algorithms to obtain a measurable intensity with a good spatial resolution.

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0.4.64 Manganese(2+) ions in the design of multifunctional molecular materials exhibiting humidity-sensitive photoluminescence

Speaker: Hoffman Aleksander

Manganese(2+) ions in the design of multifunctional molecular materials exhibiting humidity-sensitive photoluminescence

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In recent years molecule-based materials exploring coordination complexes of earth-abundant metals, such as manganese, chromium, iron, or cobalt, have evoked increasing scientific interest due to their potential in substituting rare-earth or precious heavy transition metals for applications in organic light-emitting diodes (OLEDs), optical storage, and optical sensing, as well as due their broad set of accessible magnetic, magneto-optical, and magneto-chiral functionalities.^[1–6]

Herein, we present a novel multifunctional luminophore based on Mn(II) complexes with Me-dppmO₂ (bis(diphenylphosphino)-1,1-ethane dioxide) ligands, that is a hybrid organic-inorganic salt, [Mn(Me-dppmO₂)₃]MnCl₄ (**1**), that crystallizes in a polar Cc space group, which invokes SHG phenomena (Figure 1). The presented material exhibits also a series of humidity-sensitive physical properties, including strong yellow (maximum at ca. 560 nm) photoluminescence in the solid state at room temperature (Figure 1), slow magnetic relaxation effects below 10 K, and the dielectric relaxation switchable by the presence of water molecules of crystallization in the material. The humidity sensing potential of this system, considered from the viewpoints of its optical, magnetic, and electrical properties, is discussed.

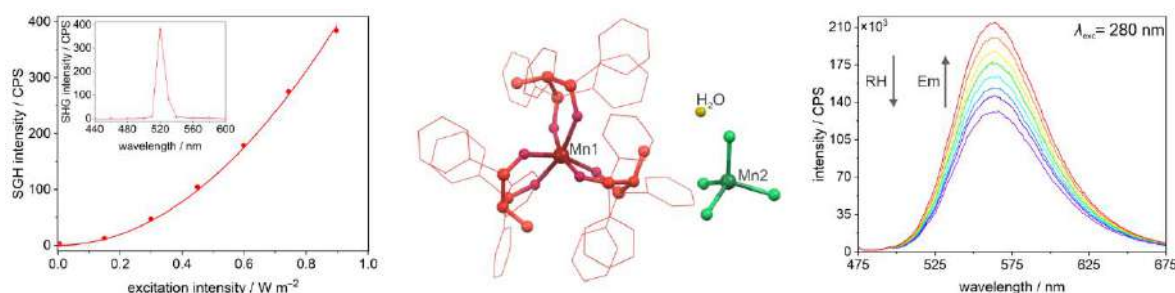


Figure 1. Room-temperature SHG signal of **1** presented within its laser power dependence as well as the wavelength dependence in the inset (left), the crystal structure of **1** (center), and the relative-humidity-dependent solid-state photoluminescence spectra at room temperature (right).

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0.4.65 Mn⁵⁺ activated A₅(VO₄)₃Cl (A = Sr²⁺, Ba²⁺) apatite phosphors for Near-Infrared luminescence thermometry

Speaker: Mullins Abbi

Mn⁵⁺ activated A₅(VO₄)₃Cl (A = Sr²⁺, Ba²⁺) apatite phosphors for Near-Infrared luminescence thermometry

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Biological applications for luminescence thermometry require both excitation and emission to pass through the skin. Biological window 2 (BW-2: 1000-1350 nm) allows for the greatest depth of penetration.¹ Mn⁵⁺ is one of the few transition metals that emit within this range alongside having transitions that allow for BW-1 (650-950 nm) excitation.²

The apatite structure A₅(BO₄)₃X (*P*₆₃/*m*) contains three cation sites (A1, A2, B) and one anion site (X) which allows for many possible chemical formulae and differing structures that can affect site symmetries and crystal field strength.

A₅(V_{1-x}O₄)₃Cl:Mn_x (A = Sr²⁺, Ba²⁺; x = 0.01, 0.03, 0.05) were synthesized first by solid-state method to establish the ideal Mn⁵⁺ concentration of x = 0.03. Sol-Gel synthesis was then employed alongside addition Cl reagent to give pure samples.

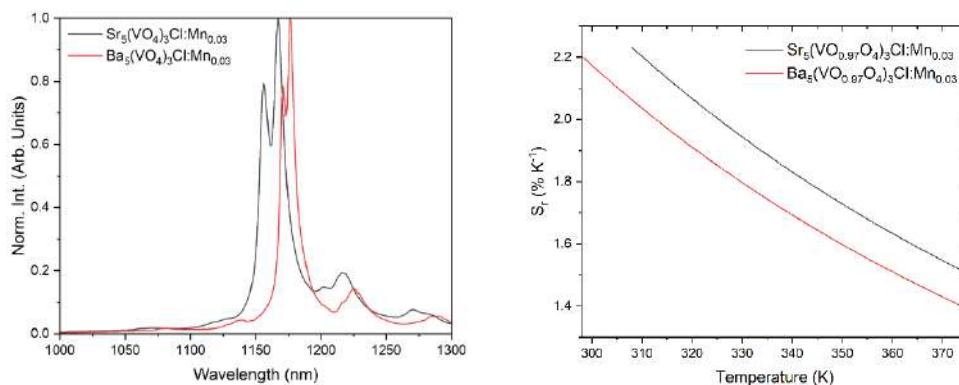


Figure 1: a) Mn⁵⁺ emission of A₅(V_{0.97}O₄)₃Cl:Mn_{0.03} (A = Sr²⁺, Ba²⁺); b) Calculated relative sensitivities.

Variable temperature thermometric analysis was undertaken on Sr₅(V_{0.97}O₄)₃Cl:Mn_{0.03} and Ba₅(V_{0.97}O₄)₃Cl:Mn_{0.03}. LIR thermometry of the ³T₂/¹E emission bands produced relative sensitivities of 2.2% K⁻¹ and 2.1% K⁻¹ respectively at 308K. Average temperature resolution was calculated to be 0.15 K and 0.34 K respectively at 308K. Quantum yields were found to be 46.8% and 50.5% respectfully.

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0.4.66 Molecular Design of FR/NIR Emitting Materials for Bioimaging and Utilization of Host-Guest Interactions as a Way of Increasing Fluorescence Intensity

Speaker: Smolka Rastislav

Molecular Design of FR/NIR Emitting Materials for Bioimaging and Utilization of Host-Guest Interactions as a Way of Increasing Fluorescence Intensity

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Photoluminescent materials based on organic conjugated molecules have been attracting considerable attention for decades due to their unique optical properties, color-tunability, and potential application in various fields [1]. The intense solid-state fluorescence (SSF) is desirable for light-emitting field-effect transistors, organic light-emitting diodes (OLEDs), or water-dispersible nanoparticles for bioimaging. In this study, emphasis will be placed on the characterization of photoluminescence materials and their potential use as nanoparticles for *in vivo* bioimaging. Fluorescence imaging has advanced biological and biomedical research, most notably fluorescence-guided surgery (FGS) [2]. The utilization of fluorescence imaging faces limitations typical for biological samples. To overcome these limitations, novel photoluminescence materials capable of fluorescence in the FR/NIR region are presented. By utilizing FR/NIR emitting materials, fluorescence imaging benefits from decreased self-fluorescence and the reduction of light scattering. Moreover, NIR light demonstrates exceptional penetrability in biological tissue. This allows for higher optical contrast and reduced photodamage. In this study, to obtain NIR fluorescence, an intramolecular electronic transition of charge-transfer (CT) character is utilized. This transition takes place in electron donor-acceptor (DA) systems. Unfortunately, such systems result in narrow band-gap organic materials and inevitably lead to reduced solid-state fluorescence quantum yields due to the promotion of intramolecular non-radiative processes. To overcome this, reduction of exciton migration via self-trapping is pursued. Crystal engineering methods are used to achieve either excimer-type NIR fluorescence or utilize so-called host-guest systems (HG), in which the effect of resonance energy transfer increases the solid-state fluorescence quantum yield of a fluorophore beyond its usual level. Such systems are deployed in the form of nanoparticles, showing increased QY of new π -conjugated fluorescent molecules based on derivatives of DPA-DPS-EWG [3] (DPA – diphenylamine; DPS – 2,5-diphenyl-stilbene building block; EWG – electron withdrawing group), such as DPA-DPS-IOO (IOO – indandione) from 5 % to 14 % at 693 nm. This demonstrates the potential of such an approach as a way of obtaining nanoparticles with increased fluorescence intensity in the FR/NIR region, which is desirable for their application in NIR bioimaging.

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0.4.67 Molecular design of thermally activated delayed fluorescence of phenazine-5,10-diyl-dibenzonitriles

Speaker: Püschel Dietrich

Molecular design of thermally activated delayed fluorescence of phenazine-5,10-diyl-dibenzonitriles

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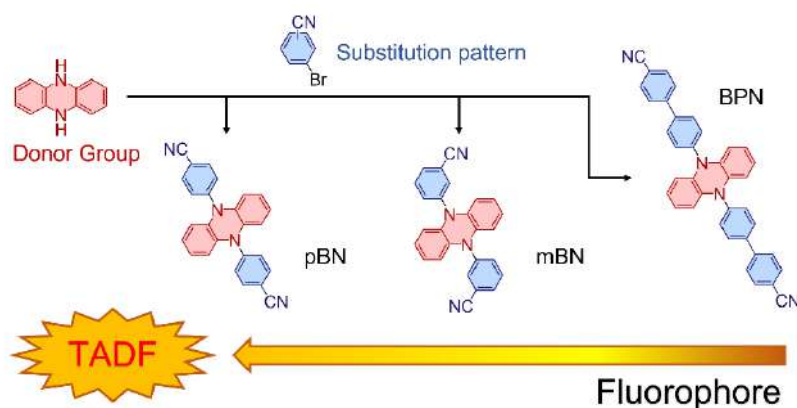
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Thermally activated delayed fluorescent (TADF) emitters are a currently emerging class of purely organic, metal-free materials with potentially 100% internal quantum yield upon electric charge carrier injection. One generally successful strategy in the design of organic TADF emitters is the covalent ligation between an electron-rich donor and electron-poor acceptor moiety in a twisted fashion. We started with an established TADF emitter, 4,4'-(phenazine-5,10-diyl)dibenzonitrile (**pBN**) reported by Adachi's group^[1] and explicitly modified structural elements of this template to investigate the impact on the TADF properties using temperature-dependent time-resolved luminescence studies, investigations of solvatochromism and advanced density functional theoretical (DFT) calculations. With a *meta* substitution pattern of the acceptor groups (**mBN**) the effective energy gap decreases to almost 0 eV ($\Delta E_{ST} < 0.01$ eV) and TADF is less pronounced. This can be assigned to the cumulative effect of both a twist between donating dihydrophenazine and accepting benzonitrile moieties but also a general overlap mismatch due to the *meta* positioning of the nitrile groups relative to the dihydrophenazine moiety. The charge transfer-type nature is still evident according to the solvatochromic studies. In contrast, introduction of additional phenylene units (**BPN**) increases the effective distance between donor and acceptor and thus, makes charge transfer ineffective. Overall, this demonstrates how the charge transfer properties mandatory for the observation of TADF in the class of dihydrophenazine-based dyes can be chemically very easily controlled and implies an important and yet chemically intuitive design principle for potential materials.



Graphical abstract

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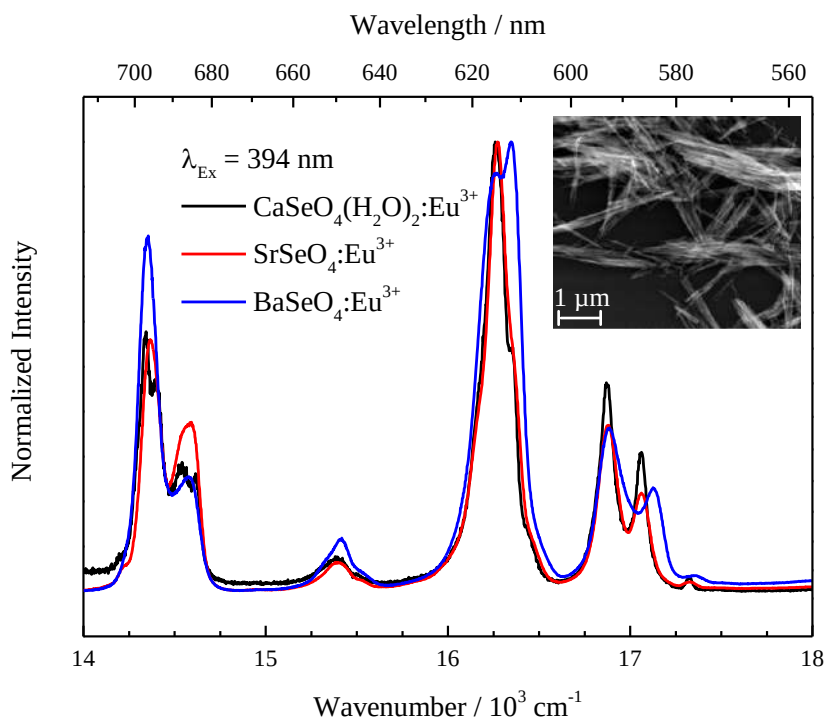
0.4.68 MSeO₄:Eu³⁺ - New alkaline earth nanowires

Speaker: Kuhlmann Natalie

MSeO₄:Eu³⁺ - New alkaline earth nanowiresNatalie Raupach,¹ and Prof. Dr. Claudia Wickleder^{1,*}¹ Department chemistry-biology, University of Siegen, Siegen, 57234, Germany

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Up to now, no selenate nanoparticles have been described even though much research has been done on oxidic compounds such as sulfates [1] and phosphates [2]. For the first time, alkaline earth selenates of the formular MSeO₄ (M = Ca, Sr, Ba) could be synthesized as nanoparticles or nanorods. For this purpose, a micro emulsion method was applied using CTAB as surfactant. In X-ray diffraction measurements phase pure compounds could be proven. Furthermore, the nanoparticles were analyzed by raster electron microscopy (cf. figure below) and dynamic light scattering measurements. Finally, the nanomaterials were doped with Eu³⁺. Incorporation of Eu³⁺ lead to strong red-emitting nanoparticles as expected. Successful doping was demonstrated by fluorescence measurements in the region of 18 000 to 14 000 cm⁻¹ (550 – 715 nm, cf. figure below). Low temperature measurements at 10 K allow conclusions to be made about the site symmetry of the Eu³⁺ ion on the alkaline earth site [3]. This knowledge can be used as another indication for the successful incorporation of Eu³⁺ in the host lattice. Red-emitting alkaline earth selenates are not described in literature up to now.



Emission of MSeO₄ nanoparticles under excitation of 394 nm at room temperature. The inset in the top-right corner depicts a REM image of the SrSeO₄ nanoparticles.

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0.4.69 Multifunctional photoluminescent nanosystems based on CdTe quantum dots

Speaker: Costa Pedro

Multifunctional photoluminescent nanosystems based on CdTe quantum dots

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Luminescent multifunctional nanomaterials have received great attention because of their diverse applications, such as bioimaging, thermometry and chemical sensing. In this context, the quantum dots (QDs) have been highlighted due to their optical properties, such as high quantum yield, broad absorption band, intense luminescence emission, easy emission tunability, and long lifetime.¹ The QDs are versatile materials and have been used as oxygen sensors with higher efficiencies than conventional sensors. Additionally, due to their nanometric size, the QDs allows the development of nanodevices for application in specific systems.² In this work, we present the development of CdTe QDs with high brightness. Due to the particle growth, it was possible to tuning the QDs emission from $\lambda = 500$ to 800 nm (Fig.1). The *in-situ* emission monitoring developed by LEMAF research group allowed the particle size control as a function of the emission wavelength during the reaction. This system proved to be very useful for applications that need the material with specific emission range. The QDs presented a particle diameter between 2 and 10 nm measured by transmission electron microscopy. Also, the particle size was correlated with the bandgap energy determined by UV-Vis spectroscopy. These results indicate the ability of CdTe QDs for use as oxygen sensors and their potential to be combined with other nanomaterials aiming the development of multifunctional platforms.

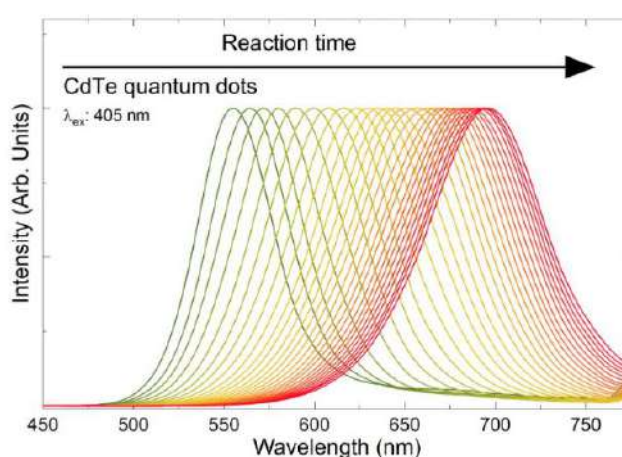


Fig. 1 - *In-situ* monitoring of water-soluble CdTe QDs emission.

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0.4.70 Multifunctionality of non–equiatomic $\text{Lu}_{3.09}\text{Al}_2\text{Ga}_3\text{O}_{12}:\text{Ce}$ single crystal: toward hybrid persistent luminescence color converters

Speaker: Bartosiewicz Karol

Multifunctionality of non-equiatom Lu_{3.09}Al₂Ga₃O₁₂:Ce single crystal: toward hybrid persistent luminescence color converters

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In the past few decades, light-emitting diodes (LEDs) have become more popular for a wide range of lighting uses due to their high efficiency, low cost, small size, and long device lifetimes, etc. [1]. However, even the best-performing phosphors suffer from thermal quenching at high temperatures and droop or saturation quenching at high light intensities. These undesirable consequences are frequently observed under lighting operating conditions [2]. Thermal quenching mitigation is unquestionably important for applications. Therefore, defect-composition engineering can result in additional functionalities including energy- and charge-transfer processes or quenching of the luminescence. When appropriate defects are introduced in the host lattice, additional trapping and de-trapping pathways are realized, which can steer the temperature-dependent behavior of the phosphor. Another benefit of such energy storage is persistent luminescence that can last for hours after excitation has stopped [3].

The non-equiatom Lu_{3.09}Al₂Ga₃O₁₂:Ce composition grown from the rapidly cooled melt served as a research model. The crystallized phase and atom distributions were studied by XRD and SEM-EDS techniques. The luminescence intensity as well as fast and slow decay curves of the Ce³⁺ ions were studied in the wide temperature range (8-650 K). The CIE chromaticity coordinates (CIE 1931), luminous efficacy, and luminous intensity under blue LED and laser diode excitation were estimated. Thermally stimulated luminescence and persistent luminescence properties were also systematically studied and discussed in detail.

Acknowledgments: National Science Centre Poland No.: 2020/39/D/ST3/02711.

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0.4.71 Multimodal non-contact luminescence cryothermometry aided by oxides doped with Cr³⁺ and Mn⁴⁺

Speaker: Mykhaylyk Vitaliy

Multimodal non-contact luminescence cryothermometry aided by oxides doped with Cr³⁺ and Mn⁴⁺

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Accurate temperature sensing in harsh environments, where physical contact is restricted, presents a significant challenge. Luminescence thermometry offers an elegant non-contact solution by utilizing the temperature-dependent variation of emission characteristics in selected luminescence materials. Extending the application of the luminescence thermometry towards cryogenic temperatures relies upon identification of further materials with luminescence properties suitable for temperature sensing in this range. The great promise for such application represents the systems where thermally induced processes of particle exchange between excited levels and thermal quenching require low activation energy that can then translate in the tangible changes of a luminescence parameter with temperature.

Motivated by this idea we carried out systematic studies of the temperature-induced changes in the luminescence of Cr³⁺ and Mn⁴⁺ doped oxides (Al₂O₃, Ga₂O₃, Y₃Al₅O₁₂, YAlO₃) [1, 2] and alloys (Al₂O₃-Ga₂O₃) [3] over the 4.5-300 K temperature range. The responsivity of the luminescence characteristics that can be used for the non-contact measurements of temperature i.e. luminescence intensity ratio, wavelength shift and decay time constant, is examined and the chief features influencing thermometry over the cryogenic temperature range are identified. This is complemented by comprehensive analysis and interpretation of thermometric properties of the crystals under study. We applied suitable theoretical models to explain the observed temperature dependences by the changes in the dynamics of the excited levels population due to i) thermalization, ii) electron-phonon interaction, iii) nonradiative multiphonon relaxation and iv) thermal depopulation of higher states. It is shown that the intensity ratio of R-lines of Cr³⁺ and Mn⁴⁺ at low temperatures is predominantly controlled by the process (i) responsible for redistribution of particles between the upper and lower levels. The process (ii) is the cause of wavelength shift while the explanation of the temperature change of decay rate requires to take into account combined effect of all factors. We will show that developed models provide adequate interpretation of the processes as can be judged from the high quality of fits obtained for the measured temperature dependences of luminescence intensity ratio, wavelength shift and decay time constant in the materials under study. The results of the fits yielded a number of quantitative parameters that allowed us to establish how the energy structure of the emission centre and phonon dynamics in different hosts influence the luminescence properties and what effect it has upon the different modes of non-contact luminescence temperature sensing. Finally, we will evaluate the performance of different materials and methods of temperature sensing used in cryothermometry and highlight the benefits of intrinsic redundancy enabled by multimodal luminescence sensors.

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0.4.72 Nanothermometry based on an ultra-long lifetime from Pr³⁺ and Na⁺ doped yttrium tantalate scintillating nanoparticles for nanomedicine advances

Speaker: Do Prado Labaki Hayra

Nanothermometry based on an ultra-long lifetime from Pr³⁺ and Na⁺ doped yttrium tantalate scintillating nanoparticles for nanomedicine advances

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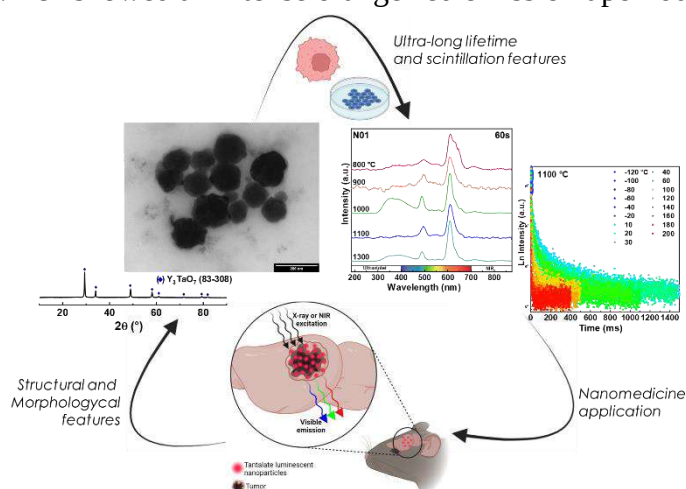
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Luminescent nanoparticles exhibiting a long lifetime are extremely important in the nanomedicine field given that the lifetime of most biological molecules is below the nanosecond level, and a long-lived emission that could remain detectable after removing the excitation for several seconds is noteworthy. In the present work, we report the synthesis, structural, morphological, and spectroscopic characterization of a multifunctional material: the Pr³⁺, Na⁺-doped yttrium tantalate nanoparticles designed by an original sol-gel route. The X-ray diffraction analysis illustrated the presence of the Y₃TaO₇ or M'-YTaO₄ phases. Transmission Electron Microscopy depicts nanoparticles with an average size of 132 nm. Photoluminescence measurements revealed an intense orange emission, as well as in the NIR II and IIb biological windows. A primary nanothermometer was also successfully developed ($S_T=1,5\%K^{-1}$). The ¹D₂ lifetime values show an extremely long lifetime of 432 ms upon UV excitation, for the sample annealed at 1100 °C. The lifetime was also temperature-dependent indicating that a sensible nanothermometer further arises. It is important to point out that no literature reports a long lifetime as in this work. Radioluminescence studies were also performed, and outstanding scintillation properties were observed for the M'-YTaO₄ phase, which showed an intense orange-red emission upon 60 s of irradiation.



TEM images, XRD diffractogram, radioluminescence spectra, and lifetime decay as a function of the temperature (153 a 473 K) for the Pr³⁺ and Na⁺ yttrium tantalate nanoparticles.

0.4.73 Near infreared emitting luminescent solar concentrators

Speaker: Andre Paulo

Near infreared emitting luminescent solar concentrators

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The world's energy is mainly consumed by three sectors: buildings, industry, and transportation, in which the building sector represents the world's largest energy consumption. Windows, which account for a significant part of heat gain/losses, can be transformed into energy-harvesting/generating units through the luminescent solar concentrator (LSC) concept [1]. In order to maximize the output of the LSCs without jeopardizing the indoor light quality, transparent devices should be fabricated by the use of UV-absorbing or NIR-emitting centres, which are scarce in the literature and mostly through the use of quantum dots raising environmental concerns [2]. The possibility of using natural renewable materials for LSC applications has been pointed out [3], justified by the combined use of bio-based compounds to increase human health and decreased environmental concerns, considering the use of natural sources instead of synthetic alternatives.

In this work, we propose a large area (10×10 cm²) LSC prototype based on bacteriochlorophyll, a photosynthetic pigment that occur in phototrophic bacteria, dispersed in Styrene-Ethylene-Butylene-Styrene (SEBS), a thermoplastic elastomer with enhanced thermal and UV stability. This material presents emission in the red/NIR spectral range with an emission quantum yield ~5%, which is remarkable for a natural NIR-emitting emitting material. This is the first example of a large-area LSCs based on nature-based optically active centers with red/NIR, which yielded optical and power conversion efficiency values of up to ~2.6 % and ~0.04 %, respectively, which are comparable values regarding state-of-the art natural-based LSCs.

