

# IS-OM10



Lyon

July 6<sup>th</sup> - 10<sup>th</sup> 2026

## 10<sup>th</sup> International Symposium on Optical Materials



## Book of abstracts



**Monday 6<sup>th</sup>**

**Tuesday 7<sup>th</sup>**

**Wednesday 8<sup>th</sup>**

**Thursday 9<sup>th</sup>**

**Friday 10<sup>th</sup>**

**Posters**



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# Monday 6<sup>th</sup>

## Weekly summary

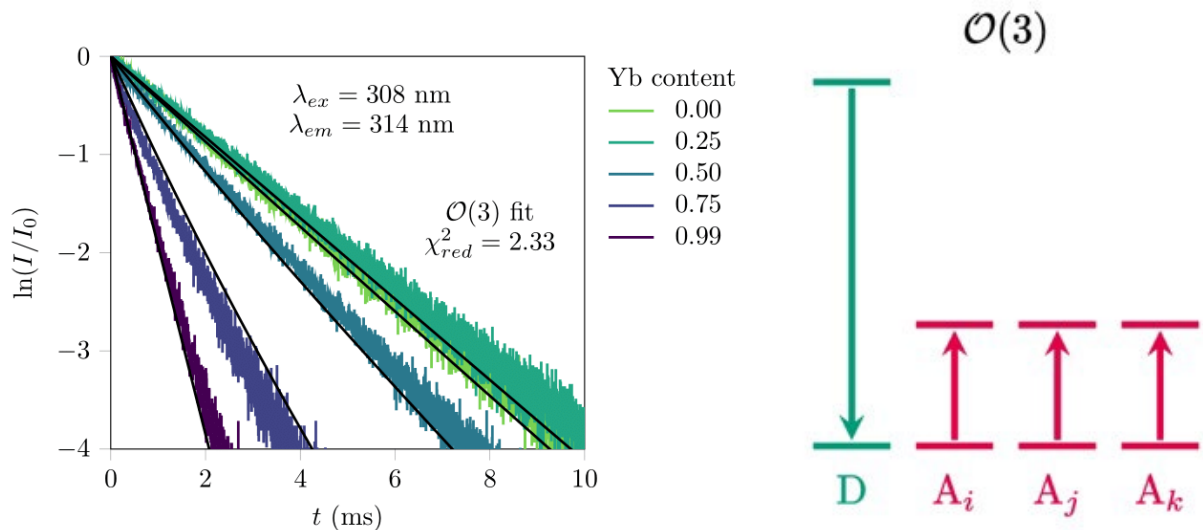
# WORKING TOGETHER IN LUMINESCENCE

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In the field of luminescence initially the spectroscopic properties of individual ions were explored and also applied, e.g. in lamp phosphors as  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  or x-ray phosphors as  $\text{Gd}_2\text{O}_2\text{S}:\text{Pr}^{3+}$ .<sup>1</sup> During his long and impressive career professor Georges Boulon demonstrated the beneficial effects of combining different types of ions, both lanthanides and transition metal ions, to realize brighter luminescence and better lasers.<sup>2,3</sup> The same principle was demonstrated by Georges in working together with colleagues and students, in his laboratory and at conferences and summer schools in Erice and Wroclaw, resulting in exciting discoveries and brighter students. In this presentation I will look back at what we have learned about energy transfer and cooperative processes involving lanthanides and transition metal ions working together. Recent results on cooperative energy transfer from a single lanthanide to two or even three neighboring ions will be discussed (including Georges' favorite lanthanide  $\text{Yb}^{3+}$ )<sup>4</sup> as well as insights in energy transfer mechanisms by modelling luminescence decay curves with the discrete shell model.<sup>5-7</sup> The implications for applications in for example luminescence thermometry and solar cells will illustrate the importance of working together in luminescence.



**Fig. 1** – Luminescence decay curves of the  $\text{Gd}^{3+}$  emission in  $(\text{Y},\text{Yb})_2\text{O}_3:\text{Gd}^{3+} 1\%$  with curve fitting using the shell model for cooperative energy transfer from one  $\text{Gd}^{3+}$  to three  $\text{Yb}^{3+}$  neighbors depicted on the right hand side.

Not all interactions are however beneficial and the role of bad neighbors, defects and quenching sites, is well-known but poorly understood. Defects play a crucial role in the performance, limiting efficiency, stability and performance but the nature and role of defects has remained



elusive.<sup>1,8</sup> In the second part of my presentation I will discuss the role of defects that cause strong variations in luminescence efficiency, spectra and afterglow induced by ppm levels of impurities and defects in micro- and nanocrystalline phosphors as well as single crystals and transparent ceramics where again Georges' work contributed to understanding the importance of optimized synthesis methods and studying ion and defect distributions on a microscopic scale to optimize (laser) performance.<sup>9,10</sup> After an outlook on future developments and how by working together we can solve the remaining puzzles in the field of luminescence, I will share some memories on working together with professor Georges Boulon for 35 years, starting with his lectures at the ESTE and Erice Summerschools when I was a PhD student and continuing with his seminal contributions to our field, his role as editor of Optical Materials and his strong commitment to the ICL conferences until the end.

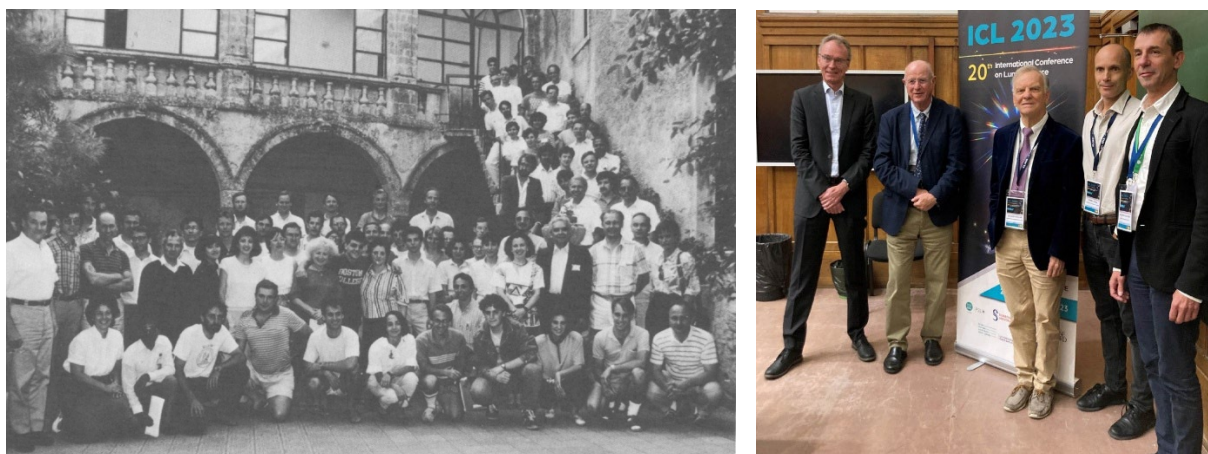


Figure 2 – (left) Group picture of my first Erice summerschool in 1989 with professor Georges Boulon as lecturer, (right) Photograph taken at the 2023 ICL meeting in Paris.

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# PHOTOLUMINESCENCE AN EFFECTIVE METHOD FOR THE NON-INVASIVE ANALYSIS OF GEMSTONES OF CULTURAL HERITAGE MASTERPIECES

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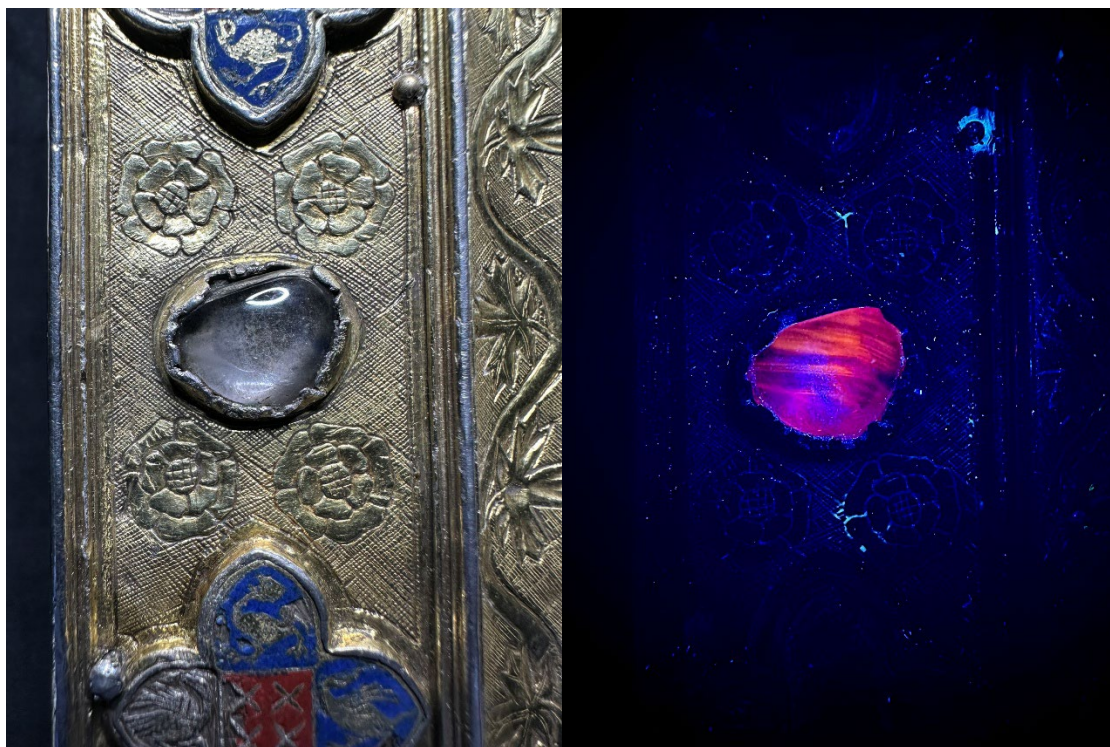
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The detailed scientific characterization of cultural heritage jewels or masterpieces is an essential challenge for 1) their historical knowledge, 2) the identification of possible replacements and restorations, 3) their traceability and 4) their insurance value. The identification of gemstones and of their imitations contributes to this knowledge. If, on site, non-invasive, Raman analysis, optical absorption and XRF elemental analysis are necessary, photoluminescence PL provide a specific spectral fingerprint, which can be used to identify very rapidly the nature of the mineral host matrixes such as: rubies (corundum  $\text{Cr}^{3+}:\text{Al}_2\text{O}_3$ ), spinels ( $\text{MgAl}_2\text{O}_4$ ), sapphires ( $\text{Fe}^{2+}\text{-Ti}^{4+}$ ,  $\text{Cr}^{3+}:\text{Al}_2\text{O}_3$ ), emeralds ( $\text{Cr}^{3+}:\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ ) and fluorite ( $\text{Ln}^{3+}:\text{CaF}_2$ ) [1,2]. Therefore, they can efficiently be differentiate from glass or glass-ceramic imitations.



**Fig.** Colorless leuco-sapphire revealed by its  $\text{Cr}^{3+}$  red fluorescence and its growing zonation under UV (365 nm) illumination (Gospel of Saint-Denis, Latin 9387 inf., BnF, manuscript 9th cent.; cover binding 13th cent.).

Precise examples are given with the gemstones set (Fig.) on the precious bindings of Medieval manuscripts of the French national library (BnF, Paris). PL is proof to be an efficient and essential tool to characterize gemstones of patrimonial objects.

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# THE ROLE OF INTERFACES IN PHOTOEXCITATION AND CHARGE TRANSFER IN DIAMOND

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Diamond is an unconventional semiconductor with a wide bandgap and a remarkable ability to host defects and intrabandgap states, enabling applications in quantum technologies with NV centers as well as catalysis using B and N doping. Unlike most semiconductors, diamond surfaces do not form a native oxide layer but are instead terminated by surface atoms and molecular groups ( $sp^2$  reconstructions,  $-OH$ ,  $=O$ ,  $-H$ ,  $-N$ ,  $-F$ , etc.). These terminations introduce localized states within the bandgap, strongly modify surface electron affinity and band bending, can be photoexcited, lead to charge separation and trapping [2], and evolve depending on the environment and usage. Understanding and controlling these effects is essential for designing the diamond-based applications of tomorrow.

In this talk, I will show how different diamond surface terminations control electronic structure and interfacial charge-transfer processes, and how these properties change under operating conditions. Using state-of-the-art synchrotron X-ray spectroscopies (NEXAFS, depth-resolved XPS, *in situ* XAS) [1] combined with laboratory experiments [2,3,7], we probe a variety of diamond interfaces. From this understanding, I will illustrate how nitrogen-terminated diamonds [3–5] stabilize the  $NV^-$  charge state compared to oxidized surfaces [6], and how functionalized nanodiamonds and B- and N-doped diamonds can be engineered for electro- and photoelectrochemical applications, including  $CO_2$  reduction [7,8].

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**Monday 6<sup>th</sup>**

# **Non Linear Optic**

# NEW CONTRIBUTIONS TO THE MODELING OF SPONTANEOUS PARAMETRIC DOWN-CONVERSION IN PHASE-MATCHED CRYSTALS

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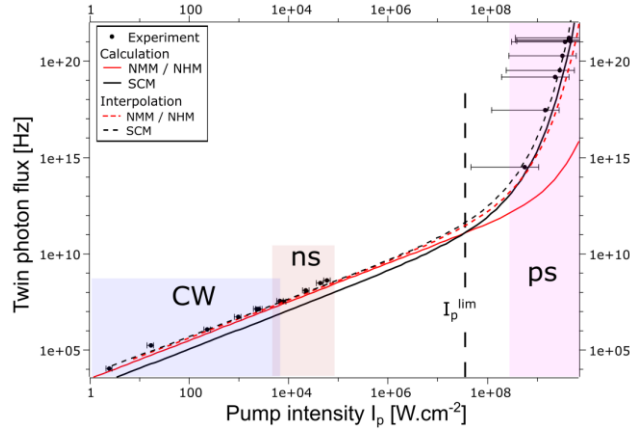
This keynote presentation deals with spontaneous parametric down-conversion (SPDC) which is a second-order nonlinear process in which a pump photon is split into two photons of lower energy. Nowadays, bulk crystals, photonic crystals or waveguides are used as nonlinear media [1]. Photon-pairs are at the very heart of several non-classical properties, such as for example the squeezing of quantum fluctuations, or quantum entanglement that is the most intriguing [2]. These quantum aspects are the key element in a large number of demonstrations such as quantum cryptography, quantum teleportation and quantum information in the broadest sense, or the detection of gravitational waves [3]. While the quantum properties of photon pairs are extremely well known, it is still extremely difficult to predict their flux as a function of pump intensity. Major efforts have been made in recent years to develop semi-classical models [4] and quantum models [5] of SPDC. The present work falls within this framework, with the ambition of further improving quantitative predictivity based on a semi-classical approach [6].

The classical part of the model is based on the coupled differential equations relative to the spatial derivative of the complex amplitudes of the interacting waves, *i.e.*  $\partial E_a / \partial Z$  with  $a = (p, s, i)$ , in the undepleted pump approximation (UPA), *i.e.*  $\partial E_p / \partial Z = 0$ , and in a collinear phase-matching configuration, *i.e.*  $\omega_p n_p - \omega_s n_s - \omega_i n_i = 0$  where  $n_a$  is the refractive index at the circular frequency  $\omega_a$ . The quantum part of the model corresponds to the quantum fluctuations of vacuum that are taken as the initial values of the amplitudes of the generated fields, *i.e.*  $E_{s,i}(Z=0) \equiv \Delta E_{s,i}^{\text{vacuum}} = \sqrt{\Delta \omega_{s,i} \hbar \omega_{s,i} / 4\pi c \epsilon_0 n_{s,i} S}$  where  $\Delta \omega_{s,i}$  is the spectral linewidth of the generated photons, and  $S$  the cross section of the overlap between the pump and stimulation beams. Then, it comes for the flux of the generated triplets:

$$N_{\text{pairs}}(L) = \frac{\epsilon_0 n_s c S}{4 \hbar \omega_s} \left[ \Delta E_s^{\text{vacuum}} (\cos h(\beta L) - 1) + \sqrt{\frac{\omega_s n_i}{\omega_i n_s}} \Delta E_i^{\text{vacuum}} \sinh(\beta L) \right]^2 \quad (1)$$

$L$  is the crystal length,  $\beta = \chi_{\text{eff}}^{(2)} E_p(0) \sqrt{\kappa_s \kappa_i}$  with  $\kappa_{s,i} = \omega_{s,i} / 2n_{s,i} c$  and  $\chi_{\text{eff}}^{(2)}$  the second-order effective coefficient.

We have validated our model by performing an experiment for which the pump intensity at 532 nm or 527 nm ranges from 2.4 W.cm<sup>-2</sup> to 3.7 GW.cm<sup>-2</sup>, leading to the generation of twin-photons around 1000 nm with a flux from 1.1x10<sup>4</sup> Hz to 1.2x10<sup>21</sup> Hz [6]. The corresponding curve is given in the following figure that also gives the calculation by two quantum models, *i.e.* the nonlinear momentum model (NMM) [7] and the nonlinear Hamiltonian model (NHM) [812], as well as by our semi-classical model (SCM) [6].



**Fig.** Measured and calculated photon-pair flux generated by SPDC that is phase-matched along the x-axis of a 1-cm-long KTP crystal pumped in continuous (CW), nanosecond (ns) and picosecond (ps) regimes at 532 nm or 527 nm.  $I_p^{\text{lim}}$  is the pump intensity delimiting the low and high pump intensity regimes.

Our semi-classical model allows a satisfying description of the experimental data, with a much better agreement at high intensity than the quantum models: the difference with respect to experiment reaches seven orders of magnitude with the quantum models, whereas it is one order of magnitude with our model. The figure also shows that there exists two SPDC regimes regarding the pump intensity: one below  $40 \text{ MW.cm}^{-2}$  for which the flux increases linearly, and the other one above  $40 \text{ MW.cm}^{-2}$  for which it behaves exponentially. We have also calculated at this limit the ratio between the magnitudes of the electric fields of the generated photons – signal or idler - and of vacuum  $\|E_{s,i}\|^{\text{lim}} / \|\Delta E_{s,i}^{\text{vacuum}}\|$  that is equal to 1.718 [9]. This relation of order regarding the electric fields allows us to confirm and well understand that the quantum fluctuations of vacuum governs SPDC in the small-signal regime, *i.e.*  $\|E_{s,i}\| < \|\Delta E_{s,i}^{\text{vacuum}}\|$  meaning that the pump photons splitting into photon-pairs is a spontaneous process, while the splitting is stimulated by the signal and idler photons in the high-signal regime, *i.e.*  $\|E_{s,i}\| > \|\Delta E_{s,i}^{\text{vacuum}}\|$ , which corresponds to a regime of parametric amplification.

Then our study complements previous works reporting different quantum properties of the photon-pairs generated by SPDC as a function of the pump intensity, from entangled state of the signal and idler fields in the low-signal regime to highly-squeezed EPR states in the high-signal regime.

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# All-Photonic Terahertz Detection Using Microcomb-Referenced Dual Optical Carriers for Low-Noise W-Band Wireless Reception

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Terahertz (THz) wireless systems are a key technology for future beyond-5G/6G networks, where seamless convergence between optical fiber and wireless links is required. However, conventional electronic THz receivers suffer from bandwidth limitations, phase-noise degradation caused by frequency multiplication, and difficulties in direct integration with photonic systems. To address these challenges, we propose and demonstrate an all-photonic THz detection scheme based on THz-to-optical carrier conversion using dual optical carriers referenced to a soliton microcomb.

In this approach, mutually coherent dual wavelengths generated from a microresonator-based optical frequency comb are injection-locked to semiconductor lasers to form a stable optical reference separated by a THz-rate spacing. An incoming W-band THz signal is applied to an electro-optic polymer modulator equipped with a patch-antenna array, where the THz field induces optical phase modulation. The generated optical sideband is heterodyned with the second optical carrier, enabling nonpolarimetric electro-optic downconversion of the THz signal directly into the RF domain without requiring an electrical local oscillator.

We experimentally demonstrate reception of a 106-GHz OOK-modulated THz signal at 2.97 Gb/s. The proposed dual-carrier configuration significantly enhances the signal-to-noise ratio compared with a single-carrier scheme, enabling clear eye opening and error-free detection with a Q-factor of 5.78 and a bit-error rate of  $3.7 \times 10^{-9}$ . These results confirm that microcomb-referenced dual carriers provide a compact and scalable platform for low-phase-noise photonic THz receivers.

The demonstrated architecture establishes a pathway toward fully photonic wireless-to-optical interfaces, offering frequency scalability beyond the W-band and compatibility with future high-capacity THz communication systems.

This research was supported by MIC/FORWARD#JPMI240910001.

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# PROBING THE ORGANIZATION OF LIQUIDS BY SECOND HARMONIC GENERATION

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Liquid molecular organization as well in the bulk or at interfaces like gas-liquid or liquid-liquid interfaces, is involved in many physical, chemical, or medical relevant processes. At interfaces, the inherent asymmetry of the forces present dramatically modifies their properties and determines in large part its specific chemical composition, molecular structure, dielectric and transport properties, compared with its bulk counterparts. This asymmetry also drives important chemical reactions occurring in chemical and biological processes, including liquid extraction, catalysis, membrane processes, or drug delivery, to mention a few. In the bulk, this organization is also of utmost importance to understand hydration and more generally solvation, ions dissolution and precipitation, protein folding and activity, all result from the interaction of ions with solvent molecules. Charged solutes and ions interact with dipolar molecules through ion-dipole interactions and perturb the dipole-dipole interaction network present in pure dipolar liquids. The structure and the dynamics of liquids have been extensively studied with experimental methods based on neutrons, X-rays or UV-to-IR optical spectroscopy as well as theoretical methods like molecular dynamics. More recently, nonlinear optical methods [1, 2,3] and Hyper Raman spectroscopy [4] have been proposed with great success. The existence of long-range orientational correlations over nanometer distances have been experimentally demonstrated in water as well as the role of ions in disrupting this network [2]. In this context, we have used Second Harmonic Generation (SHG) as a tool to probe the structure of liquids from interfaces to the bulk phase. Indeed, this non-linear optical process whereby two photons at a fundamental frequency are converted into one photon at the harmonic frequency, is intrinsically sensitive to interfaces and very sensitive to the liquid structure or the electrostatic environment.

In this presentation, I will focus on the possibility of applying nonlinear optics to probe the molecular organization of liquids. We applied the SHG technique through the Second Harmonic Scattering geometry to study bulk phases. Two kinds of liquids have been investigated: aqueous solutions (pure water and electrolytes) and ionic liquids. We will show that the combination of SHG and quantum mechanical calculations provides valuable information on the structure of the liquids on scales ranging from the very short distance [5] (solvation shells) to the long distance (orientation correlations) [3].

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# THERMAL TREATMENT CONDITIONS FOR FORMATION OF SCATTERING CENTERS IN CsLiB<sub>6</sub>O<sub>10</sub> CRYSTALS

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Deep-ultraviolet (DUV) pulsed light sources based on infrared solid-state lasers and frequency conversion can provide high photon energy, high beam quality, and high repetition rates suitable for microfabrication of advanced materials. CsLiB<sub>6</sub>O<sub>10</sub> (CLBO) is a nonlinear optical crystal used for DUV light generation. CLBO-based DUV laser systems have demonstrated long-term, high-power continuous operation.<sup>1,2)</sup> However, after long-term operation, beam-pattern degradation has been observed, which is critical for industrial applications.<sup>2)</sup>

Previous studies showed that the degradation correlates with visible-light scattering intensity inside the CLBO crystal,<sup>3)</sup> suggesting that clarifying the formation conditions of these scattering centers and preventing their formation are important for improving the long-term stability of DUV light generation. Similar light-scattering phenomena were also observed in CsB<sub>3</sub>O<sub>5</sub> (CBO), where the formation mechanism of scattering centers was investigated through post-growth thermal treatments.<sup>4)</sup> In our previous studies on CBO, scattering centers can be effectively removed by heating near the melting point (835 °C) followed by rapid cooling, whereas they remain when the crystal is heated at lower temperatures or slowly cooled. These behaviors have been discussed in terms of a two-step process: Cs deficiency caused by evaporation of the Cs component at high temperatures, followed by precipitation of a secondary phase during cooling near 650 °C. We confirmed that, as in CBO, the scattering intensity in CLBO after heating near the melting point (850 °C) depends on the cooling rate.<sup>5)</sup> In this research, we investigated the holding-temperature dependence of scattering-center formation and the temperature range in which scatterers precipitate.

CLBO single crystals were grown by the Kyropoulos method<sup>6)</sup> and cut into 5 mm × 5 mm × 10 mm samples (four-sided polished) along the type-I SHG phase-matching direction for 532 nm laser light. Post-growth thermal treatments were conducted in a gas-replacement furnace under flowing Ar (0.5 L/min). Light scattering was observed by passing a linearly polarized green laser (wavelength: 543.5 nm, average power: 2.5 mW) through the sample and imaging the scattered light with a DSLR camera. The scattering intensity was evaluated from the images taken under fixed camera settings (exposure time: 90 s).

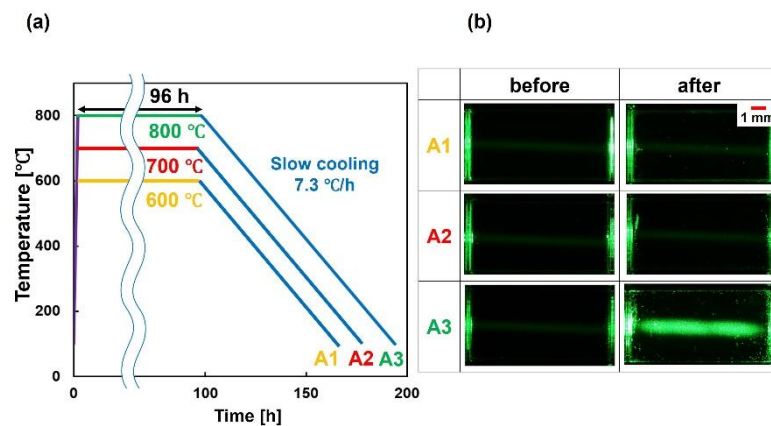
To examine the temperature dependence of scattering-center formation, post-growth thermal treatments were performed at different holding temperatures. Figure 1(a) shows the thermal treatment programs A1-A3. The samples were held at 600, 700, and 800 °C for 96 h

and then slowly cooled at 7.3 °C/h. Figure 1(b) shows the light scattering observed in the samples before and after thermal treatment. For samples A1 and A2, in which the holding temperature was 700 °C or lower, no change in scattering intensity was observed compared with that before the thermal treatment. In contrast, for holding at 800 °C (sample A3), the scattering intensity increased significantly after the thermal treatment. These results indicate that a high-temperature hold of approximately 800 °C is required for scattering centers to form during slow cooling. As with CBO, we regard evaporation of crystal components during heating at 800 °C as a possible cause of the formation of defects related to scattering centers; however, this point is still under investigation.

Next, to identify the temperature range in which scatterers precipitate, we applied slow cooling (7.3 °C/h) only within a selected temperature range and rapid cooling (700 °C/h) elsewhere. Scattering intensity increased when slow cooling was applied in the 200-100 °C range, indicating that scatterers precipitate over time in the temperature range of 200-100 °C.

In summary, we identified the high-temperature range under which defects related to scattering centers are formed (800 °C) and the temperature range in which scatterers precipitate (200-100 °C). This understanding will be used to improve crystal growth conditions.

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**Fig. 1.** (a) Post-growth thermal treatment programs with different holding temperatures (600–800 °C) under the same slow-cooling condition, and (b) observation of light scattering before and after post-growth thermal treatment (exposure time: 90 s).

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# ELECTRICAL CONTROL OF PERSISTENT SPIN HELIX ORIENTATION IN DUAL-GATED GaAs QUANTUM WELLS

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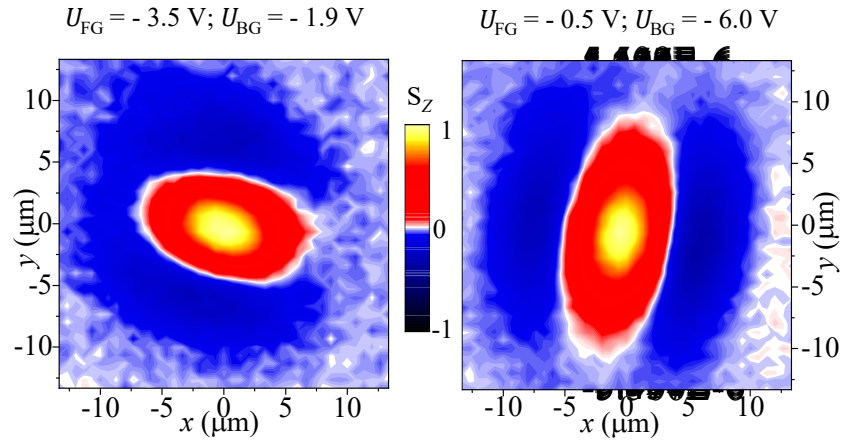
The persistent spin helix (PSH) represents a unique symmetry-protected spin state in two-dimensional electron gases (2DEGs), arising when Rashba and Dresselhaus spin-orbit coupling (SOC) terms are balanced [1,2]. In this regime, spin dephasing is strongly suppressed, enabling long spin lifetimes and coherent spin transport over micrometre length scales. Following its initial realization, numerous studies have focused on the mechanisms that stabilize or limit the PSH. Experimental and theoretical work has shown that higher-order SOC terms, notably the cubic Dresselhaus contribution, impose fundamental limits on PSH lifetimes, while factors such as carrier density, temperature, and electric fields influence both spin diffusion and relaxation [3-7]. Together, these advances highlight both the robustness and fragility of the PSH state, as well as the delicate interplay of structural, electronic, and dynamic factors that govern spin coherence.

While previous studies have demonstrated gate control of the PSH condition, direct electrical manipulation of the PSH *orientation* has remained elusive due to leakage-current limitations and the inherent constraints of single-gate architectures. Here, we demonstrate electrical switching of the PSH orientation by 90° in a gate-controlled GaAs double quantum well structure using time-resolved Kerr rotation microscopy. The device is equipped with independent front and back gates, allowing separate control of the electron density and the electric field across the quantum wells. By tuning the two gate voltages in opposing directions, we invert the Rashba SOC parameter while maintaining a nearly constant carrier density and avoiding gate leakage. This controlled sign reversal of the Rashba interaction, combined with an essentially constant Dresselhaus contribution, enables switching between two orthogonal PSH states aligned along the principal crystallographic directions, see Figure 1.

Spatially and temporally resolved Kerr rotation maps directly visualize the evolution and reorientation of the spin polarization patterns. Fourier analysis of the measured spin textures yields quantitative values of the SOC parameters, revealing that the Dresselhaus coefficient remains nearly invariant over the explored gate-voltage range, whereas the Rashba parameter depends linearly on a specific combination of front- and back-gate voltages. This confirms that differential gate tuning provides direct control over the internal electric field and, consequently, over the Rashba interaction.

Our results establish dual-gate quantum well architectures as a powerful platform for precise spin-orbit engineering. Beyond demonstrating direct electrical control over PSH orientation, this approach

overcomes fundamental limitations of single-gate systems and provides a robust route toward reconfigurable spin textures. Such controllability is highly relevant for spintronic applications, including spin-based logic devices, long-distance spin interconnects, and coherent spin routing in two-dimensional semiconductor systems.



**Fig.1** 2D maps of spin polarization, illustrating the manipulation (a 90-degree rotation of the PSH pattern) of the PSH by varying front-gate  $U_{FG}$  and back-gate  $U_{BG}$  voltages. The delay time for all the measurements was fixed at  $t=500$  ps. This figure shows only a representative subset of the full set of measurements.

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The background features a collection of light gray, irregular geometric shapes, primarily pentagons and hexagons, scattered across the white canvas. These shapes are separated by thin white lines, creating a fragmented, crystalline pattern.

**Monday 6<sup>th</sup>**

**Up converting nanoparticles**

# **A SYMPHONY OF PHOTONS: UPCONVERSION AND DOWNSHIFTING LUMINESCENCE IN THERANOSTIC PLATFORMS BASED ON RARE EARTH DOPED NANOPARTICLES**

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Since first reported, luminescent rare earth doped nanoparticles have attracted a great deal of interest. In the last decade, however, the field has rapidly taken off, progressing from the basic understanding of the photophysical properties governing their nanoscale luminescence, in particular upconversion, to their use in a plethora of applications, with considerable focus in biology and medicine. This interest stems primarily from the ability to stimulate these luminescent nanoparticles with near-infrared (NIR) light as well as their diverse emission wavelengths spanning the UV to the NIR. Therefore, with a single NIR excitation wavelength, it is possible to observe higher energy luminescence, known as upconversion, or single photon NIR emission (known as down-shifted luminescence). The former upconversion process proceeds through the sequential absorption of multiple NIR photons through the long-lived  $4f$  electronic energy states of the tri-positive rare earth ions. As a result, upconversion is several of orders more efficient than conventional multiphoton absorption processes. This is especially interesting for applications in theranostics (therapy + diagnostics on the same platform) where the upconverted light can be used to trigger another light activated modality (therapy) while the NIR luminescence can be used for bioimaging and nanothermometry (diagnostics). Here, we present a personal journey of our work on the synthesis and development of various NIR excited (and emitting) core/shell rare earth doped nanostructures/nanoplatfroms and demonstrate how their various emissions could be harnessed for applications in biology and nanomedicine.

# Nanostructured Oxyfluoride Glass-Ceramic Fibers for Enhanced Upconversion

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Upconversion (UC) of near-infrared excitation into visible emission in rare-earth doped materials has been investigated intensively due to the potential applications in several areas such as 3D displays, visible solid state lasers and amplifiers, solar energy conversion, medical imaging, photodynamic therapy, sensors, security and so on. The UC efficiency is strongly governed by the host matrix, particularly by its phonon energy: low-phonon environments reduce non-radiative multiphonon relaxation, thereby enhancing radiative transitions and emission efficiency. Among various host materials, transparent oxyfluoride glass-ceramics can combine the favorable properties from both fluoride crystal and oxide glass matrix, i.e., low phonon energy and high mechanical and chemical stabilities. While bulk oxyfluoride systems have been extensively investigated, the translation of these advantages into optical fiber geometries poses significant scientific and technological challenges, particularly regarding controlled nanocrystallization, transparency preservation, and propagation losses.

In this work, we report the fabrication and characterization of  $\text{Er}^{3+}$ - $\text{Yb}^{3+}$  co-doped  $\text{LaF}_3$ -based glass-ceramic optical fibers prepared by the rod-in-tube method using borosilicate cladding. Controlled post-drawing heat treatments induce the precipitation of  $\text{LaF}_3$  nanocrystals within the fiber core, providing a low-phonon crystalline environment for the rare-earth ions.

The  $\text{Er}^{3+}$ - $\text{Yb}^{3+}$  codoping strategy enhances absorption at 980 nm via efficient  $\text{Yb}^{3+} \rightarrow \text{Er}^{3+}$  energy transfer, resulting in intense green and red UC emissions together with a weak blue component. The UC mechanisms were investigated through excitation power dependence and time-resolved analysis of the green and red emissions. Power-dependent measurements indicate intermediate-state saturation, while temporal dynamics provide strong evidence that the UC process predominantly proceeds via energy-transfer upconversion mediated by  $\text{Er}^{3+}$ - $\text{Yb}^{3+}$  interactions.

The results demonstrate that controlled nanocrystallization in  $\text{Er}^{3+}$ - $\text{Yb}^{3+}$  co-doped  $\text{LaF}_3$ -based glass-ceramic fibers enables enhanced optical performance, positioning these materials as promising candidates for applications in photonics devices.

# Decoupling Structural Stabilization and Luminescence: A Strategy for Monitoring RE-Dopant Distribution in HfO<sub>2</sub> Nanoparticles

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Rare earth (RE) doping is often used to activate fluorescence, scintillation, or upconversion in several materials. The precise spatial distribution of these dopants throughout the host lattice plays a crucial role in optimizing the materials optical properties, as phenomena such as clustering or segregation can detrimentally affect their optical performance. In materials like HfO<sub>2</sub>, trivalent RE ions play a dual role: they activate luminescence but also induce, above specific amounts, the room temperature stabilization of high-symmetry polymorphs. When doping aims at upconversion (UC), for example through the incorporation of Er<sup>3+</sup> and Yb<sup>3+</sup>, efficiency and spectral purity depend on short-range energy transfer among the doping ions, together with the host crystal geometry. This doping-related polymorphism makes it difficult to determine whether changes in optical performance stem from lattice symmetry or simply from dopant concentration.

In this talk, the multifunctional role of RE doping in the activation of luminescence and on the nanocrystals host structure will be discussed. A doping strategy utilizing optically silent Lu<sup>3+</sup> ions allows to independently control structural stabilization and active dopant concentration.<sup>1</sup> This approach allows us to decouple the respective influences of structure and composition on luminescence. Upconverting nanoparticles show distinct emission profiles and UC efficiency between cubic and monoclinic hafnia allow for phase-specific luminescent labelling. By tailoring the material composition, tuneable UC chromaticity spanning from green to red is achieved.<sup>2</sup>

This is particularly relevant in mixed-phase systems resulting from intermediate doping levels, where UC spectral features can reveal the non-uniform, short-range repartition of ions between phases, acting as a powerful optical tool for monitoring nanoscale dopant distribution.

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# EFFECT OF La SUBSTITUTION ON THE BLUE UPCONVERSION LUMINESCENCE OF $\text{Gd}_2\text{Zr}_2\text{O}_7\text{:Tm}^{3+}/\text{Yb}^{3+}$ PYROCHLORE PHOSPHORS

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The choice of A-site cation in the  $\text{A}_2\text{Zr}_2\text{O}_7$  pyrochlore family is a powerful strategy for modulating upconversion behaviour in rare-earth-activated oxides, as it directly alters both the local crystal field environment and the defect/phonon landscape around activator ions. Replacing host cations with ions of different size or electronic configuration can influence their 4f–4f transition probabilities, modify  $\text{Yb}^{3+} \rightarrow \text{Tm}^{3+}$  energy-transfer dynamics, suppress or enhance non-radiative relaxation, and control oxygen-vacancy formation [1]. Despite these advances, the explicit interplay between A-site substitution, defect structure, and upconversion efficiency in zirconate pyrochlores remains incomplete motivating the present investigation.

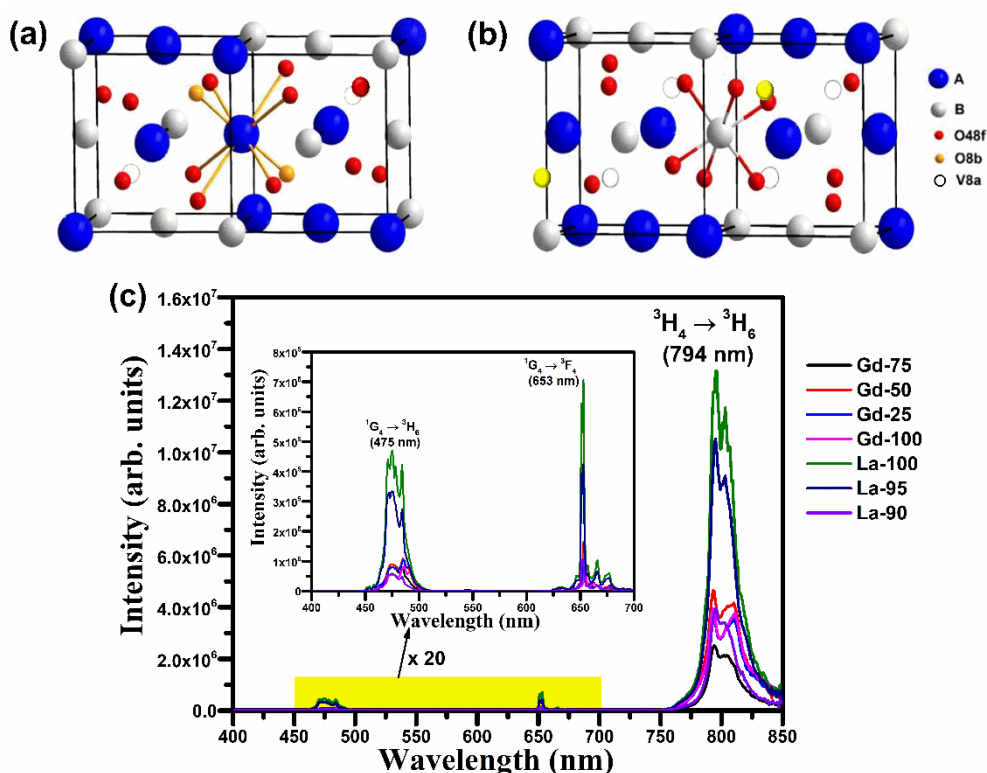
The  $\text{A}_2\text{Zr}_2\text{O}_7$  pyrochlore family is uniquely suitable for such studies, owing to its structural flexibility, low phonon energy, and capacity to accommodate extensive cation disorder. According to the ionic radius ratio criterion proposed by Subramanian et al. [2], if  $r_A/r_B$  lies between 1.46 and 1.78 a stable ordered cubic pyrochlore structure ( $\text{Fd}\bar{3}\text{m}$ ) is favoured. However, if it varies below 1.46 this tends to yield a defective fluorite phase ( $\text{Fm}\bar{3}\text{m}$ ), whereas values above 1.78 drive formation of monoclinic layered perovskites. In this work, the  $\text{Gd}^{3+}$ -ions (smaller ionic radius) and  $\text{La}^{3+}$ -ions (larger ionic radius) lie on opposite ends of this stability window, making the  $\text{Gd} \leftrightarrow \text{La}$  substitution series an ideal platform to probe how cation ionic radius-driven structure and defect evolution influences  $\text{Tm}^{3+}/\text{Yb}^{3+}$  upconversion. Additionally,  $\text{A}_2\text{Zr}_2\text{O}_7$  pyrochlores are technologically relevant for harsh-environment photonics, scintillators, thermal barrier coatings, and near-infrared emitters.

In this research the spectroscopic properties of  $\text{A}_2\text{Zr}_2\text{O}_7$  synthesized via microwave hydrothermal method were investigated with the A-cation site being occupied different proportions of  $\text{La}^{3+}$  and  $\text{Gd}^{3+}$ , with the La proportion varying from 0% (i.e.  $\text{Gd}_2\text{Zr}_2\text{O}_7$ ), 5%, 10%, 25%, 50%, 75% or 100% (i.e.  $\text{La}_2\text{Zr}_2\text{O}_7$ ) to capture the full transition from defective pyrochlore to ordered pyrochlore structure. The phosphor samples were co-doped with  $\text{Tm}^{3+}$  (2%) and  $\text{Yb}^{3+}$  (5%). The powder X-ray diffraction analysis confirmed the anticipated structural crossover from defective cubic pyrochlore ( $\text{Fm}\bar{3}\text{m}$ ) in Gd-rich samples to ordered pyrochlore ( $\text{Fd}\bar{3}\text{m}$ ) in La-rich compositions (specifically when  $\text{La} \geq 75\%$ ), in agreement with established disorder–radius correlations [3]. Further, the morphology from scanning electron microscopy with energy dispersive X-ray spectroscopy revealed nanoscale agglomerates confirming expected elemental stoichiometry and successful dopant incorporation.

The diffuse reflectance spectra showed the host band edge near 210 nm, with direct optical band gap varying between 5.15 eV to 5.40 eV for Gd- rich to La-rich samples respectively. Further, the Gd-rich samples exhibited a sharp absorption band near 278 nm corresponding to the  $^8\text{S}_{7/2} \rightarrow ^6\text{G}_7$   $\text{Gd}^{3+}$  f-f absorption, while the doped samples displayed the sensitizer-specific 980 nm absorption corresponding to  $\text{Yb}^{3+} \ ^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$  transition, confirming consistent optical activation pathways across the series. Under 980 nm excitation, all the doped samples exhibit well-resolved upconversion emission bands at 475 nm (blue,  $^1\text{G}_4 \rightarrow ^3\text{H}_6$ ), 653 nm (red,  $^1\text{G}_4 \rightarrow ^3\text{F}_4$ ) and 794 nm (infrared,  $^3\text{H}_4 \rightarrow ^3\text{H}_6$ ) corresponding to characteristic  $\text{Tm}^{3+}$  emissions. A clear

composition-dependent variation was observed, with the emission intensity increasing with increasing proportion of La in the host. The possible enhancement in observed UC emission spectra arose either from reduced defect density, or optimized Tm–O/Yb–O coordination symmetry, or suppressed phonon-assisted non-radiative processes in the ordered La-rich lattice. Further, the lifetime decay values are found to be longer in La-rich ( $\tau_{475\text{ nm}} = 0.33\text{ ms}$ ;  $\tau_{797\text{ nm}} = 0.45\text{ ms}$ ) sample compared to Gd-rich ( $\tau_{475\text{ nm}} = 0.26\text{ ms}$ ;  $\tau_{797\text{ nm}} = 0.39\text{ ms}$ ) sample which support improved radiative probability in La-rich hosts, consistent with established 4f-level behaviour in oxide pyrochlores [4].

Overall, this systematic study demonstrated that A-site cation engineering is a powerful design strategy for modulating upconversion efficiency in Tm<sup>3+</sup>/Yb<sup>3+</sup> activated zirconate pyrochlores. The combined structural and spectroscopic insights highlight the potential of A<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> materials as tunable platforms for possible applications in photonics, bio-imaging, anti-counterfeiting, and high-stability optical devices, aligning strongly with the evolving demands of advanced optical materials research.



**Fig.** Schematic of (a) ordered pyrochlore, (b) defective pyrochlore crystal structures and (c) upconversion luminescence emission spectra of synthesized samples under  $\lambda_{\text{ex}} = 980\text{ nm}$ .

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# DUAL-WAVELENGTH EXCITED UPCONVERSION IN RARE-EARTH-DOPED $\text{CaF}_2$ FOR LOW-COST NIR-TO-MIR INFRARED DETECTION

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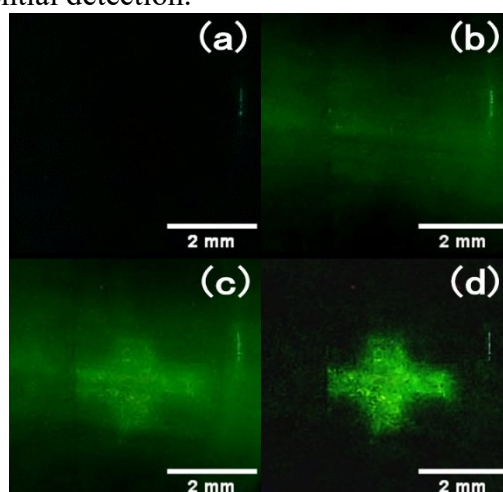
Infrared (IR) imaging from the near-IR (NIR) to mid-IR (MIR) is an essential technology for telecommunications, non-destructive inspection, and molecular sensing, yet high-performance IR cameras require specialized semiconductor materials such as InGaAs and HgCdTe, which are costly and often necessitate cryogenic cooling. To address this challenge, wavelength conversion offers a promising route to convert IR photons into visible (VIS) or NIR emission for detection with mature silicon CMOS/CCD sensors. In this work, we develop dual-wavelength excited upconversion (UC) in rare-earth-doped  $\text{CaF}_2$  crystals and demonstrate its utility as a solid-state IR quantum counter platform. In this scheme, a pump beam (pre-excitation) prepares population in an intermediate level of the rare-earth ion, and an IR signal beam drives excited-state absorption (ESA) to generate shorter-wavelength emission. This two wavelength scheme produces strong UC emission only when both beams are simultaneously present, thereby enabling wavelength-selective infrared detection. Below, we report on the confirmation and quantification of UC characteristics in  $\text{Er}:\text{CaF}_2$ , the extension to multiple rare-earth ions covering a broader wavelength range, and the demonstration of two-dimensional UC imaging.

We first systematically investigated the fundamental characteristics of dual-wavelength excited UC in  $\text{Er}^{3+}$ -doped  $\text{CaF}_2$ . By simultaneously irradiating the crystal with 800-nm pre-excitation and a 1510-nm signal beam, we observed strong green UC emission near 540 nm. Since this emission falls within the sensitivity range of silicon cameras, it enables NIR detection using low-cost silicon-based detectors. We defined the dual-wavelength increment as  $\Delta I = I(2\lambda) - I(800) - I(1510)$  and performed detailed power-dependent measurements of both excitation beams, revealing that  $\Delta I$  follows an approximately bilinear dependence  $\Delta I \propto P(800) \cdot P(1510)$ . We further introduced the normalized contrast  $C = \Delta I / (I(800) + I(1510))$  and analyzed its excitation-density dependence, finding that  $C$  peaks at moderate power levels and decreases at high powers due to saturation and parasitic single-color UC. To describe this behavior, we constructed a compact model combining a bilinear numerator with effective power-law backgrounds, establishing a practical design guideline for optimizing excitation conditions to maximize dual-wavelength UC selectivity.

To extend the target wavelength range of our dual-wavelength UC scheme, we systematically compared the absorption and transmission spectra as well as UC responses of  $\text{CaF}_2$  crystals

doped with several different rare-earth ions. In Ho:CaF<sub>2</sub>, we identified pronounced absorption lines near 1158 nm and 1442 nm and demonstrated clear enhancement of UC emission in both the visible and around 950 nm under dual-wavelength excitation. This result confirms that the platform is applicable beyond Er<sup>3+</sup> to a range of rare-earth dopants. Furthermore, as an extension toward MIR detection, we developed a new ESA-only dual-wavelength scheme in Er:CaF<sub>2</sub>. A 1550 nm (telecom-band) pump populates the long-lived <sup>4</sup>I<sub>13/2</sub> manifold, while a 2.8- $\mu$ m MIR signal beam drives ESA to enhance emission in the 980-nm band (observed near 970 nm). In our experiment, the 970-nm peak increased by approximately 7.5% ( $\Delta I \approx 300$  counts) upon MIR irradiation, exceeding the noise floor at a statistically significant level ( $z \approx 2.5$ ). To the best of our knowledge, this is the first demonstration of MIR-to-NIR conversion in a CaF<sub>2</sub>-based dual-wavelength UC platform and points to clear routes for sensitivity improvement through higher MIR photon flux and optimized differential detection.

Finally, we demonstrated two-dimensional IR imaging using the dual-wavelength UC platform. Figure 1 shows the spatial distribution of UC emission from Er:CaF<sub>2</sub> crystal captured by a silicon camera under various excitation conditions. Under illumination with the 1510-nm signal beam alone, virtually no emission is observed (Fig. 1a), while the 800-nm pump beam alone produces only weak background UC (Fig. 1b). In contrast, simultaneous dual-wavelength excitation yields a bright UC emission image at the beam overlap region (Fig. 1c). Subtracting the pump-only image from the dual-wavelength image produces a differential image (Fig. 1d) in which only the UC component attributable to the 1510 nm signal is extracted with high contrast. This differential imaging approach demonstrates that wavelength selectivity is achieved at the two-dimensional image level. Taken together, these results establish that dual-wavelength UC in CaF<sub>2</sub> is a promising platform for low-cost, room-temperature, wavelength-selective NIR-to-MIR sensing using only silicon detectors and mature telecom laser technology.



**Figure 1** Er:CaF<sub>2</sub> under single- and dual-wavelength excitation. (a) 1510 nm signal only. (b) 800 nm pump (pre-excitation) only. (c) Dual-wavelength excitation (800 nm + 1510 nm). (d) Differential image (c)-(b) highlighting the 1510-nm gated signal. Scale bars: 2 mm.

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# HOW TO SYNTHESIZE HIGHLY EFFICIENT RED EMITTING SMALL YVO<sub>4</sub>:Eu<sup>3+</sup> NANOCRYSTALS?

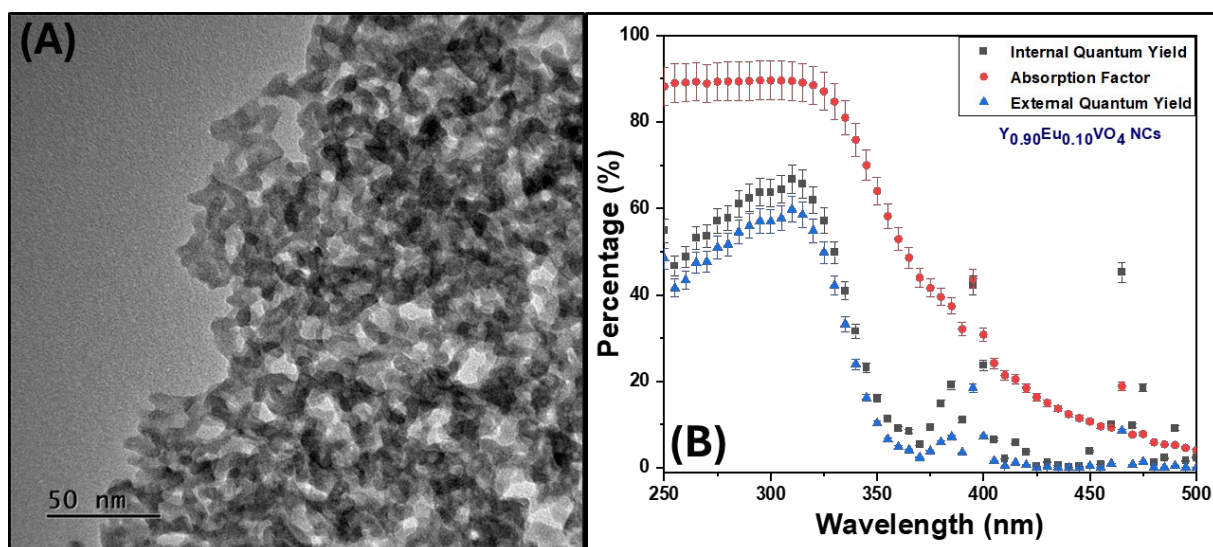
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In recent years, small YVO<sub>4</sub>:Eu<sup>3+</sup> nanocrystals (NCs) with high luminescence quantum yield received greater interest because of their potential application in high resolution LED displays and biomedical fields [1]. The increased surface-to-volume ratio of smaller nanocrystals enhances packing density and reduces the loading requirements in solid-state optical devices. In this study, we ideally synthesised YVO<sub>4</sub>:Eu<sup>3+</sup> nanocrystals using hydrothermal method and capped them with etidronic acid as ligand, modifying the wet chemical synthesis reported by K. Riwotzki *et al.* [2,3]. We conducted the detailed structural, morphological and optical studies with various characterization techniques. Three distinct Eu<sup>3+</sup> doping concentrations (5, 10, and 15 mol%) were systematically synthesized to investigate the influence of activator (Eu<sup>3+</sup>) content on the structural and photoluminescence properties. The effective concentrations of yttrium, europium, and vanadium were quantitatively determined using inductively coupled plasma–optical emission spectroscopy (ICP-OES). X-ray diffraction and Rietveld Refinement studies disclose that Eu<sup>3+</sup> ions substitute Y<sup>3+</sup> ions, forming a well-crystalline and uniform zircon-type structure. TEM images reveals that the synthesized NCs are ellipsoidal in shape with the length of 18 nm and width of 10 nm (**Figure 1A**). Raman and FT-IR spectroscopies were employed to verify the successful surface functionalization of the nanocrystals with etidronic acid, while thermogravimetric analysis (TGA) and CHN elemental analysis were used to quantitatively determine the mass fraction of the capping ligands bound to the NC surfaces. Upon UV excitation, the samples exhibit an intense red emission corresponding to the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> transition of Eu<sup>3+</sup> ions at 619 nm. Optimization of the Eu<sup>3+</sup> concentration revealed that nanocrystals doped with 10 mol% Eu<sup>3+</sup> achieve an external quantum yield (ePLQY) of 60% without additional thermal treatment (**Figure 1B**). Moreover, the absorption factor of NCs reaches ≈90% in the UV region (≤325 nm), followed by a controlled decrease toward the visible range, where distinct Eu<sup>3+</sup> f–f transition bands remain observable (**Figure 1B**). This strong UV harvesting capability, combined with characteristic defect and activator-related absorption factor, underscores the efficient excitation dynamics of the system. Our results demonstrate a critical Eu<sup>3+</sup> concentration of 10 mol% in our NCs, i. e. twice the value that is commonly reported for the bulk and for the YVO<sub>4</sub>:Eu<sup>3+</sup> NCs described by K. Riwotzki *et al.* Comprehensive photophysical analyses were conducted to investigate the Eu<sup>3+</sup> concentration-dependent energy transfer mechanisms in YVO<sub>4</sub>, with particular attention to short-range exchange interactions and lattice-related quenching pathways. Emission, excitation, and lifetime measurements were systematically performed to elucidate the factors governing radiative and non-radiative processes and to clarify the origin of the observed quantum efficiency. Spectroscopic analyses indicate that the high ePLQY is primarily governed by well-ordered D<sub>2d</sub> Eu<sup>3+</sup> centres located within the crystalline core, while Eu<sup>3+</sup> ions at the surface promote non-radiative pathways through interactions with ligands and structural defects. This proposed mechanism provides a clear and rational explanation for their enhanced performance. Overall, these findings demonstrate that the synthesized YVO<sub>4</sub>:Eu<sup>3+</sup> nanocrystals are promising

candidates for next-generation miniaturized optoelectronic devices and biomedical applications.



**Figure 1.** (A) TEM images and (B) PLQY measurements of synthesized  $Y_{0.90}Eu_{0.10}VO_4$  NCs.

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# OPTICAL MATERIALS FOR THE NEXT GENERATION OF SMART IMPLANTS

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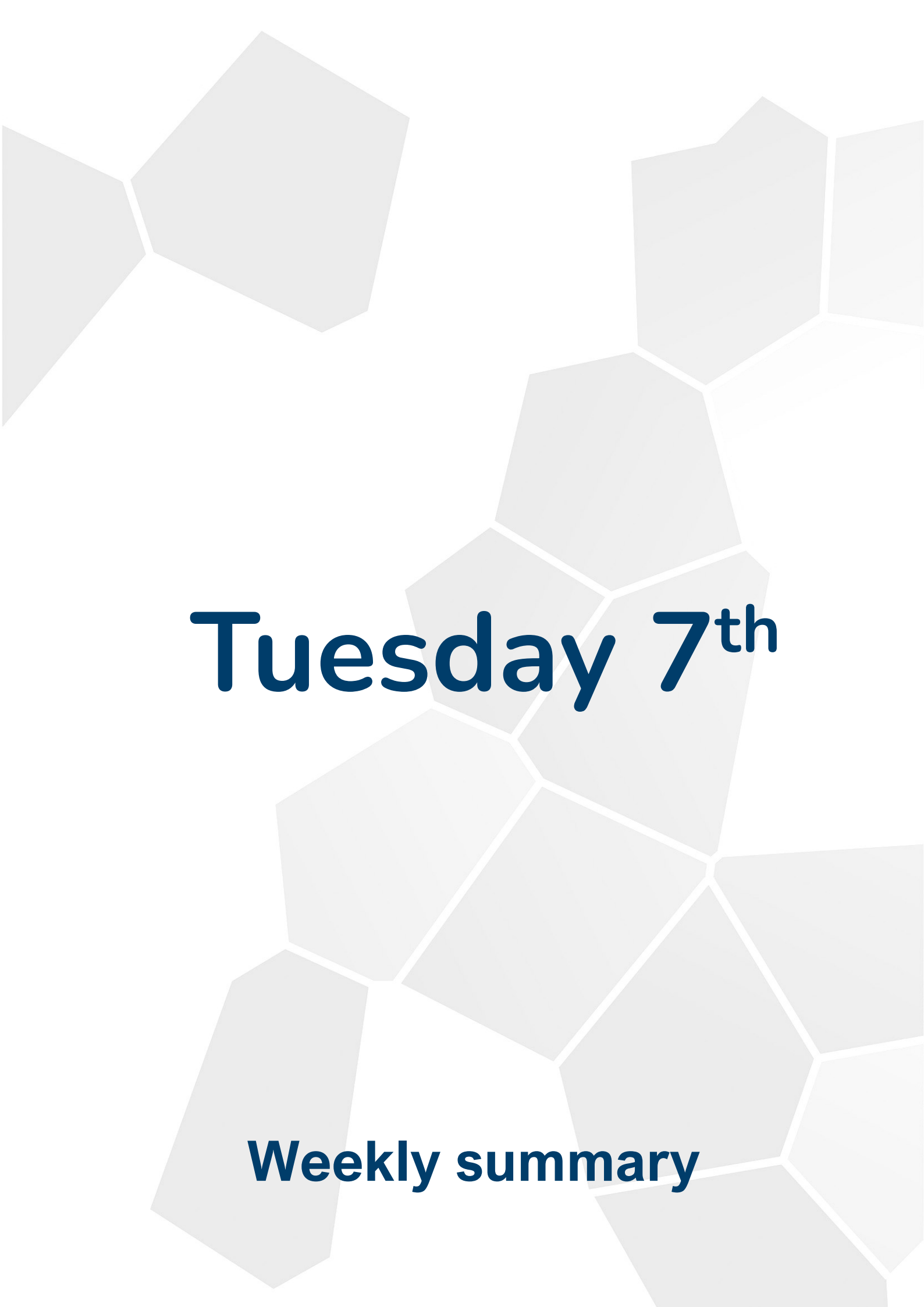
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Cardiovascular stents have revolutionized the treatment of coronary artery disease, yet once implanted they remain passive devices that provide no direct information about the biochemical state of the surrounding arterial tissue. As a consequence, the monitoring of plaque progression or implant performance still relies on indirect and often invasive imaging techniques. Developing implants capable of reporting molecular information from within the artery therefore represents an important unmet clinical challenge.