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0.4.74 New translucent films with improved up conversion yield

Speaker: De Mattos Elaine

New translucent films with improved up conversion yield

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The up conversion phenomenon occurs when two or more lower-energy photons are converted into one higher-energy photon. This phenomenon can be applied in different areas such as bioimaging, solar converters, etc. One of its main limitations is the phenomenon's inherent low yield, and in order to mitigate this problem, we studied the enhancing effect of metallic nanoparticles on cellulose-based polymeric transparent composites with upconverting properties.

For this purpose, yttrium fluoride nanoparticles doped with ytterbium and erbium were prepared by a solvothermal method and incorporated into hydroxypropyl methylcellulose (HPMC) films using a drop-casting process. Simultaneously, metallic nanoparticles with surface plasmon resonance were added to these composites. X-ray fluorescence nanomapping registered at the Carnaúba beamline from Sirius Synchrotron facility was used to understand the interaction between UCNps and MNPs in the composite and, showed, serendipitously, that the gold nanoparticles interact preferentially with the fluoride nanoparticles over the carbonyl ends of the HPMC. Finally, the photoluminescence study showed an intensification of the up-conversion phenomenon in the presence of gold nanoparticles.



Figure 1: Photograph of the HPMC/UCNps+AuNps film in white light and with 980 nm laser excitation, and upconversion spectra of the HPMC/UCNps with added AuNps and without.

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0.4.75 Ni:CGGG single crystal as potential luminescent concentrator emitting in the SWIR range

Speaker: Caraud Nicolas

Ni:CGGG single crystal as potential luminescent concentrator emitting in the SWIR range

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Luminescent concentrators (LC) are new sources of incoherent light, pumped by printed circuit board LEDs, combining power and brightness. They were demonstrated in the yellow spectral range thanks to a Ce:YAG single crystal concentrator [1]. This work focus on the development on new LC emitting in the SWIR (Short-Wave Infrared). For this purpose, calcium-gallium-germanium garnet (CGGG), doped by nickel (and nobium for electroneutrality) was selected as it can well absorb in the visible and emit in the SWIR range [2] ($\text{Ca}_3\text{Ga}_{2(1-3y/4)}\text{Ni}_y\text{Nb}_{y/2}\text{Ge}_3\text{O}_{12}$, y from 0.0011 to 0.23). The pumping transition centered around 700 nm corresponds to $^3\text{A}_2(^3\text{F}) \rightarrow ^3\text{T}_1(^3\text{F})$ transition whereas an emission centered around 1480 nm is assigned to transition from $^3\text{T}_2(^3\text{F})$ to $^3\text{A}_2(^3\text{F})$ (figure 1(a)). Fluorescence decay was measured with y Ni content from 0.0011 (5.10^{18} ions. cm^{-3}) to 0.23 (10^{21} ions. cm^{-3}) (figure 1(b)). To maximize absorbance while keeping high fluorescence lifetime (high quantum yield), the Ni content $y = 0.011$ was selected. It is the highest concentration with a mean lifetime above 90% of the maximum lifetime measured at very low Ni concentration (figure 1(b)). A single-crystal with this starting concentration ($\text{Ca}_3\text{Ga}_{1.98}\text{Ni}_{0.011}\text{Nb}_{0.01}\text{Ge}_3\text{O}_{12}$) was synthesized by optical floating-zone method (figure 1(c)). Its optical characterizations are in progress and will be presented at the conference.

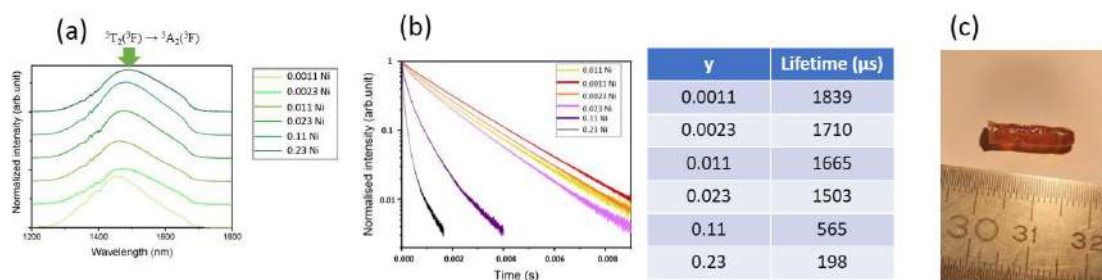


Fig. 1 (a) emission spectra of $\text{Ca}_3\text{Ga}_{2(1-3y/4)}\text{Ni}_y\text{Nb}_{y/2}\text{Ge}_3\text{O}_{12}$, y from 0.0011 to 0.23. (b) fluorescence decay (excitation 750 nm) of $\text{Ca}_3\text{Ga}_{2(1-3y/4)}\text{Ni}_y\text{Nb}_{y/2}\text{Ge}_3\text{O}_{12}$, y from 0.0011 to 0.23, and corresponding mean lifetime. (c) picture of a single-crystal of $\text{Ca}_3\text{Ga}_{1.98}\text{Ni}_{0.011}\text{Nb}_{0.01}\text{Ge}_3\text{O}_{12}$

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0.4.76 Non-isomeric impurity-induced phosphorescence in carbazole derivatives

Speaker: Mazarevics Arturs

Non-isomeric impurity-induced phosphorescence in carbazole derivatives

Arturs Mazarevics,^{1,2} Kaspars Leduskrasts,¹ and Edgars Suna^{1,*}

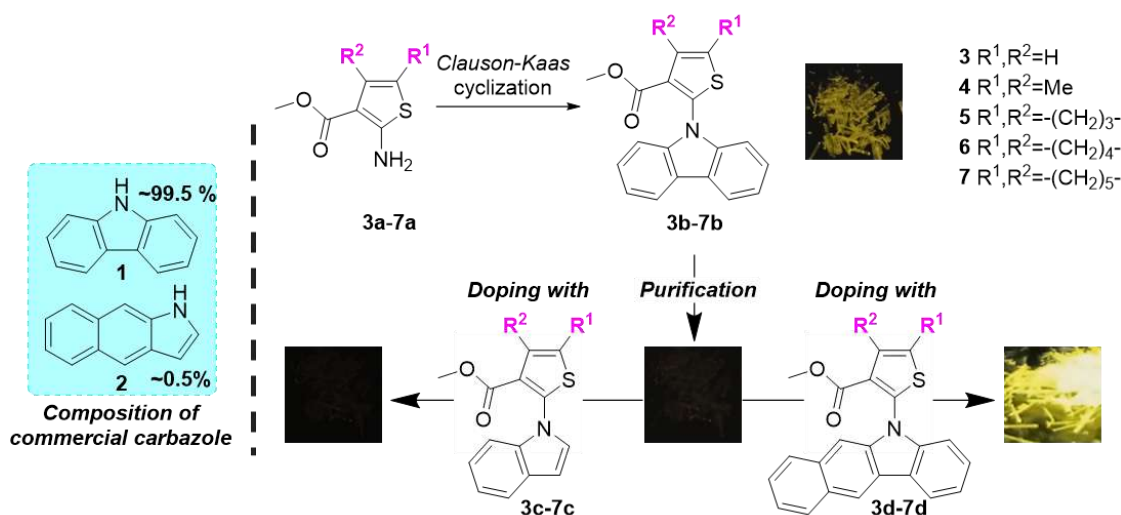
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Efficient phosphorescence is routinely achievable in organometallic complexes, but costly synthesis, high toxicity and lack of stability limit the use of such materials. To overcome the aforementioned drawbacks, purely organic phosphorescent materials (phosphors) have recently attracted a large interest due to their biocompatibility, low cost and limitless design possibilities.¹ These organic phosphors generally contain extended π -systems and heteroatoms that provide n-type orbitals to achieve fast intersystem crossing.

Carbazole **1** subunit is a broadly implemented moiety in the field of purely organic phosphorescence, but recently it was shown that commercially available carbazole has an isomeric impurity (**2**), that induces phosphorescence in carbazole containing luminophores.² Herein, we report the synthesis of carbazoles **3b–7b** in which the carbazole ring was formed through *Clauson-Kaas* cyclization, thus avoiding commercial impurities. Initially, carbazoles **3b–7b** showed phosphorescence, however, after laborious purification, it disappeared. By doping the purified carbazoles **3b–7b** with byproducts formed during the *Clauson-Kaas* reaction, two component systems were obtained. When indole derivatives **3c–7c** were used as dopants, no phosphorescence was observed. In contrast, employing benzo[*b*]carbazoles **3d–7d** as dopants lead to an intense phosphorescence emission with ultra-long lifetimes.



Impurity induced phosphorescence in carbazoles **3b–7b**

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0.4.77 Novel lanthanide compounds based on perfluoro benzoates for luminescent applications

Speaker: Malvestiti Ivani

Novel lanthanide compounds based on perfluoro benzoates for luminescent applications

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Perfluoro benzoic acid (LH) can yield coordination complexes with trivalent lanthanide ions, Ln(III), with distinct structures, particularly, mono-, di-, and polymetallic compounds [1]. The composition and structure of the complexes depend on the Ln(III), the synthetic method, and on the crystallization conditions, where rarely a pure phase is obtained [1]. Two structures were synthesized: a novel framework **1Ln**, $[\text{Ln}(\text{L})_2(\text{LH})(\text{H}_2\text{O})_4](\text{Cl})(\text{LH})(\text{H}_2\text{O})_2$, and known bimetallic complexes **2Ln**, $[\text{Ln}_2(\text{L})_6(\text{H}_2\text{O})_8](\text{H}_2\text{O})_2$, with Ln = Eu, Gd, Tb, EuGd, EuTb, and GdTb. Their syntheses were performed at room conditions or at 80 °C, followed by crystallization. The crystals are soluble in water and the Eu(III) compounds presented low quantum efficiency (8%) and emission lifetimes of 0.3 ms. Novel **3Ln** (Ln = Eu, Gd, Tb) compounds, with still unknown structure, were synthesized in a closed reactor at 120 °C. The powder presented high crystallinity and is not soluble in water or several organic solvents (e.g., methanol, ethanol, acetone, acetonitrile, etc.). The emissions of **3Eu** presented a larger number of Stark components than **1Eu** and **2Eu**, suggesting a stronger ligand field and lower symmetry [2] around the Ln(III). However, no multiplicities higher than $2J + 1$ were observed, indicating a single site for the Ln(III) ion. The ligand centered $\pi-\pi^*$ transitions are more intense in the excitation spectrum of **3Eu** and are comparable to the Eu(III) $^5\text{L}_6 \leftarrow ^7\text{F}_0$ transition. The emission lifetime (0.6 ms) and quantum efficiency (18%) are higher for **3Eu** than **1Eu** and **2Eu**. However, **3Tb** has a much shorter emission lifetime (0.28 ms) than the framework counterpart **1Tb** (0.82 ms). These results emphasize the versatility of perfluoro benzoic acid in yielding different Ln(III) structures with improved luminescent properties.

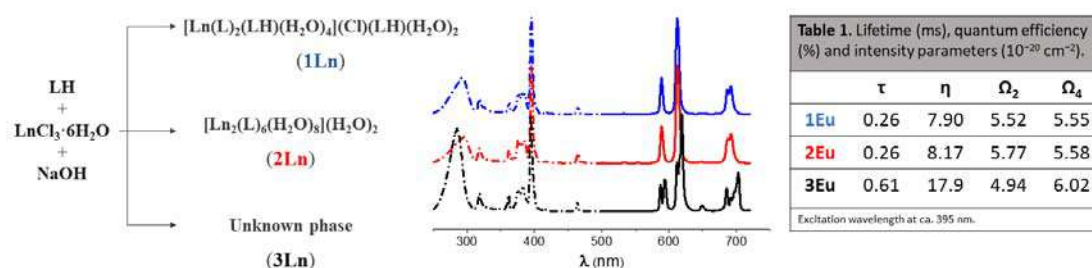


Figure. Synthesis, excitation and emission spectra, and table with photophysical properties.

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0.4.78 Novel luminescent low molecular weight gelator with enhanced photoluminescence quantum yield

Speaker: Mahashaya Rahul

Novel luminescent low molecular weight gelator with enhanced photoluminescence quantum yield

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The study of fluorescent supramolecular gels derived from the self-assembly of low molecular weight gelators (LMWGs) have received considerable attention in recent years due to their numerous applications as soft emissive materials in nanoscience and nanotechnology. Herein, we explored the role of dendrimer on gelation of a blue emissive single molecule. Interestingly, the resulting poly (aryl ether) based dendron, as a novel luminescent material was found to show enhanced photoluminescence quantum yield of 59 %. The gelator molecules assembled via various non-covalent interactions such as hydrogen bonding, π - π stacking, donor-acceptor and hydrophobic interactions was found to show helical and fibrous as two different kinds of morphology in same solvent system. For the first time, we report on separating the two morphologies using the solvophobic effect. The motivation behind studying the supramolecular organization of this blue emissive gelator is to gain precise control over their interchromophoric interaction, which is highly relevant in the context of their utility in organic-electronic device applications. Further, the computational calculations indicate a well separated HOMO-LUMO distribution leading to photon up conversion from the low-lying triplet (T_1) to the singlet (S_1) state. As a consequence, delayed fluorescence was observed from the assembly. The role of molecular architecture and self-assemblies, including chiral helical for the un-conventional design would open a new avenue for the future designs and fabrication of cost-effective and efficient luminescent emitters for varying applications.

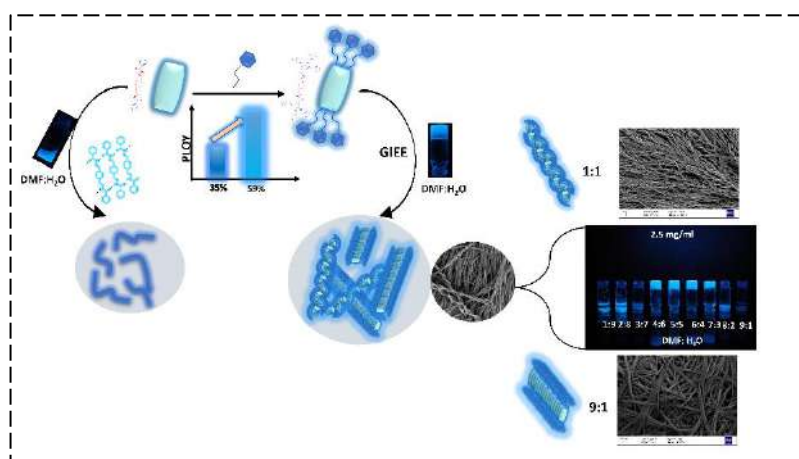


Figure. Schematic representation of the working principle

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0.4.79 On the development of core-shell persistent phosphors functionalized with europium β -diketonate complexes

Speaker: Francisco Leonardo H. C.

On the development of core-shell persistent phosphors functionalized with europium β -diketonate complexes

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With the ever-increasing growth of nanotechnology, several novel bottom-up engineering methods have been widely studied for the fabrication of multifunctional persistent phosphors with potential applications in various fields, ranging from energy conversion and storage to biomedicine. [1,2] Hence, in this work, we prepared single and double-shell $\text{MAl}_2\text{O}_4\text{:Eu}^{2+},\text{Dy}^{3+}$ and $\text{M}_2\text{SnO}_4\text{:Cr}^{3+}$ (M: Sr, Mg or Zn) persistent phosphors, and functionalized them with Eu^{3+} - β -diketonate (tta, dbm) complexes coordinated on ancillary ligands (*N*-picNO) via a SiO_2 polymeric network using a fast and energy-saving microwave-assisted synthesis. The materials were investigated by XRPD, FTIR, UV, and Vacuum-UV spectroscopy using synchrotron radiation, where it was possible to infer the dependency of the ligands on the optical properties of the compounds. Interestingly, phosphors functionalized with the tta complex exhibited an increased persistent luminescence decay time with mainly Eu^{2+} emission, while the same cannot be said for materials containing the dbm complex. Additionally, on double-shell materials, Eu^{3+} luminescence was predominant, revealing the influence of shell thickness and distance in energy transfer and migration processes.

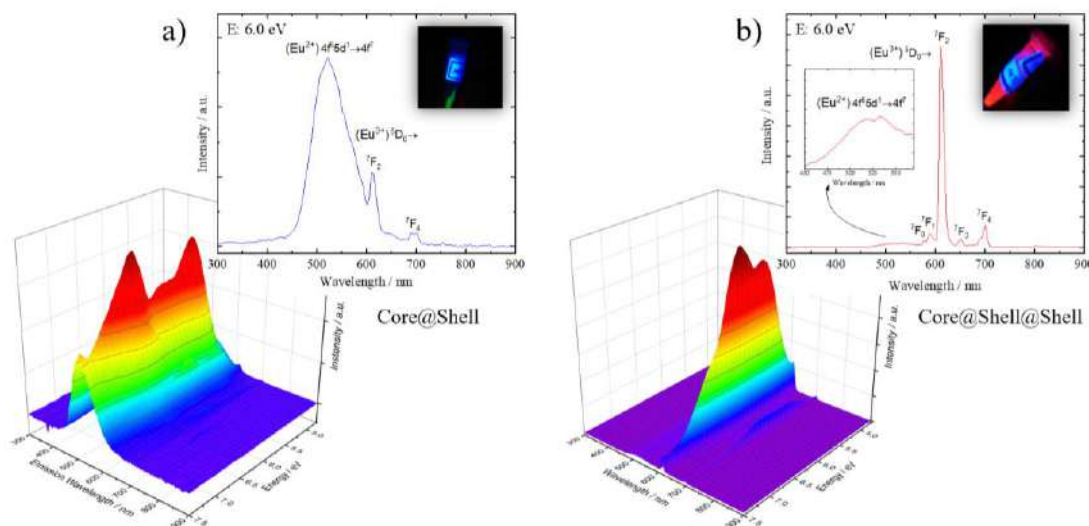


Figure 1. Luminescence Vacuum-UV spectra of a) single-shell and b) double-shell $\text{MAl}_2\text{O}_4\text{:Eu}^{2+},\text{Dy}^{3+}$ phosphors functionalized with the $\text{Eu}^{3+}(\text{tta})_3(\text{N-picNO})_2$ complex. Photographs were taken under a UVA lamp.

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Funding: FAPESP 2021/08111-2

0.4.80 On the intramolecular energy transfer efficiency in Eu³⁺ chelates

Speaker: Blois Lucca

On the intramolecular energy transfer efficiency in Eu³⁺ chelates

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Lanthanide chelates are undoubtedly major players in the photoluminescence and photonics field.^{1,2} In this regard, organic ligands are used to overcome the electric-dipole-forbidden nature of the 4f-4f transitions, harvesting the excitation energy and transferring the energy to the lanthanide ion. This intramolecular energy transfer (IET) process has been thoroughly investigated (theoretically and experimentally), however, the concept of energy transfer efficiency has remained somewhat eerie. Concerning the energy transfer yield in Eu³⁺ complexes, we have explored how it varies in regard to kinetic parameters, mainly: *i*) the ratio between the S₁ → T₁ intersystem crossing and the singlet relaxation rate ($\beta_L = k_{ISC}/k_{S_1S_0}$); *ii*) the ratio between the overall energy transfer from S₁ to a thermally excited Eu³⁺ ion at the ⁷F_J level and the singlet relaxation rate ($\alpha_{ET}^J = W_{ET}^{S_1J}/k_{S_1S_0}$) and *iii*) the corresponding ratio of the latter for the T₁ ($\gamma_{ET}^J = W_{ET}^{T_1J}/k_{T_1S_0}$). Our calculations show that the energy transfer efficiency can be expressed as:

$$\phi_{IET} = \frac{1}{Z} \sum_{J=0}^6 (2J+1) \frac{\gamma_{ET}^J (\beta_L + \alpha_{ET}^J)}{(1 + \gamma_{ET}^J)(1 + \beta_L + \alpha_{ET}^J)} e^{-\frac{E_J}{kT}}$$

where Z is the canonical partition function for the ⁷F_J manifold. By considering that $\gamma_{ET}^J \cong 1 + \alpha_{ET}^J$, which was already proven by some experiments involving transient absorption spectroscopy,^{3,4} we can plot the energy transfer efficiency for a Eu³⁺ by truncating the sum at J = 1 for 298 K (Figure 1). Our results show that when $(\alpha_{ET}^1, \beta_L) \approx (1,1)$ the gradient of the energy transfer efficiency rises, as shown by the concentration of the contour lines near (0,0). Moreover, a small variation in the ligands' kinetics (β_L) may lead to huge differences in the efficiencies of the energy transfer process.

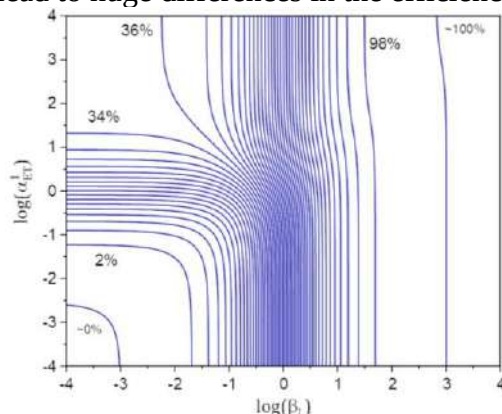


Figure 1. Contour lines of the energy transfer efficiency as a function of the kinetic parameters α_{ET}^1 and β_L .

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0.4.81 On the Optical Properties of the Solid Solution $\text{LiBaLa}_{1-x}\text{PrxWO}_6$ with $x = 0.0$ to 1.0

Speaker: Pier Tim

On the Optical Properties of the Solid Solution $\text{LiBaLa}_{1-x}\text{Pr}_x\text{WO}_6$ with $x = 0.0$ to 1.0

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Rare earth containing tungstates of various molecular compositions, have been of major interest for optical applications for decades already [1,2]. Quaternary tungstates according to the general composition $\text{M}^{\text{I}}\text{M}^{\text{II}}\text{LnWO}_6$ ($\text{M}^{\text{I}} = \text{Li}^+, \text{Na}^+, \text{K}^+$, $\text{M}^{\text{II}} = \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}$) crystallize in a double perovskite structure and represent a relatively new family of tungstates. Since their first description in 1974 only a handful of studies have been published, highlighting the need for further investigation into these kinds of compounds [3]. This study concerns the optical properties of the novel Pr^{3+} -doped LiBaLaWO_6 phosphor. The luminescent features were investigated dependent on activator concentration and temperature. The results of these investigations were interpreted and relations between the optical and structural properties were drawn.

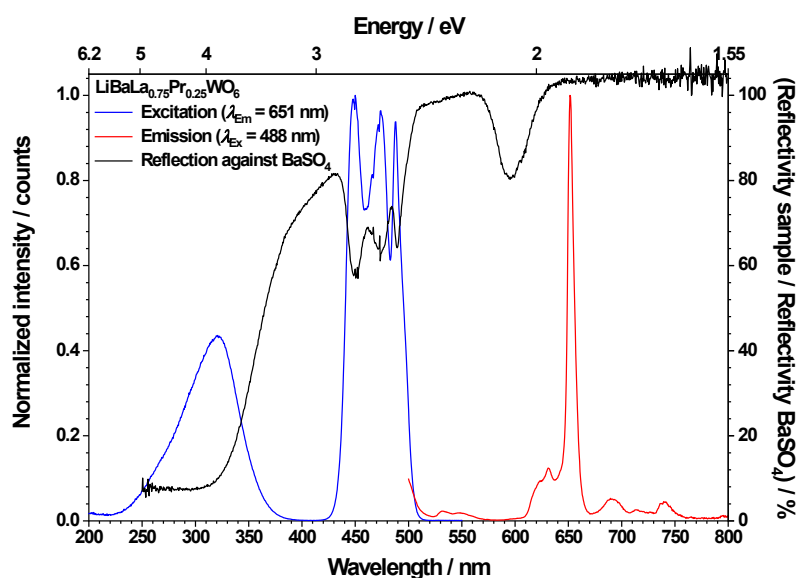


Figure 1: Excitation, emission, and diffuse reflection spectra of $\text{LiBaLa}_{0.75}\text{Pr}_{0.25}\text{WO}_6$.