In this talk, I will present our recent efforts toward the development of light-enabled cardiovascular implants based on clinically used stents functionalized with near-infrared (NIR-II) emitting Ag<sub>2</sub>S nanoparticles. These luminescent nanostructures transform conventional stents into active optical devices capable of generating infrared signals that can be detected through biological tissue. I will discuss the design of the nanomaterials, their integration onto clinical-grade stents, and the optical principles that allow the implanted device to act as a nanoscale light source within the artery. I will also introduce a recently developed sensing strategy based on tissue-induced spectral distortions, in which wavelength-dependent changes in the broadband emission of the nanoparticles provide information about the biochemical composition of the surrounding arterial environment. Finally, I will illustrate how this approach may enable fluorescence-based visualization of stent implantation and discuss its potential for future non-invasive monitoring of lipid-rich atherosclerotic plaques and implant status.

The background of the slide features a collection of light gray, irregular geometric shapes, primarily pentagons and hexagons, scattered across a white field. These shapes are outlined in a slightly darker gray, creating a subtle, crystalline pattern.

# **Tuesday 7<sup>th</sup>**

## **Weekly summary**

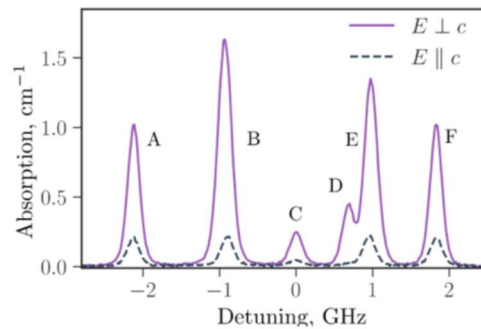
# RARE EARTH DOPED CRYSTALS FOR INTEGRATED QUANTUM PHOTONICS

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Systems with both spin and optical transitions offer a range of functionalities for quantum technologies. They allow storage and entanglement of photonic quantum states for quantum communications, interfacing processing nodes with optical networks for distributed quantum computing, or efficient detection for quantum sensing. Among various solid-state systems currently considered, rare-earth doped materials stand out as they combine, at cryogenic temperatures, long-lived optical and spin quantum states. In addition, they offer optical transition in a wide spectral range, including telecom wavelengths, high chemical stability, and easy doping in many hosts, thus enabling using large ensembles of centers with uniform properties.

Quantum-grade rare earth doped materials are developed in different forms. They include bulk crystals, as well as nanostructured materials such as nanoparticles, thin films, or molecular crystals, aiming at integration into nanophotonic devices. The latter offer small footprints, low energy consumption, high stability, scalability, and stronger interactions between light and rare earth ions. In this talk, we will present some of our recent results in the field [1-5], as well as the challenges to be addressed to bring rare-earth doped materials up to the highly demanding requirements of quantum technologies.



Narrow optical absorption lines in  $^{171}\text{Yb}^{3+}:\text{CaWO}_4$  showing resolved hyperfine structures [1].

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# EXPERIMENTAL AND COMPUTATIONAL $\text{Bi}^{4+/3+}$ CHARGE TRANSITION LEVEL ENERGIES RELATIVE TO THE VACUUM LEVEL

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The location of the bismuth charge transition levels (CTLs) with respect to the host valence or conduction band controls many fascinating properties of bismuth activated materials. Like for lanthanides, it determines the preferred valence state ( $\text{Bi}^{2+}$ ,  $\text{Bi}^{3+}$ , and  $\text{Bi}^{4+}$ ), it determines whether bismuth is a potential hole trapping or electron trapping center, and also how deep those charge carrier traps are. Luminescence quantum efficiency and thermal quenching temperature have always been difficult to fully understand. Like for the lanthanides it is often linked to electron transfer to the conduction band (CB) or hole transfer to the valence band (VB) and again CTL locations are crucial

Around 1970, in the early career of Georges Boulon, the  $\text{Bi}^{3+}$  doped rare earth (La, Y, Sc) sesquioxides and rare earth orthovanadates were studied [1]. Many papers on  $\text{Bi}^{3+}$  luminescence have appeared since then, and today bismuth is actively studied for different applications. Bismuth, in the form of  $\text{Bi}^{2+}$ ,  $\text{Bi}^{3+}$ , and  $\text{Bi}^{4+}$ , is utilized in luminescence phosphors, scintillators, afterglow phosphors, and storage phosphors. The  $\text{Bi}^{4+/3+}$  charge transition level energy relative to the vacuum level is equivalent to the vacuum referred binding energy (VRBE) in the ground state of  $\text{Bi}^{3+}$ . Methods for obtaining  $\text{Bi}^{3+}$  VRBEs in inorganic compounds have become available past ten years. One method uses experimental data on Bi spectroscopy combined with the semi-empirical chemical shift method that was originally developed for the lanthanides. Another method is fully computational. The  $\text{Bi}^{4+/3+}$  CTL location above the valence band (VB) top is first computed. A separate computation with the slab and vacuum method provides the energy at the VB-top relative to the vacuum level. Here we will compare the results of both methods to explore to what extent they are consistent with each other.

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The background of the slide is composed of various light gray, irregular polygonal shapes of different sizes and orientations, scattered across a white background. These shapes resemble fragments of a crystalline structure or abstract architectural elements.

**Tuesday 7<sup>th</sup>**

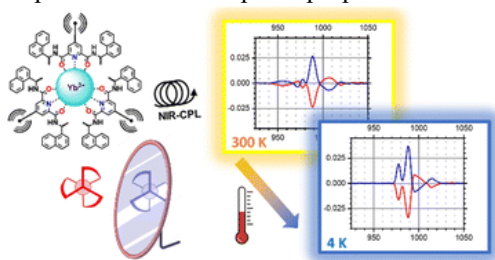
**Rare earth-organic complexes**

# UNUSUAL CIRCULARLY POLARIZED LUMINESCENCE APPLICATIONS OF F-ELEMENTS

Bruno Baguenard, Amina Bensalah-Ledoux, François Riobé, Laure Guy, Boris Le Guennic, Stéphan Guy, Olivier Maury\*

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Lanthanide-coordination complexes exhibit fascinating optical and chiroptical properties, due to the 4f-4f transitions leading to applications in various fields in materials science or biology. We recently developed an artefact-free CPL set-up<sup>1</sup> and revisited the CPL properties of 4 and 5f-element and in particular the role of the temperature<sup>2</sup> and the experimental bandwidth.<sup>3</sup> We also explore unusual chiroptical properties in biology<sup>4</sup>...



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# ROBUST OPTICAL COHERENCE IN A CHEMICALLY TUNABLE EU(III) MOLECULAR CRYSTAL

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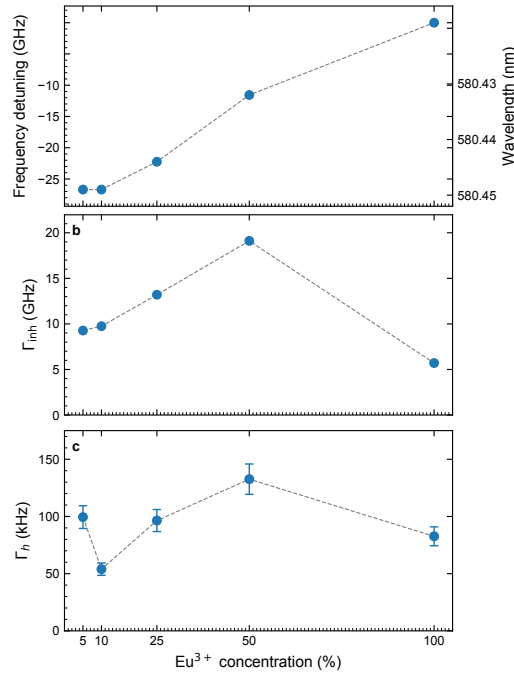
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Rare-earth ions embedded in crystalline solids constitute a leading platform for long-lived optical and spin coherence in the solid state [1] \cite{Goldner:2015ve}. In particular, trivalent europium (Eu(III)) has attracted sustained interest owing to its remarkably narrow  ${}^7F_0 - {}^5D_0$  optical transition [2], reaching the hundreds-of-hertz regime in optimized systems, combined with exceptionally long nuclear spin coherence times [3]. In inorganic hosts such as yttrium orthosilicate ( $\text{Y}_2\text{SiO}_5$ ) [2,3], these properties establish Eu(III) as a benchmark system for optical quantum memories [4].

Despite their outstanding coherence properties, inorganic oxide crystals offer limited flexibility for systematic chemical modification. The local crystal field, phonon spectrum, and interionic distances are largely dictated by the host lattice, restricting bottom-up materials design strategies. In contrast, molecular coordination compounds provide a chemically versatile platform in which ligand identity, coordination geometry, intermolecular spacing, and lattice dynamics can be engineered through synthetic control. Such tunability enables systematic structure--property investigations and opens the possibility of designing quantum-coherent materials through chemical and isotopic strategies [5].

We report here recent results about the structure–coherence relationship in the molecular crystal  $\text{Eu}(\text{TMHD})_3(\text{phen})$  and its dilution series in the isostructural host  $\text{Y}(\text{TMHD})_3(\text{phen})$ . We additionally examine a partially deuterated analogue of the complex. The optical inhomogeneous linewidth of the  ${}^7F_0 \rightarrow {}^5D_0$  transition near 580.4 nm exhibits a pronounced concentration dependence, ranging from 6 to 20 GHz (Fig. 1(a)), while the transition frequency shifts by up to  $\sim 25$  GHz across the dilution series (Fig. 1(b)). Homogeneous linewidths remain within the 50–130 kHz regime below 1.5 K across the whole concentration series (Fig. 1(c)) and after partial deuteration.



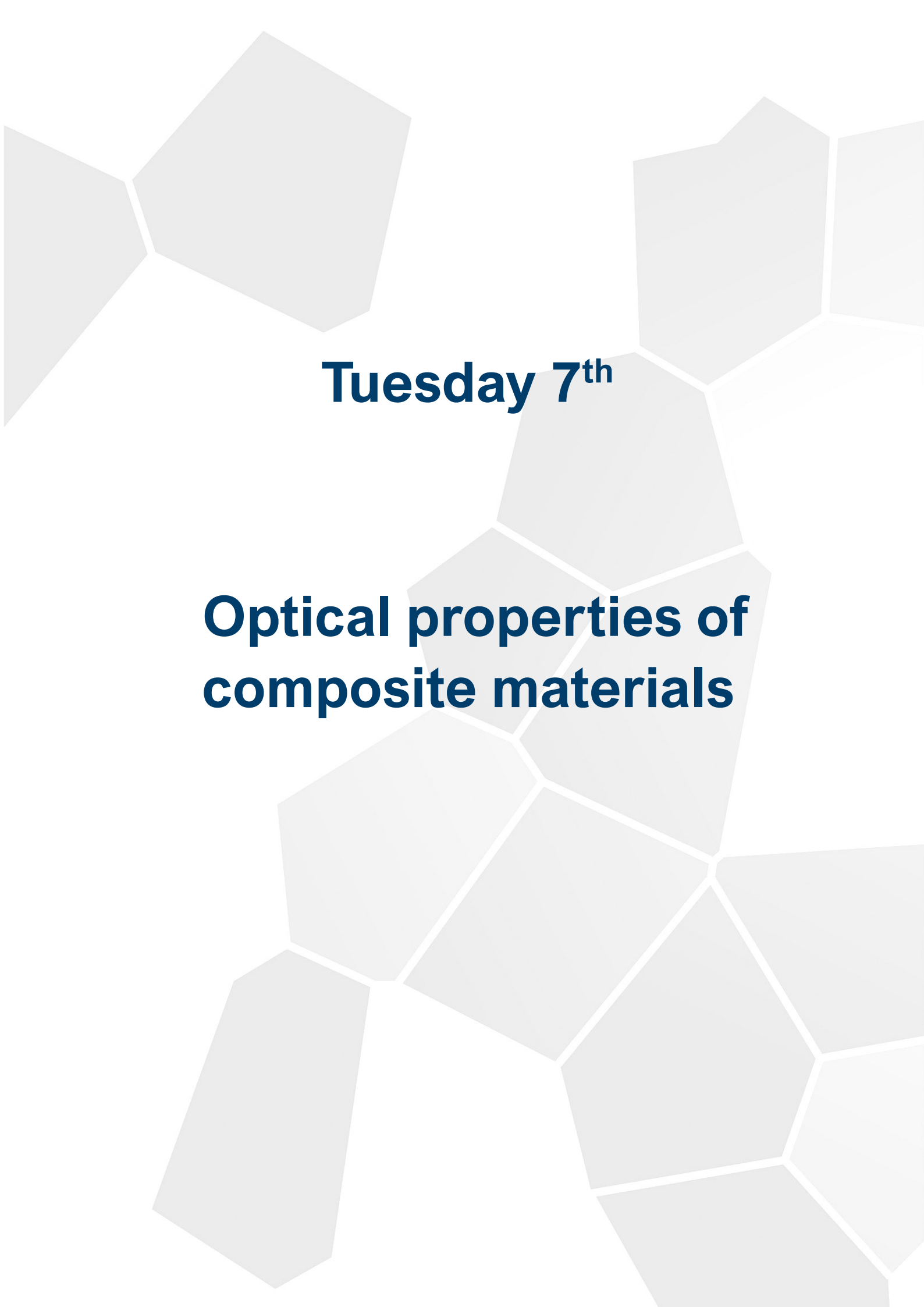
**Fig.** Concentration dependence of the optical properties of the  ${}^7F_0 \rightarrow {}^5D_0$  transition in  $\text{Eu}(\text{TMHD})_3(\text{phen})$  diluted in  $\text{Y}(\text{TMHD})_3(\text{phen})$ . (a) Transition frequency detuning relative to the 100% Eu sample, shown in GHz (left axis) and corresponding wavelength (right axis). (b) Inhomogeneous linewidth  $\Gamma_{\text{inh}}$  as a function of Eu concentration measured at 10 K. (c) Homogeneous linewidth  $\Gamma_h$  extracted from two-pulse photon echo measurements at 1.4 K. While the inhomogeneous linewidth exhibits pronounced concentration-dependent variations at the gigahertz scale, the homogeneous linewidth remains in the sub-100 kHz regime with only weak dependence on concentration.)

The weak concentration dependence of the homogeneous linewidth indicates that direct Eu–Eu interactions are not the dominant decoherence pathway. Similarly, the limited impact of deuteration on the homogeneous linewidth rules out magnetic noise associated with ligand proton dynamics as the primary dephasing mechanism in this molecular crystal. Temperature-dependent measurements and spectral diffusion analysis further constrain the role of lattice dynamics and the surrounding nuclear spin bath.

Our results confirm that  $\beta$ -diketonate europium coordination crystals can sustain optical coherence in the 100 kHz regime while exhibiting a chemically tunable optical transition at the gigahertz scale.

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The background of the slide is composed of several light gray, irregular polygonal shapes of various sizes and orientations, scattered across a white background. These shapes resemble fragments of a broken surface or crystalline structures.

**Tuesday 7<sup>th</sup>**

**Optical properties of  
composite materials**

# WHAT IS ESSENTIAL IS INVISIBLE TO THE EYE – FUNCTIONAL MATERIALS FOR CHEMICAL SENSING

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The design, synthesis, and precise optimization of modern functional materials with strictly defined physicochemical properties remain among the key challenges in contemporary materials science, particularly when targeting advanced sensing applications. The translation of a theoretical concept into a functional device imposes rigorous requirements on the material, including high thermal stability, chemical resistance, and well-defined optical responses. Chemical sensors based on luminescent organic dyes offer several advantages, such as high sensitivity, operation in both reversible and irreversible modes, and a clear optical output. However, their practical application requires preparation in forms that ensure ease of use, durability, and compatibility with existing technological platforms. One of the most effective strategies is the incorporation of organic dyes into inorganic or hybrid matrices, with silica-based systems being particularly attractive due to their optical transparency and mechanical stability.

Despite the widespread use of sol-gel technology, hybrid systems involving organic compounds still face important limitations. These include the limited solubility of many high-performance dyes in sol-gel precursors and their tendency to form non-emissive aggregates in solid matrices. In addition, the fabrication of stable thin films often requires high-temperature treatment exceeding 300°C. A holistic approach—combining molecular design of fluorophores, careful selection of host matrices, and optimization of processing conditions—enables these limitations to be addressed. The integration of organic dyes with silica-based and liquid crystalline matrices allows the development of a new generation of functional materials with enhanced stability and performance. These systems open new opportunities for multi-modal sensing of temperature, pH, and chemical analytes in complex environments, with potential applications in environmental monitoring, industrial process control, and medical diagnostics.

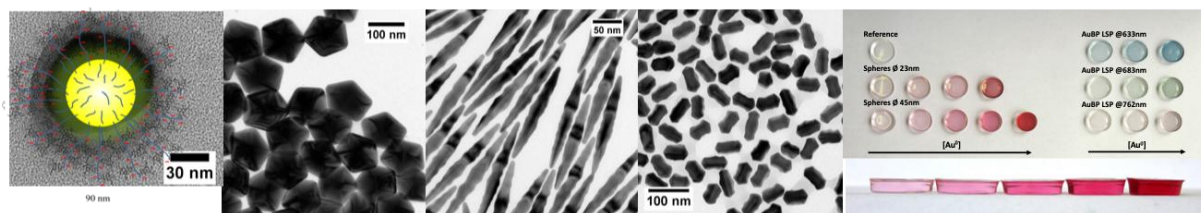


# TUNING THE PLASMONIC PROPERTIES OF GOLD NANOPARTICLES: SINGLE PARTICLES, ASSEMBLIES AND PLASMONIC GLASSES

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Metal nanoparticles possess unique optoelectronic properties that can be exploited in various fields, including electronics, solar cells, biology, medicine, and catalysis. However, their synthesis remains challenging, particularly at large scales for industrial applications [1,2]. The use of single objects to fine-tune the optical properties of hybrid materials will be explored (Fig. 1) [3,4]. Introducing chirality into such colloidal materials represents another significant challenge in optics. Recent advances in the synthesis of pentatwinned gold nanoparticles and their use as substrates for the growth of chiral particles will be discussed [5]. Insights into the origin of chirality will be presented based on both experimental and theoretical data. Additionally, strategies for controlling colloidal assembly will be proposed to expand the range of particle properties [6,7]. Finally, the preparation of hybrid plasmonic glasses for optical applications will be introduced [8,9], along with a discussion of experimental challenges related to their fabrication and characterization.



**Fig.1** Examples of architectures, from single particles to plasmonic glasses

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# NANOSCALE STRAIN ENGINEERING OF OPTICAL PROPERTIES IN MONOLAYER MoS<sub>2</sub> VIA NANOPARTICLE CHAINS

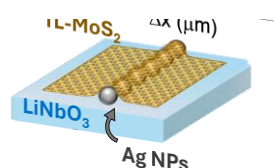
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Monolayer transition metal dichalcogenides (1L-TMDs) constitute a fascinating class of atomically thin materials in which d-electron interactions give rise to rich phenomena with strong impact on optoelectronics, electronics, and spintronics. In particular, 1L-MoS<sub>2</sub> has attracted considerable attention as a direct-bandgap two-dimensional semiconductor with highly tunable optical properties, whose excitonic landscape can be tailored using various physical and chemical approaches for optoelectronic applications.

Here, we investigate the optical response of 1L-MoS<sub>2</sub> transferred onto a metallic chain of silver nanoparticles (Ag NPs) self-assembled on a periodically poled LiNbO<sub>3</sub> ferroelectric substrate. These Ag NP chains act as nanometrically localized strain sources, inducing well-defined nano-wrinkles in the overlying MoS<sub>2</sub>. Spatially resolved photoluminescence spectroscopy shows that the resulting strain gradients efficiently modulate the bandgap and promote exciton-to-trion conversion within ~50 nm wide regions, without the need for large strain amplitudes or invasive local probes. In particular, cryogenic temperatures enhance quasiparticle localization, leading to a marked increase of more than 50% in trion generation (see Fig. 1) with respect to flat regions.<sup>1</sup>

The results highlight long, nanometer-wide Ag NP chains as a platform for one-dimensional, strain-quasiparticle confinement. In this context, the charged nature of trions provides strong sensitivity to external fields, opening opportunities for trion-based circuits and next-generation quantum technologies.



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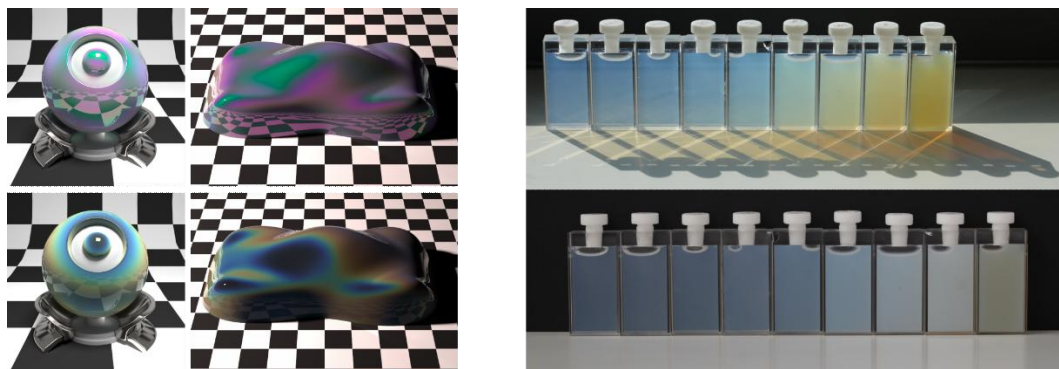
# DISORDERED NANOSTRUCTURES FOR VISUAL APPEARANCE DESIGN

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Nature offers us beautiful visual appearances. The most resplendent of them, from the iridescence of opals and the wings of some butterflies to the bright colors of some birds and fruits, are mostly due to interference effects created by nanostructures. These last decades have witnessed the emergence of new research themes, intrinsically multidisciplinary, aiming at understanding the microscopic origin of visual effects produced in nature, at reproducing these effects by artificially structuring matter, and at creating new ones - without equivalents in the natural state - for new applications. The design of visual appearance represents nowadays indeed a key challenge in many industrial sectors.

This presentation aims at providing some insights on the potential of designed disordered nanostructures – either nano-objects randomly arranged on a substrate [1,2] or colloidal suspensions of small particles [3] – for creating exotic visual effects at the macroscopic scale (see Figure). Specifically, I will discuss the relationships between nanostructure parameters (particle size, shape, composition, density, spatial arrangement) and visual attributes (color, gloss, translucency, etc.), and present the achievements of my colleagues in Bordeaux [2] and in Lyon [3] in realizing materials with targeted visual appearances by bottom-up techniques.



**Fig.** Exotic visual effects created by disordered nanostructures (Left) Physically realistic synthetic images of macroscopic objects covered by engineered nanostructured surfaces. Adapted from [1]. (Right) Photographs of liquid samples containing dielectric nanoparticles at different densities. Adapted from [3].

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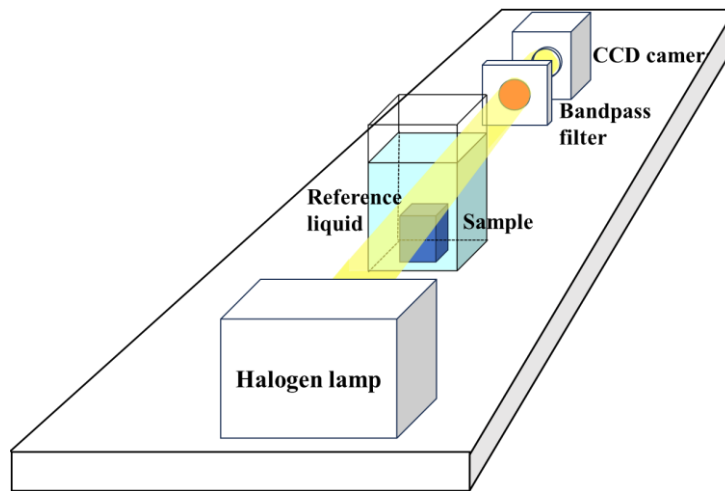
# INDEX MEASUREMENT OF TRANSPARENT MATERIALS AND SELLMEIER DISPERSION OF SUGAR SOLUTION

**Mayuko KOGA<sup>1</sup>, Hiroki NAKATA<sup>1</sup>, Hanayo TAKENAKA<sup>1</sup>, Yugo AKABE<sup>2</sup>, Marilou CADATAL-RADUBAN<sup>2,3</sup>, Nobuhiko SARUKURA<sup>2</sup>, Noriko CHIKUMOTO<sup>2</sup>, and Toshihiko SHIMIZU<sup>2</sup>**

<sup>1</sup> Graduate school of Engineering, University of Hyogo, Himeji, Hyogo, Japan; <sup>2</sup> Institute of Laser Engineering, The University of Osaka, Suita, Osaka, Japan; <sup>3</sup> Unitec Institute of Technology, Auckland, New Zealand

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We present a simple and non-destructive method for measuring the refractive index and dispersion of transparent materials, including those with irregular shapes that are difficult to process<sup>1</sup>. Our approach uses a sugar solution with a known refractive index as an immersion medium. By immersing the sample in the solution and analyzing the disappearance of boundary contrast in CCD-captured images, the refractive index is determined (See Figure). To characterize the sugar solution's dispersion, a dual-prism configuration with an imaging spectrograph was employed<sup>2</sup>. Multiple bandpass filters allow dispersion measurements across different wavelengths. The results showed precision on the order of  $10^{-2}$ , demonstrating the feasibility of this proof-of-concept. This technique requires no polishing or sample processing, making it ideal for rapid evaluation of unpolished, irregular, or fragile optical materials.



**Fig.** Experimental setup of non-destructive refractive index measurement.

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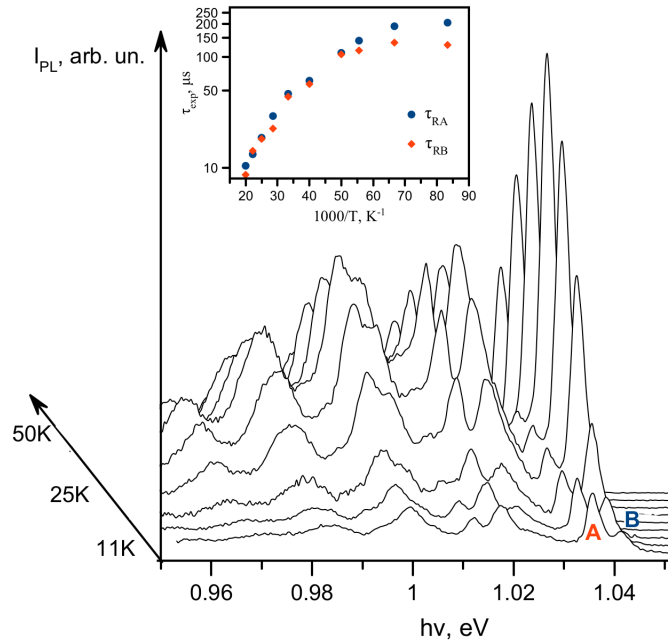
# RADIATIVE DECAY KINETICS OF BOUND EXCITON STATES IN BULK MoSe<sub>2</sub> CRYSTALS INTERCALATED WITH I<sub>2</sub> MOLECULES

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In recent years, the physical and chemical properties of Transition Metal Dichalcogenides (TMDs) have drawn significant interest due to their potential in creating functional heterostructures for photonics [1]. While mono-atomic layers of TMDs are of great interest due to their direct band gap, the properties of layered materials can be strategically tuned by intercalating various species into the van der Waals gap [2]. This work focuses on bulk single crystals of molybdenum diselenide (2H-MoSe<sub>2</sub>) intercalated with iodine molecules (I<sub>2</sub>), investigating the temporal characteristics of bound exciton photoluminescence (PL).

The 2H-MoSe<sub>2</sub>:I<sub>2</sub> single crystals used in this study were grown from primary components via chemical vapour transport (CVT) using iodine as the transport agent. The resulting layered crystals were exfoliated to obtain smooth surfaces for measurement, with sample thicknesses of a few tens of microns. Steady-state PL measurements were performed in a temperature range of 12-100 K using a 447 nm CW laser. To investigate temporal kinetics, the PL was excited with a solid-state pulsed laser at 532 nm (pulse duration 10 ns). Optimized technological growth conditions provided an increased concentration of unambiguously embedded into the van der Waals gap halogen molecules ( $\sim 10^{19} \text{ cm}^{-3}$ ), enabling an intense radiative recombination of the excitons bound on neutral halogen molecules [3, and ref. therein].



**Fig. 1.** Steady-state luminescence spectra of the 2H-MoSe<sub>2</sub>:I<sub>2</sub> layered crystals at different temperatures (in the inset: Photoluminescence decay times of excitonic lines A and B).

The high intensity of luminescence, as well as the relatively large energy gap between exciton levels A and B ( $\Delta_{BA} = 5.6 \text{ meV}$ ) allowed, to our knowledge, for the first time, to measure the decay kinetics for each zero-phonon spectral line of the bound exciton emission separately. The PL spectra of MoSe<sub>2</sub>:I<sub>2</sub> exhibit a characteristic zero-phonon exciton doublet, labeled A ( $E_A =$

1.0360 eV) and  $B$  ( $E_B = 1.0416$  eV), assisted by several phonon replicas [4]. Time-resolved measurements revealed that at low temperatures ( $T=12$  K), the exponential decay times of these lines differ significantly with  $\tau_{RA} \approx 210 \mu s$  and  $\tau_{RA} \approx 1.6\tau_{RB}$  demonstrating that the two exciton states are not in thermal equilibrium at low temperatures. As temperature increases, this difference diminishes. Above  $T = 20$  K, the kinetics of both lines become identical ( $\tau_{RA} \approx \tau_{RB}$ ), indicating the onset of thermal equilibrium. The temperature dependence of the steady-state luminescence intensity  $I_{SS}(T)$  shows an initial increase up to 35 K, attributed to the population of the faster radiative state  $B$  ( $\tau_B \ll \tau_A$ ), followed by thermal quenching at higher temperatures due to exciton dissociation and extrinsic self-trapping processes [3].

It is shown that the observed different behaviour of the temperature dependences of the decay times of  $A$  and  $B$  exciton states is due to the fact that the rate of radiative recombination of state  $B$  ( $\tau_B^{-1}$ ) is significantly higher than the probability of phonon-induced non-radiative transitions of holes from  $B$  to the  $A$  state ( $\tau_B^{-1} > \tau_{BA}^{-1}$ ,  $\tau_{AB}^{-1} = (g_B/g_A) \cdot \tau_{BA}^{-1} \cdot e^{-\Delta_{BA}/kT}$ , wherein  $g_A = 3$  and  $g_B=1$  are the degeneracy factors). To model this kinetics, a system of two rate equations was employed. The analysis suggests that the formation of a bound exciton in state  $A$  always precedes the emergence of the higher-energy state  $B$ , populated thermally due to phonon-induced radiativeless transitions. This model successfully describes the observed temporal behaviour and the transition to thermal equilibrium at higher temperatures. These results quantitatively characterize bound exciton dynamics in halogen-intercalated TMDs and show that intercalant concentration governs access to otherwise unresolvable kinetic regimes.

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The background consists of several light gray, irregular geometric shapes, primarily pentagons and hexagons, arranged in a non-uniform pattern. These shapes are separated by thin white lines, creating a mosaic-like effect. The overall composition is minimalist and modern.

**Tuesday 7<sup>th</sup>**

**Laser**



# GETTING BOTH MORE - AND LESS - FROM YOUR RARE-EARTH DOPANTS

**John BALLATO**

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In optical applications, rare-earth dopants are most commonly employed as light emitters. The “more and less” aspects of this talk will focus on rare-earth-doped optical fibers and instances where the rare-earth is a source of all-optical heating (more!) but also all-optical cooling (less).

While representing opposite ends of the thermal spectrum, these extremes share some commonalities: all-optical heating through complete multiphonon quenching at very high rare-earth doping levels<sup>1</sup> and all-optical cooling through anti-Stokes fluorescence, which requires electron-phonon coupling.<sup>2</sup>

The physical and spectroscopic mechanisms will be discussed as will be how the associated fibers are fabricated and the requisite optical materials science that enable both efficient heating and cooling from rare-earth-dopants.

Lastly, in honor of Prof. Boulon, this keynote aims to have fun with rare-earths outside their noble, yet normal purposes.

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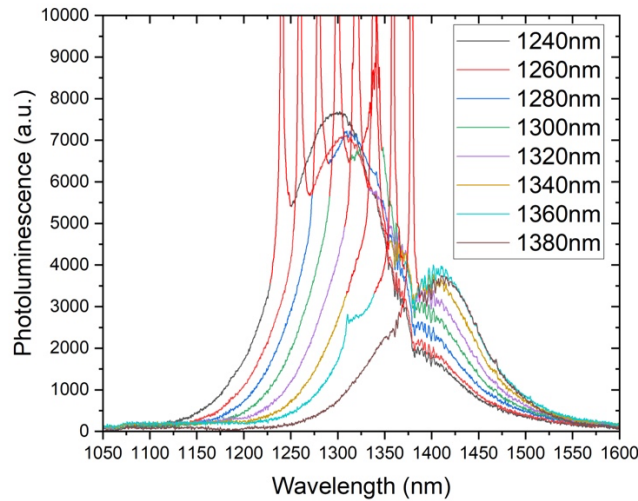
# ON THE NEAR INFRARED PROPERTIES OF BISMUTH-DOPED FIBERS

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Since its discovery in the late 1990s, the infrared photoluminescence (PL) of bismuth-doped silicate glasses has continued to attract the interest of numerous groups worldwide [1, 2]. This interest is primarily driven by the fact that this PL is accompanied by optical gain in spectral ranges not covered by rare-earth ions. This therefore enabled the advent of Bismuth-Doped Fiber Lasers (BDFL) and Bismuth-Doped Fiber Amplifiers (BDFA) with properties complementary to the well-known Neodymium-, Ytterbium-, Erbium or Thulium- Doped Fiber Amplifiers (NDFA, YDFA, EDFA, and TDFA). Although high-level performances have been reported, the nature of the Bismuth Active Center (BAC) responsible for PL in silicate glasses of different compositions still remains an open question. Our work focuses on the fabrication and characterization of bismuth-doped preforms and fibers for optical amplification in the O-band (1260-1360 nm) of telecommunications. To this end, two optical fiber preform manufacturing processes based on the Modified Chemical Vapor Deposition (MCVD) method were compared. In both cases, a phosphosilicate core material was synthesized, but the type of bismuth precursor and its incorporation technique were modified. The optical and amplifying properties of the fibers thus produced were evaluated [3, 4].



**Fig 1.** Evolution of the emission band of a bismuth-doped phosphosilicate fiber as a function of the pumping wavelength.

Alongside these application-oriented studies, we focused also on some characteristic properties of bismuth-doped fibers, such as the different BACs using absorption and PL spectroscopies,

and the analysis of the spectral dependence of the unsaturated absorption of the fibers. Several results obtained in this context will be presented during the conference, as illustrated by the excitation wavelength dependence of the PL illustrated on Fig. 1.

This work was supported in part by the SIMBADE project financed by Bpifrance and by the French government under the France 2030 ANR program "PEPR Networks of the Future" (ref. ANR-25-PEFT-0001, PLEIADES project). This work was carried out within the Contrat de Plan Etat-Region (CPER) WaveTech@HdF and the Initiative of Excellence of the University of Lille within the frame of CDP C2EMPI (R-CDP-24-004-C2EMPI).

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# CONFINED TAMM LASER DIODES

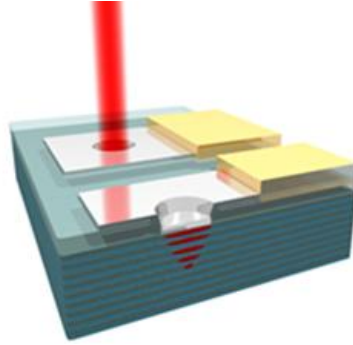
**J. Bellessa<sup>1,\*</sup>, M. Laupretre<sup>1</sup>, C. Symonds<sup>1</sup>, J.M. Benoit<sup>1</sup>, A. Lemaitre<sup>2</sup>**

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The integration of metallic elements into semiconductor laser architectures has emerged as an efficient approach to improve device performance through enhanced optical confinement at the micro- and nanoscale. Tamm plasmons, which correspond to optical modes located at the interface between a distributed Bragg reflector (DBR) and a metallic layer, occupy an intermediate position between metal–semiconductor cavities and spasers. A Tamm mode can be viewed either as a cavity mode within a cavity of effectively zero thickness or as a surface mode, since its field amplitude decreases away from the metal/semiconductor interface. Because of this surface-bound nature, optical confinement at the microscale in Tamm plasmon structures can be achieved simply by patterning the thin metallic layer, which determines the modal geometry<sup>1</sup>. This method makes it possible to realize complex confinement geometries that would be extremely difficult to fabricate by etching several hundred nanometers into a semiconductor material within a vertical cavity configuration. In addition, the metallic patch responsible for optical confinement can also function as an electrical contact for current injection. In Tamm lasers, subwavelength structures patterned into the metallic layer can strongly influence the laser properties. Due to the surface-mode nature of Tamm plasmons, the nanostructure is effectively embedded within the cavity and therefore directly affects the emission characteristics of the laser.



**Fig.** *Schematic of the Tamm laser diode structure*

Based on these concepts, we demonstrate an electrically injected Tamm plasmon laser obtained by integrating a silver microdisk with a GaAs/AlAs DBR containing InGaAs quantum wells located at the electric-field antinodes. Under electrical injection and cryogenic operation at 95 K, the device exhibits clear lasing behavior, reaching a maximum output power of 200  $\mu$ W at 906 nm. Spectral measurements reveal the emergence of optical gain together with strong mode confinement, ultimately leading to lasing characterized by pronounced spectral and angular narrowing<sup>2</sup>. Dispersion imaging further supports these findings by confirming lasing from the fundamental confined Tamm mode. These results highlight the potential of Tamm plasmon lasers as compact, integrable, and possibly reconfigurable coherent light sources.

Beyond the demonstration of a Tamm laser diode, we also explore the integration of nanostructures within the metallic film to control the emission properties. In particular, unusual polarization behaviors are observed. The polarization characteristics as well as the spatial intensity distributions are presented and discussed.

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# Chirowaveguide and circularly polarized evanescent waves: achievement and perspectives

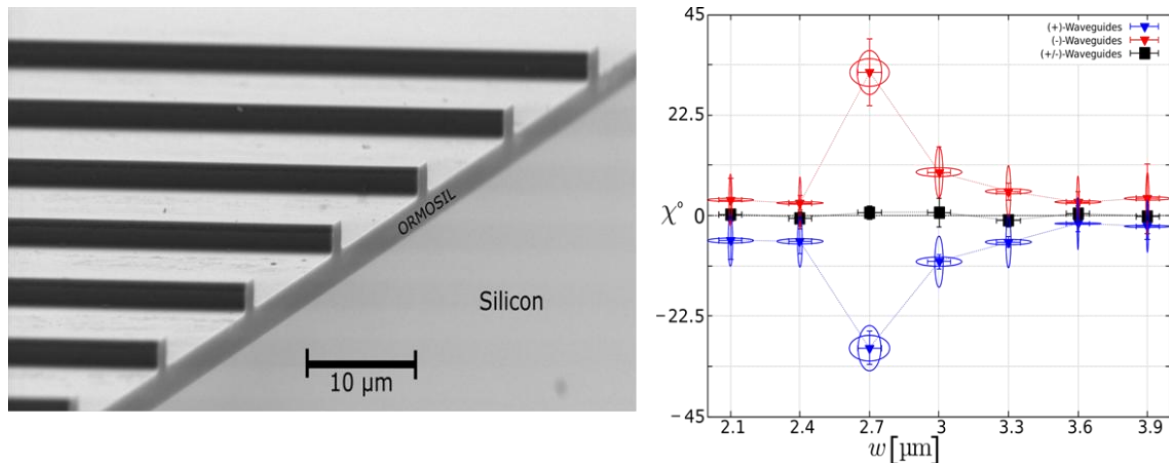
Stéphan GUY<sup>1</sup>, Hoshang SAHIB<sup>1</sup>, Amina Bensalah-Ledoux<sup>1</sup>, Bruno Baguenard<sup>1</sup>, Alban Gassenq<sup>1</sup>, Laure GUY<sup>2</sup>, Clémence Gounon<sup>2</sup>

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An object is said to be chiral when it is not superimposable with its mirror image. The two mirror-related forms are called enantiomers. Chirality is a fundamental property of molecules in living systems, where the two enantiomers of the same molecule can exhibit markedly different biological activities—for example, differing taste, therapeutic effects, or toxicity. Chirality also plays an important role in optics because circularly polarized light is itself chiral. As a result, chiral light–matter interactions depend on the enantiomer involved, giving rise to well-known spectroscopic signatures such as optical rotation (OR) consequence of the circular birefringence of the chiral material (CB), circular dichroism (CD), and circularly polarized luminescence (CPL).

Here, we demonstrate how chiral materials can be used to fabricate optical *chirowaveguides* that support circularly polarized eigenmodes. In conventional optical waveguides fabricated on planar optical chips, the rectangular geometry imposes linearly polarized eigenmodes of either TE or TM type, corresponding to electric or magnetic field oscillations parallel to the substrate plane, respectively. By employing chiral materials with high circular birefringence, we experimentally show that this constraint can be overcome, enabling eigenmodes with different polarization states.



We developed a robust and low-cost fabrication approach based on sol–gel chemistry for the synthesis of chiral materials combined with PDMS soft-stamping for waveguide

patterning<sup>1</sup>. The material consists of a binaphthyl-based organically modified silica exhibiting an optical rotation of approximately 30°/cm. Dip-coating this material onto silicon wafers followed by PDMS imprinting yields well-defined rib waveguides. The ribs are typically 2 μm high and 1–5 μm wide, extending over lengths of about 4 cm. Scanning electron microscopy confirms the structural quality (see Figure left), while optical measurements indicate very low propagation losses.

We show that the eigenpolarization states are governed solely by the ratio between the linear birefringence (LB) induced by the waveguide geometry and CB of the chiral material. In the ideal case, circularly polarized eigenmodes occur when  $LB \ll CB$ . By tuning the waveguide geometry, we modulate the linear birefringence within this regime, enabling continuous control of the eigenpolarization ellipse from linear to circular polarization (figure right).

Finally, we exploit the strong sensitivity of the eigenpolarization to linear birefringence to measure birefringence in chiral waveguides<sup>2</sup>. This method is particularly effective when the linear birefringence is comparable to the circular birefringence (on the order of  $10^{-5}$ ). We apply this technique to investigate the influence of humidity on sol–gel-based chirowaveguides.

Potential applications in chiral sensing and active CPL light-emitting devices will also be briefly discussed.

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# Room temperature bonding and properties of Cr:LiSAF and sapphire composite materials

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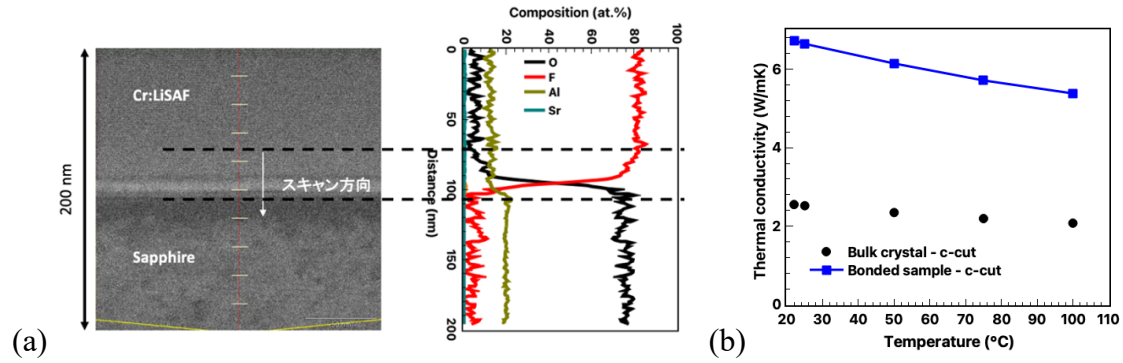
## 1. Introduction

Recently, 800-950 nm CW lasers, such as Ti:Sapphire, became widely used in quantum computer science as trap lasers and optical pincets for <sup>87</sup>Rb-based quantum bits [1]. However, the limited available output power of Ti:Sapphire lasers due to a low efficiency multi-step pumping process is now the main limitation of atom arrays size. A promising alternative could be using Cr<sup>3+</sup>:LiSrAlF<sub>6</sub> (Cr:LiSAF) which also exhibits broadband emission between 770 nm and 1.1 μm but with the advantage of being pumped by commercially available red laser diodes with an efficiency of about 50% [2]. However, the maximum output power obtained with Cr:LiSAF remain below 3 W due to low thermal conductivity of the material (~2.5 W/mK) and the thermal quenching of the emitting level appearing from ~69°C. In this work we present an original approach to improve thermal management inside Cr:LiSAF and scale up its output laser power.

## 2. Experimental results and discussion

To improve the heat extraction inside Cr:LiSAF crystal, bonding between this gain medium and high thermal conductivity heat sink (36 W/mK for sapphire) was performed using room temperature inter-layer surface activated bonding (il-SAB) technique [3]. By doing such stacks of low and high thermal conductivity materials, we aim to improve the effective thermal conductivity of Cr:LiSAF as it has already been demonstrated using Nd:YAG/sapphire stacks [4]. First tests were performed using uncoated 5 mm diameter 1 mm thick c-cut sapphire crystal and 5 mm diameter, 0.5 mm thickness c-cut Cr:LiSAF crystals. Surface activation using ion beams is performed under high vacuum conditions (below 10<sup>-5</sup> Pa) after a careful cleaning of the samples' surfaces. After this activation step, an interlayer was deposit on the surfaces to ensure proper bonding between the two materials with different chemical compositions. The samples were then pressed together. Under these conditions, a successful bonding between Cr:LiSAF and sapphire was obtained. The same experiment was conducted without the inter-layer but using AR coating on the Cr:LiSAF to match the refractive index mismatch between Cr:LiSAF and sapphire (1.39 and 1.68, respectively) and successful bonding was also achieved.

The bonded samples were then cut in half to analyze the bonding interface between Cr:LiSAF and sapphire. The interface was observed using TEM (60 keV) and the elemental composition through the interface was check using Energy Dispersive X-ray analysis (0.1 nm diameter electron beam) along the 200 nm length TEM window observable (Fig. 1.a). For the samples bonded with an interlayer, the results mainly show the diffusion of Oxygen and Fluoride through the bonding interface between Cr:LiSAF and sapphire. The thickness of the amorphous layer forming the bonding interface can be estimate at around 40 nm. Also, the bonding interface seems more extended on the Cr:LiSAF side indicating a longer diffusion depth of Oxygen (compared to Fluoride diffusion in sapphire) and a higher sensitivity to the ion beam performed for surface activation. Analysis of the bonding interface for the AR coated samples shows a thinner amorphous layer of around 23 nm between Cr:LiSAF and the outer layer of SiO<sub>2</sub> from the coating on the sapphire side.



**Fig. 1** TEM image of Cr:LiSAF/sapphire bonding interface and corresponding EDX analysis (a); Effective thermal conductivity of composite material compared to bulk Cr:LiSAF (b).

Firstly, the thermal diffusivity  $D$  of bulk Cr:LiSAF and of Cr:LiSAF/sapphire bonded sample were measured by laser flash method in the 22 to 100°C range. The bonded material presents a  $\sim 3$  times higher thermal diffusivity (2.693 mm<sup>2</sup>/s at 22°C) compared to the bulk Cr:LiSAF (0.961 mm<sup>2</sup>/s at 22 °C). Also, the difference between measured and calculated thermal diffusivity of the bonded sample was estimated to be similar to the standard deviation of the measurement ( $\sim 3\%$ ). In that case, the thermal resistance of the bonded layer can be neglected.

In addition, a measurement of the Cr:LiSAF bulk specific heat was also performed in the -20-200°C to accurately calculate its thermal conductivity using the relation  $\kappa(T) = D(T) \cdot C_p(T) \cdot \rho(T)$ , with  $\rho(T)$  the volume mass estimated using the thermal expansion coefficients [5]. Finally, the effective thermal conductivity of the bonded material  $\kappa_{\text{eff}}$  was calculated to be around 6.6 W/mK,  $\sim 2.5$  times the one of bulk Cr:LiSAF (2.5 W/mK).

### 3. Conclusion

Successful bonding at room temperature between low thermal conductivity Cr:LiSAF and sapphire was demonstrated using il-SAB technique. Bonding analysis revealed that Cr:LiSAF is more sensitive to FAB compared to sapphire, resulting in a 40 nm thick amorphous layer between the bonded materials, more extended on the Cr:LiSAF side. In addition, accurate measurements of bulk and composite thermal properties were performed, showing a  $>2.5$  times higher effective thermal conductivity for the bonded sample. To power scale Cr:LiSAF laser emission, effective thermal conductivity of composite chips should be over 10 W/mK, corresponding to bonded thickness of Cr:LiSAF around 4 times thinner than sapphire length.

### ACKNOWLEDGEMENT

This work was supported by the Moonshot project (JPMJMS2269) and by the ARIM-NEXT project (JPMXP1225MS1046).

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The background of the slide features a collection of light gray, irregular geometric shapes, primarily pentagons and hexagons, scattered across the white surface. These shapes are separated by thin white lines, creating a mosaic-like effect. The shapes vary in size and orientation, with some appearing more prominent than others.

**Tuesday 7<sup>th</sup>**

# **LED and Phosphors**

# HF-FREE SOLID-STATE SYNTHESIS OF $\text{K}_2\text{SiF}_6\text{:Mn}^{4+}$ FOR HIGH-PERFORMANCE RED-EMITTING PHOSPHORS IN WHITE LEDS

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Katia ARAUJO DA SILVA<sup>1</sup>, Damien BOYER<sup>1</sup>**

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Solid white light-emitting diodes (WLEDs) have emerged in the 21st century as next-generation energy-saving light sources, progressively replacing conventional lighting technologies in commercial, residential, and specialty markets. Their success relies on phosphor-converted architectures in which down-converting materials transform part of the blue emission from InGaN chips into longer wavelengths to generate white light [1]. Currently, the dominant configuration combines a blue-emitting chip with the yellow phosphor  $\text{Y}_3\text{Al}_5\text{O}_{12}\text{:Ce}^{3+}$  (YAG:Ce), producing cool white light with high correlated color temperature (CCT > 4500 K) but insufficient color rendering index (CRI < 80) for high-quality lighting applications. To achieve warm white light (CCT 2700–3500 K) with improved CRI, a red-emitting phosphor must be incorporated [2]. Among available red emitters, the  $\text{Mn}^{4+}$  doped  $\text{K}_2\text{SiF}_6\text{:Mn}^{4+}$  (KSF-Mn) has emerged as the benchmark material due to its sharp line emission centered around 630 nm, minimal parasitic emission above 650 nm, and excellent overlap with the human eye sensitivity curve [3]. In contrast to  $\text{Eu}^{2+}$ -activated nitrides and oxynitrides, whose broad emission bands reduce luminous efficacy, KSF-Mn ensures high spectral efficiency and optimal color rendering [4]. Furthermore, as a rare-earth-free phosphor, KSF-Mn addresses economic and environmental concerns associated with rare-earth element exploitation, a strategic issue for the European Union [5]. Many synthesis methods have been experienced already for the preparation of KSF-Mn but most of them, however, use hazardous and non-eco-friendly aqueous HF as fluorine source. This highly corrosive contact-poison can cause severe skin burns and eye damage, is fatal if swallowed, fatal in contact with skin and fatal if inhaled. Substitution of aqueous HF to another source of fluorine ions is therefore highly recommended and has entailed a lot of interest in recent years [6].

Since 2012, our research group at ICCF has developed an original research program on KSF-Mn. This work led to the patenting of a sol-gel-assisted synthesis in 2017 [7] and, more recently, to the development of a breakthrough solid-state synthesis route in 2021 [8]. This innovative approach relies on solid/gas equilibria and enables the rapid (<3 h), cost-effective, and HF-free production of KSF-Mn without harmful by-products. In contrast with conventional industrial processes which are typically based on aqueous HF chemistry and require post-synthesis stabilization treatments, our strategy avoids hazardous reagents while offering tunable particle size control through fluorination parameters.

This approach has enabled the production of reproducible batches of up to 10 g of micrometer-sized KSF:Mn powders with a D90 of ~6.5  $\mu\text{m}$  (Fig. 1a, 1b and 1c). Photoluminescence studies indicate it achieves an external quantum efficiency (EQE) of 65% under blue LED excitation, demonstrating excellent down-conversion performance. The powder disperses easily and uniformly in silicone, enabling direct fabrication of remote phosphor films that are fully compatible with current LED manufacturing processes (Fig. 1d and 1e).

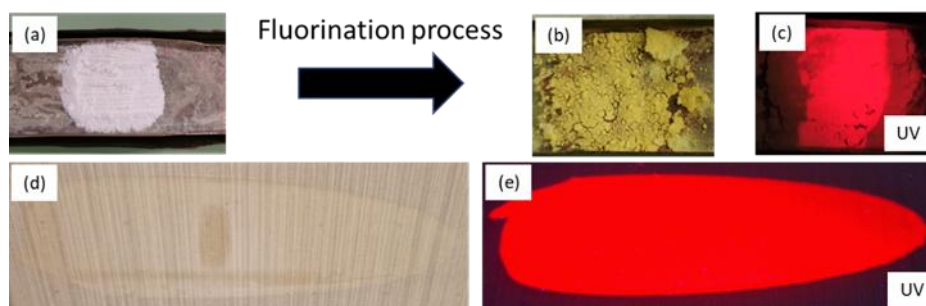


Figure 1. Photos of KSF-Mn precursor mixture (a) before and (b,c) after fluorination, and silicon film with 30 wt.% KSF-Mn under (d) daylight and (e) UV light

Overall, these results highlight KSF:Mn as a scalable, high-performance, and environmentally friendly red phosphor for next-generation WLEDs and display technologies.

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# Process-Induced Carbon Contamination and Its Suppression in Composite Ceramic Phosphors for High-Efficiency Laser Lighting

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Recent advances in high-performance electronic materials, characterized by high speed, high efficiency, and long lifetime, have significantly improved the quality of modern life. Among emerging technologies, laser lighting has attracted considerable attention as a next-generation light source due to its high brightness, high directionality, and high efficiency. It has already been implemented in practical applications such as automotive headlights and is expected to expand further into a wide range of fields.

Ceramic phosphor-based laser lighting systems have reached a practical stage, where oxide-based phosphors such as Ce:YAG are currently dominant. However, under high-power excitation conditions, the phosphor temperature increases due to self-heating, resulting in performance degradation such as reduced emission efficiency and thermal quenching. Therefore, the development of materials and structures that can maintain stable luminescence under high-temperature conditions is strongly required.

In this study, we focus on oxide-based materials and investigate composite ceramic phosphors consisting of Ce:YAG and a high-thermal-conductivity matrix of Al<sub>2</sub>O<sub>3</sub>. The introduction of Al<sub>2</sub>O<sub>3</sub> is expected to enhance heat dissipation and improve luminescence performance under high-power operation. As a result, an improvement in emission characteristics was achieved. However, the obtained samples exhibited noticeable blackening, which was found to be a major factor contributing to the reduction in quantum efficiency.

The fabrication of these bulk samples was carried out using the spark plasma sintering (SPS) process, which is widely employed for densifying difficult-to-sinter ceramics within a short processing time. However, SPS typically utilizes graphite components, and the sintering is conducted under vacuum or inert gas atmospheres within a stainless-steel chamber. Under these conditions, carbon contamination originating from graphite components is unavoidable. This contamination leads to increased optical absorption, causing blackening of the samples and directly degrading the quantum efficiency.

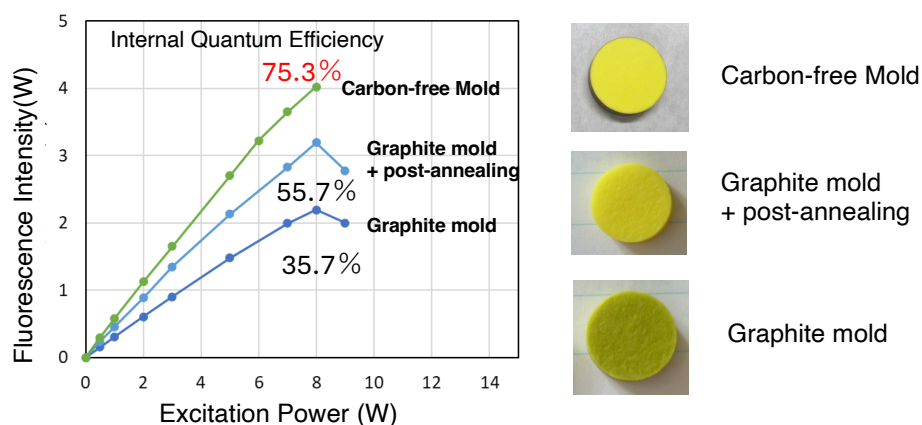
Furthermore, our investigation revealed that carbon impurities and associated defects are trapped within the highly densified bulk during sintering. As a result, these defects cannot be sufficiently removed by post-annealing treatments. This indicates a fundamental limitation of conventional approaches relying on post-processing to recover material properties. Instead, it is essential to suppress impurity incorporation and defect formation during the sintering process itself.

Based on this understanding, we propose a new processing approach that focuses on controlling both the sintering atmosphere and the structural components of the sintering system. Specifically, we have developed a carbon-free high-speed hot-press system that eliminates the

use of graphite components and enables sintering under a controlled atmosphere. This system allows for significant suppression of carbon contamination during the densification process.

Figure shows the relationship between excitation power and luminescence intensity for Ce:YAG–Al<sub>2</sub>O<sub>3</sub> composite ceramics fabricated using the newly developed carbon-free mold. For comparison, results obtained using conventional graphite molds and those subjected to post-annealing in air are also presented. The results clearly demonstrate that the use of graphite molds has a significant detrimental effect on luminescence performance. Moreover, even in oxide-based materials, post-annealing in air is insufficient to completely eliminate the effects of carbon contamination.

In contrast, the samples fabricated using the carbon-free mold exhibit a substantial reduction in carbon-related defects and a marked improvement in luminescence intensity. These results indicate that the reduction of carbon contamination directly leads to enhanced quantum efficiency.



**Fig.** Relationship between excitation power and fluorescence intensity of Ce:YAG–Al<sub>2</sub>O<sub>3</sub> composite ceramics fabricated using a carbon-free mold and a graphite mold, with and without post-annealing. Photographs of the corresponding bulk sample are also shown.