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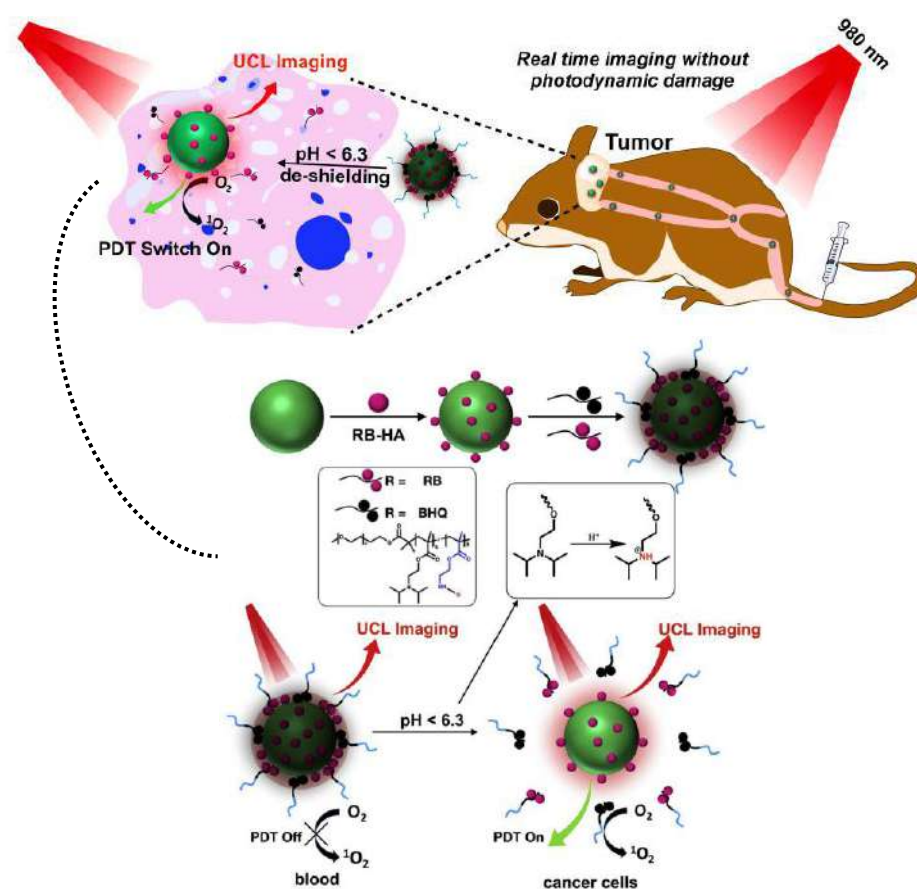
0.4.82 Optical imaging and pH-awakening therapy by upconversion nanophotosensitizers

Speaker: Jun Yuan

OPTICAL IMAGING AND pH-AWAKENING THERAPY OF DEEP TISSUE CANCER BASED ON SPECIFIC UPCONVERSION NANOPHOTOSENSITIZERS

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Keywords

pH-awakening PDT; real-time imaging; tumor intracellular responsive; upconversion

0.4.83 Optical properties of number of layers controlled two-dimensional perovskites

Speaker: Naoi Kota

Optical properties of number of layers controlled two-dimensional perovskites

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The multiple-quantum-well (MQW) structure consists of alternating stacked barrier and well layers. When light with a resonance frequency is incident on the MQW, the light propagates through the barrier layers and excitons are generated in the well layers. When the excitons in each well layer have exactly the same energy, light and the excitons are combined to form a state called MQW polariton. MQW polaritons lead to energy splitting of the excitons and the appearance of super-radiant modes. In order to investigate the characteristic optical properties of MQW polaritons, which are different from those of bulk samples, we have measured luminescence and time-resolved luminescence measurements on two-dimensional (2D) perovskite $[\text{CH}_3(\text{CH}_2)_{17}\text{NH}_3]_2\text{PbI}_4$ samples. It is difficult for ordinary semiconductors to achieve a perfectly constant well layer thickness. However, 2D perovskites are ideal materials for the study of MQW polaritons because of their perfectly uniform well widths [1]. In this study, we used samples in which the number of well layers was controlled by the Langmuir-Blodgett (LB) method [2].

Figure 1 shows the absorption spectra near exciton resonance with different number of layers. Exciton peaks are clearly observed at 487 nm and the absorbance increases linearly with the number of layers, indicating that the samples with the desired number of layers have been fabricated. For the sample with a small number of layers, time-resolved measurements showed a relatively short relaxation time compared to the related single crystal sample. We discuss these characteristic exciton dynamics in terms of MQW polaritons.

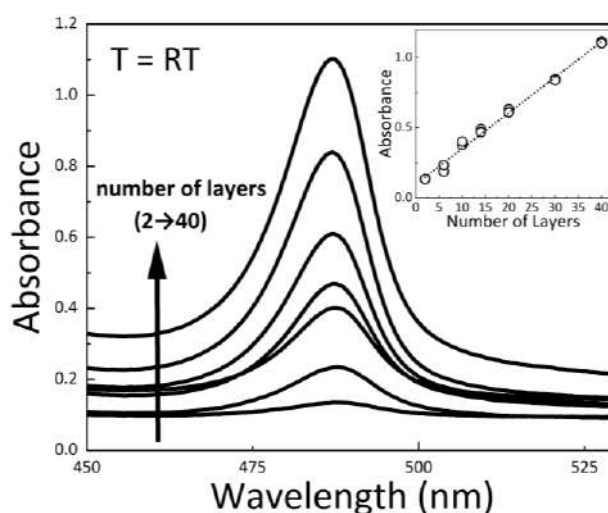


Fig. 1 Number of layers dependence of absorption spectra near exciton resonance at room temperature (RT).

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0.4.84 Performing Single Molecule Spectroscopy on Lanthanide Complexes and Aggregates

Speaker: Bailey Anna

Performing Single Molecule Spectroscopy on Lanthanide Complexes and Aggregates

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Lanthanide (Ln) complexes have unique and characteristic light emission with narrow spectral widths and long excited state lifetimes, which gives them a range of light emitting applications [1]. However, understanding the photophysics of Ln complexes has proved challenging, as energy transfer and loss mechanisms occurring within the molecule are difficult to measure [2]. This research applies the cutting edge technique of single molecule spectroscopy (SMS) to understand, design and therefore deliver novel and highly efficient Ln complexes for use in light emitting materials. SMS measures individual Ln complex molecules or molecular aggregates and their light emission allows photon statistics to be analysed [3]. Using time-correlated single photon counting, photon antibunching graphs can be constructed and the number of independent emitting sites estimated. Processes occurring within the molecule/aggregate such as singlet-singlet annihilation can also be observed using time-resolved analysis. Data for the Ln complex [Eu(hfac)₃(pd)] (hfac = hexafluoroacetylacetonate, pd = 1,10-phenanthroline-5,6-dione) [4] within a host matrix (Figure 1) as aggregates with ~8 emitting chromophores (a) and single molecules with <2 emitting chromophores (b) are presented.

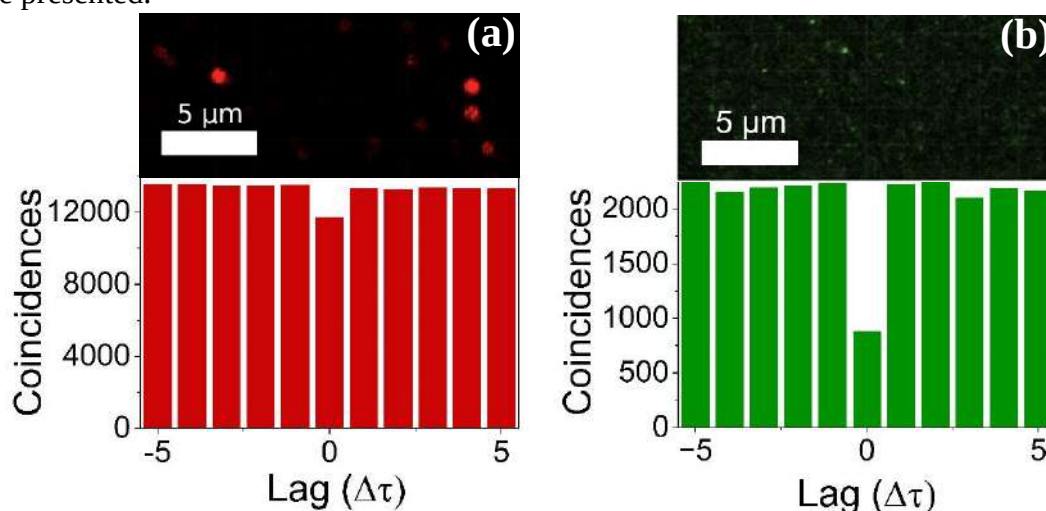


Figure 1: (top) SMS images of aggregate (a) and single molecule (b) spots of Eu(hfac)₃(pd) with the corresponding photon antibunching graphs (bottom)

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0.4.85 Persistent Luminescence in Garnet Single Crystals

Speaker: Viana Bruno

Persistent Luminescence in Garnet Single Crystals

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In persistent luminescence materials, energy can be stored in controlled traps/defects located within the bandgap of the material. The materials can be “charge” under brief irradiation, namely few minutes under various wavelengths ranging from natural daylight to x-rays [1]. This energy is then released at room temperature for several hours via light emission once the excitation is stopped.

The present work is focused on the analysis of the persistent luminescence properties on single crystals of Ce³⁺ and Cr³⁺ co-doped gadolinium-yttrium-aluminum-gallium garnets of general formula Y_{3-x}Gd_xAl₂Ga₃O₁₂ (GYAGG), to promote new applications of the persistent materials. Such single crystals elaborated by the Czochralski method are interesting to better understand the persistent luminescence phenomena. Examples of the obtained crystals are presented in Figure 1 right. First, tuning both the amount of Ce³⁺ and Cr³⁺ dopants and the Y³⁺/Gd³⁺ ratio, different afterglow curves at room temperature have been obtained after excitation at 455 nm (Figure 1 left). Second, volume [2] and transparency effects of the crystals could be analyzed: thicker transparent crystals exhibit more intense afterglow than thinner crystals as larger volume of the sample is excited. Surfaces of the crystals have been polished with different qualities: (i) one laser quality with very good transparency within the faces and (ii) one de-polished quality where scattering occur towards the surface of the crystal. Furthermore, when charging these materials by X-Rays, intensive persistent luminescence is obtained opening the path to new applications such as storage and anti-counterfeiting, x-rays imaging, etc.

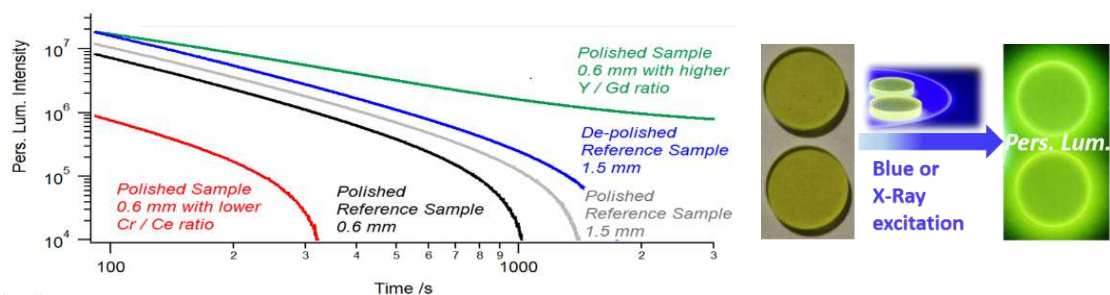


Fig. 1 (left) Pers. Lum. intensity decay profiles after excitation during 10 min with a 455 LED (1.1 W) for various crystals with different cationic compositions (for instance in green: (Gd_{0.26}Y_{0.74})_{3.08}Ce_{0.008}(Al_{2.36}Ga_{2.54}Cr_{0.001})O₁₂, 0.6mm, polished (see ref 4 for others compositions) (right) Example of Pers. Lum. obtained with garnet crystals.

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0.4.86 Persistent luminescence nanoparticles for biosensing

Speaker: Becerro Ana Isabel

Persistent luminescence nanoparticles for biosensing

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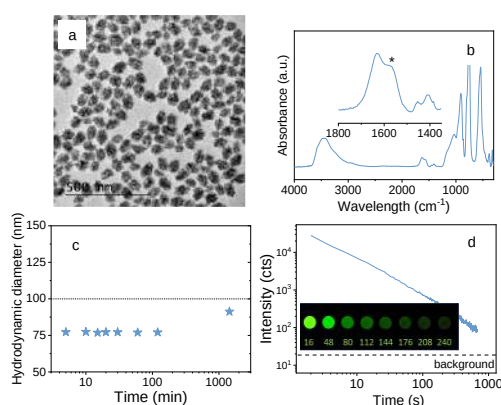


Figure 1: TEM micrograph (a), FTIR spectrum, *=PAA (b) colloidal stability (c), and afterglow curve (d) of $\text{Zn}_2\text{GeO}_4:0.5\%\text{Mn}^{2+}$ PLNPs in PBS. Inset: Digital photographs at different times of the PLNPs after UV irradiation for 5 minutes.

ellipsoidal shape (57 nm x 80 nm, Fig. 1a), functionalized with carboxylate groups (Fig. 1b), were obtained following a microwave-assisted, one-pot method from an aqueous solution of Zn and Mn nitrates and GeO_2 , using polyacrylic acid (PAA) as additive. The PLNPs were very stable towards aggregation with time in phosphate buffer saline (PBS, Fig. 1c) and demonstrated excellent chemical stability for, at least, one week. Excitation of the PLNPs with UV light gave rise to a strong green luminescence that persisted long after the excitation was stopped (Fig. 1d). The PLNPs were then used to fabricate a generic sandwich immunoassay (SI) to detect interleukin-6 (IL-6) in undiluted human serum. IL-6 is a pro-inflammatory cytokine whose presence in serum is a clear sign of infection. The presence of carboxylate groups on the PLNPs surface was essential for their conjugation to the detection antibodies involved in the SI (Fig. 2). The SI was able

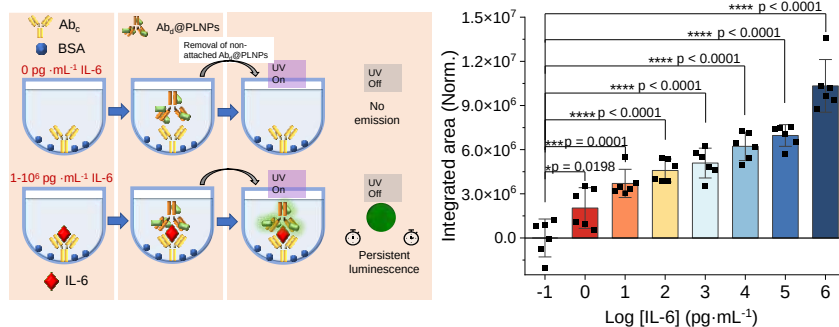


Figure 2: Scheme of the SI and calibration curve in human serum.

Persistent luminescence nanoparticles (PLNPs) are very interesting as nanoprobes for biosensing as they allow for the elimination of the background autofluorescence characteristic of biological species. Apart from their nanometer size and long persistent luminescence, PLNPs for biosensing must fulfill a number of requisites, namely: i) regular shape and uniform size, ii) high colloidal and chemical stability, and iii) availability of functional groups for subsequent anchoring to biomolecules. We herein present a simple synthesis route to obtain PLNPs that meet all the mentioned requisites. Specifically, uniform $\text{Zn}_2\text{GeO}_4:\text{Mn}^{2+}$ PLNPs with

to detect as low as $1 \text{ pg}\cdot\text{mL}^{-1}$ of IL-6 spiked in human serum. This study demonstrates that the one-pot synthesized $\text{Zn}_2\text{GeO}_4:\text{Mn}^{2+}$ PLNPs are ideal candidates for biosensing.

0.4.87 Phase transitions of CsPbHal₃ perovskite nanocrystals in borogermanate glass

Speaker: Babkina Anastasiia

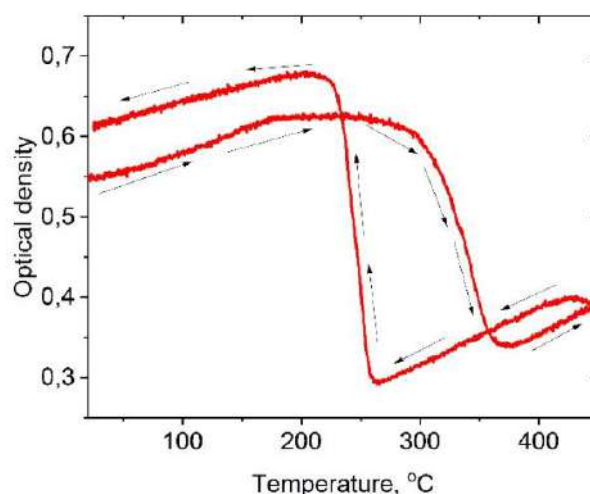
Phase transitions of CsPbHal₃ perovskite nanocrystals in borogermanate glass

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Perovskite nanocrystals are direct-gap semiconductors, have high absorption and emission coefficients, narrow luminescence bands, and also make it possible to obtain radiation in the entire visible range by changing the size of nanocrystals and the ratio of halogens [1]. They can be used in solar cells, LEDs, various detectors, scintillators, etc. [2], but many of their properties remain unexplored. A series of borogermanate glasses of the system B₂O₃–GeO₂–Na₂O–ZnO–P₂O₅–TiO₂–K₂O–Cs₂O–PbO–x Br–(1–x) I mol.%, where x = 1; 0.6; 0.5; 0.4; 0.25; 0. Glass was synthesized in an air atmosphere at a temperature of 950°C for 30 min. Perovskite CsPb(Br_xI_{1–x}) nanocrystals precipitated in the glass matrix upon annealing from 470°C. The glass transition temperature of the obtained glasses lies in the range 440–450°C. During the experiment, samples of glass-ceramics with perovskites were heated from room temperature to the temperature at which the absorption of nanocrystals disappeared (370–500°C), i.e. they melted in the glass matrix. After reaching this temperature, the glass ceramics were cooled to room temperature. At temperatures of about 200–250°C, the absorption intensity returned to its initial values.



Optical density changes at the exciton absorption maximum of CsPbBr_{0.5}I_{0.5} nanocrystals upon heating and cooling the glass sample

This research was supported by Russian Science Foundation (Agreement #19-72-10036).

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0.4.88 Photoluminescence and radiation-induced luminescence properties of Tb-doped SrF₂-Al₂O₃-B₂O₃ glasses

Speaker: Kimura Hiromi

Photoluminescence and radiation-induced luminescence properties of Tb-doped SrF₂-Al₂O₃-B₂O₃ glasses

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Scintillators are kind of luminescent materials, and they immediately convert the absorbed energy of ionizing radiation into many low energy photons. The combination of a scintillator and a photodetector is used for a typical scintillation detector. To date, the material forms of commercial scintillators were mostly used single crystals because of their optical qualities. Recently, K. Shinozaki *et al.* have reported the scintillation properties of oxyfluoride glasses such as AEF₂-Al₂O₃-B₂O₃ (AE = Mg, Ca, Sr, Ba), and these glasses showed high quantum yields and scintillation light yields [1]. In addition, glasses have a lot of advantages such as low cost and easy productivities in comparison with single crystals. In this study, we synthesized xTbF₃-(30-x)SrF₂-20Al₂O₃-50B₂O₃ glasses (x = 0.1, 0.5, 1.0, 5.0, 10, and 20 mol%) and investigated optical and radiation-induced luminescence properties.

Fig. 1 illustrates PL excitation/emission map of 10% Tb-doped glass as a representative example. Under the excitation of 340–380 nm, the 10% Tb-doped glass showed some sharp emission peaks in the range of 480–630 nm. The spectral shape is similar to Tb-doped glasses reported elsewhere [2, 3]. Among the prepared glasses, the quantum yield of 10% Tb-doped glass was the highest (~100%). The PL decay curve of 10% Tb-doped glass is shown in Fig. 2. The decay curve was well-approximated by a single exponential decay function. The lifetime of 10% Tb-doped glass was 2.7 ms, and this value was typical for the 4f-4f transitions of Tb³⁺ ions [3]. In this conference, we will report the optical and radiation-induced luminescence properties in detail.

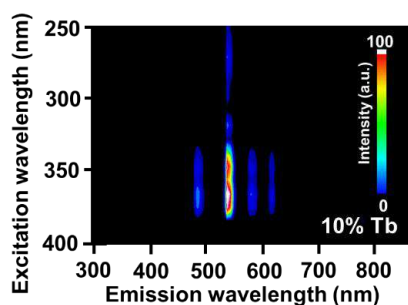


Fig. 1. PL excitation/emission map of 10% Tb-doped SrF₂-Al₂O₃-B₂O₃ glasses.

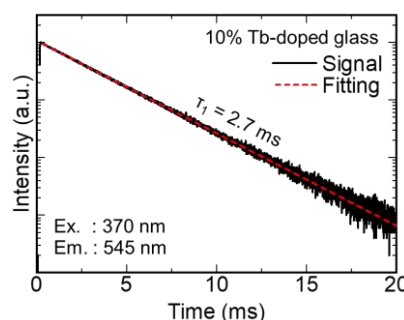


Fig. 2. PL decay curves of 10% Tb-doped SrF₂-Al₂O₃-B₂O₃ glasses.

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0.4.89 Photon-avalanche-like mechanism in $\text{Nd}_x\text{Y}_{1.00-x}\text{Al}_3(\text{BO}_3)_4$ particles excited at 1064 nm

Speaker: Moura Andre

Photon-avalanche-like mechanism in $\text{Nd}_x\text{Y}_{1.00-x}\text{Al}_3(\text{BO}_3)_4$ particles excited at 1064 nm

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The trivalent Neodymium ions (Nd^{3+}) can emit radiation at around 1064 nm due to the electronic transition $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$, which has been exploited for fundamental and applied purposes with, for example, the development of lasers and random lasers, and the operation of luminescent thermometers. Regarding the laser applications, the end state of this transition is far from the ground state ($^4\text{I}_{9/2}$), and at room temperature it is practically empty, which favors the population inversion for the stimulated emission. Furthermore, the 1064 nm light is not resonant with ground-state absorption transitions from the Nd^{3+} , which minimizes the losses of radiation by light reabsorption. In spite of that, the excitation of Nd^{3+} at 1064 nm can be feasible by phonon annihilation from the host lattice in order to compensate the energy mismatch for the **nonresonant** ground-state absorption (GSA) transition $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{3/2}$. Another excitation route for light at 1064 nm is by thermal excitation from the ground state to the upperlying state $^4\text{I}_{11/2}$ followed by **resonant** excited-state absorption (ESA) $^4\text{I}_{11/2} \rightarrow ^4\text{F}_{3/2}$. At room temperature, both nonresonant GSA and resonant ESA transitions present low probabilities. But, once excited at the $^4\text{F}_{3/2}$ state, the Nd^{3+} ion can interact with a neighbor ion at the ground state, and by means of a cross-relaxation, both ions can end at the $^4\text{I}_{15/2}$ level. Due to the low energy gap with lowerlying states, both ions are expected to relax nonradiatively with phonon emissions in the sequence $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2} \rightarrow ^4\text{I}_{11/2}$. Once at the $^4\text{I}_{11/2}$ level, both ions can be excited by resonant ESA to the $^4\text{F}_{3/2}$ state. In resume, starting with low probabilities processes, one excited Nd^{3+} at the $^4\text{F}_{3/2}$ state can lead to two ions at this state after a sequence of cross-relaxation, nonradiative relaxations with phonon emissions, and resonant ESA. Upon repeating this sequence of events, the population of the $^4\text{F}_{3/2}$ level can double at every iteration reaching giant populations, i.e., there is the establishment of a photon avalanche (PA) mechanism, which we have been observing in $\text{Nd}_x\text{Y}_{1.00-x}\text{Al}_3(\text{BO}_3)_4$ particles [1]. The nonradiative relaxations with phonon emissions from the Nd^{3+} increase the $\text{Nd}_x\text{Y}_{1.00-x}\text{Al}_3(\text{BO}_3)_4$ particles temperature, which favors both nonresonant GSA and resonant ESA. The temperature increase by intrinsic relaxations of Nd^{3+} or by heating the particles externally, is one fundamental ingredient for the PA [2]. In other words, the process is not only due to electronic transitions from the Nd^{3+} , because of that, we named the process PA-like. In addition to the light emission at 880 nm ($^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$), we observed light emission from 530 nm to 1800 nm, whose emitting levels are populated by ladder thermal excitations from the $^4\text{F}_{3/2}$ state. Thanks to the large nonlinearities in PA, it can be exploited for super-resolution imaging [3]. Also, theranostics can be exploited due to the intrinsic heating, and the operation of optical thermometers [1].

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0.4.90 Photonic integrated quantum memory in rare-earth doped solids

Speaker: Liu Chao

Photonic integrated quantum memory in rare-earth doped solids

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An optical quantum memory is a device that can store photonic quantum information and release it after a controlled time. It is an essential component for overcoming channel losses in large-scale quantum networks, either through the approaches of quantum repeaters or transportable quantum memories. Optical quantum memories have been demonstrated with various physical systems including atomic gases, single atoms in optical cavities and rare-earth-ion doped solids. Now quantum memories are marching towards miniaturization and integration for large-scale practical applications. Solid state systems stand as a natural choice due to the physical stability and ease of micro or nano fabrication using well-established techniques. In the past decade, considerable efforts have been devoted to developing photonic integrated quantum memories, i.e., quantum memories based on micro/nano-photonic structures manufactured in solids. Remarkable performances have been achieved with integrated quantum memories, with the advantages of low consumption, small volumes, large storage densities and easy implementations. I will introduce the basic concepts of optical quantum memories, the state-of-the-art technologies for fabricating integrated quantum memories, and our recent works on photonic integrated quantum memories based on femtosecond laser micromachining.

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0.4.91 Polarized spectroscopy of stoichiometric KEu(WO₄)₂ crystal

Speaker: Baillard Amandine

Polarized spectroscopy of stoichiometric KEu(WO₄)₂ crystal

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Trivalent europium ions (Eu³⁺, electronic configuration: [Xe]4f⁶) are widely used in red phosphors and more recently, they appeared attractive for watt-level deep-red lasers [1]. Monoclinic (sp. gr. *C2/c*) double tungstates feature high stimulated-emission (SE) cross-sections for polarized light for the dopant rare-earth ions, high available doping levels and weak luminescence quenching due to the large RE³⁺ - RE³⁺ distances. We report on a detailed spectroscopic study of a stoichiometric KEu(WO₄)₂ crystal. In this compound, Eu³⁺ ions reside in low-symmetry (*C*₂) sites. KEu(WO₄)₂ is biaxial and its spectroscopic properties are described in the optical indicatrix frame {*N*_p, *N*_m, *N*_g}. The 2-fold symmetry axis is parallel to the *N*_p one.

We focused on the polarization anisotropy of visible emissions of Eu³⁺ ions in this crystal related to transitions from the metastable state ⁵D₀ to the group of lower-lying ⁷F_J multiplets (*J* = 0 – 6, ⁷F₀ is the ground-state). The ED and MD forbidden ⁵D₀ → ⁷F₀ emission is observed only for light polarized along the 2-fold symmetry axis. For the purely ED transitions ⁵D₀ → ⁷F₂ (red) and ⁵D₀ → ⁷F₄ (deep-red), the SE cross-sections were determined for light polarizations *E* ∥ *N*_p, *N*_m, *N*_g, Fig. 1(a), and the electronic transitions as well as the irreducible representation of the Stark sub-levels Γ_i were assigned based on LT (12 K) spectroscopy. The deep-red Eu³⁺ transition is suitable for RT laser operation. For the purely MD transition ⁵D₀ → ⁷F₁, the emission spectra depend on the light polarization *E* and its propagation direction *k*, Fig. 1(b). Polarization selection rules are suggested based on the orientation of the magnetic field vector *H* [2].

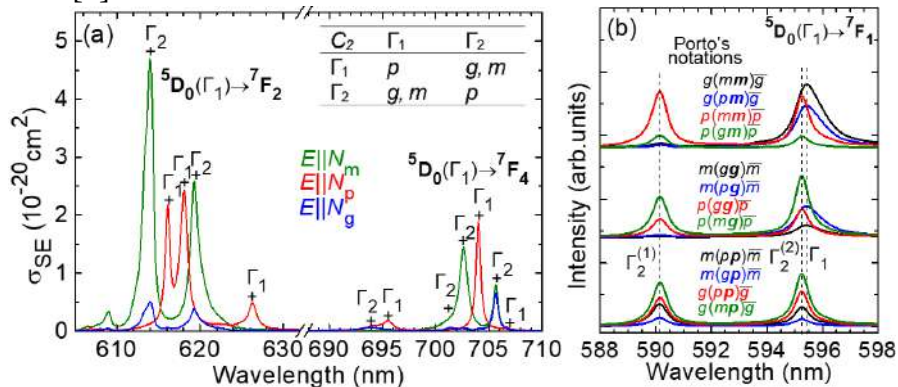


Figure 1. Polarized emission spectra of Eu³⁺ ions in KEu(WO₄)₂: (a) SE cross-sections for the ⁵D₀ → ⁷F₂ and ⁵D₀ → ⁷F₄ ED transitions; (b) the ⁵D₀ → ⁷F₁ MD transition. "+" – electronic transitions, Γ_i – irreducible representations.

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0.4.92 Probing the interaction of lanthanide-doped core@multi-shell nanoparticles with surface acoustic waves

Speaker: D. D. Couto Jr. Odilon

Probing the interaction of lanthanide-doped core@multi-shell nanoparticles with surface acoustic waves

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Hierarchically structured lanthanide-doped multi-shell nanoparticles are nanoscale-engineered systems with potential applications as multifunctional materials, since their multi-shell structure allows one to combine, in the same nanosystem, the remarkable optical emission and magnetic properties usually presented by lanthanide^{III}-based nanoparticles. These systems have been used as self-calibrated luminescent thermometers due to the high sensitivity of their molecular emission spectra to environment changes [1]. On another perspective, surface acoustic waves (SAWs) have been successfully employed over the last decades in microelectronic circuits and devices as an efficient mean to transport and decode classical information. Moreover, it is recognized that large SAW powers can lead to local heating in these devices. In this contribution, we investigate the effects of a 220 MHz SAW beam on the emission spectra of NaYDy F₄ @NaY F₄ @NaGdErYb F₄ @NaGdNd F₄ core@multi-shell nanoparticles. We studied nanoparticle clusters presenting hexagonal crystalline phase [1] placed on piezoelectric LiNbO₃ substrates with lithographically fabricated SAW transducer devices. We used a Ti-Saph laser emitting in the near infrared to predominantly excite the neodymium ions which transfer their energy to erbium ions. By detecting the light emission in three temperature ranges (5 K, 200 K and 300 K), we study the SAW-induced heating dynamics of these nanoparticles by probing the evolution of the three main Er^{III} upconverted emission bands in the visible range under different laser excitation and SAW power conditions. We are able to observe the molecular state filling dynamics of the ⁴S_{3/2} to ⁴I_{15/2} individual Stark levels as the SAW power is increased, thus demonstrating that high SAW powers can really affect the local temperature experienced by the clusters, particularly at low environment temperatures. These observations may contribute to create perspectives for using these materials as sensitive mesoscopic/nanoscale heat probes in future SAW-based quantum information circuits.

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0.4.93 Quantitative assessment of GaAs doping at the nanoscale by cathodoluminescence

Speaker: Collin Stéphane

Quantitative assessment of GaAs doping at the nanoscale by cathodoluminescence

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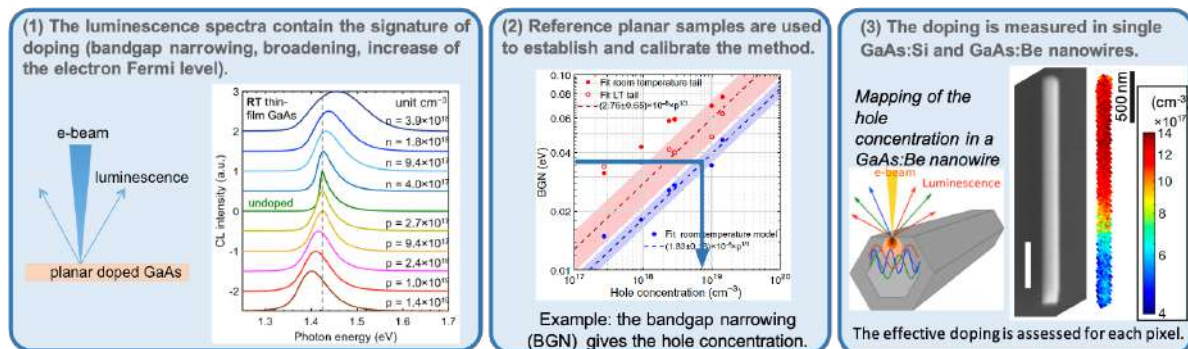
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Doping, a fundamental property of semiconductor devices. In this contribution, we take advantage of the signature of the charge carrier concentration in the luminescence of semiconductors, and we show how cathodoluminescence mapping can be used to provide a contactless, quantitative assessment of active doping at the nanoscale. The method is applied to n-doped (Si, Be) and p-doped (Te) GaAs nanowires.

First, we analyze a wide range of p-type and n-type GaAs thin films with carrier concentrations spanning from 2×10^{17} to $1 \times 10^{19} \text{ cm}^{-3}$. The luminescence spectra are fitted with the generalized Planck law and with a refined absorption model that takes into account the bandgap narrowing and the band filling induced by the doping. They are used as references to fit and calibrate cathodoluminescence (CL) measurements, and to provide a rigorous method for the quantitative assessment of p-type and n-type carrier densities by CL [1,2].

Second, we apply this method to analyze the doping concentration profiles in single GaAs nanowires (NWs) [3,4]. High-resolution maps of the hole concentration demonstrate the homogeneous doping in pure zincblende segments of GaAs:Be NWs. For Si-doped GaAs NWs, the electron Fermi level and the FWHM of low-temperature CL spectra are used to assess the electron concentration to approximately 3×10^{17} to $6 \times 10^{17} \text{ cm}^{-3}$, limited by doping compensation [3]. We also investigate GaAs:Te nanowires and we evidence higher electron concentrations, with gradients along the nanowire axis from $1 \times 10^{18} \text{ cm}^{-3}$ to $3.3 \times 10^{18} \text{ cm}^{-3}$ [4]. **Overall, these results show that high-resolution hyperspectral CL mapping is an efficient tool for contactless assessment of carrier densities at the nanoscale. The method can be extended to other semiconductors, nanostructures and devices.**



Main steps illustrating the use of luminescence spectra to map the doping at the nanoscale.

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0.4.94 Quenching mechanisms in Pr, Dy and Yb-doped ZrO₂

Speaker: Carrera Peralta Rosalba

Quenching mechanisms in Pr, Dy and Yb-doped ZrO₂

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Quenching processes in lanthanide doped compounds are of paramount importance. In this regard, it is found that in ZrO₂ doped with some lanthanides and synthesized by the polymerizable complex method, the luminescence is quenched as the annealing temperature increases. Here, we investigate in a systematic way the effect of the annealing temperature on the relative tetragonal/monoclinic phase concentration, and on the photoluminescent properties of ZrO₂ doped with Pr³⁺, Dy³⁺ and Yb³⁺ at 1 mol %. Two experiment rounds were performed. In the first one, samples were annealed at 800 °C and 1100 °C during 1h, and the luminescence intensity between these treatments dropped significantly. On the second one, after an initial heat treatment at 800 °C for 1 h, several treatments at different annealing temperatures in increasing steps of 50 °C up to 1100 °C were done. In this case, the luminescent intensity quenches gradually. To further assess the correlation between photoluminescent intensity and the crystalline phase, tetragonal yttrium stabilized zirconia were synthesized. Finally, the luminescence quenching mechanism for each of the three lanthanides is discussed.

0.4.95 Rare Earth – Diamond hybrid structures for optical quantum technologies

Speaker: Ionut Gabriel Balasa

Rare earth-diamond hybrid structures for optical quantum technologies

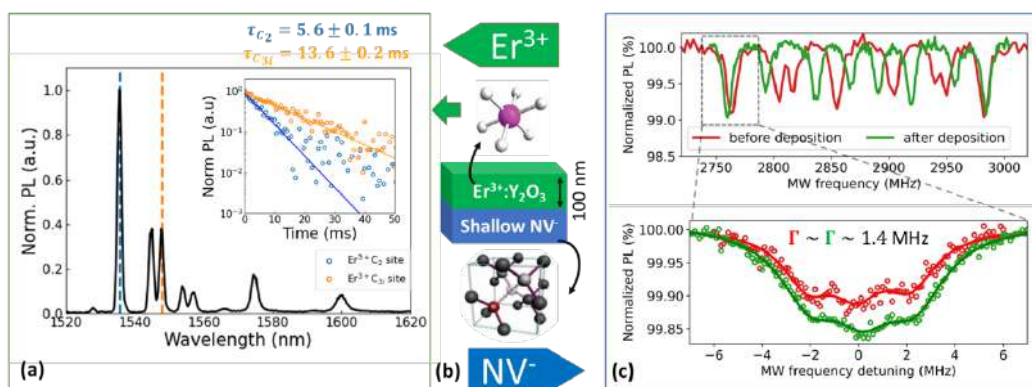
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The challenge of developing hybrid quantum materials aims to associate distinct optically active centers to achieve new functionalities while preserving the underlying properties of each component. In this work, we combine two optically active materials that have been broadly used for quantum applications and are compatible with scalable fabrication techniques: shallow NV⁻ color centers in diamond [1] and rare earth (RE) ions in thin films [2]. Here, we present a hybrid structure sketched in Fig. (b) that consists of an Er³⁺ doped Y₂O₃ thin film deposited by direct liquid injection chemical vapor deposition (CVD) on a diamond substrate in which shallow NV⁻ were implanted. We investigate the crystallinity of the thin film and the optical properties of the embedded Er³⁺ ions, and how the spin and optical properties of the NV⁻ are affected by the thin film. The photoluminescence spectrum of the ⁴I_{13/2}-⁴I_{15/2} Er³⁺ transition measured at 10 K is reported in Fig. (a) and confirms that Er is in the trivalent configuration in the cubic phase of Y₂O₃. The inset of Fig. (a) also presents the decays of the two Er occupational sites in Y₂O₃: C₂ and C_{3i}, measured at 10 K. The obtained decay times are 5.6 ± 0.1 ms and 13.5 ± 0.2 ms respectively and are comparable to bulk crystal references (8.5 ms and 14.6 ms [3]) thus proving that no major non-radiative or quenching effects arise in the nanostructured thin film. Optical and spin properties of the NV⁻ before and after the thin film deposition are reported in Fig. (c). The top of Fig. (c) presents a wide optically detected magnetic resonance (ODMR) spectrum where the 8 peaks correspond to the degeneracy lift due to 4 distinct projections of the applied magnetic field on the NV axis for two different spin projections ($m_s = \pm 1$). The bottom part of Fig. (c) is a zoom into one of the spin transitions indicating a constant linewidth around 1.4 MHz, before or after deposition. The spin properties of the NV⁻ at the diamond/film interface have thus not been altered. In conclusion, this is a first proof of the possibility of integrating the rare-earth ions with NV⁻ centers at the nanoscale level for developing hybrid solid state quantum systems.



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0.4.96 Rare Earth – Diamond hybrid structures for optical quantum technologies

Speaker: Mariá Arranz-Martinez

Rare Earth – Diamond hybrid structures for optical quantum technologies

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The challenge of developing hybrid quantum materials aims to associate distinct optically active centers to achieve new functionalities while preserving the underlying properties of each component. In this work, we combine two optically active materials that have been broadly used for quantum applications and are compatible with scalable fabrication techniques, the shallow NV⁻ color centers in diamond [1] and the rare earth (RE) doped thin films [2]. Here, we present a hybrid structure that consists of an Er³⁺ doped Y₂O₃ thin film deposited by direct liquid injection chemical vapor deposition (CVD) on a diamond substrate in which shallow NV⁻ were implanted. We investigate the crystallinity of the thin film and the optical properties of the embedded Er³⁺ ions, and how the spin and optical properties of the NV⁻ are affected by the thin film deposition. The photoluminescence spectrum of ⁴I_{13/2}-⁴I_{15/2} Er³⁺ transition measured at 10K confirms that erbium is in the trivalent configuration in the cubic phase of Y₂O₃. The decays of the two erbium occupational sites in Y₂O₃, C₂ and C_{3i}, were measured at 10 K. The obtained decay times are 5.6 ± 0.1 ms and 13.5 ± 0.2 ms respectively and are similar to the bulk references (8.5 ms and 14.6 ms [3]) thus proving that no major non-radiative or quenching effects arise in the nanostructured thin film. Optical and spin properties of the NV⁻ before and after the thin film deposition show that the spin transition linewidth is around 1.4 MHz and it has not been affected by the film deposition. Thus the spin properties of the NV⁻ at the diamond/film interface has not been altered. In conclusion, this is a first proof of the possibility of integrating the rare-earth ions with NV⁻ centers at the nanoscale level for developing hybrid solid state quantum systems.

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0.4.97 Red-emitting lifetime-based luminescence manometer on SrGdAlO₄ Mn⁴⁺

Speaker: Pieprz Mateusz

Red-emitting lifetime-based luminescence manometer on SrGdAlO₄ Mn⁴⁺

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Luminescence manometry enables quick and minimally invasive diagnostic, which is crucial for various applications. Currently, most luminescent manometers rely on the spectral response of the phosphor [1][2]. Nevertheless, this method of measurement is susceptible to disturbance when the emitted light interacts with a highly scattering or absorbing medium. Hence, there is an urgent need to explore new measurement techniques to ensure accurate and dependable pressure readings under such circumstances.

In the present work, a new approach to luminescence manometry is proposed, which take advantage of the lifetime elongation of the ²E state of Mn⁴⁺ ions in SrGdAlO₄:Mn⁴⁺. The spectroscopic properties of this red emitting phosphor were studied as a function of applied pressure and temperature. As it will be shown the lifetime of the ²E states elongates monotonically in the ambient to- 4GPa pressure range. Additionally in this host material the kinetics of the ²E→⁴A₂ luminescence is not affected by the temperature in the 260-365K range, which provides the temperature invariant pressure readout. The maximal relative sensitivity to pressure changes reaches S_{R,p}=19.7%/GPa at 2.1GPa

Acknowledgement

This work was supported by National Science Center Poland (NCN) under project No. UMO-2020/37/B/ST5/00164.

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0.4.98 Research of polymer matrices toward the fabrication of submicrometric dye-doped films – potential candidates for application as a humidity sensor and for photonics

Speaker: Duda Łukasz

Research of polymer matrices toward the fabrication of submicrometric dye-doped films – potential candidates for application as a humidity sensor and for photonics

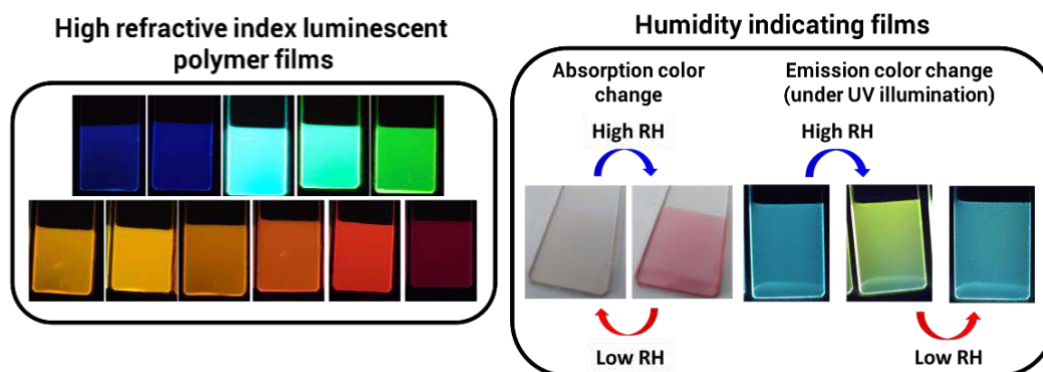
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Embedding of organic luminescent dye into some matrices may induce specific interaction between them [1]. This in turn may influence the luminescent properties of the dye due to presence of its different forms *e.g.* aggregated, neutral and/or protonated. A variety of organic luminescent dyes and polymer matrices (including polyelectrolytes) enables fabrication of films with designed properties, such as refractive index and spectral range of emission, as presents in Figure below.



Fabricated high refractive index and humidity indicating luminescent films on soda-lime glass substrates. RH – relative humidity.

In this study the fabrication of polymer films using dip-coating technique as well as their characterization, is presented. Poly(benzyl methacrylate) (PBzMA), polystyrene (PS), polycarbonate (PC) and polysulfone (PSU) films on soda-lime glass substrates were obtained. The thickness of the layers was in the submicrometric range and their refractive index was higher than 1.51, which was determined using profilometry and spectroscopic ellipsometry. Numerical calculations confirmed that fabricated polymer films meet the criteria to work as planar waveguides on soda-lime glass substrates. Spectroscopic techniques such as absorption, luminescence excitation and emission showed that organic luminescent dyes from various chemical groups could be used in dye-doped PSU. Their emission covers the entire visible spectral range. Moreover, the luminescent properties of two dyes exhibiting either solvatochromism (Nile Red) or tendency to aggregation (Rhodamine 6G) turned out to be strongly dependent on the polymer matrix. We expect that the fabricated films could be used in planar photonic systems as waveguiding films or in light conversion and light amplification systems. Moreover, fabrication of polyelectrolyte films together with their potential application as optical humidity indicators is discussed.

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The research was co-financed by the Foundation for Polish Science from the European Regional Development Fund within the project POIR.04.04.00-00-14D6/18 "Hybrid sensor platforms for integrated photonic systems based on ceramic and polymer materials (HYPHA)" (TEAM-NET program). Ł.D. would like to thank the Ministry of Science and Higher Education in Poland for the Grant No. DWD/4/64/2020 in the frame of Implementation Doctorate Programme.

0.4.99 Scintillation screens for Imaging with Neutrons

Speaker: Walfort Bernhard

Scintillation screens for Imaging with Neutrons

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Neutron imaging detectors based on a light-sensitive camera, which observes the emitted light from a scintillator screen have become a standard tool at many facilities. Meanwhile, there are systems available for very large field-of-view (FOV), very high spatial resolution, high frame rate and those for sophisticated new methods (like centroiding or “event-mode”-imaging). Each of them has specific requirements in particular related to the scintillator screen - one of the key components.

Clearly, the two most relevant specifications of the scintillation screens are the light output and the resolution, but to fully evaluate the performance of the screen also the “signal to noise ratio”, the light attenuation and the neutron capture efficiency should be taken into account.^[1]

Here we will give an overview of the different type of scintillation screens and their advantages and disadvantages in the use of different applications or beamline surrounding.

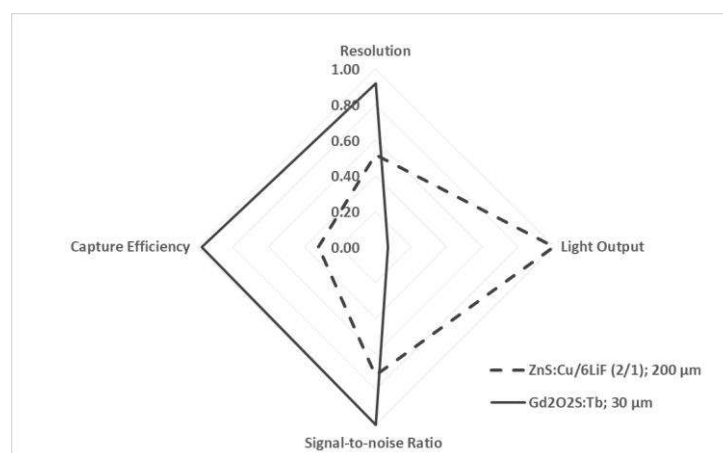


Fig. 1: Comparison of the different features of the most used scintillation screens within a net diagram (measured at Neutra (PSI)).

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0.4.100 Self-decontaminating surfaces in 3D prints through ultraviolet radiation generated in situ by upconversion nanoparticles

Speaker: Makiyama Lays

Self-decontaminating surfaces in 3D prints through ultraviolet radiation generated in situ by upconversion nanoparticles

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This work reports on 3D printing with self-decontaminating surfaces obtained by photopolymerization of upconversion nanocomposites leading to in situ UV production. Although the integrated intensity of UV radiation generated by the proposed process is low, monitoring assays of viral inactivation over surfaces with a virus model are being performed to evaluate the effectiveness of the local effective flux of UV radiation generated by nanoparticles near these contaminants. Upconversion nanoparticles (UCNPs) of Ca_2LaF_7 doped with Yb^{3+} and Tm^{3+} ions were synthesized by hydrothermal route ^[1] aiming *in situ* decontamination purposes by the generation of UV radiation in nanocomposites with UCNP, forming innovative 3D printing resins for additive manufacture. To achieve a higher intensity of a 363 nm UV emission from Tm^{3+} ($^1\text{D}_2 \rightarrow ^3\text{H}_6$) ^[2], the ratio of $\text{Yb}^{3+}/\text{Tm}^{3+}$ concentrations was chosen to improve in each matrix the IR $\rightarrow$ UV UC from 980 nm excitation through four photons sequential energy transfer from Yb^{3+} , based on the APTE (Auzel Effect) between Yb^{3+} - Tm^{3+} ions, looking at the same time to the cross-relaxation processes between Tm^{3+} - Tm^{3+} ions ^[2-3]. In the Ca_2LaF_7 composition studied the optimal concentrations for IR $\rightarrow$ UV UC were up to 20% (mol) for Yb^{3+} and 0.2% (mol) for Tm^{3+} . A study of the use of Fe^{3+} ions as a dopant in the crystalline matrix of composition was also executed, where it was verified that Fe^{3+} ions contributed significantly to the IR $\rightarrow$ UV UC. The synthesized Ca_2LaF_7 UCNPs had an average size of 30 nm, as a mix of two crystalline phases: cubic (CaF_2) and hexagonal (LaF_3). The synthesized UCNPs were incorporated into photopolymerizable resins for 3D printing, and as a result, a UC luminescent photopolymerizable nanocomposite (UCNCFP) was produced, which was subsequently printed in a 3D MSLA Phrozen Sonic Mini 8K high-resolution printer in discs shaped, for viral inactivation surface assays. Strategies were established to increase the intensity of the UV emission by the UCNPs and UCNCFPs, as well as new mechanisms for Vis $\rightarrow$ UV UC instead of IR $\rightarrow$ UV UC to move the excitation to the visible region, monitored by microbiological tests for the analysis of the decontamination capacity by UV radiation ^[4] generated in situ at the UCNCFP excited surfaces.

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0.4.101 Silica-titania based integrated optic systems for new on-chip sensing devices

Speaker: Prokop Kacper

Silica-titania based integrated optic systems for new on-chip sensing devices

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A new construction of Mach-Zehnder interferometer based on a sol-gel SiO₂-TiO₂ (silica-titania) material platform is proposed. According to the current experience on this topic [1,2], the silica-titania waveguide platform proves its advantage due to low cost, low loss, and easy-to-develop integrated optics systems. The integrated photonic circuits studied here were obtained for very attractive optical platforms: Si/SiO₂ and Si/SiO₂/SiO₂:TiO₂. The SiO₂:TiO₂ thin films were deposited via a sol-gel dip-coating method. Such systems, modelled in detail are capable of operating from visible to near-IR wavelength ranges. The Mach-Zehnder configurations investigated in this work are attractive for on-chip sensing devices. Fabricating highly effective and economical photonic devices of such is the final purpose of discussed research.

The study is organized into two parts. In the first part, a detailed investigation of photolithography parameters' is presented. The determination of best factors such as UV exposure dose, development time or hard-baking temperature was very important. The search for the best parameters was aimed at obtaining continuous, defect-free, well-separated waveguides (WG) of Mach-Zehnder structures with specific separation between WGs. In the second part, the results of etching silica-titania waveguiding structures, based on optimized lithographic patterns, are presented.