The developed atmosphere-controlled high-speed hot-press system enables the suppression of carbon contamination and the fabrication of low-defect ceramic phosphors with high quantum efficiency. These findings highlight the critical importance of process design in achieving high-performance ceramic phosphors for laser lighting applications. In this invited lecture, we present these results and discuss the extension of this approach to nitride-based materials.

We would like to acknowledge the members of SK Medical Electronics Co., Ltd. for their valuable advice on the high-speed hot-pressing method. This work was partially supported by a research grant from the Amada Foundation.

# High Luminescence Quantum Efficiency Of $\text{Yb}^{2+}/\text{CN}^-$ Co-Doped Potassium Chloride Crystals Applied As White Light-Emitting Phosphors

**L. H. C. Andrade<sup>a,\*</sup>, C. Y. Morassuti<sup>a</sup>, S. Finoto<sup>a</sup>, J. R. Silva, L. A. O. Nunes<sup>b</sup>, S. M. Lima<sup>a</sup>**

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The development of white light-emitting diodes (WLEDs) has brought about significant advancements in lighting technology, offering benefits such as energy efficiency and longevity. In an effort to improve the performance of WLEDs, the exploration of novel white light phosphors is critical. This work describes the synthesis and characterization of  $\text{Yb}^{2+}/\text{CN}^-$  co-doped KCl crystals for application as white light phosphors. The results confirmed formation of the  $\text{Yb}^{2+}/\text{CN}^-$  pair in the crystal, with high optical absorption in the UV-Vis range, a broad emission band from 400 to 700 nm, and high internal quantum yield (IQY, ~95%), which are fundamental for photonic devices., which are fundamental for photonic devices. It was observed that the emission shifted to longer wavelengths when the KCN concentration in the crystal was increased, presenting color coordinates from white/yellow to orange/red regions in the International Commission on Illumination -CIE 1931 color diagram, with high Color Rendering Index-CRI Ra (71-93) and very short distance of color coordinates to plankian locus- Du'v'. All these characteristics indicated the usefulness of  $\text{KCl}:\text{Yb}^{2+}/\text{CN}^-$  as a phosphor for WLEDs and red compensation, which was demonstrated with a prototype.

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# DOWN-SHIFTING IN $\text{Ce}^{3+}$ - $\text{Tb}^{3+}$ CO-DOPED PHOSPHATE GLASSES FOR SOLAR CELLS APPLICATION

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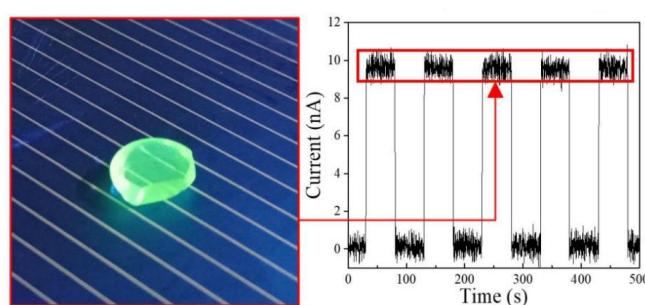
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The Down-Shifting (DS) of UV photons into the visible range has been attracting much attention for lighting appliances and solar cells. In this study, a series of phosphate glasses codoped with  $0.5 \text{ Ce}^{3+}$ - $x\text{Tb}^{3+}$  was synthesized using the melt-quenching method to investigate the energy transfer producing downshifting to  $\text{Tb}^{3+}$  ions.

Our focus was on photoluminescence and decay time of  $\text{Ce}^{3+}$  and  $\text{Tb}^{3+}$ , revealing trends of higher  $\text{Tb}^{3+}$  concentration leading to increased photoluminescence intensity and decreased luminescence intensity of  $\text{Ce}^{3+}$ . Additionally, investigation into down-shifting luminescence in  $\text{Ce}^{3+}$ - $\text{Tb}^{3+}$  co-doped phosphate glasses unveiled energy transfer from  $\text{Ce}^{3+}$  to  $\text{Tb}^{3+}$ . Placement of a codoped glass over a silicon solar cell generated photocurrent after UV excitation at 280 nm, indicating a potential for improve the solar cell efficiency.



**Fig.** a) Photo of a monocrystalline silicon solar cell with a co-doped glass sample on the top under 280 nm excitation and b) Temporal measurements of the photocurrent in a solar cell with and without sample under an excitation at 280 nm

# Dy<sup>3+</sup>-ACTIVATED Ln<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (Ln=Gd,Y) PYROCHLORES: STRUCTURAL AND PHOTOLUMINESCENCE INSIGHTS FOR WHITE LIGHT EMISSION

Houda ELBARHOUMI <sup>1</sup>, Faïçal KHLISSA <sup>1</sup>, Inocencio Rafael Martin <sup>2</sup>,  
Sana HRAIECH<sup>1</sup>, Ahlem GARBOUT <sup>1</sup>

<sup>1</sup>Physical Chemistry Laboratory of Mineral Materials and their Applications, National Center of Research in Materials Science, B.P. 73, 8027 Soliman, Tunisia

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Rare-earth-activated titanate pyrochlores are considered promising multifunctional materials due to their structural flexibility, chemical stability, and exceptional optical properties, making them ideal candidates for solid-state lighting applications [1]. In this study [2], we explore the structural, vibrational, and photoluminescence properties of Dy<sup>3+</sup>-substituted (Ln<sub>1-x</sub>Dy<sub>x</sub>)<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (Ln = Gd, Y) pyrochlores, synthesized over the full compositional range (0 ≤ x ≤ 1) via a conventional solid-state reaction method. X-ray diffraction (XRD) analysis, combined with Rietveld refinement, confirmed the formation of single-phase cubic pyrochlores crystallizing in the Fd3m space group. The refinement results revealed that Dy<sup>3+</sup> ions successfully substitute Ln<sup>3+</sup> sites and induce a systematic variation in lattice parameters due to ionic radius mismatch. This substitution also leads to subtle distortions in the pyrochlore lattice, reflecting changes in local symmetry and bonding environment.

To further investigate the effect of Dy<sup>3+</sup> incorporation on the lattice dynamics, complementary Raman spectroscopy was performed. The Raman spectra revealed pronounced shifts and intensity changes of the characteristic vibrational modes with increasing Dy<sup>3+</sup> concentration, highlighting structural distortion and local symmetry modifications consistent with the XRD observations.

Dy<sup>3+</sup> ions, acting as sensitive spectroscopic probes, were then used to examine local site symmetry and photoluminescence properties. Under 350 nm excitation, all phosphors exhibited strong yellow emission at 580 nm, corresponding to the hypersensitive <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>13/2</sub> electric dipole transition. The intensity of this emission reflects the occupation of non-centrosymmetric sites by Dy<sup>3+</sup> ions, slightly displaced from inversion centers in the cubic D<sub>3d</sub> lattice [3]. Maximum photoluminescence intensity was observed for x = 0.03 in Gd-based pyrochlores and x = 0.01 in Y-based pyrochlores, with concentration quenching occurring at higher Dy<sup>3+</sup> content. Time-resolved photoluminescence studies revealed non-exponential decay behavior, which was well-described using the Inokuti-Hirayama model. The results indicate that energy transfer between Dy<sup>3+</sup> ions is predominantly mediated by dipole-dipole interactions via cross-relaxation processes, accounting for the observed quenching at higher dopant levels.

Finally, the chromaticity coordinates (CIE) and correlated color temperatures (CCT) were calculated from the emission spectra. The values fall within the white light region, confirming that these Dy<sup>3+</sup>-activated Ln<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> pyrochlores are highly promising candidates for solid-state lighting applications. This comprehensive study highlights the interplay between structure, lattice vibrations, and optical properties, providing insights for the rational design of efficient phosphor materials.

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The background of the slide is white, featuring several light gray, irregular geometric shapes. These shapes are scattered across the page, with some overlapping. They resemble stylized rock formations or abstract architectural elements. The shapes are composed of various polygons, mostly pentagons and hexagons, with some having more complex, multi-sided forms. The overall effect is a clean, modern, and abstract design.

# **Wednesday 8<sup>th</sup>**

## **Weekly summary**

# ENABLING MATERIALS – OPTICAL AND FUNCTIONAL COMPOSITES

**Dorota Anna PAWLAK<sup>1</sup>**, Piotr PIOTROWSKI<sup>1,2</sup>, Monika TOMCZYK<sup>1</sup>, Katarzyna SADECKA<sup>1</sup>, Nada AGHAD<sup>1</sup>, Kingshuk BANDOPADHAY<sup>1</sup>, Ali ABBAS<sup>1</sup>, Krzysztof MARKUS<sup>1</sup>, Andrzej MATERNA<sup>1</sup>, Hamid REZA-DARABIAN<sup>1</sup>

<sup>1</sup> Ensemble<sup>3</sup> Centre of Excellence, Warsaw, Poland

Recently, we proposed the idea of utilizing directional solidification as a method for manufacturing metamaterials [1] and plasmonic materials [2]. We develop two methods: (i) method based on directionally-grown self-organized eutectic structures [3-5]; and (ii) NanoParticles Direct Doping method (NPDD) based on directional solidification of dielectric matrices doped with various nanoparticles [6-9]. In both of these methods we can easily use all available resonant phenomena to develop materials with unusual electromagnetic properties. Utilizing described above methods we demonstrated: (i) volumetric eutectic-based material with localized surface plasmon resonance at visible wavelengths [10-11]; (ii) enhanced luminescence and up-conversion processes in the eutectic material exhibiting LSPR and co-doped with erbium ions [6]; (iii) volumetric matrix-nanoparticles-based materials with plasmonic resonances at visible [6, 12] and IR wavelengths based on silver (Ag), antimony-tin-oxide (ATO) and titanium nitride nanoparticles (TiN); (iv) matrix-nanoparticles-based composite with enhanced photoluminescence at the telecommunication frequency of 1.5  $\mu\text{m}$ ; (v) material with subwavelength transmission at IR frequencies [13]; (vi) narrow band filter and polarizer [14-15]; (vii) surface enhanced Raman scattering in a bulk eutectic material enabling enhancement of selected Raman modes [16], (viii) materials with enhanced Faraday effect; (ix) materials for photoanodes in photoelectrochemical cells for generation of hydrogen [17-18], (x) topological insulator heterostructures [19] generating THz polarized radiation [20]. The newest achievements will be discussed.

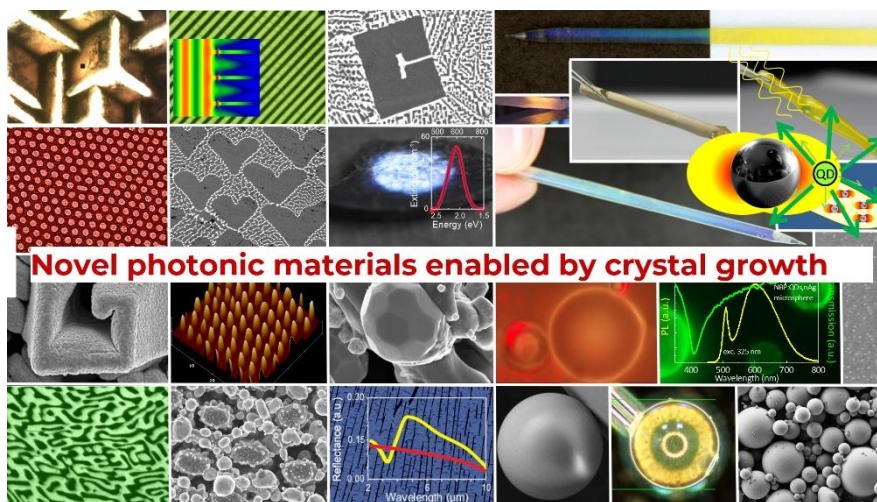


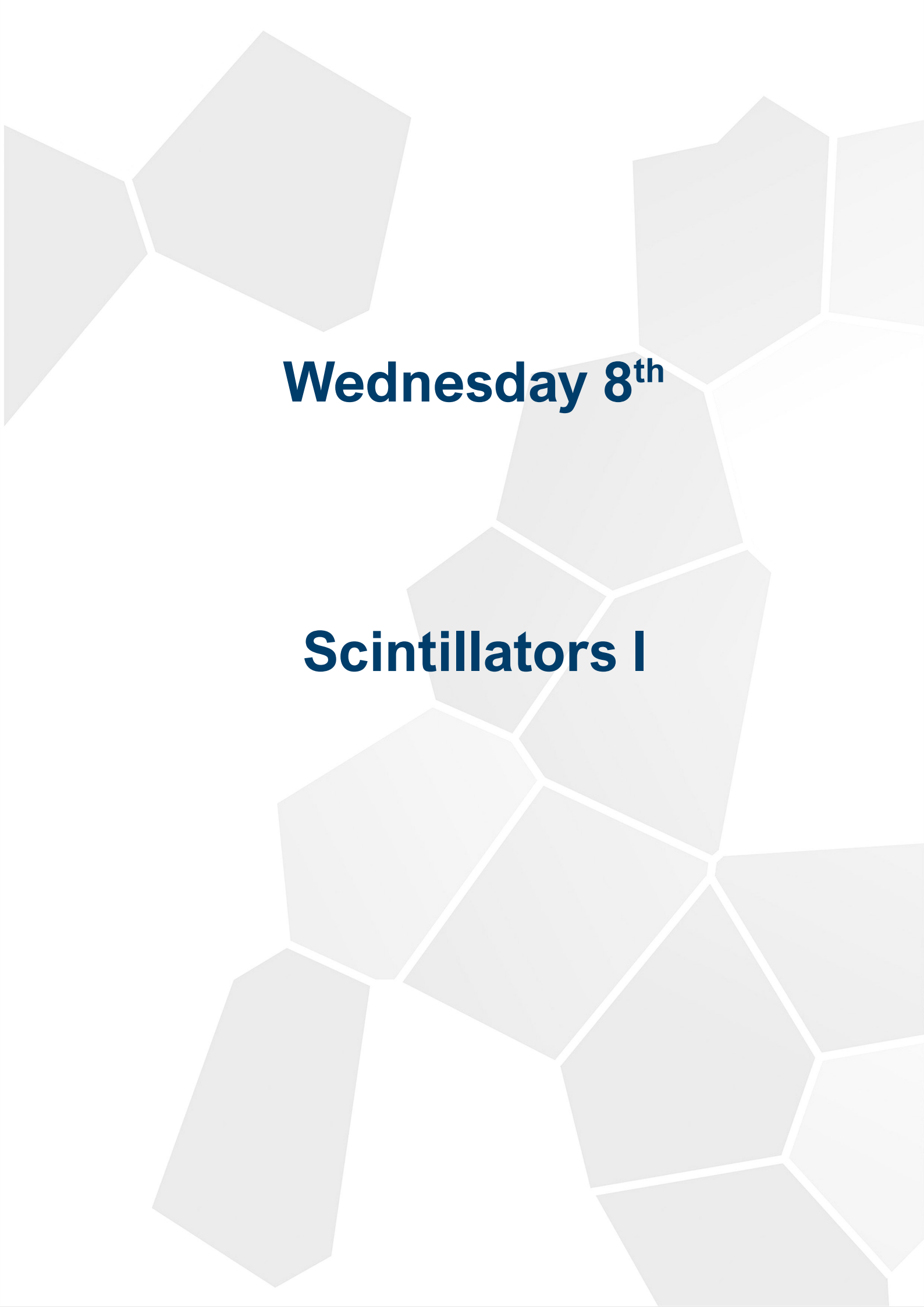
Fig. 1. Novel photonic materials enabled by crystal growth, manufactured in Ensemble<sup>3</sup>.

## ACKNOWLEDGEMENT

The authors thank the ENSEMBLE<sup>3</sup> Project carried within the International Research Agendas Programme of the Foundation for Polish Science co-financed by the European Union under the European Funds for Smart Economy and the Teaming Horizon 2020 programme of the European Commission (GA No. 857543) for supporting this work.

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**Wednesday 8<sup>th</sup>**

# **Scintillators I**

# Nanoporous scintillating aerogel for radioactive gas detection

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As the nuclear industry expands to deliver carbon-free electricity through advanced reactor concepts, including small modular reactors and fuel reprocessing technologies, the demand for precise monitoring of radioactive effluents becomes increasingly critical. In particular, the detection of pure beta-emitting noble gases such as tritium ( $^3\text{H}$ ) and  $^{85}\text{Kr}$  represents a major technological challenge for both nuclear operators and environmental safety authorities.

The short range of the emitted electrons from these radionuclides renders conventional detection techniques intrinsically limited. Existing approaches, including ionisation chambers and liquid scintillation counting, involve gas–gas or gas–liquid mixing to ensure the most efficient interaction between the emitted electrons and the active medium. Nevertheless, they fail to simultaneously provide high sensitivity, real-time capability, operational simplicity, and in-line deployment.

In this presentation, we introduce a fundamentally new detection paradigm based on a gas–solid mixing approach. We present the concept of a nanoporous scintillating medium specifically engineered to directly address the short-range electron detection challenge. Central to this development is the combination of a synthesized transparent scintillating aerogel based on  $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^4$ , an efficient coincidence-based single-photon detection chamber, and refined data analysis.

We will detail the synthesis route, nanostructural characteristics, and scintillation mechanisms governing energy relaxation within the material. Experimental results obtained under radioactive noble gas exposure—including  $^3\text{H}$  and  $^{85}\text{Kr}$  mixtures—will be presented, along with the achieved sensitivity limits. Importantly, we demonstrate for the first time a method enabling simultaneous quantification of mixed tritium–krypton atmospheres, overcoming a long-standing limitation in radionuclide metrology [1,2].

The resulting system is compact, robust, and compatible with real-time in-line monitoring of strategic radioactive gases. Beyond addressing a critical detection bottleneck, this work establishes a new conceptual framework for beta-emitting gas metrology, with broad implications for advanced nuclear facility management and environmental protection.

**Acknowledgements:** This work was performed under the project RadonNET (23IND07) which has received funding from the European Partnership on Metrology, co-financed from the European Union's Horizon Europe Research and Innovation Programme and by the Participating States. Funder ID: 10.13039/100019599

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# HEAVY GARNET SCINTILLATORS: THE MILESTONES OF THE 26 YEARS LONG R&D PATHWAY

**Martin NIKL**

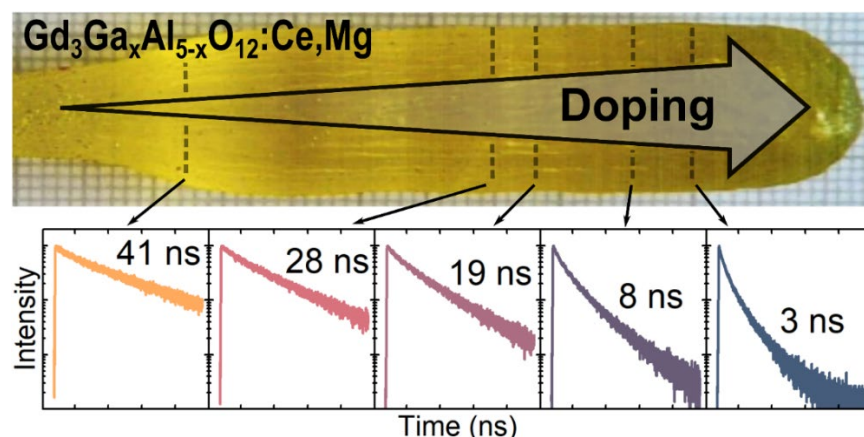
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Among aluminum garnets the  $\text{Ce}^{3+}$ -doped  $\text{Y}_3\text{Al}_5\text{O}_{12}$  (YAG:Ce) single crystals were found suitable for fast scintillators in 1970's due to fast 5d-4f emission of  $\text{Ce}^{3+}$  peaking around 530 nm with 60 ns photoluminescence decay time [1]. The first comprehensive description of YAG:Ce scintillator characteristics was reported in 1990's by Moszynski et al [2], who included this material among the high figure-of-merit oxide scintillators. Due to the need of higher density and  $Z_{\text{eff}}$  host for gamma ray detection the isostructural  $\text{Lu}_3\text{Al}_5\text{O}_{12}$  (LuAG) became of interest around year 2000 [3]: its higher density and effective atomic number ( $\rho=6.67 \text{ g/cm}^3$ ,  $Z_{\text{eff}}=63$ ) compared to YAG ( $\rho=4.56 \text{ g/cm}^3$ ,  $Z_{\text{eff}}=32.6$ ) and stable growth from the melt by the Czochralski technique provided viable industrial alternative and was commercialized immediately. At room temperature, contrary to YAG host, also the  $\text{Pr}^{3+}$  ion did provide an efficient fast 5d-4f emission in LuAG with the maximum around 310nm and much shorter decay time of 18 ns which enabled several times faster scintillation response of LuAG:Pr [4]. Given the flexibility of complex garnet lattice, various point defects can appear and so called antisite defects ( $\text{Lu}_{\text{Al}}$ ) dominate due to the lowest formation energy [5]. At the same time, such defects were found responsible for shallow electron traps in LuAG:Ce [6] which are detrimental for timing characteristics of scintillation response, i.e. lowering substantially its light yield. Thus, the most essential bottleneck in scintillation mechanism has been understood in 2007 [7] and the question arised: can the chemical composition of LuAG:Ce single crystal be modified to suppress it? Using the micropulling-down ( $\mu\text{PD}$ ) growth method, the Ga-admixed  $\text{Lu}_3(\text{Ga},\text{Al})_5\text{O}_{12}:\text{Pr}$  crystals appeared promising when the slow components in their scintillation response were diminishing, and intensity of low temperature thermoluminescence as well, with increasing amount of Ga [8]. Such a result paved the way towards the material optimization, though the observed effect was wrongly interpreted as the suppression of the antisite defects themselves. Only the following study, however, using combination of several experimental techniques and theoretical electronic band structure calculations, provided well-grounded explanation [9]. Namely, the admixture of gallium into LuAG decreases the bottom edge of conduction band and shallow electron trap become immersed in it, thus loosing the capacity to capture electrons. True breakthrough, however, came with the admixing of Gd creating so called multicomponent garnet of general formula  $(\text{Gd},\text{Y},\text{Lu})_3(\text{Ga},\text{Al})_5\text{O}_{12}:\text{Ce}$  (GGAG:Ce) reported in 2011 [10] where even in lower quality  $\mu\text{PD}$  grown crystals the best light yield values were close to 50 000 phot/MeV making a world-record in the melt-grown bulk oxide scintillation crystals. Interpretation is based on positive combination of the Ga effect described above and increase of crystal field at dodecahedral site due to Gd presence which increases the ionization barrier of 5d<sup>1</sup> excited state of  $\text{Ce}^{3+}$  making the ionization losses at room temperature negligible. Another milestone in improving performance of heavy garnet scintillators was met in 2014 where codoping of  $\text{Mg}^{2+}$  into LuAG:Ce [11] and GGAG:Ce [12] resulted in substantial



acceleration of its scintillation response due to stabilization of  $\text{Ce}^{4+}$  in the structure which provides new fast de-excitation pathway and competes with with electron traps for electron capture from conduction band. Acceleration of scintillation decay (15ns) well below the photoluminescence lifetime (58ns) was noticed in case of heavy Mg codoping in [11], but explained only later in 2018 as due to the quenching of  $\text{Ce}^{3+}$  emission in the closely spaced Ce-Mg pairs in epitaxial GGAG:Ce films [13]. It was then transferred to the bulk Czochralski grown crystals in [14]. In fact, more than ten times acceleration along the crystals was achieved upon heavy Ce doping and Mg codoping, Fig. 1. Technological transfer to CRYTUR company resulted in the growth of industrial scale volume-homogeneous accelerated garnet scintillators suitable for practical applications. Within last several years we have made an effort to replace gallium in chemical formula with scandium, i.e. to prepare GSAG:Ce crystal in much cheaper molybdenum crucible compared to iridium one necessary in the growth of GGAG. Unfortunately, the spontaneous occupation of dodecahedral garnet site by  $\text{Sc}^{3+}$  in congruent composition of the crystal grown creates a deep electron trap which results in strong deterioration of the timing and light yield characteristics [15], i.e. it appears as a blind way of no practical potential.

The presentation will summarize the achieved milestones in heavy garnet R&D during the 26 year lasting research in a broad international collaboration.



**Fig. 1** Evolution of scintillation decay along the Czochralski-grown GGAG:Ce,Mg crystal with increasing concentration of Ce and Mg [14].

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# NANOSCINTILLATORS AS NEXT GENERATION RADIOTHERAPEUTICS TO EXPAND THE THERAPEUTIC WINDOW

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More than 50% of cancer patients undergo radiation therapy during their treatment. However, delivering therapeutically effective doses of X-rays with tolerable toxicity to surrounding healthy tissues remains a challenge. To enhance the therapeutic window of radiotherapy and lead to a better prognosis for difficult-to-treat cancers, it has been proposed to use innovative nanoscintillators that can induce multifaceted radiotherapeutic effects. Nanoscintillators down-convert ionizing radiations into visible light, hence act as internal light sources remotely activated by penetrating X-ray. When accumulated in the tumor prior to radiotherapy, nanoscintillators can induce various effects that can potentially synergize<sup>1,2</sup>. When conjugated to photosensitizers, nanoscintillators can induce deep-tissue photodynamic therapy (PDT). This strategy would overcome the shallow penetration of light in tissues, one of the major limitations of PDT<sup>3</sup>. Because nanoscintillators can be made of high-Z element, their accumulation in the tumor prior to radiotherapy creates a physical radiation dose-enhancement effect<sup>4-6</sup>. This effect is initiated by a higher photoelectric absorption of orthovoltage X-rays by high-Z elements compared to soft tissues that leads to a higher production of photo- and Auger electrons, enhancing the damage to cancer tissues. Recently, we have demonstrated that nanoscintillators can also significantly delay DNA repair following radiotherapy. The combination of nanoparticles capable of modulating DNA repair pathways with a treatment modality whose therapeutic efficacy relies on inducing DNA damage represents a powerful and highly promising strategy for improving radiotherapy outcomes<sup>6</sup>.

While proof-of-concept studies demonstrating the radiotherapeutic potential of nanoscintillators have been reported by our group and others, our current focus is on establishing a comprehensive understanding of the mechanisms they induced by during radiotherapy. To achieve this, we adopt a multidisciplinary approach ranging from physics to biology, to preclinical trials. By investigating a diverse range of rare-earth-based nanoscintillators, we have identified a variety of radiophysical and radiobiological effects, which will be presented and discussed in this talk.

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The background of the slide is composed of several light gray, irregular polygonal shapes of various sizes and orientations, scattered across a white background. These shapes resemble crystalline structures or abstract architectural elements.

**Wednesday 8<sup>th</sup>**

**Luminescence (Inorganic)**

# Sb<sup>3+</sup> LUMINESCENCE PROPERTIES IN SODA-LIME GLASSES

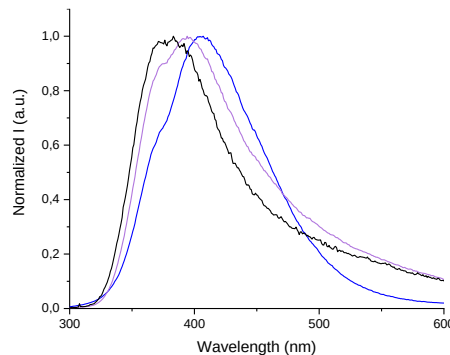
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Antimony has been used in antiquity as a decolorizing agent in glass production [1]. It also acts as a fining agent, reducing bubble formation during melting. In addition, like other heavy metal ions, antimony is of interest because of the strong nonlinear optical properties observed in highly doped glassy systems.

Sb<sup>3+</sup> ions belong to the group of 6s<sup>2</sup> luminescent centers, characterized by 6s6p excited states, similar to Bi<sup>3+</sup> and Sn<sup>2+</sup>, which exhibit comparable optical properties. Sb<sup>3+</sup> can therefore act as an efficient luminescence activator in optical materials [2]. Although the luminescence properties of Sb<sup>3+</sup> in halide crystals have been extensively investigated [2–3], highlighting the occurrence of a Jahn–Teller effect in the <sup>3</sup>P<sub>1</sub> excited state [4], its spectroscopic behavior in glass matrices has been studied in less detail. More recently, one can find some investigations on glass systems such as borate [5] or phosphate [6].

The present study explores the luminescence properties of Sb<sup>3+</sup> ions to improve our understanding of colorless Roman glasses. The photoluminescence behavior of Sb<sup>3+</sup> is strongly influenced by the local coordination environment, which depends not only on the chemical composition of the host glass but also on processing conditions, including melting and cooling rates [5]. Time-resolved measurements under 266 nm excitation performed on three Roman glasses decolorized with antimony revealed distinct emission profiles, with two main components peaking at 375 nm and 405 nm (Figure 1). However, Roman glasses contain multiple luminescent species, including Pb<sup>2+</sup> (which exhibits similar optical properties) and Cu<sup>+</sup>, making the assignment of those emission bands nontrivial. To clarify their origin, synthetic soda–lime glasses with compositions similar to ancient glasses were prepared and doped with 0.7 and 1.7 mol% Sb<sub>2</sub>O<sub>3</sub>. These samples were subsequently analyzed by photoluminescence spectroscopy.



**Fig.1** Emission spectra of Sb<sup>3+</sup> ions under 266 nm excitation in several Roman glasses

Our present results focus on the attribution and discussion of excitation and emission bands measured at various temperatures, ranging from 300 K down to 16 K. In Sb-doped synthetic soda–lime glasses, two similar emission components were observed at 370 nm and 400 nm. We assume that both components arise from the same  $^3P_1 \rightarrow ^1S_0$  emission band of  $Sb^{3+}$  and correspond to two distinct site distributions within the glass network ; their relative proportions depending on the Sb concentration

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# Probing excitonic energy transfer in Bi- and/or Eu-doped GdVO<sub>4</sub> by ultrafast spectroscopy

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Lanthanide-ion-activated orthovanadates, both downconversion (DC) and upconversion (UC) ones, have attracted great interest due to the possibility to excite intrinsic, or self-activated luminescence emissions with high quantum yields and large Stokes shifts [1]. Nanoparticles doped with small amounts of activator ions such as transition-metal and/or rare-earth (RE) ions have gained considerable attention because of the variety of their optical, magnetic, and thermal properties. Their potential as multifunctional materials is very broad, they can be used to improve photovoltaic cell efficiency through solar spectral conversion by shifting short-wavelength sunlight (ultraviolet and blue) to longer wavelengths (DC processes such as downshifting, quantum cutting...), or by shifting long-wavelength near-infrared (NIR) radiation to visible light (UC processes), where the solar cell shows the larger quantum efficiency. On the other hand, the luminescence decay times of the majority of lanthanide and transition-metal ions are much longer than those of biological materials; therefore, NPs activated with these ions show strong potential for biolabeling applications. Moreover, long-lasting emissions can be easily discriminated from the autofluorescence of biological materials using time-resolved spectroscopic techniques [2].

Gadolinium orthovanadate (GdVO<sub>4</sub>)-based materials have interesting luminescent and magnetic properties. They can be doped with a variety of other luminescent lanthanide ions because of the equal valence and alike ionic radii. They can be efficiently excited with UV radiation due to the strong absorption of the (VO<sub>4</sub>)<sup>3-</sup> anions and efficient energy transfer from these groups to lanthanide ions. However, despite of the enormous amount of theoretical and experimental data on the structural, electronic and optical properties of single and/or multidoped RE-M-LaVO<sub>4</sub> (RE=Rare-earth metals, M= other metals i.e. Bi., La= Y, Gd, Lu, Sc, ..) there are energy transfer mechanisms not yet well understood to explain some of the observed emissions from doping activators.

In this work, we performed a detailed spectroscopic analysis of impurity dopant emissions in gadolinium vanadate crystalline powders doped with Bi<sup>3+</sup> or Eu<sup>3+</sup>, or co-doped with the Bi<sup>3+</sup>-Eu<sup>3+</sup> pair. This analysis aimed to experimentally elucidate, using high-resolution time-resolved spectroscopic data, the origin of the emissions produced by the presence of these impurities, as well as the energy transfer processes that drive the respective excited states and, consequently,

the role each ion plays in the observed emissions. The study was conducted at different impurity ion concentrations below the point of appreciable luminescence concentration quenching. Our results show that the basis of the spectroscopic behavior of the  $\text{Bi}^{3+}$ ,  $\text{Eu}^{3+}$ , and  $\text{Bi}^{3+}\text{-Eu}^{3+}$  co-doped vanadate matrix is an excitonic energy transfer to the activator ions managed primarily by the  $(\text{VO}_4)^{3-}$  molecular units. The self-trapped excitons located within them, generated by the UV pumping photons, can migrate to the capture sites induced by the doping impurities. Then, exciton recombination transfer its energy to the impurity and/or generates metal-metal charge transfer (MMCT) excited states that give rise to the observed luminescence. Measurements of rise time and lifetime of emissions in pure, single-doped, and co-doped samples allow tracking the dynamic electronic processes involved between the vanadate host and the dopants, as well as estimating the rate and efficiency of energy transfer.

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# PHASE-DEPENDENT SPECTROSCOPIC PROPERTIES OF THE Nd<sup>3+</sup> ION IN NANO- AND MICRO-CRYSTALLINE BiPO<sub>4</sub> HOSTS

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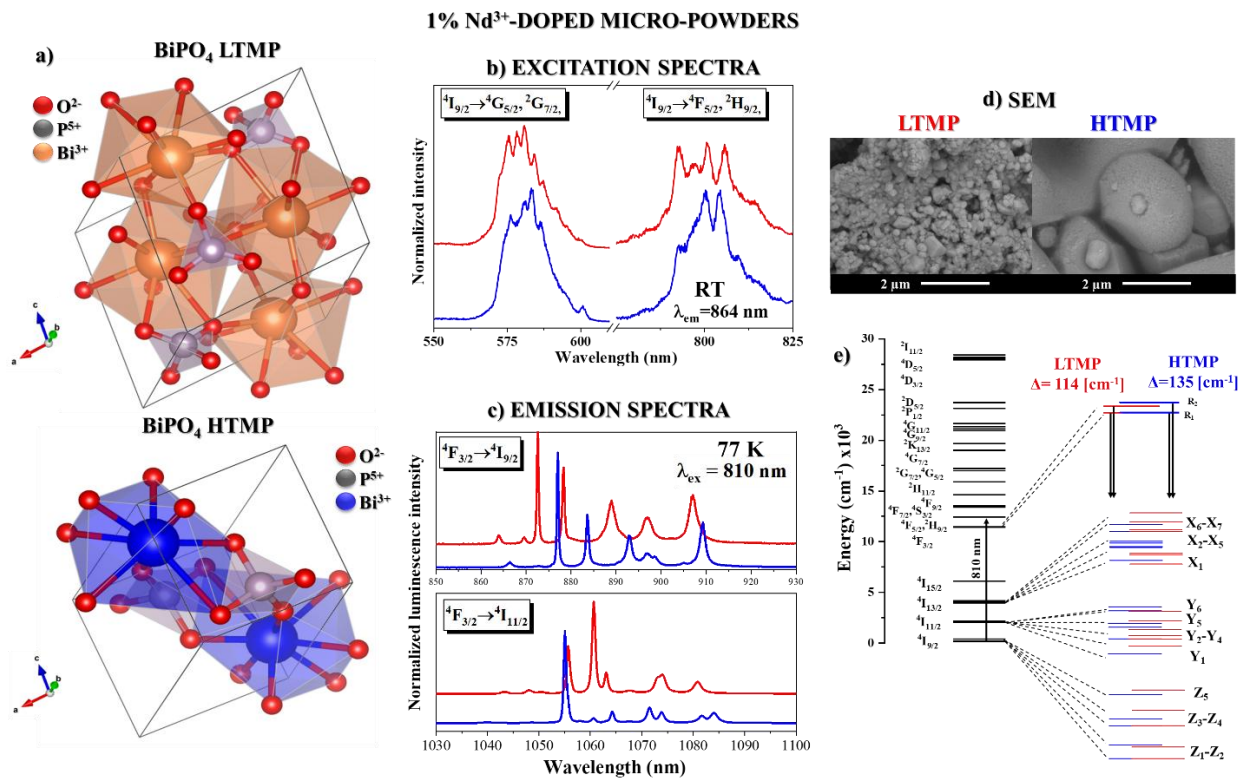
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We present a comprehensive structural and spectroscopic study of Nd<sup>3+</sup>-doped BiPO<sub>4</sub> nano- and micro-crystalline phosphors synthesized *via* ionic-liquid-assisted microwave (IL MW) and solid-state (SS) methods. Nano-powders (40 - 70 nm) were obtained exclusively in phase-pure low-temperature monoclinic phase (LTMP), whereas micro-powders (~ 0.8 - 9 μm) yielded both LTMP and high-temperature monoclinic (HTMP) polymorphs. These results highlight the strong influence of synthesis route and thermal treatment on phase formation, particle size, morphology, and crystallinity. X-ray diffraction and electron microscopy analyses confirmed that Nd<sup>3+</sup> ions effectively substitute Bi<sup>3+</sup> sites without forming secondary phases over a broad concentration range.

High-resolution absorption spectroscopy reveals nearly identical Nd<sup>3+</sup> band positions in LTMP and HTMP, indicating that the local crystal-field environment around the primary Nd<sup>3+</sup> site is preserved across phases. In contrast, photoluminescence spectra show marked phase-dependent behavior: LTMP emission originates predominantly from a single Nd<sup>3+</sup> site, while HTMP exhibits contributions from an additional site, consistent with minor additional maxima observed by absorption at 8 K. Low-temperature measurements enable the assignment of the R<sub>1</sub> and R<sub>2</sub> Stark sublevels of the <sup>4</sup>F<sub>3/2</sub> state. HTMP exhibits a larger R<sub>1</sub> - R<sub>2</sub> splitting (ΔE = 135 cm<sup>-1</sup>) than LTMP (ΔE = 114 cm<sup>-1</sup>) reflecting a stronger local crystal-field effect.

The comparison of LTMP and HTMP illustrates how subtle variations in monoclinic symmetry and local coordination selectively modulate emission properties while leaving absorption nearly unaffected. Luminescence decay times are shorter at 77 K (e.g. for nano-powders at 1% Nd<sup>3+</sup> at RT τ = 232 μs and at 77 K τ = 182 μs), consistent with previously reported behavior in other Nd<sup>3+</sup>-doped orthophosphates [1-3]. The results allow a direct comparison of the spectroscopic properties of Nd<sup>3+</sup> ions with those previously studied in tetragonal YPO<sub>4</sub> and LuPO<sub>4</sub>, as well as in monoclinic GdPO<sub>4</sub>. They establish BiPO<sub>4</sub> as a cost-effective and versatile host for near-infrared photonic, laser, and luminescent applications representing the first detailed spectroscopic characterization of Nd<sup>3+</sup> ions in monoclinic BiPO<sub>4</sub> and offering significant new insight into rare-earth-doped phosphate materials.





**Fig.** (a) Visualization of the LTMP and HTMP polymorphs. (b) Excitation spectra measured at room temperature. (c) Emission spectra recorded at 77 K. (d) SEM images illustrating the morphology of the samples. (e) Proposed energy-level diagrams of Nd<sup>3+</sup> ions in both LTMP and HTMP host lattices.

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# LUMINESCENCE OF $S_2^{\bullet-}$ IN THE MINERAL BARYTE, $BaSO_4$

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Natural baryte ( $BaSO_4$ ) is a well-known luminescent mineral that emits light from the UV to the near-IR regions of the spectrum. It has an orthorhombic structure (point group  $2/m\ 2/m\ 2/m$ ) in which sulphur is situated in tetrahedral coordination with oxygen (with the S–O covalent bond lengths ranging from 1.46 to 1.49 Å), and barium is in 12-fold coordination with oxygen. Laser-induced time-resolved luminescence enables the detection of multiple luminescence centres, including  $Ag^+$ ,  $Bi^{2+}$ ,  $Bi^{3+}$ ,  $Eu^{2+}$ ,  $Eu^{3+}$ ,  $Ce^{3+}$ ,  $Nd^{3+}$ , and  $(UO_2)^{2+}$  [1]. The previously unknown type of yellow-orange luminescence was found in the baryte under study. By time-resolved spectroscopy at 100 K, a clear vibrational structure is observed with a decay time of  $\sim 100$  ns and a vibrational period of  $540\text{--}570\text{ cm}^{-1}$ . The same luminescence was found at CW spectra at low temperatures down to 20 K (Figure). Among the luminescence centres previously known in minerals, the very similar spectral kinetic parameters are typical of  $S_2^{\bullet-}$  centres (“•” means unpaired electron) [1].

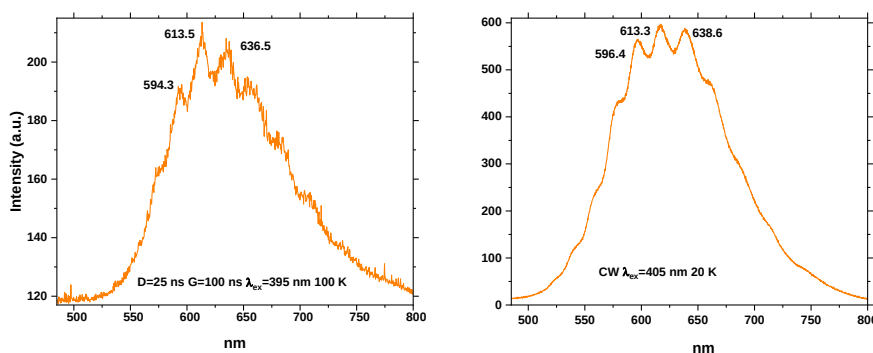


Figure. Time-resolved luminescence of baryte at 100 K with  $\tau=100$  ns and CW spectrum at 20 K

The existence of this radical anion in baryte was proved by EPR as well as the presence of a weak Raman band near  $555\text{ cm}^{-1}$  corresponding to the S–S stretching mode of  $S_2^{\bullet-}$ . Other relevant defects ( $K^+$  cations,  $SO_2^{\bullet-}$ ,  $SO_3^{\bullet-}$  radical anions, and COS neutral molecules) have been identified using IR, EPR, Raman spectroscopy, and LIBS.

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# SINGLE QUANTUM-DOT SPECTROSCOPY OF HALIDE PEROVSKITE NANOCRYSTALS

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ABX<sub>3</sub>-type metal halide perovskites, a new class of semiconductor materials, are currently receiving significant attention from the viewpoints of fundamental physics and optoelectronic device applications [1]. These materials are defined by the A-site monovalent cation [Cs<sup>+</sup>, methylammonium (MA<sup>+</sup>) or formamidinium (FA<sup>+</sup>)], the B-site divalent metal cation (Pb<sup>2+</sup> or Sn<sup>2+</sup>), and the X-site halide (I<sup>-</sup>, Br<sup>-</sup>, or Cl<sup>-</sup>). Due to their characteristic ionic bonding and crystal structure, these perovskites exhibit an extraordinary tolerance to defects within the band gap, making them highly promising materials for solar cells, as well as light-emitting diodes and lasers. Furthermore, high-quality nanocrystal (NC) samples can be fabricated via low-temperature chemical solution methods. Halide perovskite NCs exhibit nearly 100% photoluminescence quantum yields (PLQYs) without requiring specific core/shell structures. This talk provides an overview of our group's recent progress in unraveling the photophysical properties and luminescence characteristics of these halide perovskite NCs.

Single-dot photoluminescence (PL) spectroscopy is essential for revealing the intrinsic optical properties of halide perovskite NCs. Excitons, trions, and biexcitons govern their PL spectra and dynamics [2,3]. At low temperatures, weak trion and biexciton PL peaks appear in the low-energy region below the strong exciton PL peak [4-6]. By analyzing these multi-peak spectra, we accurately evaluated the binding energies of trions and biexcitons, revealing that they increase significantly as the NC size decreases [6].

In addition, multiple fine structures appear near the exciton main peak [4,5]. These peaks originate from strong exciton-phonon couplings. Since halide perovskites possess multiple longitudinal optical (LO) phonon modes, the LO-phonon-assisted PL spectra are complicated. Exciton-phonon coupling is typically discussed in terms of long-range and short-range interactions [7]. The long-range exciton-phonon coupling constants are evaluated from the Huang-Rhys factors in the PL spectrum. The short-range exciton-phonon coupling constants are also determined from the Urbach energy [8]. Our results show that both the long-range and short-range exciton-phonon interactions increase in small NCs.

Furthermore, strong exciton-phonon interactions lead to efficient anti-Stokes PL at room temperature, where the emitted photon energy is higher than the incident photon energy [9,10]. Achieving net optical cooling necessitates near-unity PLQYs. Although nonradiative carrier trapping and Auger recombination typically limit PLQYs and induce sample heating, we identified optimal experimental conditions, specifically excitation wavelength and intensity, through theoretical calculations. Using high-quality NC samples, we successfully demonstrated the laser-induced optical cooling of NCs: the observation of a decrease in the sample temperature during laser excitation [11,12].

In this talk, we discuss the size dependence of exciton-exciton and exciton-phonon interactions, as well as the fundamental mechanisms of optical cooling. We also highlight the exceptional potential of halide perovskite NCs as next-generation light-emitting device materials.

The author would like to thank many colleagues for their contributions. Part of this work was supported by JST CREST (JPMJCR21B4).

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# THERMOCHROMIC–LUMINESCENT HYBRID MATERIALS BASED ON POLYDIACETYLENE AND LANTHANIDES FOR OPTICAL TEMPERATURE SENSING

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Hybrid organic–inorganic materials combining responsive polymers with luminescent nanophosphors provide a versatile approach to temperature-responsive optical materials. In particular, integrating thermochromic polymers with lanthanide-based luminescent thermometers allows the material to record threshold temperature exposure while simultaneously providing a quantitative temperature readout [1]. Such hybrid systems are particularly relevant for sensing in sub-zero and cryogenic environments where reliable temperature monitoring is required.

In this work, we present hybrid optical films based on a poly(vinyl acetate) (PVAc) matrix integrating thermochromic polydiacetylene (PDA) derivatives with lanthanide-doped phosphate nanophosphors. The sensing mechanism is based on a bilayer polymer structure that combines two complementary optical responses within a single material platform.

The inorganic component consists of YPO<sub>4</sub> or GdPO<sub>4</sub> nanoparticles co-doped with Nd<sup>3+</sup> and Yb<sup>3+</sup> ions, which act as luminescent nanothermometers operating in the near-infrared spectral region. Upon excitation of Nd<sup>3+</sup> ions, thermally activated energy transfer to Yb<sup>3+</sup> exhibits temperature-dependent emission that can be analyzed using ratiometric luminescence thermometry. This mechanism enables reliable temperature readout across a broad temperature range extending from cryogenic conditions to elevated temperatures.

The organic component consists of a PDA derivative, activated using a UV light source, capable of undergoing an irreversible blue-to-orange chromic transition triggered by temperature. This transition originates from conformational rearrangements of the conjugated PDA backbone that disrupt  $\pi$ -conjugation and lead to a pronounced change in the optical absorption spectrum. Once activated, the chromic transition provides a persistent visual indication of temperature exposure and allows the material to record threshold temperature events without the need for continuous monitoring [2].

Both components are integrated within a PVAc-supported bilayer film, enabling the fabrication of stable hybrid optical materials. The resulting sensor provides a dual response that combines irreversible threshold indication with quantitative luminescent thermometry. In this configuration, the PDA layer records the crossing of a sub-zero temperature threshold through a permanent chromic transition, while the lanthanide-doped nanophosphate layer enables continuous temperature readout based on near-infrared emission. Such hybrid optical materials

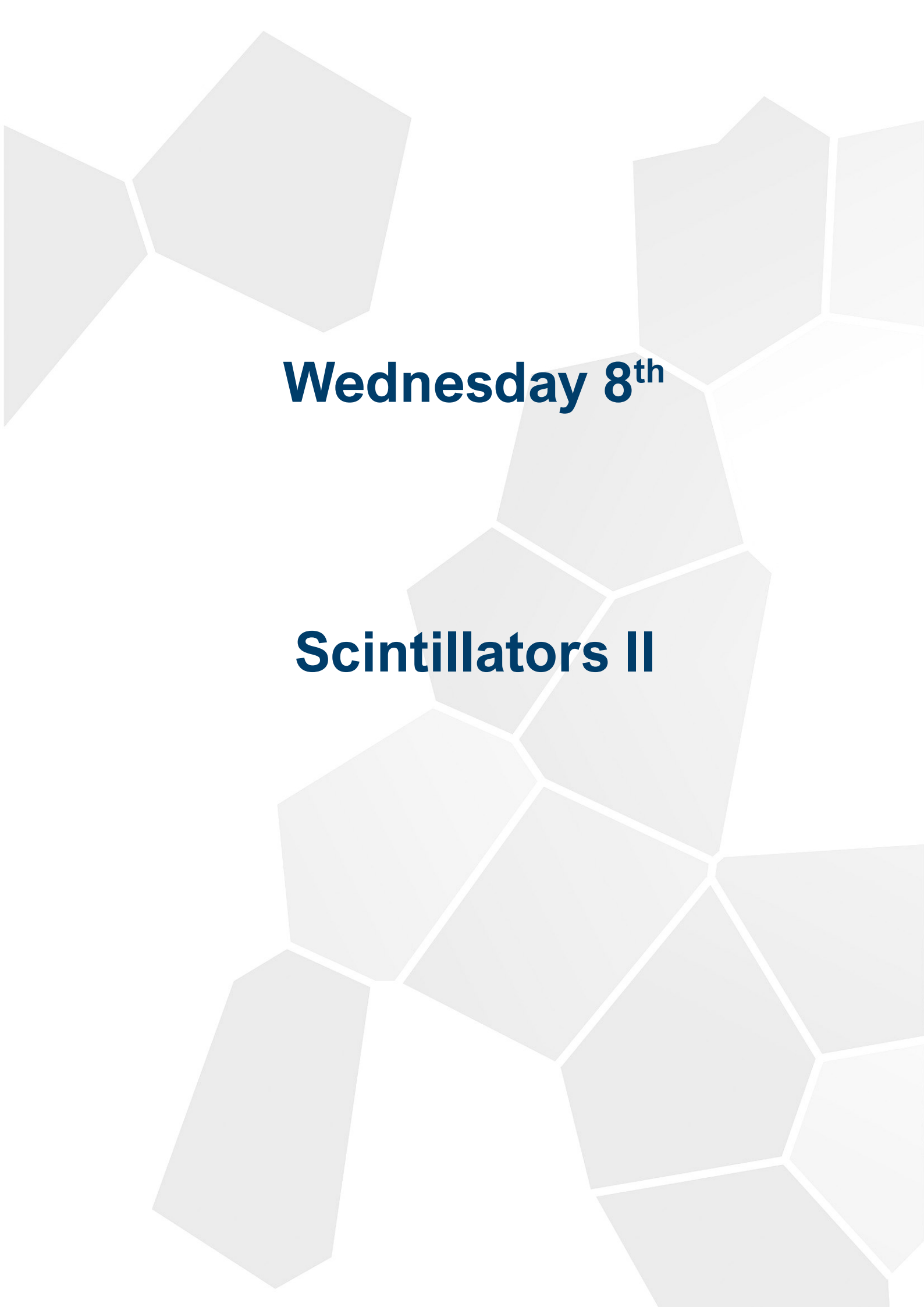
offer a practical approach for monitoring temperature in cryogenic environments relevant to cold-chain logistics, sample preservation, and preservation of biological samples.

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The background of the slide is composed of several light gray, irregular polygonal shapes of various sizes and orientations, scattered across a white background. These shapes resemble fragments of a larger structure or perhaps stylized crystals.

**Wednesday 8<sup>th</sup>**

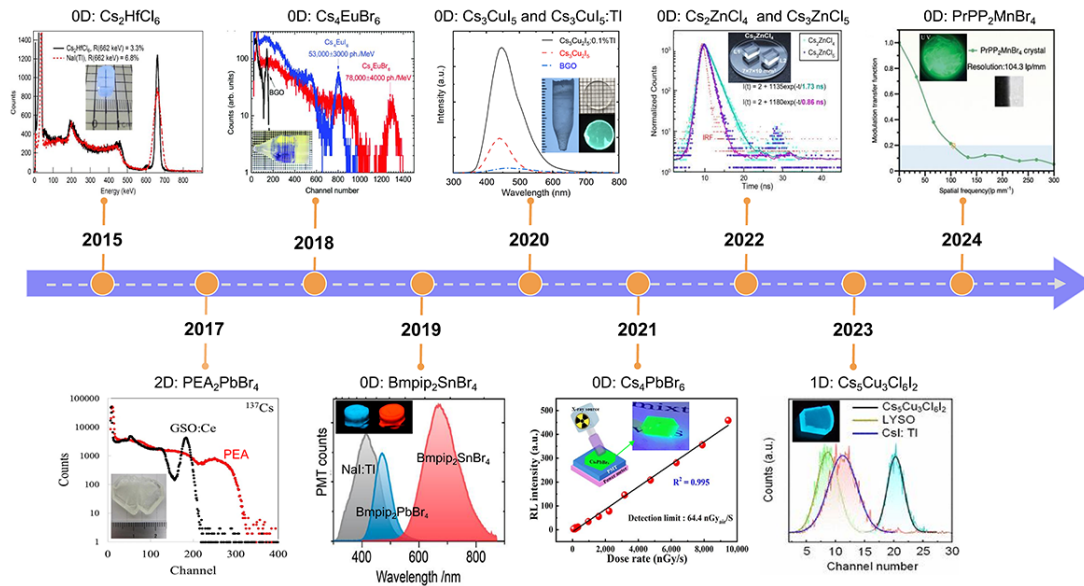
**Scintillators II**

# LOW-DIMENSIONAL HALIDES SCINTILLATORS: CHALLENGES AND OPPORTUNITIES

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Inorganic scintillators as indirect detection materials play an important role in the applications of medical imaging, non-destructive inspection, and homeland security. Classical inorganic scintillators for X-ray detection are CsI:Tl and Gd<sub>2</sub>O<sub>2</sub>S:Tb crystalline materials. In the recent years, metal halide perovskites have become promising scintillation materials for high-performance X-ray detection due to their advantages of efficient radioluminescence and ease of preparation. According to the connection mode of metal halide polyhedral units at the molecular structure level, they can be categorized into three-dimensional (3D), two-dimensional (2D), one-dimensional (1D) and zero-dimensional (0D). 3D perovskite scintillators have well-known issues, such as thermal quenching at room temperature and severe self-absorption effect. For example, the light yield of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> single crystal is 116,000 ± 23,000 photons/MeV at 8 K, but it significantly drops to about 1,000 photons/MeV at room temperature. In principle, by decreasing the structural dimension and increasing the interval spacing between the metal halide polyhedra as luminescent units, higher luminescence efficiency is expected due to stronger confinement effect. In this work, the R&D of low-dimensional halides,<sup>1-2</sup> such as lead-based, copper(I)-based, manganese(II)-based, and the associated scintillation mechanism will be reviewed.



**Fig.** Overview of recent R&D of low-dimensional metal halide scintillators.

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# DEVELOPMENT OF OPTICAL-GUIDING CRYSTAL SCINTILLATORS WITH ULTRAFINE CORES FOR HIGH-RESOLUTION X-RAY IMAGING

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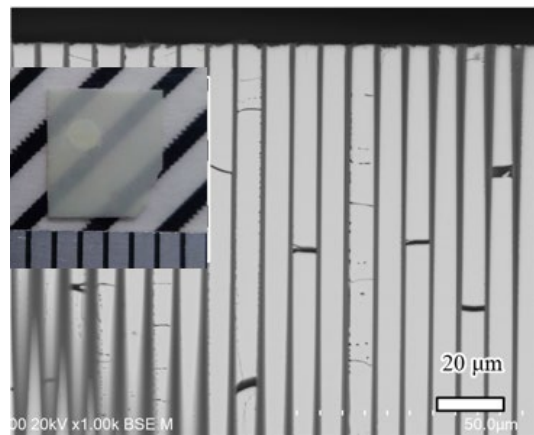
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High-resolution X-ray imaging is essential for applications such as medical diagnostics, synchrotron radiation experiments, and nondestructive microstructure analysis. Conventional scintillators including  $\text{Gd}_2\text{O}_2\text{S}$  powder screens and columnar  $\text{CsI:Tl}$  suffer from spatial-resolution degradation caused by lateral light scattering within the scintillator layer. Structured scintillators that guide scintillation photons using refractive-index contrast have therefore attracted increasing attention as a strategy to suppress optical diffusion and improve spatial resolution. Optical-guiding crystal scintillators (OCSs) are composite structures composed of high-refractive-index scintillator cores embedded in a lower-index glass matrix. Scintillation photons generated in the cores are confined by total internal reflection at the core-cladding interface, enabling optical guiding similar to optical fibers. This architecture suppresses lateral light spreading and can improve imaging contrast and spatial resolution.

In this study, bundled OCS plates with ultrafine scintillator cores of 1~4  $\mu\text{m}$  were fabricated using a hollow-fiber-based process. The structure consists of  $\mu\text{m}$ -scale cores of Tl-doped  $\text{Cs}_3\text{Cu}_2\text{I}_5$  (Tl:CCI) scintillator surrounded by a glass cladding. Unidirectional solidification along the fiber axis was applied to crystallize the scintillator cores, enabling single-grain formation and improved optical transparency. X-ray imaging experiments demonstrated a spatial resolution capable of resolving a 5  $\mu\text{m}$  test chart and a contrast transfer function (CTF) of approximately 30% at 10 lp/mm for a scintillator thickness of 500  $\mu\text{m}$ . The detailed growth technique, crystallographic evaluation, and X-ray imaging performance will be presented.



**Fig. 1** Photograph of the OCS and a backscattered electron (BSE) image of the cross-section perpendicular to the fiber direction

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# Development of Halide Scintillator Materials for Radiation Particle Identification Based on Emission Wavelength Information

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**Introduction** Scintillators represent indispensable functional materials that transduce ionizing radiation into ultraviolet or visible photons, fulfilling critical functions across medical diagnostics, nuclear physics, and particle physics. Specifically, the precise identification of radiation particles is paramount in rare-event observatories—notably within dark matter detection and neutrinoless double-beta decay experiments—to effectively discriminate veritable signals from ambient background radiation. While conventional methodologies, notably Pulse Shape Discrimination (PSD) [1], are widely employed, they are fraught with substantial impediments, including the requisite for intricate readout electronics. To circumvent these limitations, our previous research proposed and investigated a wavelength-dependent discrimination methodology that capitalizes on characteristic variations in the radioluminescence (RL) spectrum dictated by the incident radiation profile [2, 3]. We previously achieved the report demonstrating that the luminescent intensity ratio between  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  species within  $\text{CaF}_2\text{:Eu}$  exhibits a dependence on the ionizing source, varying significantly between X-ray and  $\alpha$ -particle irradiation [3]. This study aims to investigate halide crystalline scintillators optimized for implementation within this wavelength-dependent particle identification method, accompanied by a rigorous evaluation of their scintillation characteristics.

**Experimental Methods** Single crystals of  $\text{Cs}_2\text{Li}(\text{Gd,Ce})\text{Cl}_6$  and monovalent cation-doped  $\text{BaCl}_2$  were synthesized via the Vertical Bridgman (VB) technique [4]. Within the  $\text{Cs}_2\text{Li}(\text{Gd,Ce})\text{Cl}_6$  system, the Ce dopant concentration was systematically modulated between 0.1% and 30%. Conversely, the  $\text{BaCl}_2$  matrix was co-doped with  $\text{K}^+$  and select rare-earth ion (Eu) to engineer specific defect dynamics. The ensuing scintillation characteristics—encompassing RL spectra elicited under X-ray and  $\alpha$ -particle ionization, alongside the material response to heavy ion beams (proton, carbon, and titanium) generated by a tandem accelerator—were rigorously evaluated.

**Results and Discussion** Within the  $\text{Cs}_2\text{Li}(\text{Gd,Ce})\text{Cl}_6$  architecture, the concurrent emission of  $\text{Gd}^{3+}$  ( $4f \rightarrow 4f$  transitions) and  $\text{Ce}^{3+}$  ( $5d \rightarrow 4f$  transitions) was empirically verified. The RL intensity ratio between these dual components exhibited pronounced variance contingent upon whether the excitation source was X-ray or  $\alpha$ -particle irradiation. Furthermore, experiments utilizing heavy ion beam bombardments demonstrated a distinct correlation between the  $\text{Gd}^{3+}$  emission intensity and the average energy loss, postulating the material's capability to discern both particle taxonomy and their corresponding energetic states.