The fabrication of Mach-Zehnder WG structures on SiO₂-TiO₂ films was well-controlled by etch rate of the samples by utilizing dry etching technique - inductively coupled plasma reactive-ion etching (ICP-RIE). The first results showed faster and more efficient etching for silica-titania films supported on Si/SiO₂ substrates in comparison to already studied glass substrates.

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Acknowledgments

The research was co-financed by the Foundation for Polish Science from the European Regional Development Fund within the project POIR.04.04.00-00-14D6/18 "Hybrid sensor platforms for integrated photonic systems based on ceramic and polymer materials (HYPHa)" (TEAM-NET program).

0.4.102 Site-selective fluorescence and DFT studies of Nd³⁺ optical centers in BaF₂ doped crystals suitable for CNOT quantum gate

Speaker: Vagapova Ekaterina

Site-selective fluorescence and DFT studies of Nd³⁺ optical centers in BaF₂ doped crystals suitable for CNOT quantum gate

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Fluorite-type crystals and their nanoparticles activated by rare-earth ions (REIs) are of great interest for both fundamental and applied science. A promising area of special use for these materials is quantum computing, where some REIs can serve as optical centers, providing a good basis for creating quantum gates [1]. In particular, single optical centers occupying lattice sites of tetragonal symmetry (C_{4v}) in Nd³⁺-doped alkaline earth metal fluoride can be used as key elements of CNOT quantum gates, since the distance between them is suitable for the Stark blockade. The electrostatic dipole-dipole interactions between impurity REIs is almost two orders of magnitude higher than these interactions in crystals with homovalent substitution.

To study the Nd³⁺ optical centers in a BaF₂:Nd³⁺ crystal, we used the methods of site-selective time-resolved laser fluorescence spectroscopy with high spectral resolution at low temperatures ($T = 4.2$ K, 6.5K). Also, to determine the lifetimes of the $^4F_{3/2}(1)$ Stark level of the optical centers, we measured the fluorescence decay kinetics using gated photon counting.

In our studies, four different types of Nd³⁺ optical centers were observed in the BaF₂:Nd³⁺ crystal. One of them has been previously reported in the literature [2], and information about the other three is based on the results of our work. The spectroscopic measurements data, combined with DFT analysis, revealed the characteristic features underlying the formation of these three configurations that the tetragonal single Nd³⁺ center in the BaF₂ host structure can adopt. The position in the lattice of these three optical centers is characterized by a lowering of the site symmetry from C_{4v} to C_s and is associated with different stabilizing positions, which are preferred by the charge-compensating fluorine interstices in the anion sublattice with respect to one of the spatial coordinates of the impurity ion. Due to this factor, the energy of the $^4F_{3/2}(1)$ Stark level of the Nd³⁺ ion shifts differently, and the radiative lifetimes of these three optical sites become different.

It has been experimentally shown that the probability of the formation of pair centers of Nd³⁺ ions in the BaF₂ host is much lower than in CaF₂ and SrF₂. However, we still managed to select two pair optical centers with different distances between ions in a pair.

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0.4.103 SMART RHESINs—Superparamagnetic Magnetite Architecture Made of Phenolic Resin Hollow Spheres Coated with Eu(III) Containing Silica Nanoparticles for Future Quantitative Magnetic Particle Imaging Applications

Speaker: Feye Julia

SMART RHESINs—Superparamagnetic Magnetite Architecture Made of Phenolic Resin Hollow Spheres Coated with Eu(III) Containing Silica Nanoparticles for Future Quantitative Magnetic Particle Imaging Applications

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Magnetic particle imaging (MPI) is an increasingly prominent and powerful tomographic imaging technique that allows for non-invasive visualization of superparamagnetic nanoparticles (NPs) within living organisms.^[1] While MPI holds great potential for various applications, its quantitative nature in biological settings has not been fully exploited yet. To address this limitation, we propose a novel NP architecture designed to maintain nearly unchanged effective relaxation (combining Brownian and Néel relaxation) even when immobilized allowing quantification at the probe site.^[2] These superparamagnetic magnetite-filled phenolic formaldehyde resin hollow nanospheres^[3], herein named SMART RHESINs^[2], were synthesized and surface-functionalized with luminescent Eu(TTA)₃ complex-containing silica NPs (TTA: 3-thenoyltrifluoroacetate).

Besides their suitability for potential MPI applications, their accumulation in the region of the Golgi apparatus, and the absence of acute cytotoxicity, photobleaching studies revealed a remarkable observation: SMART RHESINs exhibit an unexpectedly high level of red luminescence after their uptake into living HeLa cells.^[2] The normalized fluorescence intensity of SMART RHESINs increased by approximately 20% up to 50% in different solvents compared to their initial values. The strong fluorescence enhancement indicates a gradual population of a solvent-induced long-lived dark state that could be recovered by repeated excitation, which is why the population of the presumed dark state can be attributed to the prominent fluorescence emission peak of the europium ion combined with the phenol formaldehyde resin (PFR).^[2]

The chemical stability, superparamagnetic behavior, biocompatibility and exceptional luminescence of SMART RHESINs position them as promising candidates for multimodal imaging probes. Beyond their potential applications in *in*

vitro cell biology studies, the integration of luminescence and magnetism within these NPs opens up promising opportunities for *in vivo* imaging applications. By harnessing the combined modalities of luminescence and magnetism, SMART RHESINs offer exciting advances in the field of biomedical imaging.

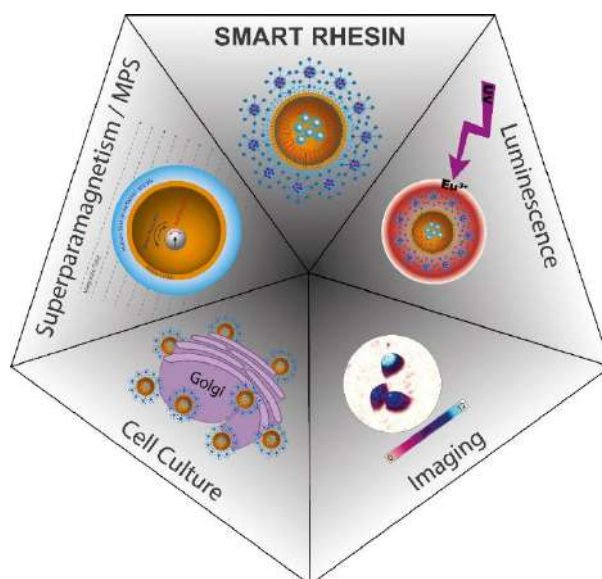


Figure 1: SMART RHESINs and their properties for multimodal biomedical applications.

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0.4.104 Spatiotemporal Microscopy of Energy Carrier Transport

Speaker: Utterback James

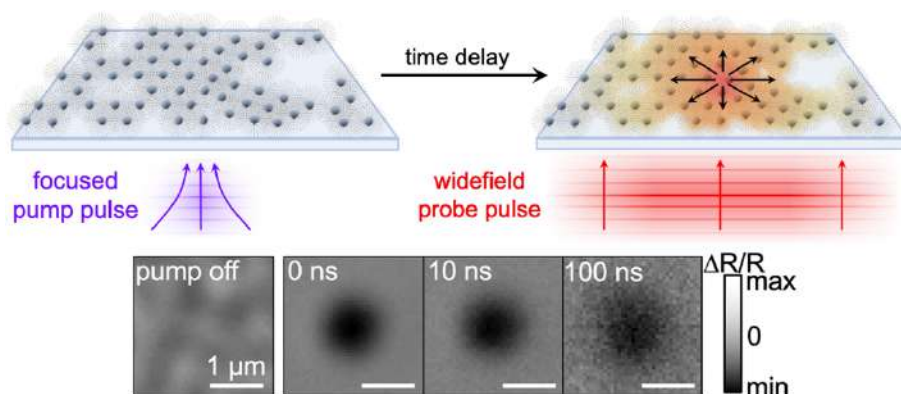
Spatiotemporal Microscopy of Energy Carrier Transport

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Optoelectronics applications require control over the generation, separation, and extraction of photoexcited charges. Yet, in many material systems, energy carrier transport must navigate defects of various natures over a broad range of length and time scales. There are many approaches to inferring microscopic energy transport through energetic, temporal, or spatial markers, but each faces limitations. Moreover, heterogeneous systems are often elusive to simple kinetic models that reveal fundamental transport parameters. To understand the principles that govern electronic and thermal relaxation dynamics in complex systems relevant to optoelectronic applications, advanced experimental techniques and theoretical models rooted in fundamental physical phenomena are needed. This presentation will focus on the following questions: How do heterogeneous environments and interfaces impact microscopic energy transport and conversion? How can we access information about energy carriers that traditionally do not have clear spectroscopic signals? I will describe pump-probe optical measurements and modeling of carrier transport in nanocrystal and semiconductor films.



Schematic depiction of spatiotemporally resolved pump-probe microscopy and sample data showing lateral expansion of photoexcited carrier distribution due to diffusion.

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0.4.105 Squeezing the sun: up-conversion driven photo-electrochemical hydrogen generation via water-splitting

Speaker: Torres-García Sheila

Squeezing the sun: up-conversion driven photo-electrochemical hydrogen generation via water-splitting

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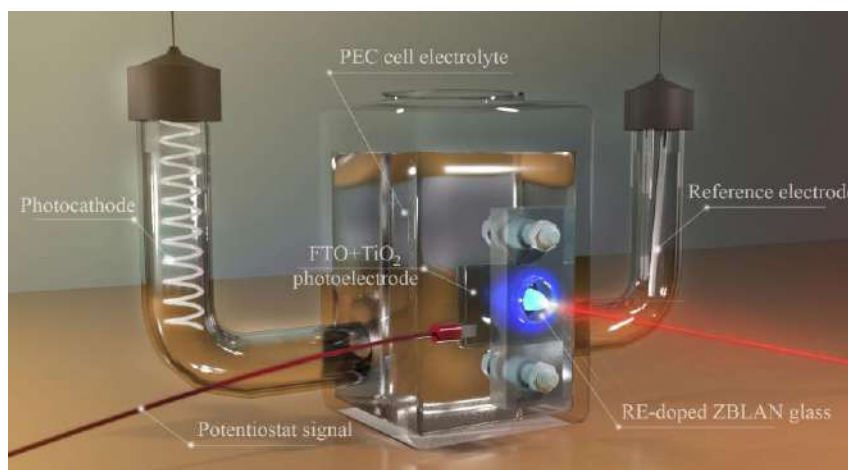
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Increasing the overall solar spectrum utilization is of crucial interest for photochemical energy harvesting and storage. In particular, rare-earth doped luminescent materials, ZBLAN glass samples doped Yb^{3+} - Er^{3+} - Tm^{3+} , with capable of NIR-to-UV-VIS spectral shaping (up-conversion) can boost “green hydrogen” production via photo-electrochemical water-splitting [1]. Here we present evidence of infrared-induced hydrogen and oxygen evolution via water-splitting in a photo-electrochemical cell using TiO_2 electrodes, by means of highly efficient spectral converting glassy materials. This approach provides a significant contribution to the state-of-the-art for effective harvesting of the near-infrared portions of sunlight, unused for conventional photocatalytic hydrogen production and environmental purification [2] at present. This proof-of-concept determines univocally the role of a solely photonic effect to split water, converting the incident NIR radiation before its interaction with the photocatalyst.



Infrared-induced hydrogen and oxygen evolution via water-splitting in a photo-electrochemical cell using TiO_2 electrodes, by means of highly efficient spectral converting (upconversion) ZBLAN glass samples doped Yb^{3+} - Er^{3+} - Tm^{3+}

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0.4.106 Stable nano-YAG:Ce³⁺ phosphors for photonic applications

Speaker: Montanarella Federico

Stable nano-YAG:Ce³⁺ phosphors for photonic applications

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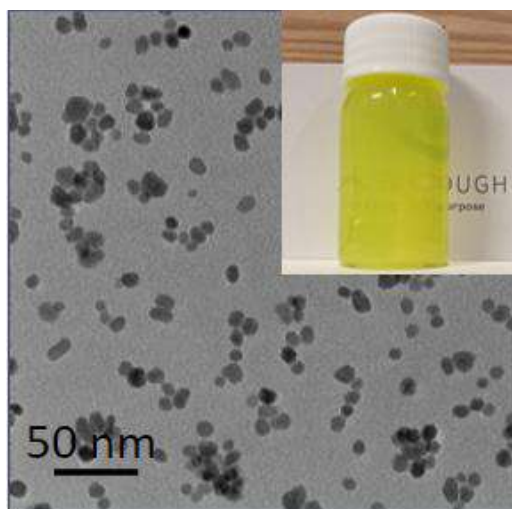
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Over the last two and half decades, Y₃Al₅O₁₂:Ce³⁺ (YAG:Ce³⁺) has served as a benchmark phosphor in lighting and display fields. Its intense green-yellow emission, extremely high robustness, strong absorption of blue light and outstanding stability makes it an ideal phosphor for a wide variety of applications. With recent miniaturization of semiconductor light emitting devices (LEDs), such as mini- and micro-LEDs, the search for stable and efficient down-converting materials with nano-to-submicron dimensions has intensified. Because of its many beneficial properties, YAG:Ce is an interesting candidate for these applications when available at the nanoscale. However, so far, efforts on the development of nano-YAG typically yield agglomerated and/or irregular particles, low absorption strengths, as well as a low energy conversion efficiency and stability issues. [1]

Here, we present an overview of our technologies on achieving stable, well-defined nano-YAG:Ce³⁺ phosphors with high energy conversion efficiencies (QY>90%). In this poster we discuss: 1) the different synthetic methods that we use, resulting in great control over the size of the nanoparticles, which can be tuned between few hundreds of nm to 10-20 nm; 2) the post-synthetic treatments and encapsulation technologies and how these influence the structural and optical properties of the materials, in particular how they improve the stability of nano-YAG:Ce³⁺ both under laser irradiation and on commercial LEDs.



Transmission electron microscopy image of nano-YAG:Ce³⁺ and (inset) digital photograph of a colloidal dispersion of YAG:Ce³⁺ nanoparticles

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0.4.107 Stimuli-responsive luminescent materials based on tetracyanonitridorhenate(V) complexes

Speaker: Liberka Michal

Stimuli-responsive luminescent materials based on tetracyanonitridorhenate(V) complexes

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Stimuli-responsive materials gain significant scientific attention in the pursuit of novel technologies as they display remarkable changes in physical properties upon even subtle changes in the surroundings.¹ They offer a fast response to such external stimuli as light, voltage, or temperature, which opens applications, e.g., in drug delivery, data storage, or lighting devices. Our goal was to construct novel luminescent systems which can be highly sensitive to external stimuli. We selected tetracyanonitridorhenate(V) complexes, $[\text{Re}^{\text{V}}(\text{CN})_4(\text{N})(\text{L})]^{2-}$ (L = organic ligand), that are strongly emissive, and their optical properties are sensitive to chemical factors and temperature.² We combined them with polar *N*-methylidabconium (Medabco⁺) cations which results in novel organic-inorganic hybrids showing strong green photoluminescence. Thanks to the cations revealing non-innocent *T*-activated dynamic vibrations, these materials show an order-disorder phase transformation demonstrated in structural, electrical, and spectroscopic studies. Moreover, this phase transition results in the unique luminescence switching effect. The tetracyanonitridorhenate(V) complexes were also combined with different pyridine-based ligands (L), which strong emission (Φ up to 0.8) is tunable from yellow to red by the applied organic ligand. We used these complexes to fabricate light-emitting devices to demonstrate that their photophysical properties make them attractive candidates for lighting applications. In addition to photo- and electroluminescence, they exhibit the extremely unique switching of photoluminescence by an applied electric field.

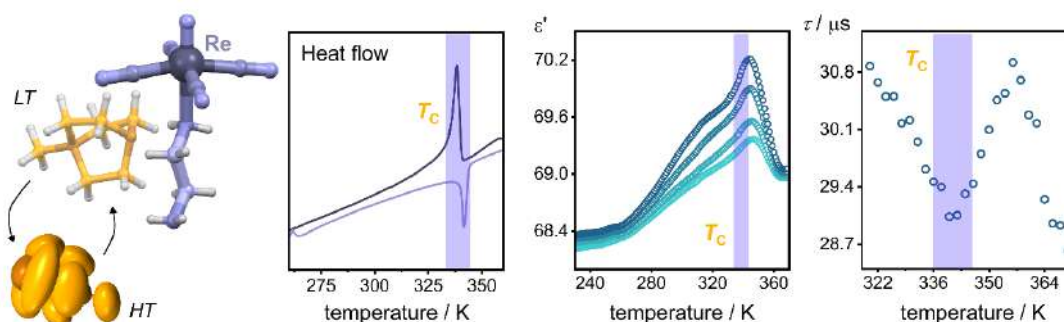


Figure 1. The crystal structure of $(\text{Medabco})_2[\text{Re}^{\text{V}}(\text{CN})_4(\text{N})(\text{L})]$ salt and its DSC curve profile, together with *T*-dependences of the dielectric permittivity and emission lifetime.

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0.4.108 Strain-mediated ion-ion interaction in rare-earth-doped solids

Speaker: Louchet-Chauvet Anne

Strain-mediated ion-ion interaction in rare-earth-doped solids

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It was recently shown that the optical excitation of rare-earth ions produces a local change of the host matrix shape, attributed to a change of the rare-earth ion's electronic orbital geometry [1]. In this work we investigate the consequences of this piezo-orbital backaction and show how it leads to a specific ion-ion interaction mediated by mechanical strain. This interaction, intimately connected to the piezospectroscopic effect, scales as $1/r^3$, similarly to the other archetypal ion-ion interactions, namely electric and magnetic dipole-dipole interactions.

We quantitatively assess and compare the magnitude of these three interactions from the angle of the instantaneous spectral diffusion mechanism, and reexamine the scientific literature in a range of rare-earth doped systems in the light of this generally underestimated contribution [2].

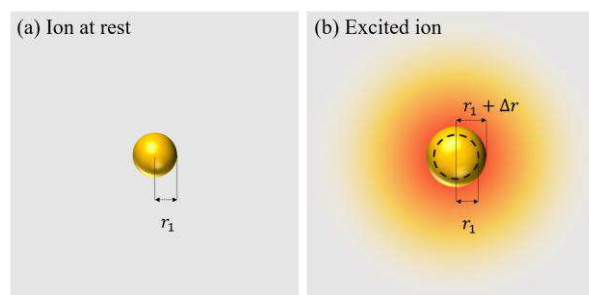


Figure : Simplified view of the piezo-orbital backaction around a spherical rare-earth ion. The stress field, symbolized by a radial color gradient around the ion, perturbs the surrounding ions via the piezospectroscopic effect.

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0.4.109 Structural characterization of Layered Double Hydroxide (LDH) nanotubes for application in photocatalysis

Speaker: Teixeira Alexandre

Structural characterization of Layered Double Hydroxide (LDH) nanotubes for application in photocatalysis

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Carbon dioxide (CO₂) is an important gas for life on the planet and it is released naturally in the breathing of living organisms, by the decomposition of organic matter, etc. From the second half of the XVIII due to the Industrial Revolution, the emission of CO₂ has been intensified beyond the acceptable limits leading several countries to start to make high investments in reducing the emission of this gas[1].

The structure of layered double hydroxides (LDH) is based on the sheet mineral brucite (MgO). Isomorphic substitution of divalent ions in the neutral brucite sheet with tri or tetravalent ions generates a positive layer charge which can be compensated by adsorption of anions between the layers. LDH nanotubes have a large surface area[2] and replacement of metals in the LDH layers by metals with photocatalytic properties such as copper[3] can enebling a possible application in the CO₂ reduction.

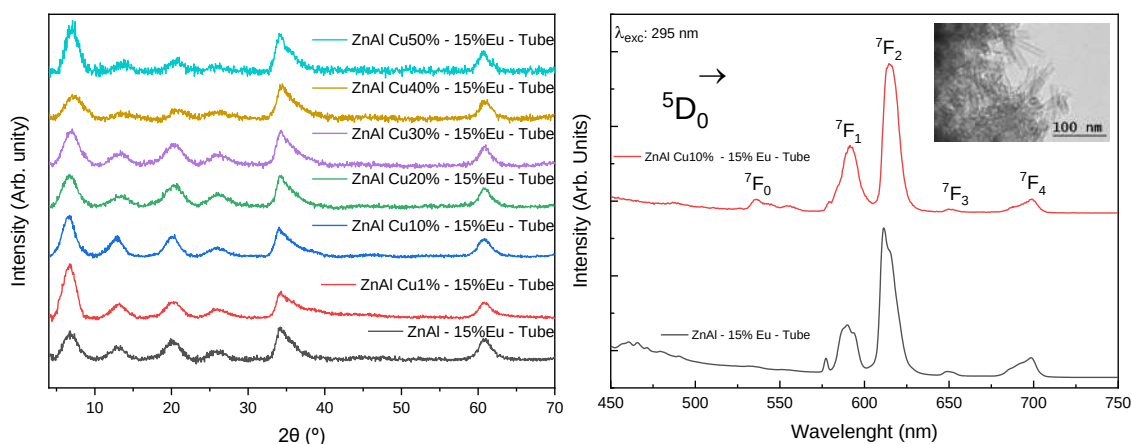


Figure1. Left: X-ray diffractograms of samples ZnAl with partial substitutions of 1%, 10%, 20%, 30%, 40% and 50% of Cu²⁺. Right: Emission spectra of the nanotubes. Red line Zn Al Cu10% - 15% Eu - Tube and black line ZnAl – 15%Eu - Tube. The inset shows the TEM image of a typical nanotubes found in those samples.

Replacement of the Zn³⁺ by Cu²⁺ in the nanotubes occurred without structural modifications for concentrations up to 10%. Beyond this concentration no formation of nanotubes was observed.

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0.4.110 Synthesis and Characterization of Terbium doped Sodium Barium Bismuth Phosphate for WLEDs Applications

Speaker: Kennedy S Masilla Moses

Synthesis and Characterization of Terbium doped Sodium Barium Bismuth Phosphate for WLEDs Applications

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The novel Tb³⁺ doped NaBaBi₂(PO₄)₃ phosphors (hereafter denoted as NBBP) were synthesized by a conventional solid state reaction method at a moderate high temperature. The prepared pure and the doped samples exhibited the same structure with a space group I-43d (220) and it was confirmed through the powder XRD peaks. The morphological analysis and the chemical composition of the phosphors were inspected through the powder SEM images along with the EDS analysis. The photoluminescent analysis showed an intense emission peak at 543 nm upon exciting the phosphor at 398 nm. The energy transfer among the nearest neighbor ions led to the concentration quenching which occurred at 0.06 mol of the Tb³⁺ ions. The increasing trend of the lifetime values and the CIE coordinates, which lay in the greenish region, were investigated. The temperature dependent lifetime was also investigated. The optimized phosphor maintained ~84% of its initial photoluminescence intensity value at 423 K, indicated its high thermal stability and could find application in the field of phosphor converted white LEDs.

0.4.111 Synthesis and photostability study of unusual $[Eu(-dkt)_2(PIB_4CH_3)_2]$ complexes

Speaker: Silva Rodolpho

Synthesis and photostability study of unusual [Eu(β -dkt)₂(PIB_4CH₃)₂] complexes

Rodolpho A. N. Silva,¹ Jean D. C. Menezes,¹ Gyovanna C. Marineli,¹ Sergio A. M. Lima,² Marco A. Cebim,¹ Marian R. Davolos,¹ and Ana M. Pires^{2,*}

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The use of coordination compounds containing lanthanide ions has increased significantly due to their applicability in the development of biomarkers, sensors, optical devices and much more. The luminescence exhibited by these compounds occurs by the well-known antenna effect, where ligands coordinated to the lanthanide ion absorb the incident radiation and transfer it to the metallic center, followed by light emission. However, the same absorbed energy can also degrade the complex, with the breaking of chemical bonds, a phenomenon known as photobleaching, common both in purely inorganic and organic systems, with emphasis on the latter.¹ Therefore, photostability studies are necessary to identify optimal working times for these complexes, as well as potential applications. In this study, complexes with the general formula [Eu(β -dkt)₂(PIB_4CH₃)₂], β -dkt = TTA, 2-thenoyltrifluoroacetyl-acetonate or BTFA, 4,4,4-trifluoro-1-phenyl-1,3-butanedione, and PIB_4CH₃ = 2-(p-tolyl)-1H-imidazo[4,5-f][1,10]phenanthroline were synthesized, characterized, and had their photo-stabilities monitored via photoluminescence spectroscopy (PLS). FTIR data revealed vibrational modes between 400 and 600 cm⁻¹ assigned to Eu-O and Eu-N bonds in the spectra of the synthesized complexes that are absent in those of the ligands, suggesting successful coordination. In addition, molecular ions related to the above-mentioned stoichiometric ratio ([M + 1 H⁺]) were detected via mass spectrometry. PLS measurements, in turn, provided the spectral profiles of the synthesized complexes and their respective photophysical parameters. Photostability measurements, Fig. 1, reveal that all complexes exhibit a drop in relative emission intensity after 5 hours of direct exposure to UV light at ~320nm (β -dkt band), with emphasis on the complex with TTA ligand, with a loss of 72.3%. It is possible to conclude, therefore, that the complexes were successfully synthesized, and that their photostability qualifies them for potential application in devices or assays that do not require prolonged exposure to ultraviolet radiation, or else, in the design of UV sensors.

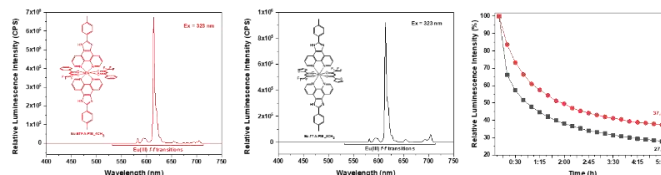


Figure 1: Emission spectra and Relative Luminescence Intensity in function of time of UV light exposure of Eu-BTFA-PIB_4CH₃ (red) and Eu-TTA-PIB_4CH₃ (black) complexes.

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0.4.112 Synthesis of superparamagnetic and ultra-high luminescent nanostructured composites via solid state reaction for application in non-destructive testing (NDT)

Speaker: Sihm Luca Michael

Synthesis of superparamagnetic and ultra-high luminescent nanostructured composites via solid state reaction for application in non-destructive testing (NDT)

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Magnetic particle inspection (MPI) is an industrial nondestructive technique that detects flaws in ferromagnetic materials like steel¹ by magnetizing it with an electric current or magnetic field, then discontinuities produce a magnetic flux leak, which draws MPI bath's magnetic particles to flaws that are exposed under UV light. Luminescent superparamagnetic nanostructured composites offer improved sensitivity, increased contrast, and fewer false positives compared to traditional microparticles².

Inspired by the outstanding behavior of the BODIPY dye, a novel fluorescent boron fluoride derivative of the classic YELLOW 101 pigment has been synthesized and investigated in prior work³. A composite of maghemite nanoparticles (γ -Fe₂O₃) and the new BYellow dye was obtained by grinding at a mass proportion of 60-40, and over several days an intriguing change in its emission was visually observed. The unusual solid-state reaction was then characterized by fluorescence spectroscopy (steady-state and time-dependent), X-Ray powder diffraction (XRD), and scanning electron microscopy (SEM). The emission exhibited a blue shift, and the integral intensity of the emission intensified threefold (Figure 1A). After 97h Yellow 101 nanocrystals were formed and the diffractogram of the composite became a mixture of γ -Fe₂O₃, Yellow 101 and BYellow patterns (Figure 1B). The solid-state reaction between BYellow and γ -Fe₂O₃ nanoparticles lead to nanorods of Yellow 101 via orientated attachment growth (Figure 1C). As the distance between the fluorescent nanorods and the γ -Fe₂O₃ nanoparticles increased, the fluorescence quenching decreased specially, the resonance energy transfer (FRET) was diminished, which resulted in an increase in the luminescence.

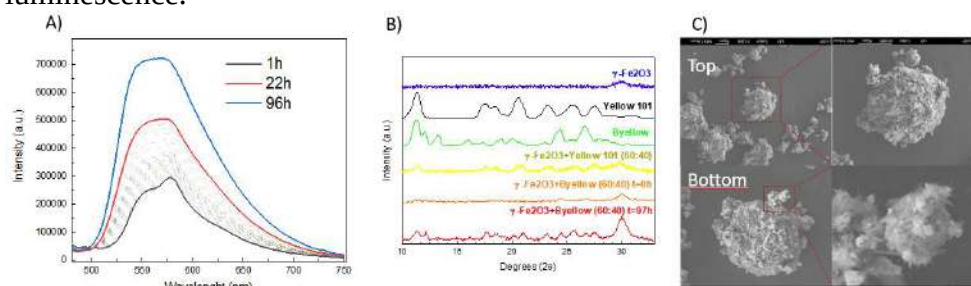


Figure 1: A) Emission of the composite of γ -Fe₂O₃ and BYellow over time (λ_{ex} = 450nm) XRD of Yellow 101, BYellow, and its composites with γ -Fe₂O₃. C) SEM on the same region of the γ -Fe₂O₃+BYellow composite in 0h (Top) and after 96h (Bottom).

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0.4.113 Synthesis of La₁-EuPO₄ nanoparticles for quantum technologies

Speaker: Valentin Grand d'Esnon

Synthesis of $\text{La}_{1-x}\text{Eu}_x\text{PO}_4$ nanoparticles for quantum technologies

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The exceptional optical properties of rare-earth ion-doped matrices make them ideal candidates for a wide range of applications. Their high optical coherence time makes their use in quantum technologies (quantum memories, quantum telecommunications, qubit, etc.) particularly interesting [1]. However, this implies a low luminescence intensity, which can be considerably enhanced by using nanoparticles in optical cavities. These devices amplify the coupling of transitions of interest with light [2]. However, coherence time is dependent on the crystalline quality of the materials: size reduction must therefore be accompanied by the preservation of this quality. This is a real challenge.

Here, we present the solid-state synthesis of a lanthanum phosphate matrix doped with europium ions, which has been shown to possess an excellent coherence time. First, the ideal doping ratio to optimize coherence time is determined by photon echo. Secondly, nanoparticles are obtained by pulverizing. Post-synthesis annealing is used to restore crystallinity and coherence time, both of which have been reduced during this stage, and are then studied in detail by Rietveld analysis and photon echo.

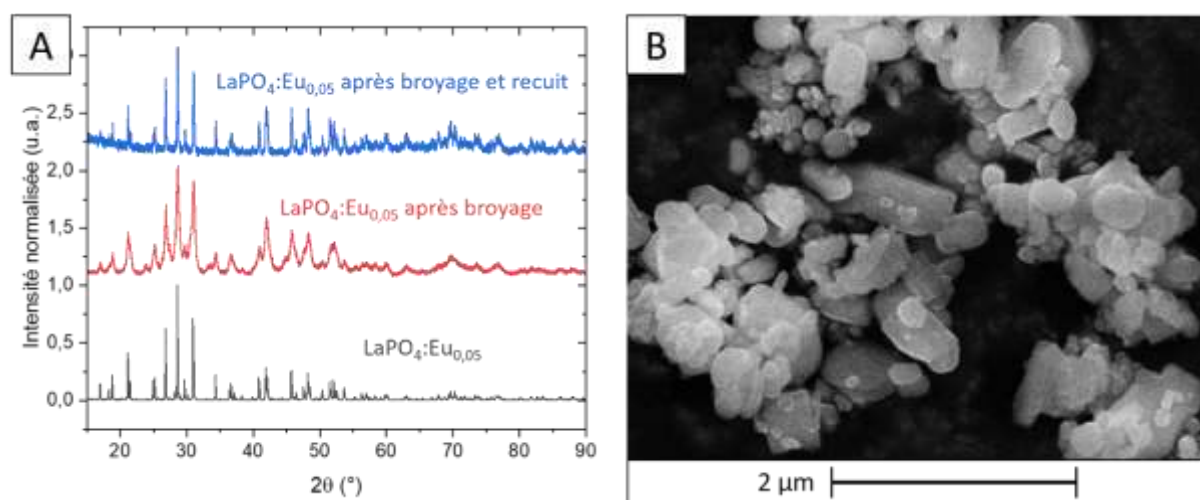


Figure 1: (A) XRD of $\text{LaPO}_4:\text{Eu}_{0.05}$ samples before grinding (black), after grinding (red) and after grinding and annealing (blue). (B) SEM image of $\text{LaPO}_4:\text{Eu}_{0.05}$ after grinding and annealing.

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0.4.114 **Synthesis, characterization and effect of heat treatment on CdS quantum dots embedded in chloroborosilicate glass matrix**

Speaker: Shasmal Nilanjana

Synthesis, characterization and effect of heat treatment on CdS quantum dots embedded in chloroborosilicate glass matrix

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CdS quantum dots (QDs) were generated in chloroborosilicate glass with composition 37.8SiO₂–27B₂O₃–18BaO–3.6K₂O–3.6Al₂O₃–10BaCl₂ (mol%), by one-step melt quench technique. The samples were characterized by transmission electron microscopy (TEM), UV-Vis absorption, excitation, and emission spectroscopy. TEM images revealed the presence of CdS QDs of size 5-20 nm in the as-prepared glass. The absorption spectrum shows a broad absorption band starting from 500 nm and centered around 400 nm, originating from various electronic transitions involving defect and trap states in CdS crystalline structure. Emission spectra revealed broad emission bands around 425 and 675 nm when excited at 350 nm and 460 nm respectively. The emission band in the lower wavelength region, shows a red shift with increasing excitation wavelength, which proves the quantum confinement effect in CdS QDs. The sample was heat treated at 650°C for several durations up to 60h. The absorption band gets slightly broader and more intense with increasing heat treatment time due to the formation of new CdS QDs as well as the enlargement of already-existing particles. The heat-treated sample was excited at different wavelengths (305, 317, 350 and 460 nm). Upon excitation in the UV (305, 317 and 350 nm) two distinct broad emission bands in the violet-blue and red are observed and there is no apparent change in spectral shape of the red band when excitation is done at 460 nm. With increasing heat treatment time, the emission bands initially show a gradual increase in intensity and then a progressive decrease accompanied by a red-shift in the peak position. The PL intensity increase (almost 10-fold) for heat treatment up to 30 h is due to two effects: i) the rise of new CdS particles and the growth of previously existing ones; ii) the crystallization of BaCl₂-based phases. This kind of enhancement is quite remarkable semiconductor QD-doped glasses and can be useful in various photonic applications.

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0.4.115 Synthesis, structure and luminescent properties of the $K_3Tb(PO_4)_2$ crystals

Speaker: Nedilko Serhii

Synthesis, structure and luminescent properties of the $K_3Tb(PO_4)_2$ crystals

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Lanthanide-containing complex oxides have been actively studied as objects with valuable optical, electrical, magnetic, and catalytic properties. Among them, the Tb^{3+} -containing materials are well-recognized phosphors for cathode ray tubes, fluorescence lamps, light-emitting diodes, field emission displays, etc. The plenty of Tb^{3+} ions emission lines in visible photoluminescence (PL) spectra is related to f - f transitions from $^5D_4$ excited level of these ions. This luminescence can be excited in the ultraviolet (UV) and vacuum UV spectral regions where fundamental light absorption bands caused by molecular phosphate anions as well as charge transfer absorption bands are located. The possibility of luminescence excitation both through the matrix and the Tb^{3+} ions absorption allows obtaining a phosphor with an adjustable visible emission.

The $K_3Tb(PO_4)_2$ crystals have been obtained via high temperature solution method starting from K_2HPO_4 , Tb_4O_7 in a molar ratio of 12:1 raw materials. The mixture of raw materials has been heated to 1500 K, kept for 2 hours under stirring, and then cooled to 800 K and poured on a copper plate. The crystallized products have been washed out from solidified melt with deionized water. The XRD patterns showed only the single phase which is isostructural to $K_3Gd(PO_4)_2$ phosphate.

The measured diffuse reflectance spectrum of $K_3Tb(PO_4)_2$ revealed a steep rise near 230 nm indicating the energy gap near 5.4 eV. The PL emission of the $K_3Tb(PO_4)_2$ in the visible spectral range is determined by $^5D_4 \rightarrow ^7F_J$ ($J = 0 - 6$) transitions. The most intensive of the PL bands corresponds to $^5D_4 \rightarrow ^7F_3$ transitions with maxima at 545 nm. The visible photoluminescence can be excited the most effectively in the 140-240 nm range where bands at 170, 185, 194, and 220 nm are peaking. The PL excitation bands in the rest of the UV and visible range (e.g. at 370 or 480 nm) have about two orders lower intensity compared to the band at 220 nm. Due to its excellent luminescence properties, the $K_3Tb(PO_4)_2$ phosphate can be considered as a perspective phosphor for lighting and display applications. The calculated CIE chromaticity coordinates for this material are $x = 0.434$; $y = 0.522$ under PL excitation at 473 nm at room temperature. These coordinates correspond to yellowish green color. It is assumed that the $K_3Tb(PO_4)_2$ can be doped with some other rare-earth ions to tune color coordinates, in particular to the red part of the visible spectrum.

0.4.116 Systematic change in the luminescent properties of ASnO_3 (A = Ca, Sr, and Ba) with doping of Eu, Dy, and Er ions

Speaker: Lee Kwan Chul

Systematic change in the luminescent properties of ASnO_3 (A = Ca, Sr, and Ba) with doping of Eu, Dy, and Er ions

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The emission profile of trivalent rare earth (RE) ions is quite sensitive to the structural symmetry around them. In this study, we investigate the relationship between the luminescent properties of rare earth ions and the structural properties of the host material in perovskite stannates, RE ion ($\text{RE} = \text{Eu}^{3+}$, Dy^{3+} , and Er^{3+})-doped ASnO_3 ($\text{ASnO}_3\text{:RE}$), where A = Ca, Sr, and Ba. X-ray diffraction and Rietveld refinement analyses confirmed that the lattice structures for A = Ca, Sr, and Ba were orthorhombic, pseudo-cubic, and cubic, respectively. The emission intensities of the three RE ions were strongest and weakest in $\text{CaSnO}_3\text{:RE}$ and $\text{BaSnO}_3\text{:RE}$, respectively. These findings indicate a strong correlation between the luminescence properties of RE ions and the structural symmetry of the host material, ASnO_3 .

References

0.4.117 Systematic Investigation of Thermally Activated Delayed Fluorescence emitters via controlling the closeness of intermediate states in fabrication of Organic Light Emitting Diodes

Speaker: Yadav Nisha

Systematic Investigation of Thermally Activated Delayed Fluorescence emitters via controlling the closeness of intermediate states in fabrication of Organic Light Emitting Diodes

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A good molecular design strategy providing high efficiency is very crucial for fabrication of cost-effective Organic Light Emitting Diodes (OLEDs). The most salient feature of achieving Thermally Activated Delayed Fluorescence (TADF) mechanism was thought to be low Singlet-Triplet energy gap (ΔE_{ST}). According to all the reported literature till now, only strategy that is being opted to tune the color is by increasing the donor strength but the decrement of Photoluminescence Quantum Yield (PLQY) is being neglected in those cases. The balance between oscillator strength (f) and ΔE_{ST} is very crucial for efficient TADF emitters. Besides this, the number and nature of intermediate states between S_1 and T_1 is equally important. We have designed a series of TADF emitters by unaltering the acceptor unit and changing variety of donor units. So, an alternative mechanism to increase the Reverse Inter-system Crossing (RISC) in spite of having moderate ΔE_{ST} and hence high External Quantum Efficiency of 22.5% was being obtained in 3BPy-mDTA. It also possess low Turn-on Voltage (V_{on}) of 2.8 V along with Power efficiency of 70.4 lm/W, Current efficiency of 78.7 Cd/A, Current density of 481 mA/cm² and Luminance of 13139 Cd/m².

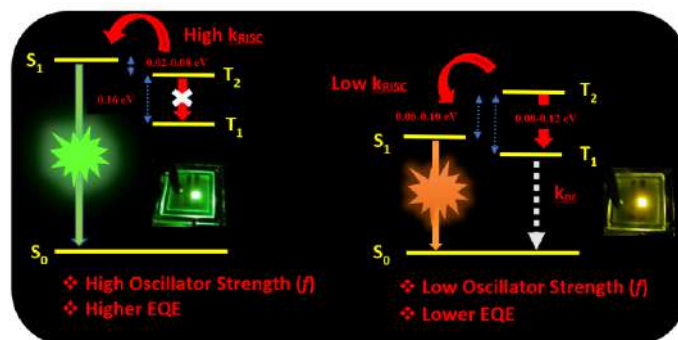


Figure : Mechanism showing role of intermediate state in enhancing RISC pathways in TADF emitters

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0.4.118 Systematic study to choose appropriate materials combination for green hyperfluorescent organic light emitting diodes

Speaker: Deori Upasana

Systematic Study to Choose Appropriate Materials Combinations for Green Hyperfluorescent Organic-Light Emitting Diodes.

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Hyperfluorescent organic light-emitting diodes (HF-OLEDs) rely on the idea of combining a thermally activated delayed fluorescence (TADF) material with a fluorescent emitter, have achieved extensive progress, as it can fully harness the advantages of both the materials. For a high-performance HF-OLED, high photoluminescence quantum yield TADF dopant and proper spectrum overlap with the terminal emitter is essential, however, there is no report till date on singlet energy difference between the materials and its impact on the efficiency roll-off of the devices. In this work, a systematic study was done by combining assistant dopants with different terminal emitters. The resulting HF-OLEDs use two efficient TADF materials, 4BPy-mDTC and 3BPy-mDTC, as assistant dopants. The device reached maximum EQE of 28% and retained EQE of 23.7% at 1000 cd/m². The energy difference between assistant dopant and terminal emitter plays a vital role in improving the device performances and roll-off characteristics. Too large energy difference may lead to inefficient transfer while too small may bring back energy transfer loss. Hence, an optimum energy gap is required between TADF dopants and terminal emitters, to improve device performance. Also, appropriate energy gap is significant to reduce the efficiency roll-off at high brightness level. This work provides an insight for developing highly efficient HF-OLEDs by modulating the energy gap between the materials.

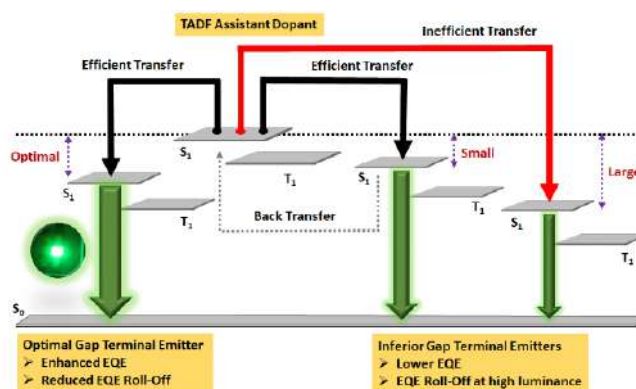


Figure : Energy transfer mechanism and lowest excited singlet energy differences between TADF assistant dopant and terminal emitters

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0.4.119 Temperature dependent photoluminescence characteristics of MBE grown Eu doped ZnMgO thin films

Speaker: Mathew Juby Alphonsa

Temperature dependent photoluminescence characteristics of MBE grown Eu doped ZnMgO thin film

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Oxide-wide-bandgap semiconductors are suitable hosts for rare earth ions owing to their availability at low cost, ease of synthesis, chemical stability, and, above all, due to the tunability of their optical and electrical properties. It is known that the bandgap of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ increases with the Mg alloying content, x . The photo-excitation-emissions of Eu ions are expected to be modified when doped inside a tunable wide-bandgap material like $\text{Zn}_{1-x}\text{Mg}_x\text{O}$. Our studies have shown that the optical activity of Europium is increased by an order of magnitude when around 10% fractional Mg is alloyed to ZnO in comparison to Eu doped pure ZnO matrix [1, 2]. However, the exact nature of Eu ion optical sites in the ZnMgO host is unknown. In this project, we explore the nature of Eu optical sites in $\text{Zn}_{0.87}\text{Mg}_{0.13}\text{O}$ thin films at a doping level around 0.5 ± 0.1 at.%. Eu doped $\text{Zn}_{0.87}\text{Mg}_{0.13}\text{O}$ thin films were grown on c- and r-oriented Al_2O_3 by Plasma assisted Molecular Beam Epitaxy, under the same ambient experimental conditions. Low temperature photoluminescence (PL) and PL Excitation analysis were performed to explore the temperature dependent activity of Eu optical sites. Two different active sites of Eu ions having different activation energies were identified from the $^5\text{D}_0$ to $^7\text{F}_0$ and $^5\text{D}_0$ to $^7\text{F}_2$ transitions. HR-XRD studies confirmed hexagonal wurtzite crystal structure for Eu doped ZnMgO films. Lattice parameters were determined accurately. Sample grown on c-Sapphire was preferentially oriented in 0002 direction. Eu: ZnMgO/C-Sapphire was found to have dominating red Eu luminescence in comparison to Eu: ZnMgO/r-sapphire which was oriented along 11-20 direction.

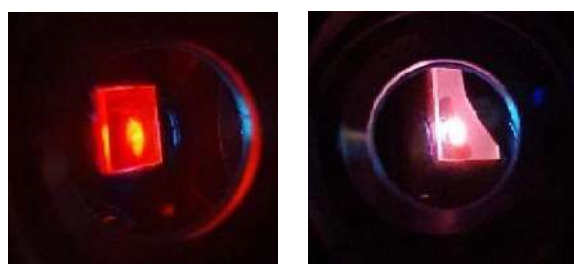


Figure: Photoluminescence observed at temperature 15K from Eu doped ZnMgO on c- Al_2O_3 (left side) and r- Al_2O_3 (right side) substrates

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0.4.120 Temporal multiplexing based on tuneable terbium-to-quantum dot Förster resonance energy transfer for DNA quantification

Speaker: Su Ruifang

Temporal multiplexing based on tuneable terbium-to-quantum dot Förster resonance energy transfer for DNA quantification

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A single Förster resonance energy transfer (FRET) pair based multiplexing strategy was developed based on terbium (Tb)-DNA-quantum dot (QD) conjugates with temporally distinct photoluminescence (PL) decays tuned by the length/orientation of Tb-DNA on QD surface¹. Tb-to-QD conjugates labeled with capture DNAs (C-DNA) were used as FRET PL probes to assembly with specific DNA targets and C-DNA conjugated magnetic bead (MB) probes through DNA hybridization. After magnetic separation and resuspension of MBs-targets-QDs, time-gated (TG) measurements of FRET-excited QD PL intensities in separate time windows after pulsed excitation can realize the specific quantification of multiple DNA targets from a single sample. This single TG-FRET-pair multiplexing can be combined with spectral resolution,² paving the way for biosensing with unprecedented high-order multiplexing capabilities.

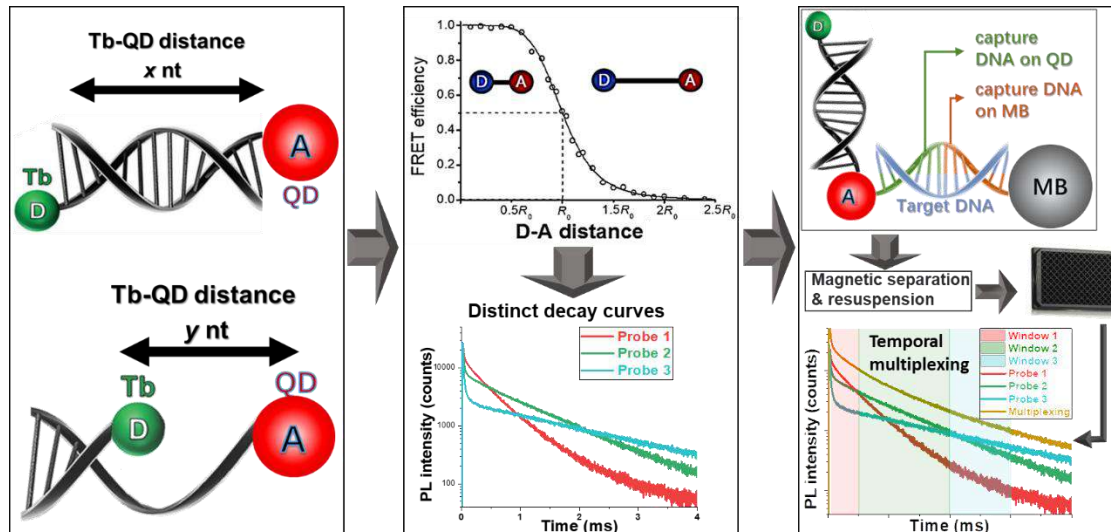


Figure. Tb-DNA-QD conjugates with distinct FRET PL decays for temporal multiplexing of DNA targets.

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0.4.121 The energy-transfer analysis of nano/micro-crystalline YPO₄ co-doped with Yb³⁺ and Nd³⁺ ions

Speaker: Pawłów Jakub

The energy-transfer analysis of nano/micro-crystalline YPO₄ co-doped with Yb³⁺ and Nd³⁺ ions

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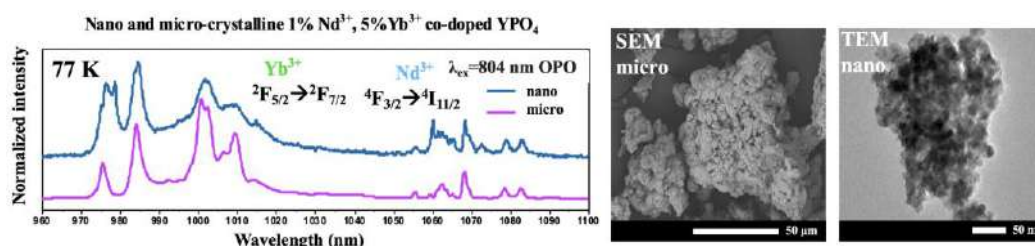
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In the last few decades, technological progress stimulated research on nano-materials with luminescent properties, which have found newer applications in the field of biomedicine or lightning. Specialized applications bring the concern to the grain size or morphology of the designed material. Due to their very small grain sizes, nanomaterials can exhibit physical and chemical properties that significantly distinguish them from analogous macroscopic materials. Moreover, change in the synthesis conditions leads to obtaining nano-materials with different grain sizes and morphology.

To investigate the possibility of modeling the morphology and its effect on spectroscopic properties LnPO₄ phosphates were selected, because of their good physico-chemical and thermal stability, as well as a large band gap, which allows them to act as a matrix for optically active lanthanide ions [1]. Among these ions, Nd³⁺ and Yb³⁺ ones are useful in a number of applications in the NIR region, like for example bioimaging.

In this study, we present the analysis of structural and spectroscopic properties of Nd³⁺; Yb³⁺-co-doped YPO₄ nano/micro-materials obtained by various methods of synthesis – microwave-assisted, hydrothermal and solid-state reaction methods. Materials with different activator concentrations were used to examine possible changes in spectroscopic properties and study the energy transfer between Nd³⁺ and Yb³⁺ ions. Electron microscopy techniques, SEM and TEM, were used to demonstrate the differences in the morphology and size of micro/nano-materials. Possible energy transfer was analyzed by using low-temperature high-resolution techniques like absorption spectroscopy at 4.2 K and tunable laser site-selective emission spectroscopy at 77 K. The strong emission of Yb³⁺ and Nd³⁺ ions was successfully achieved simultaneously for both, nano- and micro-materials. An energy transfer mechanism between these ions was proposed for the studied materials.