Regarding the  $\text{BaCl}_2\text{:K,Eu}$  framework,  $\text{K}^+$  co-doping effectively stabilized  $\text{Eu}^{3+}$  ions by engendering  $\text{Cl}^-$  vacancies for requisite charge compensation. A unique phenomenon was reported wherein  $\text{Eu}^{3+}$  luminescence is exclusively triggered by  $\alpha$ -particle irradiation, remaining entirely suppressed under X-ray excitation. This binary "ON/OFF" spectral signature introduces

robust methodology for particle identification, transcending the capabilities of conventional methods.

**Conclusion** In this study, we present two promising scintillators optimized for wavelength-dependent particle identification.  $\text{Cs}_2\text{Li}(\text{Gd,Ce})\text{Cl}_6$  and  $\text{BaCl}_2:\text{K,Eu}$  provide good discrimination resolution through dual-peak spectroscopy and yield clear, discrete spectral transitions based on thresholds. These findings establish fundamental design criteria for next-generation radiation measurement detectors and are expected to lead to advancements across multiple fields, including nuclear physics and particle physics.

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# ANALYZING PRASEODYNIUM ENERGY LEVELS IN SCINTILLATING FLUORIDE AND OXIDE GLASSES

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Rare-earth doped glasses remain promising candidates as ultrafast scintillators for laser fusion experiments. Among them, praseodymium ( $\text{Pr}^{3+}$ )-doped aluminum fluorophosphates are particularly attractive because of their wide band gaps, short absorption edges, and fast radiative decay. In our previous study, we demonstrated that aluminum-fluoride-based  $\text{Pr}^{3+}$ -doped glasses exhibit nanosecond-scale ultraviolet emission based on the energy gap between the  $4f^2$  and the  $4f5d$  configurations. In this present work, we expand this investigation to provide a systematic evaluation of  $\text{Pr}^{3+}$  energy-level structures in both fluoride and oxide glass matrices. X-ray absorption near-edge structure (XANES) measurements at the Pr LIII edge confirm the stable trivalent state of Pr across all compositions examined. Multiple spectroscopic characterization spanning the vacuum ultraviolet (VUV) to the visible (VIS) region also reveals distinct host-dependent shifts of the lowest  $4f5d$  levels relative to the  $^1\text{So}$  state of the  $4f^2$  configuration. These shifts strongly influence the competition between allowed  $4f5d \rightarrow 4f^2$  emissions and slower intraconfigurational  $4f^2$  transitions. Time-resolved radioluminescence measurements also show decay constants ranging from tens to hundreds of nanoseconds depending on the energetic separation between the  $^1\text{So}$  level and the lowest  $4f5d$  state. Hosts exhibiting larger separations favor direct  $4f5d$  emission pathways and suppress parasitic  $4f^2$  emissions, leading to faster ultraviolet scintillation. By correlating material chemistry, electronic configuration, and scintillation dynamics, our work establishes practical energy-level design criteria for optimizing  $\text{Pr}^{3+}$ -doped glass scintillators. The results provide updated guidance for designing new-generation, fast-response oxide and fluoride materials suitable for high-radiation, laser fusion experiments.

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# Compositional Engineering Toward Ce<sup>4+</sup> Dominance in Y<sub>3</sub>(Al,Ga)<sub>5</sub>O<sub>12</sub>:Ce,Mg Single-Crystal Scintillators

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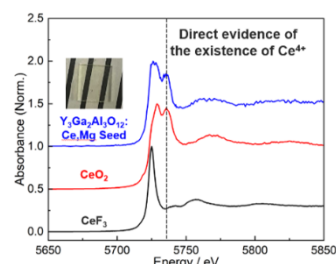
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**[Introduction]** Y<sub>3</sub>(Al,Ga)<sub>5</sub>O<sub>12</sub>:Ce (YAGG) single crystals have attracted attention as promising scintillators for photon-counting detectors (PCDs) in medical imaging and non-destructive testing [1]. This is because the K $\alpha$  X-ray energy of Y is 15 keV, which lies below the typical detection energy range of PCD systems, whereas scintillators containing Gd or Lu exhibit K $\alpha$  escape peaks at 43 keV and 55 keV, respectively, within the detection range, which can degrade energy discrimination. Recently, it has been reported that Mg co-doping on Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce enhances both the light yield and scintillation decay time, an effect attributed to a change in the valence state of Ce from 3+ to 4+ [2]. In the case of YAGG, Mg co-doping also enhances both light yield and scintillation decay time; however, the underlying mechanism of this improvement remains unknown [3]. Therefore, in this study, X-ray Absorption Near Edge Structure (XANES) analysis was employed for the direct probe of the valence state of Ce in Mg-doped YAGG as well as understanding its relationship with the scintillation properties of YAGG.

**[Materials and Methods]** Ce<sub>0.33</sub>at%, Mg<sub>0.2</sub>at% co-doped Y<sub>3</sub>(Ga,Al)<sub>5</sub>O<sub>12</sub> crystals were grown by the Czochralski (Cz) method from a stoichiometric mixture of 4N CeO<sub>2</sub>, MgO, Y<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> powders. XANES measurements were performed in fluorescence mode over the energy range 5510-5910 eV with CeO<sub>2</sub> and CeF<sub>3</sub> as reference standards.

**[Results]** The seed-side sample of the Cz-grown crystal (upper

left, Fig.1), unlike the typically yellow-coloured Ce-doped garnet, appeared colourless. Inductively coupled plasma mass spectrometry confirmed the presence of Ce. XANES analysis suggests this absence of coloration arises from the predominance of Ce<sup>4+</sup> over Ce<sup>3+</sup>. Detailed results of the scintillation properties will be presented at the conference.



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# OFZ GROWTH OF LuHfO:Ce SINGLE CRYSTALS

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While the performance of already applied scintillators have continuously been improving, scientific research focuses also on finding new scintillating materials and further characterizing less-known materials. This applies also in the field of ionizing radiation detection. One of the potential – although no yet fully investigated – systems is the pseudobinary  $\text{Lu}_2\text{O}_3\text{--HfO}_2$  system. Due to the high atomic masses of both lutetium and hafnium and the resulting high densities of their mixed oxides, these materials – with density close to  $10\text{ g/cm}^3$  – might be promising matrices with a high stopping power and radiation stability, and therefore suitable for high energy physics. The drawback for their processing is their high melting temperature (up to  $2700^\circ\text{C}$ ). These materials have so far been prepared mostly in the form of ceramics or powder, with only few reports of successful synthesis of transparent ceramics (via HIP or SPS). The compounds of the general formula  $\text{RE}_2\text{Hf}_2\text{O}_7$  crystallize in different structural types, depending on the crystal radius of the rare earth cation: either as a cubic pyrochlore ( $Fm\text{--}3m$  space group) or in a defect fluorite structure ( $Fd\text{--}3m$  space group). The smallest cations favour the formation of yet another, so-called  $\delta$ -phase of  $\text{RE}_4\text{Hf}_3\text{O}_{12}$  stoichiometry and  $R\text{--}3$  space group.

In this work, we investigated the possibility to use the optical floating zone technique (OFZ) to grow single crystals of Lu-Hf mixed oxides. First, ceramic rod-shaped preforms were prepared by a conventional solid-state reaction from oxides. These rods were then recrystallized by the OFZ.

We focused first on the growth of samples with ‘pyrochlore’  $\text{Lu}_2\text{Hf}_2\text{O}_7$  and congruent  $\text{Lu}_2\text{Hf}_3\text{O}_9$  compositions. Then, we investigated the Ce-doped crystals of both stoichiometries with focus on their optical properties.

The phase composition of the obtained solidified melts was characterized by XRD and Raman spectroscopy. Their optical characteristics were assessed via radioluminescence and photoluminescence as well as luminescence decay kinetics.

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**Wednesday 8<sup>th</sup>**

**Synthesis and Luminescence  
of Nanoparticles**

# GLASS WAVEGUIDES FUNCTIONALIZED AT THE NANOSCALE

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In the current Age of Light, Photonics is a key enabling technology for different segments: life science and health, industrial manufacturing and quality, information and communication, emerging light, electronics and displays [1]. In this context, glass-based optical waveguides play an essential role for the development of optical devices, *i.e.* the heart elements of photonic applications.

Among the various approaches explored to improve the performance of these applications, this presentation will focus on the incorporation of nanoparticles into planar waveguides and optical fibers. The idea of incorporating nanoparticles into a waveguide runs counter to the conventional wisdom, which holds that the glass should be as homogeneous as possible to enhance its transparency. However, this approach presents new opportunities. For example, regarding optical properties, the incorporation of luminescent ions (rare-earth or transition metals ions) into nanoparticles allows for the engineering of their luminescence properties through the selection of the composition and structure (amorphous or crystalline) of their immediate environment. Nanoparticles, such as SnO<sub>2</sub>, can also be used to promote the excitation of luminescent ions via energy transfers or to improve the photorefractivity of silica glass [2]. More surprisingly, recent years have shown that light scattering induced by the presence of nanoparticles opens up new possibilities both for lasers (particularly for the development of random lasers and the spectral narrowing of laser lines) and for sensors, notably through the development of new architectures [3]. Open questions and prospects will be discussed at the end of the presentation.

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# Efficient Strategies for Producing Cr<sup>4+</sup>-Doped YAG Nanoparticles

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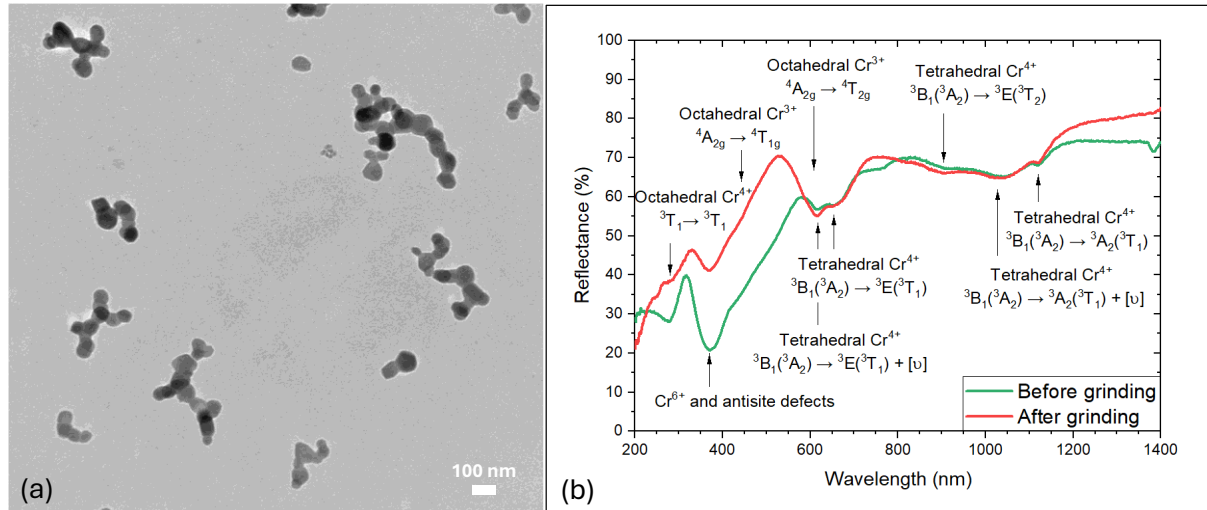
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Developing efficient infrared (IR) photonic components requires materials combining strong saturable absorption or broadband emission with an ability to be integrated on photonic platforms. Chromium-doped yttrium aluminum garnet (YAG:Cr<sup>4+</sup>) is a well-known saturable absorber around 1  $\mu\text{m}$  and an attractive near-infrared emitter (1.1–1.6  $\mu\text{m}$ ).<sup>[1]</sup> For this kind of application, Cr<sup>4+</sup> ions need to be located in the tetrahedral sites of YAG lattice (when substituting for Al<sup>3+</sup> ions, chromium ions can occupy both tetrahedral and octahedral sites). High temperature is generally required for Cr<sup>4+</sup> ions to occupy the desired tetrahedral sites, resulting in either single microcrystals or transparent ceramics.<sup>[2]</sup> Here, YAG:Ca<sup>2+</sup>,Cr<sup>4+</sup> nanoparticles and nanoaggregates are obtained through two soft-chemistry routes: the Pechini process and glycothermal synthesis. This latter way involves the elaboration of a highly porous aerogel.<sup>[3]</sup>

In both cases, optimized samples are characterized by the presence of the characteristic Cr<sup>4+</sup> absorption bands, together with a broad near-infrared emission band under 980 nm excitation. Interestingly, transient signatures of Cr<sup>6+</sup> species appear during annealing treatments, suggesting a more complex oxidation pathway than previously assumed. We propose an alternative mechanism involving the temporary formation of Cr<sup>6+</sup> ions and their subsequent reduction to Cr<sup>4+</sup>, probably directly in tetrahedral sites.

Pechini-derived powders are constituted of aggregated nanosized particles whereas the aerogel can lead, through grinding, to Cr<sup>4+</sup>-doped YAG nanoaggregates (~200 nm) that retain their tetrahedral Cr<sup>4+</sup> optical signatures (Figure 1). These aerogel-derived nanoaggregates have been redispersed in ethanol and saturable absorption measurements at 1064 nm have been carried out: a 17 % modulation depth, comparable to monolithic YAG:Cr<sup>4+</sup> crystals, has been attained, confirming the strong potential of these nanostructures as compact saturable absorbers. Finally, as a proof-of-concept for device integration, the nanoaggregates were incorporated into an organic–inorganic sol-gel matrix to fabricate transparent nanocomposite coatings via dip-coating and drop-casting. The coatings exhibit a clear Cr<sup>4+</sup> emission band under 980 nm excitation, showing the successful transfer of the nanoaggregate optical properties to the thin-film platform.

This work demonstrates new strategies for achieving highly doped YAG:Cr<sup>4+</sup> nanomaterials while maintaining optical quality and device compatibility. In particular, the glycothermal route shows that the combination of solvothermal synthesis, aerogel processing, and controlled oxidation provides a versatile pathway for engineering transition-metal-doped garnets for integrated optics, compact lasers, telecommunication devices, and IR photonics.



**Figure 1.** (a) TEM picture of a ground YAG:Cr<sup>4+</sup> annealed aerogel and (b) UV-Vis-NIR DRS spectra of the same annealed aerogel before and after grinding.

#### ACKNOWLEDGMENT

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# CESIUM LEAD HALIDE NANOCOMPOSITE SCINTILLATORS FOR RADIATION DETECTION

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In recent years cesium lead halide perovskite nanocrystals became attractive materials for many applications, including that of radiation detection. In this particular field their ultrafast excitonic emission on one hand shows perspective to boost the performance of medical imaging detectors based on the time-of-flight technique.<sup>1</sup> On the other hand, their narrow, spectrally tunable emission is recently being exploited for chromatic calorimetry in high energy physics. Within this innovative concept, the segmented detector would be able to reconstruct the longitudinal profile of the electromagnetic shower.<sup>2</sup> However, the practical usage of nanocrystals requires dealing with two major issues. Poor chemical stability can be overcome by their incorporation in a suitable, e.g. polymer, matrix to form nanocomposite. Low stopping power calls for fabrication of nanocomposites with the highest possible nanocrystalline loading keeping their reasonable level of transparency.

We focus on synthesis routes for cesium lead halide nanocrystals embedded in polystyrene enabling high nanocrystalline loading up to 40% while keeping their favourable luminescent properties and reasonable level of transparency. To achieve this, we use advanced polymerization techniques with copolymerizable ligands and fluoride nanocrystal surface passivation. The latter improves the stability of the ligand shell enabling to perform the nanocomposite synthesis up to 110 °C without deterioration of the nanocrystal properties. The developed approach can also be tuned to other polymer matrices which may show improved radiation resistance.

We study synthesis, structural and optical characteristics including the timing performance of cesium lead bromide and cesium lead bromo-chloride nanocrystals embedded in plastic matrices. Prepared nanocomposites feature significantly better time resolution under X-rays with respect to the currently used standalone conventional scintillators, such as LYSO:Ce crystal as well as considerable improvement compared to previously reported results for cesium lead bromides embedded in polystyrene.<sup>3</sup>

This work was carried out in the frame of the Crystal Clear Collaboration and was funded by the Grant Agency of the Czech Technical University in Prague, grant No. SGS23/189/OHK4/3T/14, by a grant from the Programme Johannes Amos Comenius under the Ministry of Education, Youth and Sports of the Czech Republic SENDISO project No. CZ.02.01.01/00/22\_008/0004596, Horizon Europe EIC Pathfinder project UNICORN (GA 101098649) and the grant LM2023040 Research Infrastructure for Experiments at CERN

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# SCINTILLATING COMPOSITES OF NANOCRYSTALLINE GARNETS AND POLYSTYRENE

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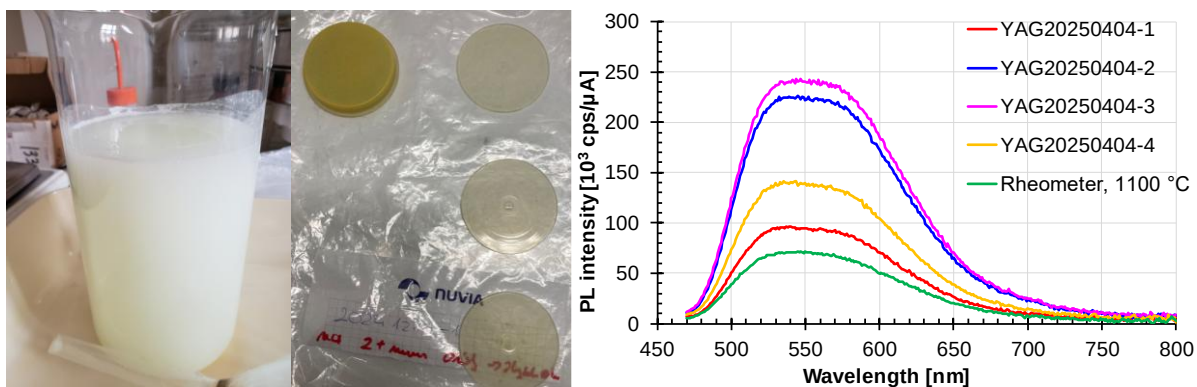
Scintillating nano-sized oxides can provide unique benefits in modern techniques for ionizing radiation detection. Ultrafast detection in e.g. ToF-PET requires a significant amount of scintillation photons within a few tens of ps from the interaction, which is hard to achieve with standard scintillators [1]. For example, the exciton luminescence in photochemical ZnO:Ga features ultrafast luminescence in near UV with a decay time in the hundreds of ps range and reasonable radioluminescence intensity [2]. Much slower, but more intense green luminescence of Ce-doped garnet materials (YAG, GGAG) can be utilized e.g. for medical imaging.

Beside their potential use as thin films or precursors for optical ceramics, the applicability of luminescent nano-oxides for ionizing radiation detection remains rather limited due to their powder or colloidal form. Heterostructure concepts that utilize such materials include e.g. the incorporation of nano-oxides into polymeric hosts [2], which are relatively cheap, easy to mass-produce and provide both reasonable structural rigidity, and machinability.

Scintillating oxide materials in nanocrystalline form, especially multi-component oxides, usually require annealing at higher temperatures to achieve sufficient luminescence intensity due to healing of defects and improvement of the charge carrier transport. However, the increased temperature negatively affects the morphology of particles by sintering, inducing intergrowth between grains and formation of very large clusters. This results in decreased transparency of heterostructure materials that lowers the applicability of such concepts for detection of ionizing radiation. Therefore, both the calcination or annealing and further treatments of the nano-oxides need to be improved upon for their incorporation into polymeric hosts.

In this work, the solid precursor for YAG:Ce prepared by photochemical synthesis in a pilot plant [3] was used as a model material for treatment optimization and incorporation methods into thermoplastic hosts.

The effect of calcination temperature of the microfiltered precursor xerogel (1100–1400 °C) was investigated in conjunction with the subsequent treatment by low-energy ball milling used to break the particle aggregates into the constituent grains or smaller particles. Wet milling was found to be essential, as the electrostatic charges produced by dry milling caused static cling (sticking) of the particles and limited the efficiency of size fractionation. Several different methods for incorporation of polystyrene (PS) were evaluated for transparency, luminescence intensity, presence of bubbles and real filling factor. These methods included mixing with PS dissolved in toluene, thermal polymerization of styrene-YAG:Ce mixtures, as well as mixing of YAG:Ce and PS pellets within a rheometer. Thorough drying and rheometer mixing of wet-milled YAG:Ce powder were found to provide the best properties of the thermoplastic heterostructure pressed into thin foils.



**Fig.** Left to right: aqueous dispersion of wet-milled YAG:Ce nanoparticles; thermally polymerized PS with YAG:Ce; photoluminescence emission spectra of YAG:Ce\_1400-PS and YAG:Ce\_1100-PS composite foils

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# SOL-GEL DERIVED LUMINESCENT $\text{Eu}^{3+}$ -DOPED $\text{YVO}_4$ POWDERS AND COATINGS

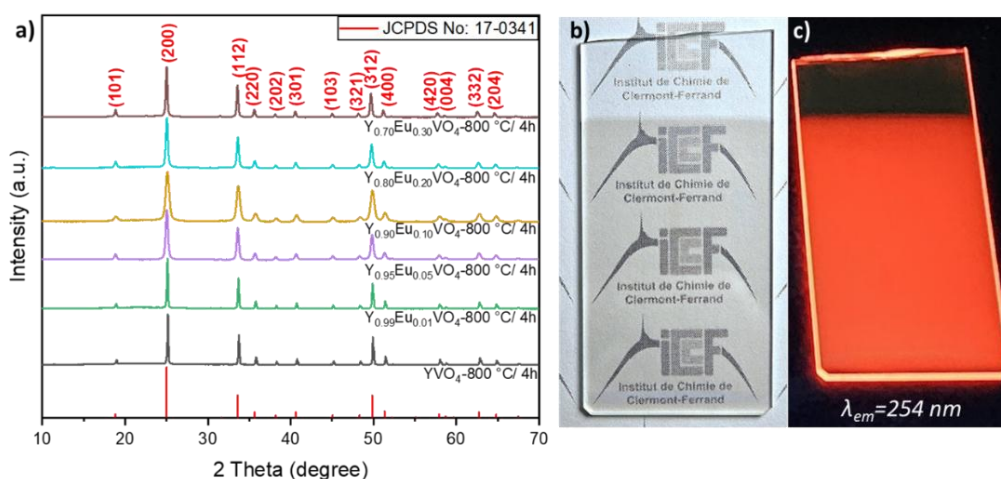
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Recent advances in optical and photonic devices have increased the demand for efficient luminescent materials in the form of size-controlled powders and uniform coatings [1]. In this context, research efforts focus on improving synthesis routes and processing methods of well-established host lattices rather than developing new material systems [2]. Europium-doped yttrium orthovanadate ( $\text{YVO}_4:\text{Eu}^{3+}$ ) remains a reference vanadate-based luminescent material due to its intense red emission upon UV excitation and high chemical stability [3].

In this work,  $\text{YVO}_4:\text{Eu}^{3+}$  materials were synthesized by an original sol-gel route using vanadium oxytrisopropoxide as the vanadium precursor and yttrium and europium chlorides as rare-earth sources. The resulting sols were either dried and sintered at 800 °C to result in crystallized powders or subsequently used to fabricate highly luminescent coatings by dip-coating deposition technique and annealing at 400°C, allowing the preparation of uniform and well-adherent thin films on glass substrate. The sol–gel method proves to be a highly promising technique, offering additional benefits such as low-temperature synthesis, uniform powder morphology, and homogeneous multicomponent coatings.

The structural and morphological studies of powders and coatings were conducted using X-ray diffraction (XRD), FT-IR and Raman spectroscopies as well as scanning electron microscopy (SEM). The XRD patterns confirm the formation of crystalline  $\text{YVO}_4:\text{Eu}^{3+}$  in all the case (Fig. 1a), while the visual appearance of the coating under daylight and UV light are shown in Fig. 1b and Fig.1c, respectively. Finally, the optical properties were recorded by photoluminescence and UV-visible spectroscopies. These results highlight the versatility of the sol–gel approach for producing  $\text{YVO}_4:\text{Eu}^{3+}$  luminescent powders and coatings.



**Fig. a)** XRD patterns of  $\text{YVO}_4$  with different  $\text{Eu}^{3+}$  concentrations, picture of prepared coating upon b) daylight, and c) UV light.

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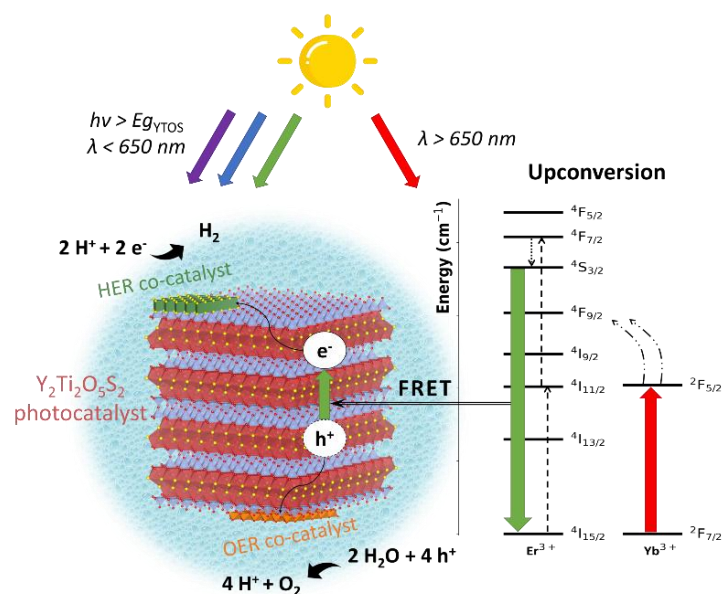
# UPCONVERTING DOPED OXYSULFIDE PHOTOCATALYST FOR THE PRODUCTION OF HYDROGEN VIA WATER SPLITTING

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Photocatalysis offers a sustainable route for solar fuel production by directly converting sunlight into chemical energy, knowing that Earth receives enough solar energy in one hour to meet the world energy consumption for an entire year<sup>1</sup>. Photocatalytic water splitting, utilizing sunlight to convert water into hydrogen and oxygen, is emerging as a promising method for producing green hydrogen. However, current solar-to-hydrogen energy conversion (STH) efficiencies remain below 5 %, necessitating further research into visible light-responsive photocatalysts<sup>2</sup>. Recently, it has been demonstrated that  $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_2$ , a narrow bandgap semiconductor, achieves stable photocatalytic water splitting under visible light when loaded with co-catalysts and with fine-tuned reaction conditions<sup>3</sup>. However,  $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_2$  can only absorb photons up to 650 nm, which represents only 50 % of the solar spectrum. Our project aims at incorporating an internal upconversion functionality via rare earth doping.  $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_2$  is a promising photocatalyst host material for rare earth ions because of its chemical stability and its low phonon energy ( $\sim 500 \text{ cm}^{-1}$  for oxysulfides), which reduces non-radiative multi-phonon relaxation between energy levels and increases the excited states lifetimes. Moreover, the ionic radius of  $\text{Y}^{3+}$  is similar to the one of most rare earth ions, avoiding large lattice distortion after doping. By integrating the upconverter directly into the photocatalyst oxysulfide matrix, atomic-level donor–acceptor contact shortens the energy-transfer distance, minimizing the interfacial losses<sup>4</sup>. In this configuration, the excited upconverter can either emit radiatively as usual or transfer energy non-radiatively via an efficient Förster resonance energy transfer (FRET) process, whose efficiency benefits from strong donor–acceptor spectral overlap and the short separation between them. By converting the low energy infrared photons into higher energy photons within the photocatalyst oxysulfide matrix, the material's STH efficiency could be enhanced by taking maximum advantage of the whole solar spectrum, including infrared photons.



**Fig.** Diagram of photocatalytic water splitting with the doped oxysulfide  $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_2:\text{Er}^{3+}, \text{Yb}^{3+}$

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The background of the slide is composed of various light gray, irregular geometric shapes, primarily pentagons and hexagons, arranged in a non-repeating pattern. These shapes are separated by thin white lines, creating a mosaic-like effect. The overall aesthetic is clean and modern.

**Wednesday 8<sup>th</sup>**

**Scintillators III**

# FROM POWDER TO BULK SINGLE CRYSTALS: UNLOCKING RARE-EARTH BINARY SULFIDES FOR SCINTILLATION AND LASER APPLICATIONS

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Sulfide-based luminescent materials have long attracted interest due to their distinctive optical properties [1], which complement those of oxides. Narrower band gaps, lower phonon energies, and enhanced covalency arising from diffuse sulfur orbitals enable unique optical functionalities, making sulfides promising candidates for scintillators, lasers, and other advanced photonic applications. Structurally, the large ionic radius of sulfur favors low-symmetry crystal frameworks, providing additional flexibility for tailoring optical properties. Despite these advantages, bulk crystal growth of sulfides remains challenging. High melting points, combined with chemical reactivity toward oxygen, moisture, and conventional crucible materials, have historically limited preparation to powders or small crystallites. Recent advances in high-temperature processing under controlled sulfidizing atmospheres are overcoming these limitations, enabling the growth of large, high-quality rare-earth sulfide single crystals.

In this contribution, we review the growth of selected bulk single crystals of  $\text{Ln}_2\text{S}_3\text{:RE}$  ( $\text{Ln} = \text{Y, La, Gd, Lu}$ ;  $\text{RE} = \text{Pr, Ce, Nd, Dy}$ ), with an emphasis on strategies that optimize crystal quality and reproducibility. We highlight  $\text{Ce}^{3+}$ - and  $\text{Pr}^{3+}$ -doped crystals for fast scintillation applications, exhibiting ultra-fast decay times below 1 ns [2], and  $\text{Nd}^{3+}$ - and  $\text{Dy}^{3+}$ -doped crystals for mid-infrared solid-state lasers, leveraging the low phonon energy to access 4f–4f emission lines often unavailable in oxides [3]. Experimental insights are complemented by advanced density functional theory calculations, including density of states and band-structure analyses, to rationalize the observed optical properties.