Emission spectra, SEM and TEM of 1% Nd³⁺, 5% Yb³⁺ co-doped YPO₄ micro- and nano-powders.

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Acknowledgments

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0.4.122 The route to obtaining high-quality photonic structures using a photolithography process and negative tone resist

Speaker: Pawłów Jakub

The route to obtaining high-quality photonic structures using a photolithography process and negative tone resist

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In recent years in the integrated optics field of science scientists were focused on optimizing processes for the mass manufacture of photonic devices [1]. One of the most common methods used to obtain waveguide structures in photonic integrated circuits (PICs) is the photolithography process, which is a remarkably efficient technique for microtechnology. It includes several sub-processes such as applying photoresist, exposing to ultraviolet (UV) light and developing the pattern. Conventional photomasks used in photolithography are rigid, fused quartz plates covered with patterned microstructures of an opaque material such as chrome.

In this work, we have investigated the effects of modifying parameters of the photolithography process carried out on soda-lime glass with a SiO₂-TiO₂ layer using fast, negative tone cross-linking photoresists based on polymers. One of the main goals of our research is to create a silica-titania optical waveguide platform and incorporate optical components using etching methods. Photolithography parameters like UV exposure dose, the development time of the resist, as well as dilution of the developer and post-processing hard-bake, were optimized in order to achieve high-quality structures on the analyzed substrates. We believe that this work will be highly beneficial for the researchers working on the photolithography process.

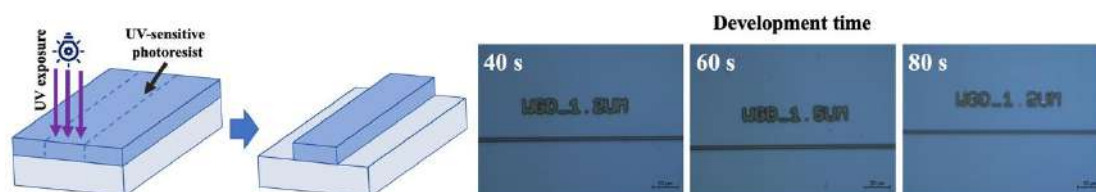


Fig. 1 Scheme of photolithography process and microscope images of obtained structures depending on the development time.

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Acknowledgements:

The research was co-financed by the Foundation for Polish Science from the European Regional Development Fund within the project POIR.04.04.00-00-14D6/18 "Hybrid sensor platforms for integrated photonic systems based on ceramic and polymer materials (HYPha)" (TEAM-NET program).

0.4.123 The Tm³⁺ ions heavy doping effect on Vis-to-UV up-conversion emission of Pr³⁺-based β -NaYF₄ and LiYF₄ NPs

Speaker: Fałat Patryk

The Tm³⁺ ions heavy doping effect on Vis-to-UV up-conversion emission of Pr³⁺-based β -NaYF₄ and LiYF₄ NPs

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Having been exposed to the flux of low-energy photons, lanthanide ions tend to sequentially absorb them within the ladder-like energy level structure, which can result in the emission of one photon of higher energy. Such a process of up-conversion (UC) was described for the very first time in the mid '60s by F. Auzel for phosphate glasses co-doped with Yb³⁺ and Er³⁺ ions [1]. The report on that unusual, i.e. anti-Stokes, phenomenon has drawn the attention of many researchers worldwide who have been investigating it up-to-date for various lanthanides compositions, which now allows the generation of upconverted radiation at almost any desired wavelength [2]. What is more, the significant research acceleration was noticed in the late '90s as the first upconverting materials at nanoscale were obtained, providing a bunch of novel bio-related applications, e.g. biosensing or tumour targeting therapy. [3]

Having the substantial impact on biologically active moieties, tissues, and living organisms, UV radiation (100-380 nm) is also a part of the electromagnetic spectrum which is generable *via* up-conversion process e.g. Vis-to-UV UC in Gd³⁺, Tm³⁺ or Pr³⁺ ions, incorporated into nanocrystalline host matrices. [4] However, the process is not reasonably effective due to low up-conversion quantum yield (UCQY < 1%) and, as a consequence, diverse ways for the enhancement are being thoroughly examined. Therefore, this study is devoted to the effect of combining Pr³⁺ ions at fixed molar concentration with Tm³⁺ ions at various concentrations within β -NaYF₄ and LiYF₄ NPs on Vis-to-UV UC emission characteristics. The recorded data are of the great importance for more efficient UV emitting NPs development and their prospective biomedical applications.

Acknowledgements

This work was supported by the National Science Centre Poland under SHENG research grant (no. 2018/30/Q/ST5/00634).

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0.4.124 Theoretical simulations and experimental verification of intended thermoluminescence dose response linearity in LiF:Mg,Ti ($TLD - 100$) by postirradiation photon excitation

Speaker: Oster Leonid

Theoretical simulations and experimental verification of intended thermoluminescence dose response linearity in LiF:Mg,Ti (TLD-100) by postirradiation photon excitation

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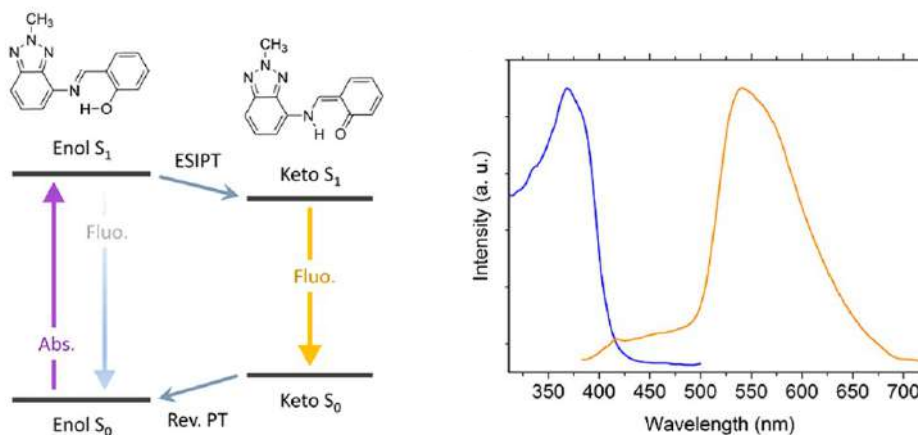
The thermoluminescent dosimeter, LiF:Mg,Ti (TLD-100), is widely used to determine patient doses in radiation diagnostics and external beam radiotherapy. The dose range of interest for radiotherapy is 1-5 Gy and in intraoperative electron radiation therapy as high as 30 Gy. Unfortunately, the thermoluminescence (TL) response of TLD-100 is non-linear (supralinear) above ~ 1 Gy reaching values of $f(D)$ (the normalized dose response) as high as 1.15-1.2 at 10 Gy and 1.5-1.6 at 30 Gy. The supralinearity is a significant drawback which requires careful calibration and correction procedures for precision applications. Theoretical Unified Interaction Model and kinetic model simulations indicated that post-irradiation photon excitation can reduce or even eliminate the supralinearity due to the alteration of the charge concentrations in the trapping centers (TCs) and luminescent centers (LCs) and preliminary experimental measurements at high levels of dose from 100 Gy to 400 Gy supported this concept. The models successfully simulate the bleaching action of the 3.65 eV photons on the increased range of linearity of the TL dose response as caused by the depletion of the occupied trapping centers and to a lesser degree charge transfer via the conduction band between the various configurations of the TC/LC system associated with composite peak 5. Photon excitation post-irradiation at 3.6 eV preferentially depletes the 3.65 eV TC/LC spatially correlated configuration thereby increasing the relative concentration of the e-h (4.3 eV) to the e-only configuration (3.65 eV) thereby reducing the supralinearity due to the greater relative contribution of the geminate nature of the e-h recombination which give rise to dose response linearity. In this manner conduction band/valence band competitive processes giving rise to the supralinearity are avoided. Photon excitation at 5 eV also alters these concentrations serendipitously in a similar manner by hole release and recapture in the TCs and LCs via V_3-V_k transformation. Measurements of $f(D=30 \text{ Gy})$ following $^{90}\text{Sr}/^{90}\text{Y}$ irradiation and over a wide range of photon fluences have now demonstrated the complete elimination of the supralinearity at photon fluences of $4 \times 10^{16} \text{ cm}^{-2}$ (5 eV) and $2 \times 10^{16} \text{ cm}^{-2}$ (3.6 eV).

Acknowledgements: This research was supported by the Israeli Ministry of Science and Technology: The accurate determination of radiation dose in clinical/medical applications. Project no. Merkava: 3-16316

0.4.125 Theory of Photoinduced Excited State Proton Transfer

Speaker: Le Dé Brieuc

Theory of Photoinduced Excited State Proton Transfer

Brieuc Le Dé,^{1,2} Simon Huppert,¹ Riccardo Spezia² and Alex W. Chin^{1,*}¹ Institut des NanoSciences de Paris (INSP), Sorbonne Université, CNRS, Paris, 75005, France² Laboratoire de Chimie Théorique (LCT), Sorbonne Université, CNRS, Paris, 75005, France*E-mail: alex.chin@insp.upmc.fr

Left: Scheme of intramolecular ESPT between an enol and a keto form. Right: Respective excitation and fluorescence spectra, showing a large Stokes shift [1].

Photoinduced Excited State Proton Transfer (ESPT) is characterized by a transfer of a proton between two moieties of a molecule when the system is photoexcited, often seen via an exceptionally large ($\geq 8000 \text{ cm}^{-1}$) Stokes shift in fluorescence spectra. The efficiency of photoinduced ESPT reactions is critical for the light reactions of photosynthesis and light-driven enzyme biosynthesis [2]. Remarkably, ESPT can be a truly ultrafast process that occurs on timescales at the limit of many experimental probes - just a few tens of femtoseconds. However, the theoretical understanding of ESPT at such very short timescales - and where quantum dynamical effects are likely to be important - still needs to be developed, and could open up novel opportunities for new light-harvesting applications. This ultrafast mechanism necessarily involves out-of-equilibrium vibronic states, which seem to be crucial for an accurate analysis. By developing simple prototype systems, we focused especially on short time behaviors parametrized by the photoexcitation shape and vibrations of the system. This surrounding environment is included with great accuracy through fully quantized theoretical simulation and powerful numerical Tensor-Network techniques [3], permitting us to include hundreds of vibrations modes, as well as an explicit description of emission and absorption process into arbitrary photonic environments (free-space, cavities, etc.). The presented study helps gain insight into the non-equilibrium dynamics of proton transfer and provides new design principles mimicking this natural and essential process.

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0.4.126 **Ti³⁺ lifetime based luminescent thermometry in LnAlO₃ (Ln = La³⁺, Gd³⁺, Lu³⁺)**

Speaker: Piotrowski Wojciech

Ti³⁺ lifetime based luminescent thermometry in LnAlO₃ (Ln = La³⁺, Gd³⁺, Lu³⁺)

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Research on phosphors doped with transition metal (TM) ions has been widely developed in recent years due to their unique spectroscopic properties [1]. TM are generally characterized by high absorption cross-section in a wide spectral range and intense emission. Moreover, the spectral location of their excitation and emission bands as well as their susceptibility to the temperature changes are strongly dependent on the host material in which they are incorporated. For this reason, TM ions are an object of interest in luminescence thermometry. In order to understand the results obtained for the new TM ions doped phosphors, the correlation between the structural and spectroscopic properties as well as the thermometric properties is sought. Such an analysis could be particularly useful in the materials engineering approach, if well-studied dependencies would be implemented to predict the properties prior to their production and thus design phosphors on demand. To date, great majority of the papers devoted to luminescence thermometry relates to chromium and manganese ions (with a dominant role of Cr³⁺ and Mn⁴⁺) [2]. However, there are also other TM ions for which only a few representative host materials have been presented so far. One such example is Ti³⁺. This is a particularly interesting case due to its 3d¹ electronic configuration, which determines that their energy diagram scheme consists of only two levels (²T₂ ground state and ²E excited state in the octahedral crystallographic site). Therefore, providing sufficient thermal energy to occupy the higher vibronic levels of the ²E excited state leads directly to its nonradiative depopulation, which guarantees a strong susceptibility of both the emission intensity and the excited level lifetime of the Ti³⁺ ions to temperature changes. The above arguments provide motivation to investigate the influence of host composition on Ti³⁺ performance in LnAlO₃ (Ln = La³⁺, Gd³⁺, Lu³⁺). The choice of host material will allow to modify the spectral position of excitation and emission bands. Due to the encouraging results obtained so far [3], it is expected that LnAlO₃:Ti³⁺ will be characterized by Ti³⁺ lifetimes of the order of a milliseconds, the value of which will be strongly temperature dependent, thus showing potential for use in luminescent thermometry.

Acknowledgments: This work was supported by the National Science Center Poland (NCN) under project no. 2022/45/N/ST5/01457.

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0.4.127 Time- resolved VUV luminescence spectroscopy at PETRA III synchrotron

Speaker: Kotlov Aleksei

Time- resolved VUV luminescence spectroscopy at PETRA III synchrotron

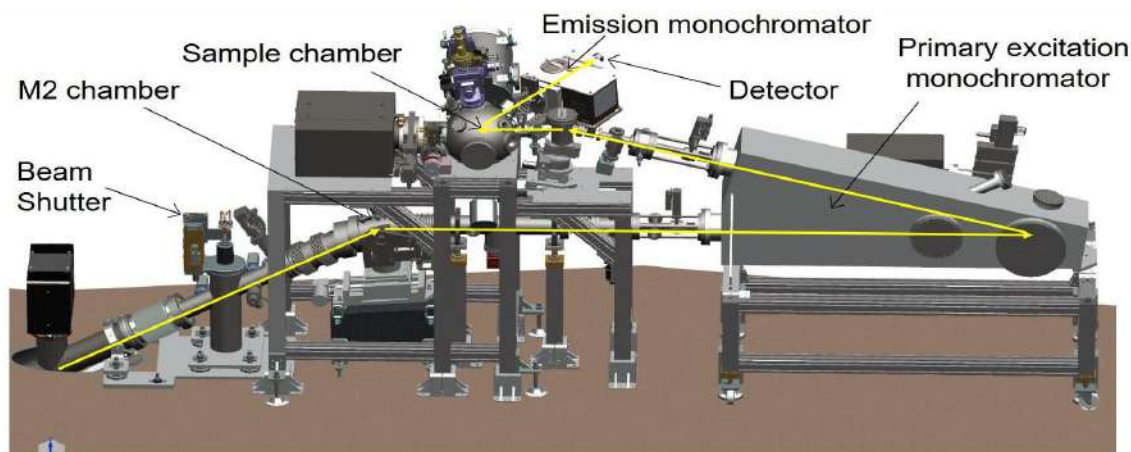
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The PETRA III P66 Time resolved luminescence spectroscopy (TRLS) beamline at Deutsches Elektronen-Synchrotron DESY (Hamburg, Germany) is a successor of the well-known SUPERLUMI station operated at DORIS ring in DESY from 1976 to 2012¹. Since year 2021 the station is re-opened and operating after a long-term relocation breakdown². The TRPL beamline is a unique facility specifically designed to study the luminescence phenomena of various materials as a function of photon energy and time with excitation by pulsed synchrotron radiation. Some specific studies, such as experimental research in short-wavelength VUV and XUV region covering the intrinsic absorption range of wide bandgap dielectrics can be realized only at the VUV spectroscopy beamline of the pulsed synchrotron source like PETRA III. On the P66 TRLS beamline, the following ranges of excitation and emitted photons are possible: 30– 330nm and 200– 1200nm, respectively³. Time resolution of the experimental setup was estimated as the full width half maximum of the Instrument Response Function (IRF), measured crossing the excitation and emission monochromators to be 870 ps. The upper boundary of the possible measured lifetime depends on the PETRA III operating mode is 192 ns between subsequent pulses in the 40 bunches mode and 16 ns for the 480 bunches mode.



Scheme of the P66 experimental installation and photon propagation

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0.4.128 Tuning of luminescence properties and proton conductivity by external stimuli in porous GdCr coordination polymer

Speaker: Heczko Michał

Tuning of luminescence properties and proton conductivity by external stimuli in porous GdCr coordination polymer

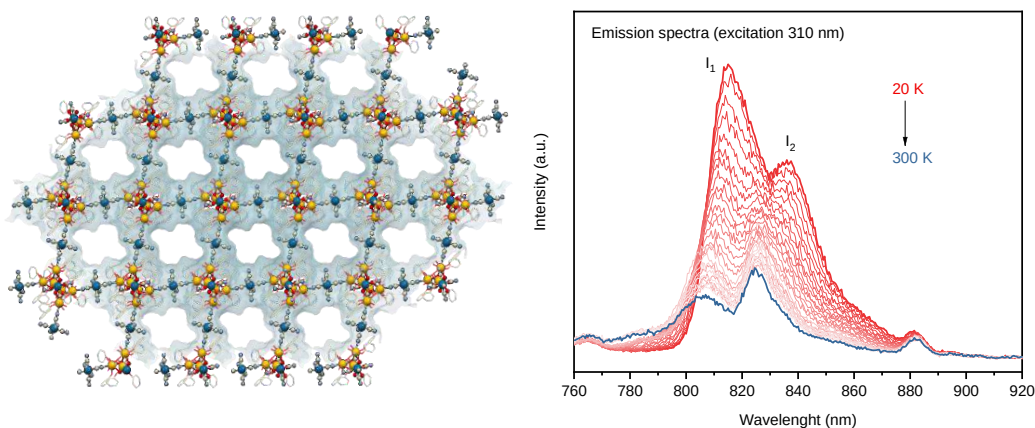
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The combination of porosity and luminescence in coordination polymers results in multifunctional materials applicable for proton conductors and optical sensors. In this regard, we performed the hydrothermal reaction between $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$, 4-OHpy (4-hydroxypyridine), and $\text{K}_3[\text{Cr}(\text{CN})_6]$ that leads to the formation of a new coordination polymer of the general formula: $\{[\text{Gd}^{\text{III}}_6(\mu_3\text{-OH})_8\text{Cr}^{\text{III}}(4\text{-OHpy})_{12}(\text{H}_2\text{O})_{12}]_{9/13}[\text{Cr}^{\text{III}}(\text{CN})_6]_3\} \cdot n\text{H}_2\text{O}$ (**GdCr**). The elevated temperature caused the partial decomposition of the anionic $[\text{Cr}(\text{CN})_6]^{3-}$ building block producing heptanuclear $\{\text{Gd}^{\text{III}}_6\text{Cr}^{\text{III}}\}$ clusters further linked through remaining $[\text{Cr}(\text{CN})_6]^{3-}$ anions into a 3D coordination network. This material can be considered as a super-expanded Prussian blue framework, in which the $\{\text{Gd}^{\text{III}}_6\text{Cr}^{\text{III}}\}$ clusters act as octahedral network nodes. In the structure, there is the presence of a 3D channels net, filled with water molecules. The sorption investigations indicated that the sorption and desorption processes are reversible, but they have different paths due to deformations of the coordination skeleton upon changing the hydration level. Moreover, **GdCr** exhibits photoluminescence due to the presence of Cr(III) centers.¹ The 310 and 390 nm irradiation allows observing two signals of luminescence in the near-infrared range. The relative intensity of observed bands and their location are dependent on the temperature and RH. The proton conductivity measurements indicated that the **GdCr** shows superionic conductivity at 100% of RH and the conductivity decreases with the lowering of the humidity. The activation energy of 0.43 eV suggests that both Grotthuss and vehicle mechanisms are presumable.²



Crystal structure of **GdCr** coordination polymer showing the channels (water molecules omitted for clarity) and emission spectra in the *T*-range of 20–300 K of the phase stable at 60% RH.

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0.4.129 Tuning of photoluminescence and persistent luminescence properties of Cr³⁺ and Ca²⁺ co-doped β -Al₂O₃-Ga₂O₃-In₂O₃ alloys

Speaker: Zhydachevskyy Yaroslav

Tuning of photoluminescence and persistent luminescence properties of Cr³⁺ and Ca²⁺ co-doped β -Al₂O₃-Ga₂O₃-In₂O₃ alloys

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Persistent luminescence properties of Cr³⁺ and Ca²⁺ co-doped β -Ga₂O₃ have been reported recently in the literature. It is known that alloying of gallium oxide with aluminum or indium oxide (creation of solid solutions) allows changing their physical properties in a wide range primarily due to modification of the crystal structure and the energy band gap of the material. When the material is activated with Cr³⁺, photoluminescence properties of Cr³⁺ ions can also be changed significantly by modification of the crystal field strength experienced by Cr³⁺ ions.

In this work, we are going to show the results of the systematic study of photoluminescence (PL) and persistent luminescence (PersL) properties of Cr³⁺ and Ca²⁺ co-doped β -Al₂O₃-Ga₂O₃-In₂O₃ solid solutions. In particular, the PL spectra, PL excitation spectra, and PL decay time of the materials were studied in the temperature range from 4 to 350 K. Besides, the afterglow decays and the thermally stimulated luminescence (TSL) after UV excitation were measured in the temperature range from 77 to 550 K. The luminescence properties have been analyzed depending on Al and In content in the base monoclinic β -Ga₂O₃ host lattice.

For this purpose, a series of samples with nominal compositions (Ga_{1-x}Al_x)₂O₃:Cr(0.05at.%), Ca(0.5at.%) ($x = 0; 0.1; 0.2$), (Ga_{1-x}In_x)₂O₃:Cr(0.05at.%), Ca(0.5at.%) ($x = 0.05; 0.1; 0.15; 0.2; 0.3; 0.4; 0.5$), and (Al_{0.33}Ga_{0.33}In_{0.33})₂O₃:Cr(0.05at.%), Ca(0.5at.%) were obtained by the sol-gel citrate method and afterward calcined at temperatures up to 1500°C. The phase composition and crystal structure of the studied materials have been analyzed in detail using powder X-ray diffraction (XRD) data.

Obtained results demonstrate wide opportunities for tuning the PL and PersL properties of the studied materials depending on the composition of the host lattice. Performed low-temperature and time-resolved PL studies shed light on the nature of the Cr³⁺ centers available in the studied alloys. The luminescence results are discussed in correlation with the crystal structure data for the studied materials.

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0.4.130 Ultra-sensitive, multimodal luminescence pressure sensor based on Cr³⁺ ions emission

Speaker: Szymczak Maja

Ultra-sensitive, multimodal luminescence pressure sensor based on Cr³⁺ ions emission

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Controlling pressure plays a crucial role in many fields - from the laboratory-scale syntheses, through food preservation, to flights of an aircraft. Hence, novel solutions to pressure monitoring are constantly being sought, and more demands are being placed on potential pressure sensors. The non-invasiveness, stability, fast readout that has high sensitivity to pressure changes and is independent of temperature are among the challenging demands. A class of pressure sensors that may meet all these requirements are luminescent manometers. Due to a number of their advantages, luminescence pressure sensors have recently constituted a branch that is being intensively studied. Accordingly, we present a luminescent manometer whose pressure readout is based on the near-infrared broadband emission of Cr³⁺ ions. The aspect that distinguishes this sensor from other luminescent manometers is the extremely large linear spectral shift of the band associated with the ⁴T₂→⁴A₂ transition, equal to 23.63 nm/GPa (in a range from ambient pressure to 7 GPa). This value is more than 60 times larger than the most widely used pressure indicator Al₂O₃:Cr³⁺ [1] and at the same time is the highest reported spectral shift so far in a context of luminescent pressure sensors. The use of the ratiometric approach resulted in a relative sensitivity S_R exceeding 120%/GPa, which is also the highest value reported in literature up to date. In addition, due to such a large pressure-induced spectral variation, it was possible to create maps of S_R, depending on the appropriately defined LIR (luminescence intensity ratio) parameter. This, in turn, allows modification of the manometric performance depending on the application requirement.

Acknowledgement: This work was supported by National Science Center Poland (NCN) under project No. UMO- 2020/37/B/ST5/00164.

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0.4.131 Ultrafast ionization of transparent materials under femtosecond laser irradiation

Speaker: Bedrane Zeyneb

Ultrafast ionization of transparent materials under femtosecond laser irradiation

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Advances in generation and control of ultrashort laser pulses have opened up new perspectives in nano-micromachining of transparent materials such as diamond. In particular, the use of femtosecond laser has proven to be a high precision technique for material modification [1]. Recently, many new applications have been found for transparent materials treated by femtosecond laser irradiation, such as laser-integrated photonic waveguides [2], color centers for quantum information technology [3], micro-drilling [4], embedded electrodes for micro-solar cell devices [5] and laser-induced periodic surface structures (LIPSS) for solar absorbers [6], where the ultimate goal for experimenters remains how to increase manufacturing precision and production yield. Therefore, to achieve more precise micromachining for manufacturing of high-quality products, the mechanism of femtosecond laser-matter interaction, including absorption and nonlinear ionization, energy transfer and thermal diffusion, should be better understood and controlled, and it is difficult to understand the deep mechanism of this complicated interaction without providing a valid theoretical support based on dynamic models.

In this work, we present a study of the fundamental processes induced during femtosecond laser-diamond interaction using Keldysh theory [7]. In this paper, we are mainly interested in the processes responsible for the thermal effect induced during the transition from a low laser-power regime to a high laser-power regime and the associated mechanisms. Our model, implemented by MATLAB software, was applied to a diamond surface irradiated by 120 fs laser pulse at 1064 nm and 532 nm wavelengths, with laser power varying from 0.2 to 10 mW. Obtained results can definitely contribute to improve the control of fs-laser processing technique to produce finer micro/nano-structures for several applications.

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0.4.132 Ultrafast Spectroscopy on Individual Light-Harvesting Complexes of *Rps. acidophila*

Speaker: Wiesneth Stephan

Ultrafast Spectroscopy on Individual Light-Harvesting Complexes of *Rps. acidophila*

Stephan Wiesneth^{*},¹ R. Hildner,² R.J. Cogdell,³ and J. Köhler¹

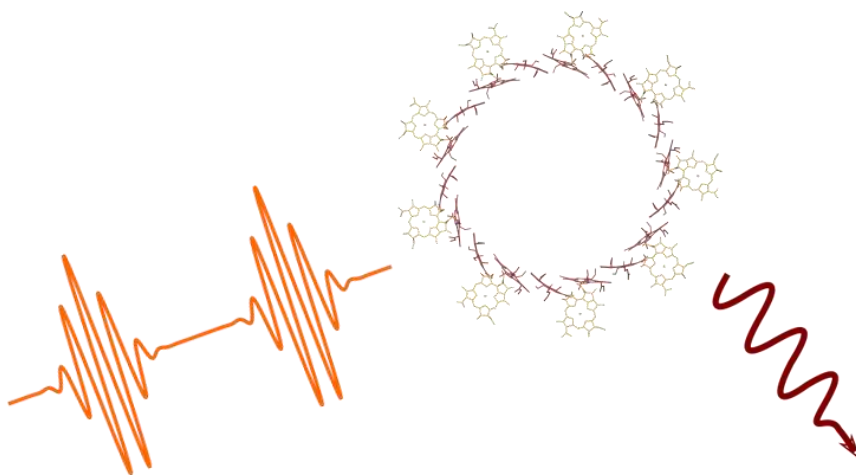
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Peripheral light-harvesting complexes LH2 play an important role in the initial steps of photosynthesis of the bacterium *Rps. acidophila* [1]. Long-lived coherences of the energy transport processes in individual complexes were detected by the van Hulst group, as well as interferograms of the absorption spectra [2,3]. We want to present the fluorescence response of individual LH2 complexes after double-pulse excitation at room temperature. The generation of the double pulses is done by pulse shaping which gives full control over the pulse delay and the phase relationship between the two pulses. The results indicate both heterogeneity of the fluorescence response between different complexes (inter-complex heterogeneity), and a temporal variation in the fluorescence response of a single complex over a long measurement period.



Schematic representation of double pulse excitation of single LH2 complexes of *Rps. acidophila* and resulting fluorescence response.

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0.4.133 Ultrathin non-doped thermally activated delayed fluorescence emitting layer for highly efficient OLEDs

Speaker: Nanda Gyana

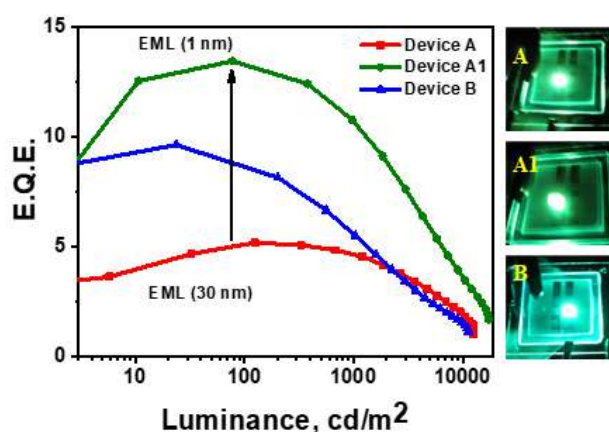
Ultrathin non-doped thermally activated delayed fluorescence emitting layer for highly efficient OLEDs

Gyana Prakash Nanda,¹ Bahadur SK,¹ Nisha Yadav,¹ Suresh Rajamanickam,¹ Upasana Deori,¹ Rahul Mahashaya,¹ Eli Zysman-Colman^{2,*} and P. Rajamalli^{1,*}

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Here we are reporting two highly efficient, non-doped green and bluish-green organic light-emitting diodes (OLEDs) using ultrathin emissive layers of two thermally activated delayed fluorescence (TADF) emitters DCBPy and DTCBPy. The neat film of both DTCBPy and DCBPy show high photoluminescence quantum yields of 70.2 and 59.8% and low delayed fluorescence lifetimes of 2.6 and 2.8 μ s, respectively, which make them eligible for the application of non-doped emitter in host free OLED devices. Because of the simplified structure and less material consumption, the non-doped ultrathin OLEDs are highly useful for large-scale device fabrication. However, due to the unbalanced mobility of holes and electrons in OLEDs, charge recombination mostly shifted to adjacent layers, and an additional emission comes. Here by reducing the EML thickness, we successfully controlled the recombination site and improved the device performance. One of the major challenges in this is the confinement of exciton within the ultrathin emissive layer, which can be overcome by a well-planned device structure. Here we have fabricated two non-doped OLEDs with different EML thicknesses (1 nm and 30 nm) using DTCBPy as an emitter. OLED with 1 nm thickness of DTCBPy showed a 2.6-fold higher external quantum efficiency (EQE_{max}) of 13.5% than the conventional (30 nm) non-doped device (5.2%). The higher performance in this ultrathin OLED is due to the proper management of holes and electrons mobility in the device.



EQE Vs Luminance plot of three OLED devices.

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0.4.134 Upconversion Random Lasing in Er³⁺/Yb³⁺ co-doped magnesium-lead-germanate glass powder

Speaker: Câmara Josivanir

Upconversion Random Lasing in Er³⁺/Yb³⁺ co-doped magnesium-lead-germanate glass powder

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Upconversion random laser (RL) based on Yb³⁺ and Er³⁺ co-doped magnesium-lead-germanate (GPM) glass powder is reported for the first time. The glass was fabricated by a conventional melt-quenching technique. Then, the GPM glass was grinded, and the resulting powder was submitted to sedimentation in isopropyl alcohol to remove the coarsest particles. Finally, a GPM glass powder with particles size between 1 and 2 μm was obtained. The sample was excited using an optical parametric oscillator (pulses of 7 ns) tuned to 980 nm, in resonance with the Yb³⁺ transition $^2F_{7/2} \rightarrow ^2F_{5/2}$ and with the Er³⁺ transition $^4I_{15/2} \rightarrow ^4I_{11/2}$. Energy transfer may occur from Yb³⁺: $^2F_{5/2}$ to Er³⁺: $^4I_{11/2}$, from which a second pump photon may be absorbed, promoting the Er³⁺ transition $^4I_{11/2} \rightarrow ^4F_{7/2}$. Nonradiative relaxation may occur to levels $^2H_{11/2}$, $^4S_{3/2}$ and $^4F_{9/2}$ giving rise to photoluminescence (PL) at about 530, 550 and 680 nm, respectively, with relaxation to the Er³⁺ ground state $^4I_{15/2}$. The input-output curve revealed RL emission at 550 nm for an excitation fluence threshold (EF_{th}) of about 0.6 mJ/mm². Temporal analysis showed that above the EF_{th} , a fast pulse in the nanosecond range is observed, corroborating the lasing process. Glass particles acted both as gain medium and scatterers, and the RL feedback mechanism is attributed to the light reflections in the particles-air interfaces, due to the high refractive index of the powder particles ($n \sim 2.0$) [1-3]. Additionally, the phenomenon of Replica Symmetry Breaking (RSB), characteristic of a photonic-phase-transition [4] was observed, by measuring the intensity fluctuations of the upconversion signal below and above the laser threshold. Pearson correlation coefficients maps were also obtained and showed that RL modes were increasingly correlated above EF_{th} . No reduction of the emission linewidth was observed above EF_{th} , which may be attributed to the inhomogeneous broadening, that is significantly higher in vitreous matrices, in comparison to crystalline hosts.

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0.4.135 Upconverting NaGdF₄ : Er³⁺,Yb³⁺ particles as theranostic agent for glioblastoma multiforme

Speaker: Dos Santos Luiz Fernando

Upconverting NaGdF₄: Er³⁺, Yb³⁺ nanoparticles as theranostic agent for glioblastoma multiforme

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Upconverting nanoparticles has opened many ways and possibilities in the development of advanced nanomaterials employed in nanomedicine and healthcare research, including photodynamic therapy, bioimaging and temperature sensors [1]. In this sense, Er³⁺, Yb³⁺ co-doped NaGdF₄ particles were prepared by EDTA assisted hydrothermal synthesis. According to Transmission Electronic Microscopy images the obtained material has spherical shape with a narrow size distribution, around 250 nm. Concerning spectroscopic features the particles displayed a high intense visible luminescence under NIR excitation (980 nm) in powder and in a colloidal dispersion in cell culture medium. The upconversion spectra show narrow bands at 520 and 545 nm assigned to ²H_{11/2} → ⁴I_{15/2} and ⁴S_{3/2} → ⁴I_{15/2} in green region and at 630 nm, assigned to Er³⁺ ⁴F_{9/2} → ⁴I_{15/2} transitions, respectively. The cytotoxic effect of these particles in different concentrations was evaluated by resazurin colorimetric test on glioblastoma multiforme tumors cells (KNS42, U87MG and T98G cells) after 3 hours incubation time. The obtained viability values remained close to 70% for U87MG and T98G, concerning the KNS42 cell line the values of viability remained around 40%. The Figure 1 depicts the spectra obtained by upconversion of the particles suspended in culture cell medium and the statistic results of viability in U87MG cells. These preliminary results suggest the potential application of RE doped fluoride based NPs in nanomedicine, acting as luminescent biomarkers and as light converters in photodynamic therapy for brain tumor treatments.

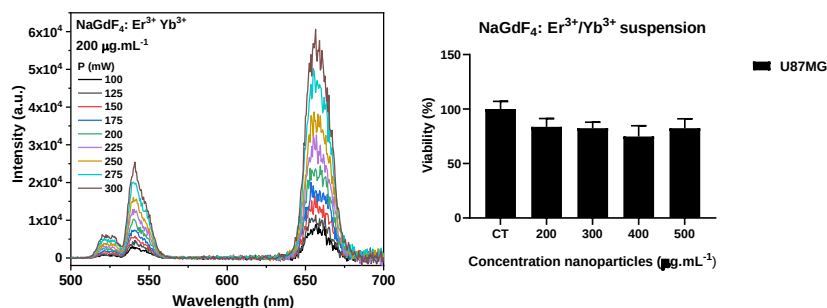


Figure 1. Upconversion spectra of NaGdF₄ colloidal suspension in a culture cell medium and cell viability obtained by the colorimetric assays.

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0.4.136 Visible and NIR emission in Yb and Y doped CaSnO₃

Speaker: Padilla-Rosales Isela

Visible and NIR emission in Yb and Y doped CaSnO₃I. Padilla-Rosales,^{1,2} G. López-Pacheco,¹ O.G. Morales-Saavedra,² and F. González^{1,*}¹ Departamento de Ingeniería de Procesos e Hidráulica, Universidad Autónoma Metropolitana-Iztapalapa, Ciudad de México, 09310, México² Instituto de Ciencias Aplicadas y Tecnología, Universidad Nacional Autónoma de México, Ciudad de México, 04510, México*E-mail: fgg@xanum.uam.mx

Ceramic powders of Ca_{1-x}Yb_xSnO₃ (x = 0.0, 0.00625, 0.0125, 0.025 and 0.05) and Ca_{1-x}Y_xSnO₃ (x = 0.00125, 0.00625, 0.0125 and 0.025) were synthesized by the polymeric complex method and annealed at 1300 °C for 1 h. Formation of both compounds series was confirmed by X-ray diffraction. Broad absorption bands in the UV range ascribed to the fundamental transition are compatible with excitation bands when Yb³⁺ emission (~970 nm) is monitored (Fig. 1a). The photoluminescent excitation and emission spectra show that NIR photon downshifting via host sensitization is achieved in Ca_{1-x}Yb_xSnO₃ samples (Fig 1). These samples have luminescence in two main regions; in the visible (VIS) which can be originated from the self-trapped calcium stannate excitons [1], and in the near-infrared (NIR) region associated with the ²F_{5/2}→²F_{7/2} transition of Yb³⁺ [2]. To demonstrate that the energy is transferred from the visible region to the NIR region, Ca_{1-x}Y_xSnO₃ samples were synthesized in the same way than the Yb-doped ones, showing that this mechanism of energy transfer is only observed for Ca_{1-x}Yb_xSnO₃ samples. Finally, it is shown that the solid solutions may downshift photons from UV to wavelengths where a crystalline-silicon photovoltaic solar cell has a better spectral responsivity.

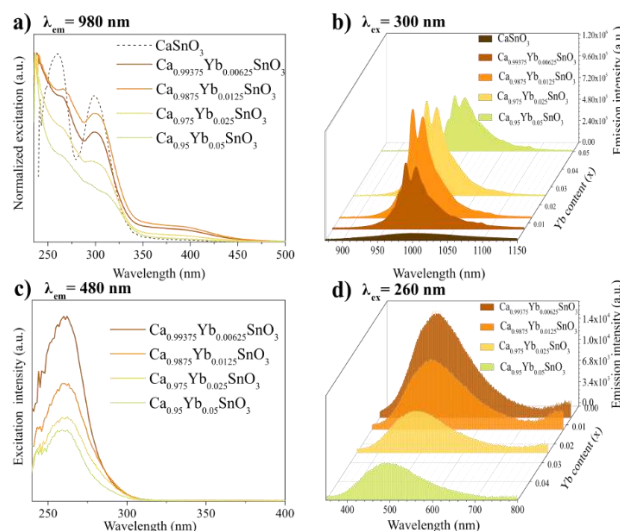


Fig. 1: Luminescence spectra of Ca_{1-x}Yb_xSnO₃ (x = 0.0, 0.00625, 0.0125, 0.025 and 0.05) samples; (a) normalized excitation spectra monitoring at λ_{em} = 980 nm, (b) emission spectra upon λ_{ex} = 300 nm, (c) excitation spectra monitoring at λ_{em} = 480 nm, and (d) emission spectra upon λ_{ex} = 260 nm.

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0.4.137 Visible and NIR luminescence for nanothermometry with silver sulfide (Ag₂S) and oxide nanoparticles

Speaker: Naillon Thomas

Visible and NIR luminescence for nanothermometry with silver sulfide (Ag₂S) and oxide nanoparticles

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Temperature is one of the most common physical quantities and greatly contributes to chemical reactivity and biological processes. Luminescence nanothermometry is related to temperature measurements at the nanometric scale with high spatial and temporal resolution using nanoparticles (NPs) for which, for instance, the controlled parameter is an extinction of luminescence observed during a rise of temperature (*Figure 1a*)¹. Nanothermometry has many applications since it reflects physical, chemical or biological phenomena. For example, in medicine, the measurement of nanothermometry would allow earlier diagnosis of certain diseases.

In this field, silver sulfide (Ag₂S) has demonstrated its effectiveness and low toxicity. Ag₂S NPs are able to be excited in the first window of transparency of biological tissues (NIR-I) and to emit in the second biological window (NIR-II). The variation of the luminescence with heating allows to calibrate the temperature probes with a very good sensitivity and this effect has been investigated in the present study for different ligands. An optimization work needs to be performed to better understand the process and to make this material more efficient. In this approach, the presence of hydrogen peroxide (H₂O₂) was studied in contact with Ag₂S NPs. The results present a strong dependence of the luminescence according to the nanoparticles coating (*Figure 1b*)².

In a second approach, various oxide structures (such as ZGGO, YAG, ...) doped with rare earths cations open up a whole range of interesting nanothermometers for consolidated measures. Indeed, metal transition and rare-earth doping makes possible the design of nanothermometers which emit visible and NIR wavelengths or dual emission bands sensitive/insensitive to temperature variations for a double temperature reading³.

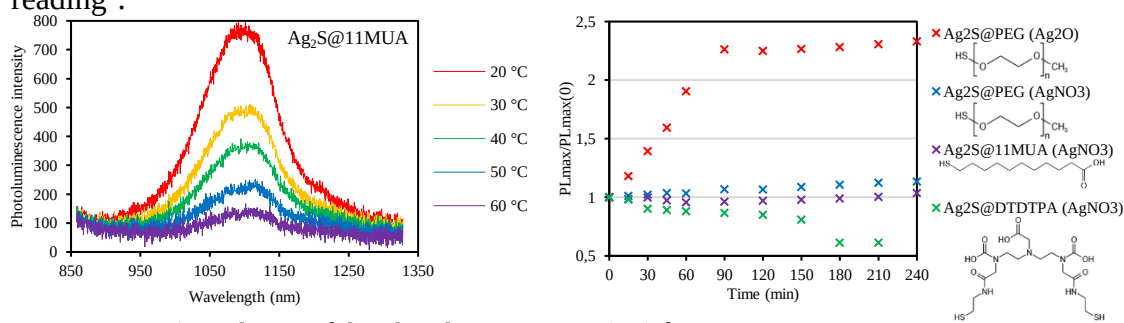


Figure 1 : a) Evolution of the photoluminescence (PL) for temperature increase on Ag₂S NPs coating with 11MUA ; b) Impact of H₂O₂ on the PL maximum (PL_{max}) pic of Ag₂S NPs during 4h after addition of H₂O₂. NPs with 3 different coating (11MUA, DTDTPA, PEG) and 2 different silver precursors (Ag₂O, AgNO₃) were studied.

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0.4.138 X-ray activated UV-A long persistent luminescence of Ce³⁺ doped Sr₃MgSi₂O₈ material

Speaker: Doke Guna

X-ray activated UV-A long persistent luminescence of Ce³⁺ doped Sr₃MgSi₂O₈ material

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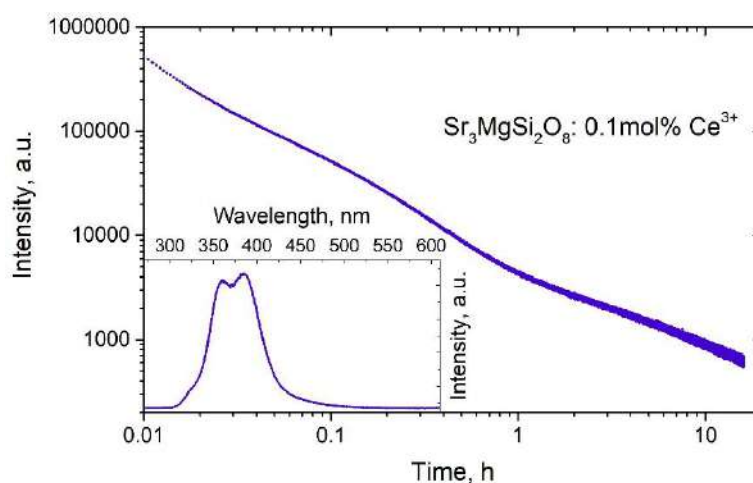
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Persistent luminescence also called afterglow or long-lasting phosphorescence is a type of luminescence characterised by the emission of radiation from a few seconds to several days after the excitation source is turned off. Most established persistent luminescence materials have emission in the visible part of the spectrum; however, for the last few years, research interest in UV-emitting persistent phosphors has emerged. Such materials have been tested for photocatalytic, sterilization, anti-counterfeiting and other applications.

Here, we report on X-ray activated UV-A long persistent luminescence of Ce³⁺-doped Sr₃MgSi₂O₈ material for the first time. It was concluded that when irradiated with X-rays for 3 min, a sample with 0.1 mol% concentration of Ce³⁺ can be characterised with afterglow in 300 – 450 nm range for more than 16 h.

Samples with varied Ce³⁺ concentrations were produced using solid-state reaction synthesis in an ambient atmosphere. Thorough investigations using photoluminescence, electron paramagnetic resonance, and thermally stimulated luminescence spectroscopy methods have been performed. Summarising the results, conclusions are drawn about the processes of long persistent luminescence of Ce³⁺-doped Sr₃MgSi₂O₈ material and its potential applications.



Persistent luminescence decay profile of Sr₃MgSi₂O₈: 0.1 mol% Ce³⁺ sample after irradiation with X-rays for 3 min. Inset: corresponding emission spectrum.

Latvian Council of Science, project “Defect engineering of novel UV-C persistent phosphor materials”, project No. LZP-2021/1-0118 is gratefully acknowledged.

0.4.139 X-ray excited optical luminescence at Carnaúba, the Sirius X-ray nanoprobe beamline

Speaker: Teixeira Verônica

X-ray excited optical luminescence at Carnaúba, the Sirius X-ray nanoprobe beamline

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Carnaúba is a tender to hard X-ray multi-analytical nanoprobe beamline from Sirius, the new Brazilian synchrotron light source, one of the pioneers among the 4th generation machines [1]. X-ray excited optical luminescence (XEOL) is one of the techniques available at the Carnauba beamline and currently can be performed in both spectral (energy scan) and hyper-spectral imaging modes, with high spectral and spatial resolution. It can be recorded simultaneously with other techniques such as X-ray fluorescence (XRF) for a complete correlation among chemical composition and optical emitter centers.

In the Fig. 1 (a) we show the experimental setup for optical measurements at the Carnaúba first endstation, called Tarumã, in which one reaches beamsizes in order of 230(H) x 200(V) nm², and Fig. 1 (b) and (c) show, respectively, hyper-spectral XRF and XEOL mapping of HPMC-ZnGa₂O₄:Mn²⁺ composites (HPMC = Hydroxypropyl Methyl Cellulose), under 9.75 keV irradiation. The films were prepared by drop-casting considering 1g/cm² surface concentration of the particles, are transparent and exhibited green persistent luminescence arising from Mn²⁺ ⁴T₁ → ⁶A₁ transition, which is correlated with Zn and Ga chemical distribution. The XEOL spectrum (Fig. 1 (c)) also showed a broadband from defect emission, which is only present under X-ray irradiation, and is a critical information to understand luminescence mechanism of this material.

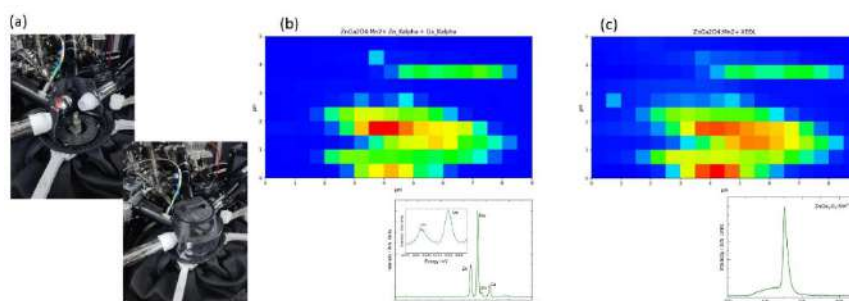


Figure 1. (a) XEOL experimental setup at the Tarumã@Carnaúba beamline, (b) XRF and (c) XEOL hyper-spectral mapping of HPMC-ZnGa₂O₄:Mn²⁺

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0.4.140 X-Ray induced Persistent Luminescence in Rare Earth-doped Strontium Sulfide materials: investigating structural defects and mechanisms

Speaker: Fonseca Karina Torre

X-Ray induced persistent luminescence in Rare Earth-doped Strontium Sulfide materials: investigating structural defects and mechanisms

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Persistent luminescence is an optical phenomenon in which a material emits light over long periods of time after the excitation source has been removed [1]. The mechanism that drives persistent luminescence consists in a gradual release of charge carriers from trapping centers, which are directly associated to lattice defects in a material, thus leading to significantly longer than expected luminescence decay times. [2,3].

SrS is a highly efficient host for persistent luminescent materials and also a potential X-ray absorber, which favors new X-ray induced mechanisms for optical luminescence and persistence. Measurements of the X-ray excited optical luminescence (XEOL) around strontium and sulfur edges, along with XANES, provide an interesting tool to identify the contribution of each atom on the final emission and its decay time under X-ray irradiation. Substitutional defects are expected to be formed in SrS matrix with doping, leading to bond length variations and also structural disorder, which can be obtained respectively as ΔR and Debye-Waller parameters in EXAFS analysis.

In this work, crystalline structure, oxidation states and X-ray induced persistent luminescence of $\text{SrS:RE}^{2+/3+}$ and $\text{SrS:Eu}^{2+}, \text{RE}^{3+}$ materials (RE: Eu^{2+} , Sm^{3+} and Ce^{3+}) were investigated with synchrotron radiation techniques. Phase purity and crystal parameters were obtained through XRD in Debye-Scherrer geometry. The incorporation of rare-earth dopants in SrS structure was studied with EXAFS, around Sr K-edge. XANES and XEOL simultaneously provided the correlation between X-ray absorption around specific edges, subsequent optical luminescence intensities and persistent luminescence decay times.

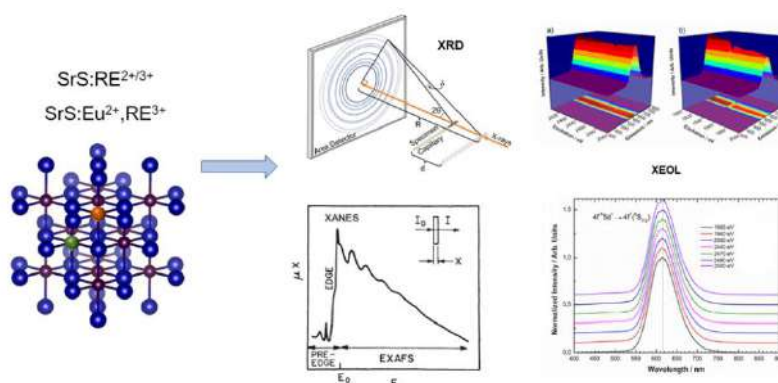


Figure 1. Crystal structure of rare-earth doped SrS materials and synchrotron radiation studies. XRD scheme was adapted from B. S. Hulbert and W. M Krivier, *J. Appl. Crystallogr.* **56**, 160-166 (2023).

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