By combining growth strategies, luminescence characterization, and theoretical modeling, this review provides a comprehensive perspective on current capabilities and emerging directions in the field of single-crystal sulfide research.

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## ACKNOWLEDGEMENT

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# Electronic Structure Elucidation of Oxide Luminescent Materials Using Synchrotron Radiation

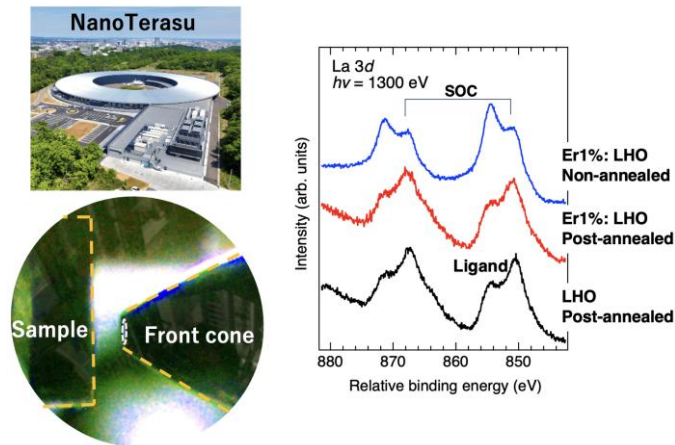
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Wide-bandgap oxide materials, such as ZnO and  $\text{La}_2\text{Hf}_2\text{O}_7$  (LHO), are of paramount importance in the field of luminescence<sup>1,2,3</sup>. A comprehensive understanding of their electronic structures is essential, as it directly governs the recombination dynamics of electrons and holes. While synchrotron radiation-based photoelectron spectroscopy (PES) is a highly anticipated and powerful tool for probing these electronic states, accurate measurements of wide-bandgap oxides are often severely obstructed by surface sensitivity and charging effects typical of insulators.

In this study, we report the precise elucidation of the electronic structure evolution in oxide luminescent materials by leveraging high-brightness synchrotron radiation and advanced experimental methodologies. As illustrated in Fig. 1, by utilizing the ambient pressure PES system at NanoTerasu—a newly constructed synchrotron radiation facility commissioned in 2024—we overcame charging issues and measured distinct electronic structures even for highly insulating LHO crystals. Our results demonstrate that the observed electronic variations originate from specific ligand structures, revealing them as crucial factors governing the luminescence process. These fundamental insights offer the robust basis for the design of novel optical materials.



**Fig. 1** PES measurements of LHO crystals achieved using the ambient pressure PES system at NanoTerasu.

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# **YPO<sub>4</sub>:Ce nanoscintillators for a novel biological application : triggering biorthogonal photoclick reactions *in vivo***

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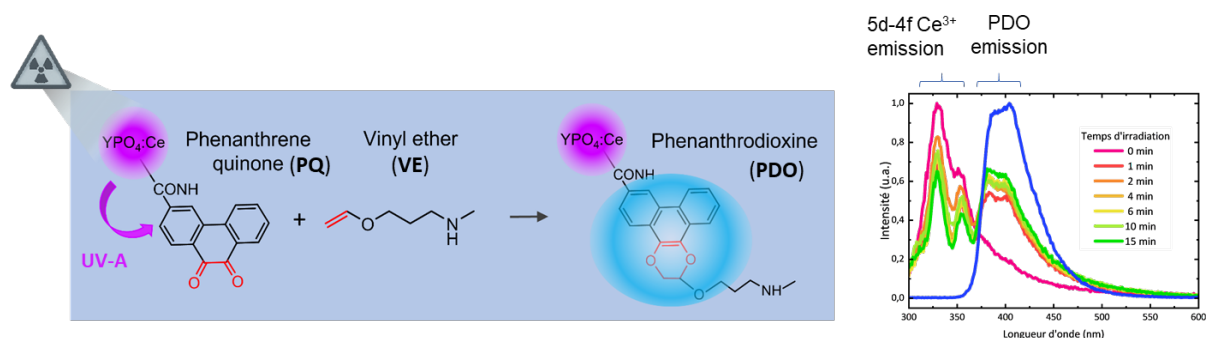
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Nanoscintillators emerged in the early 2000s and have rapidly evolved from materials of purely fundamental interest into versatile tools for a wide range of applications. Beyond radiation detection, their nanoscale dimensions make them particularly well suited for biological uses, notably in cancer theranostics. We have recently reviewed the field and identified five major theranostic applications of nanoscintillators [1]. In this presentation, we propose an additional and high potential biological application: the *in vivo* triggering of a bioorthogonal photoclick reaction.

Click chemistry refers to a class of simple, fast, and highly selective reactions that efficiently join molecular building blocks under mild conditions [2]. Bioorthogonal photoclick chemistry is a light-activated click reaction that can proceed inside living systems without interfering with native biochemical processes, enabling precise spatial and temporal control of biomolecule labeling [3]. Triggering such reactions *in vivo* therefore holds tremendous potential.

In this presentation, we will describe the strategy we are developing to trigger a bioorthogonal photoclick reaction using nanoscintillators (Figure 1). Cerium-doped YPO<sub>4</sub> nanoscintillators were synthesized *via* a microwave-assisted hydrothermal synthesis and subsequently grafted with the phenanthrequinone (PQ) photoclickable moiety. We demonstrate that the photoclick reaction yielding the blue-emitting phenanthrodioxine (PDO) can be successfully triggered at the surface of the nanoscintillators, highlighting their potential as remote activators of bioorthogonal chemistry *in vivo*.



**Figure 1:** Objective: triggering the biorthogonal photoclick reaction between phenanthrenequinone (PQ) and a vinylether (VE) to yield phenanthrodioxine (PDO) using a nano-scintillator emitting in the UV-A spectral range (left) and photoluminescence spectra obtained after various irradiation times of YPO<sub>4</sub>:Ce nanoparticles grafted with PQ in a solution containing VE.

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# Optical and Scintillation Properties of Undoped and Rare-Earth Doped $\text{Lu}_3\text{TaO}_7$ Single Crystals

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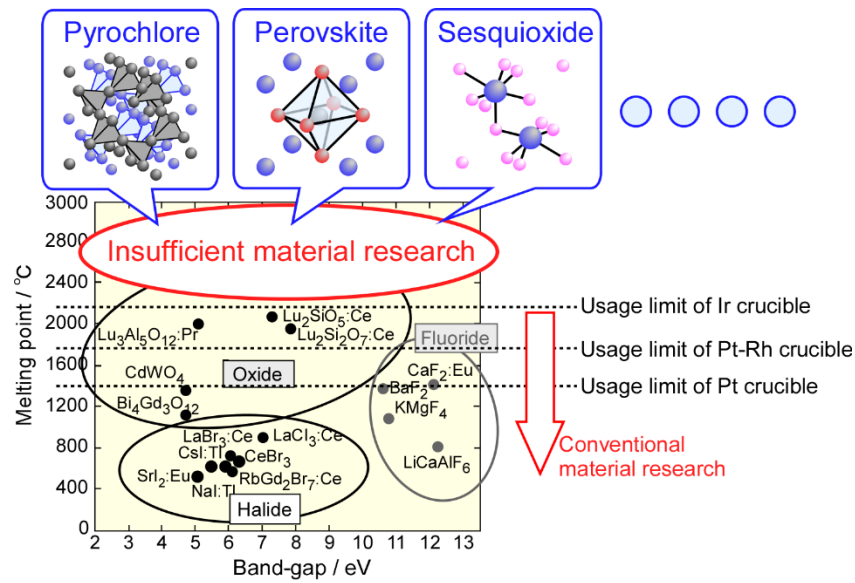
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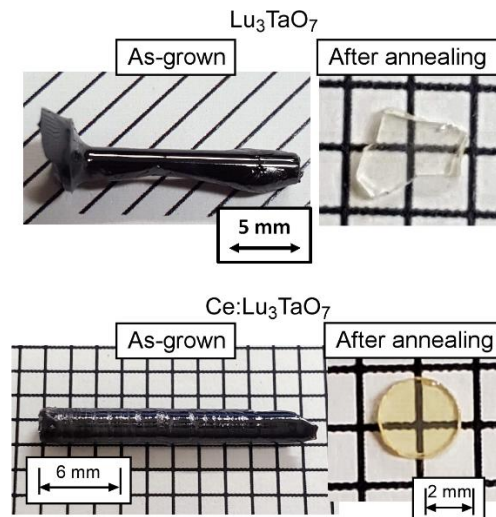
Bulk single crystals of many oxide materials have been grown from the melt using melt-growth techniques such as the Czochralski(Cz), Bridgman (BS) and Floating Zon (FZ) methods. The micro-pulling-down ( $\mu$ -PD) method is also one of the melt-growth techniques that uses a crucible with a die at the bottom to grow a fiber single crystal efficiently. Generally, oxide single crystals with relatively high melting point (m.p.) have been grown using Platinum (Pt) and Iridium (Ir) crucibles in the  $\mu$ -PD method. On the other hand, these precious metal crucibles cannot be used over 2200°C due to the limitation of use, although the high temperature range contains attractive materials as functional single crystals (Fig. 1). Therefore, we have developed a novel crystal growth method for oxide single crystals with m.p. over 2200°C [1], which uses a tungsten (W) crucible and deoxygenated insulator. Single crystals of  $\text{La}_2\text{Zr}_2\text{O}_7$  (m.p.: 2283°C) and  $\text{La}_2\text{Hf}_2\text{O}_7$  (m.p.: 2418°C) could be grown by the advanced crystal growth method, and Eu- or Er-doped  $\text{La}_2\text{Zr}_2\text{O}_7$  and  $\text{La}_2\text{Hf}_2\text{O}_7$  single crystals showed emission peaks derived from the dopant ions in the photoluminescence and X-ray radioluminescence spectra [1-3]. In this study, we tried to grow undoped  $\text{Lu}_3\text{TaO}_7$  (m.p.: 2380°C) and Rare-Earth (RE) doped  $\text{Lu}_3\text{TaO}_7$  single crystals using the advanced crystal growth method.  $\text{Lu}_3\text{TaO}_7$  has extremely high density of 9.7 g/cm<sup>3</sup>, and is expected to be used as a scintillator with high stopping power for  $\gamma$ -ray.

Undoped and RE-doped  $\text{Lu}_3\text{TaO}_7$  single crystals were grown by the advanced  $\mu$ -PD method using the W crucible with  $\phi 3$  or 5 mm die and deoxygenated  $\text{ZrO}_2$  insulators. Crystal growth was performed in Ar or Ar+2%H<sub>2</sub> atmosphere, and pulling-down rate was 0.01~0.1 mm/min. Grown crystals were annealed in air at 1000°C to compensate oxygen defects generated during the crystal growth.

Figure 2 shows as-grown and post-annealed crystals of undoped and Ce-doped  $\text{Lu}_3\text{TaO}_7$ . As-grown crystals are black due to the oxygen defect. Therefore, the crystals became transparent after the post-annealing in air. They showed a broad emission peak around 330 nm in the photoluminescence and X-ray radioluminescence spectra. In the presentation, details of optical and scintillation properties of undoped and RE-doped  $\text{Lu}_3\text{TaO}_7$  single crystals will be reported.



**Fig.1** Relationship between band-gap and melting point for oxide, fluoride, and halide scintillator single crystals with usage limit of crucibles.



**Fig.2** As-grown and post-annealed crystals of undoped and Ce-doped  $\text{Lu}_3\text{TaO}_7$ .

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# Effect of magnesium codoping on vacancy type defects in $\text{Y}_3\text{Al}_2\text{Ga}_3\text{O}_{12}:\text{Ce}$ garnet scintillators studied by positron annihilation lifetime spectroscopy

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As is well-known, magnesium codoping is an effective way of improving scintillation properties of cerium doped multicomponent garnets. The effects are different between  $\text{Gd}_3\text{Al}_2\text{Ga}_3\text{O}_{12}:\text{Ce}$  (GAGG:Ce) and  $\text{Y}_3\text{Al}_2\text{Ga}_3\text{O}_{12}:\text{Ce}$  (YAGG:Ce). Both exhibits a shortening of the luminescence decay time, but only YAGG:Ce shows an enhancement in light yield [1,2]. Several models have been proposed to explain the mechanism of magnesium codoping. However, it remains unclear. A new approach is needed to solve this issue. For this purpose, we have investigated the formation of vacancy type defects in YAGG, YAGG:Ce, and YAGG:Ce, Mg crystals using positron annihilation lifetime spectroscopy (PALS). So far, PALS studies have been carried out for GAGG:Ce [3] and  $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}$  (LuAG:Ce) [4]. Positron annihilation lifetimes were compared to clarify the effect of magnesium codoping on non-stoichiometric compositions of the host garnet crystals.

From the analysis of PALS spectra for YAGG and YAGG:Ce crystals, positron annihilation lifetimes and relative intensities changed remarkably with cerium doping. This result contrasts with the findings that positron annihilation lifetimes and relative intensities were almost unchanged for GAGG and GAGG:Ce crystals. This suggests that cerium doping changes the lattice site of vacancy type defects in YAGG. It is particularly worthwhile that cerium doping reduced the relative intensity of the long-lived component in PALS spectra. In YAGG, more cerium ions occupy the positions of 16a and 24d lattice sites than in GAGG. In this case, tetravalent cerium ions may be preferred at these positions to achieve the size match as possible.

As reported previously, magnesium codoping into YAGG:Ce caused a shortening of the scintillation decay time and an enhancement of the light yield. It reduced vacancy-type defects at the positions of 16a and 24d lattice sites, because magnesium ions are preferentially introduced at these positions. Ce-L<sub>III</sub> edge XANES spectra revealed that magnesium codoping relatively enhances the trivalent cerium L<sub>III</sub> peak. This implies that magnesium ions effectively act as charge compensators instead of tetravalent cerium ions. Hence, the concentration of trivalent cerium ions increases with magnesium codoping, resulting in enhanced light yield in YAGG:Ce, Mg.

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# OPTICAL SPECTROSCOPY AND TIME-RESOLVED LUMINESCENCE OF SWIFT HEAVY-ION IRRADIATED WIDE-BANDGAP SCINTILLATORS

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Wide-bandgap scintillators are core components of detectors for high-energy physics,  $\gamma$ -spectrometry, medical imaging, safety systems, space instrumentation, and industrial monitoring. In many of these applications, the detector is exposed to accumulated radiation dose, and the resulting degradation is governed not only by the loss of optical transparency but also by changes in the scintillation time profile. Swift heavy-ion irradiation generates stable defect populations (color centers, defect aggregates) that introduce additional carrier trapping and non-radiative losses, reshaping energy conversion and transfer to activator centers.

In this work, we investigate radiation effects in technologically relevant Ce-activated wide-bandgap scintillators, focusing on  $\text{Gd}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$  (GAGG) and  $(\text{Lu,Y})_2\text{SiO}_5:\text{Ce}$  (LYSO) crystals irradiated by 156 MeV Xe ions over a fluence range spanning isolated-track to track-overlap conditions. Complementary reference materials (e.g.,  $\text{Y}_3\text{Al}_5\text{O}_{12}$  (YAG),  $\text{Tb}_3\text{Ga}_5\text{O}_{12}$  (TGG)  $\text{PbWO}_4$ ,  $\text{PbF}_2$ ) are used to benchmark defect-related optical signatures.

The key element of the study is the determination of time parameters of  $\text{Ce}^{3+}$  luminescence under excitation-energy selectivity across a broad photon-energy range (4–1200 eV). This enables a comparative analysis of  $\text{Ce}^{3+}$  decay kinetics under (i) direct  $\text{Ce}^{3+}$  excitation, (ii) excitation in the excitonic / near-band-edge region, and (iii) high-energy excitation, where primary relaxation and carrier thermalization pathways differ substantially. Time-resolved measurements are performed at dedicated luminescence endstations at large-scale facilities, including photoluminescent setup at FinEstBeAMS beamline of MAX IV synchrotron [1,2] and SUPERLUMI setup at P66 beamline of PETRA III at DESY [3], providing excitation-selective kinetic benchmarking across irradiation doses.

Induced optical absorption bands are observed in irradiated crystals and are consistent with the formation of F-type centers, which correlate with additional non-radiative losses during charge-carrier thermalization and with degradation of excitation spectra in the VUV range [4,5]. The obtained fluence-dependent trends of  $\text{Ce}^{3+}$  temporal characteristics in GAGG and LYSO constitute the central outcome of this work and provide a direct quantitative probe of defect-controlled energy conversion in irradiated scintillators, complementing steady-state intensity/absorption metrics.

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**Wednesday 8<sup>th</sup>**

**Thin films**

# AMORPHOUS THIN FILMS : THE KEY TO GRAVITATIONNAL WAVE DETECTION

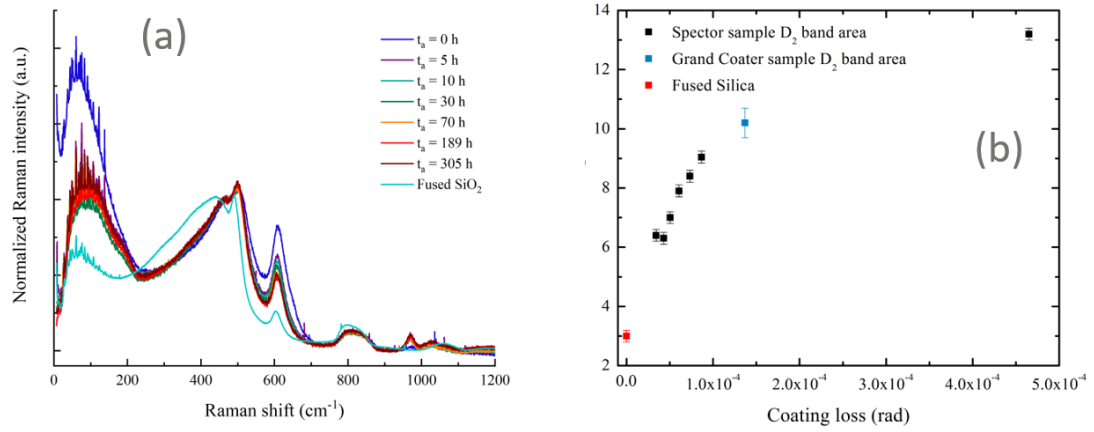
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On February 11, 2016, researchers from the LIGO-Virgo collaboration announced that the first direct detection of gravitational waves (GW) had taken place a few months earlier on September, 2015. This first signal, corresponding to the merger of two black holes, opened the door to a better understanding of the universe and its formation. There are 4 GW detectors in the world: 2 in USA, 1 in Japan and Virgo in Europ. A GW is a distortion of the space-time geometry generated by masses in movement. As a consequence, gravitational wave leads to very tiny variation of distances and laser interferometry is the most suitable technic to detect these very tiny variations. When a GW passes through the detector, it alternatively shrinks an arm while stretching the other one. The amplitude of GW is very small so the sensitivity of the detector should be very good. The lower the sensitivity, the better. To improve this detection limit, noises should be decreased. The different fundamental noises limiting the detection come from the laser, the injection and the detection. This presentation will focus on the thermal noise, coming from the mirrors of the detector called “test masses”. Thermal noise of a material leads to modification of the surface driven by temperature which is very detrimental for the detection. GW detector mirrors are Bragg mirrors composed of alternatively high index and low index amorphous oxide coatings deposited on a 20cm thick silica substrate by ion beam sputtering. The thermal noise coming from the 6µm thick coatings is much higher than the 20cm thick substrate. At the moment, the low index coating is silica and the high index is titania doped tantala but research is being conducted within the international collaboration to get a better high index material. This presentation will focus on silica which is in its bulk form the material having the lowest thermal noise at ambient temperature. The aim of this presentation is to provide insights on the structural origin of this noise<sup>1</sup>. The structure at short and mid-scale (probed by Raman spectroscopy) of bulk silica and those of silica thin film will be compared and the impact of annealing will be presented. In parallel, the mechanical loss which are directly linked to thermal noise will be also reported.



**Fig. 1** (a) Raman spectra of SiO<sub>2</sub>: comparison of the as-deposited coating ( $t_a = 0$  h) to fused silica and thermally-treated coating with different cumulative annealing time  $t_a$  (b) correlation between normalized D<sub>2</sub> area (D<sub>2</sub> is the spectroscopic signature near 600 cm<sup>-1</sup>) and coating loss (the blue point is from another IBS silica film with different deposition parameters and the red one is from bulk silica)

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# PULSED LASER ABLATED SnO<sub>2</sub>:Eu THIN FILMS FOR LUMINESCENT TRANSPARENT CONDUCTING OXIDES

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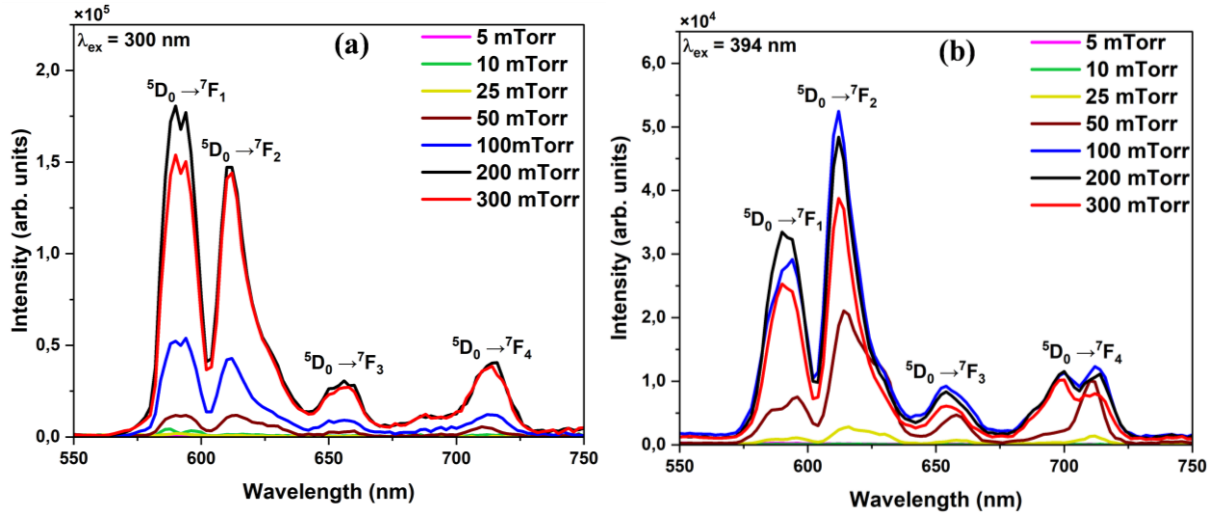
Transparent conducting oxides (TCOs) are materials that combine high optical transparency in the visible range with electrical conductivity. These properties make TCOs essential components in a range of optoelectronic applications such as touch-screen flat-panel displays, smart windows and solar cells [1]. TCO materials are not generally luminescent in the visible range, but adding this functionality may allow niche applications such as luminescent touchscreens or buttons. In this work we produced SnO<sub>2</sub>:Eu<sup>3+</sup> thin films using pulsed laser ablation and evaluated them for potential application as luminescent TCOs.

Powder SnO<sub>2</sub> doped with 2 mol% Eu was produced using a solution combustion process [2]. After annealing at 600 °C for 2 h in air, the powder was pressed into a pellet to act as a target for producing the thin films using pulsed laser ablation. The target was ablated using 30 000 pulses from a frequency quadrupled Nd:YAG laser (wavelength 266 nm, beam diameter 1.58 mm, energy 50 mJ, duration 8 ns) under varying background oxygen (O<sub>2</sub>) gas pressures ranging from 5 mTorr to 300 mTorr, producing films on quartz substrates held 4.5 cm away kept at a constant temperature of 350 °C.

Scanning electron microscopy of cross-sections of the films, as well as X-ray photoelectron spectroscopy depth profiles obtained by Ar<sup>+</sup> ion sputtering, showed that the thicknesses of the films varied between 1–2.5 µm. The variation was not correlated to the background O<sub>2</sub> pressure, nor was it consistent between the two measurement methods, so the variation was attributed to the films having non-uniform thickness over the substrate surface. Scanning electron microscopy of the film surfaces showed a transition from smooth to rough as the O<sub>2</sub> background pressure increased to 50 mTorr and above. This was confirmed by atomic force microscopy measurements of the mean square surface roughness values which increased from 0.81 nm for 5 mTorr, to 2.9 nm for 50 mTorr and 37 nm for 300 mTorr. Consistent X-ray diffraction patterns were obtained from the samples having greater surface roughness (O<sub>2</sub> background pressure of 100, 200 and 300 mTorr), although the peak intensities varied from the powder sample which was consistent with tetragonal SnO<sub>2</sub> (JCPDS 41-1445). The smoother films showed severe but inconsistent preferred orientation, while in the case of the lowest O<sub>2</sub> background pressure (5 mTorr) there was a broad band near 30° which has been attributed to amorphous SnO [3].

Optical transmission measurements were made between 300 – 800 nm. In general, the transmission increased with increasing wavelength for all the samples. The smoother samples produced at lower O<sub>2</sub> background pressures exhibited interference fringes which were absent from the samples having greater surface roughness. However, the samples produced at O<sub>2</sub> background pressures of 25 mTorr or less had poor transmission (less than 60% at 400 nm) making them unsuitable for TCO applications. The samples prepared with O<sub>2</sub> background pressures of 50, 100 and 200 mTorr had good transmission above 80% in the range 500-700 nm, although the transmission decreased when the O<sub>2</sub> background pressure increased to 300 mTorr. Photoluminescence excitation spectra showed a broad charge transfer band centred near 300 nm as well as numerous sharp *f-f* transitions characteristic of Eu<sup>3+</sup> ions, most prominently the <sup>7</sup>F<sub>0</sub> – <sup>5</sup>L<sub>6</sub> transition with corresponding wavelength 394 nm. Emission of the

films excited at 300 nm and 394 nm are shown in (a) and (b) of the figure. The general trend was for stronger luminescence from the samples prepared under greater O<sub>2</sub> background pressure, particularly 100 mTorr and above. Since there was no systematic change in the film thickness, this is attributed to the film characteristics. X-ray photoelectron spectroscopy measurements showed an increase in O:Sn elemental proportion for the films from 1.37 for 5 mTorr to 1.82 for 300 mTorr, revealing an oxygen deficiency in the films prepared under lower O<sub>2</sub> background pressure. Therefore oxygen vacancies in films produced at lower O<sub>2</sub> background pressure may be responsible for luminescence quenching.



**Fig.** Emission spectra of 2 mol% Eu<sup>3+</sup> doped SnO<sub>2</sub> thin films with excitation wavelengths of (a)  $\lambda_{ex} = 300$  nm and (b)  $\lambda_{ex} = 394$  nm, for pulsed laser deposition background O<sub>2</sub> pressures ranging from 5 to 300 mTorr.

The photoluminescence produced when exciting at 300 nm has maximum intensity near 587 nm corresponding to the  $^5D_0 - ^7F_1$  magnetic dipole transition. This transition is generally dominant when Eu<sup>3+</sup> ions occupy centrosymmetric sites. Since the Sn<sup>4+</sup> ion in tetragonal SnO<sub>2</sub> is at a centrosymmetric site, this indicates that the luminescence originates from mostly Eu<sup>3+</sup> ions substituting the host lattice cations. However, direct *f-f* excitation of the Eu<sup>3+</sup> ions using a wavelength of 394 nm produces luminescence where the  $^5D_0 - ^7F_2$  electric dipole transition corresponding to 612 nm dominates, which shows that Eu<sup>3+</sup> ions also occur at non-centrosymmetric sites, e.g. associated with defects or at grain boundaries or surfaces.

Electrical 4-point probe measurements showed the best conductivity (lowest sheet resistance  $3.89 \times 10^4 \Omega/\square$ ) for the film deposited at an intermediate O<sub>2</sub> background pressure of 50 mTorr. Considering the goals of transparency, conductivity and luminescence, films produced using pulsed laser ablation with a background O<sub>2</sub> pressure in the range 50 – 100 mTorr show the best potential for luminescent TCO applications.

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# ELECTRO-INDUCED LIGHT EMISSION IN HETEROSTRUCTURES OF TRANSPARENT OXIDES AND D- $\pi$ -A QUINOLINE DERIVATIVES

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Transparent metallic oxides coupled with organic semiconductors have increasing possibilities for applications in optoelectronics. Thin film heterojunctions of semiconductor metallic oxides, usually n-type even in the undoped form, paired as a heterostructure with quinoline derivatives (QD), organic materials that may present p-type conduction characteristics, lead to diode-like rectifying characteristics, which can be exploited to provide electroluminescence in the blue range. The QD used in this communication is the molecule 4-(6-(diethylamino)-4-phenylquinolin-2-yl) benzoic acid, which is solubilized in organic solvents (acetone and tetrahydrofuran - THF) for deposition via spin-coating. This organic compound is a D- $\pi$ -A molecule where ligands as diethylamine and phenol act as electron donors. On the other hand, the presence of benzoic acid, which exhibits 2 oxygen atoms, introduces electron acceptor nature for some parts of the molecule.

Fig. 1 displays some relevant results related to this communication. Main fig. 1 shows current -voltage (I-V) results for two heterostructure formed by QD and the transparent semiconductor tin dioxide (SnO<sub>2</sub>). Increase in intensity of electric current is observed in the forward bias regime after the threshold voltage of 14 V, for the DQS01 device (QD dissolved in acetone), and a threshold voltage of 10 V for the DQS02 device (QD in THF). Conduction is more effective for the device where the QD has been dissolved in THF, but the rectification is more pronounced (reverse polarization) in the device with QD dissolution in acetone. Anyway, the diode-like behavior is quite evident, which means that the p-type nature of the QD molecule is dominant in this situation. It is also interesting to mention that this sort of heterostructure has provided higher interfacial conduction when biased parallel to the interface barrier, when compared to individual layers [1]. Thin films of undoped titanium dioxide (TiO<sub>2</sub>) and QD were also arranged in a heterostructure, with data shown in the superior inset of fig. 1. Two data series were taken, and the diode behavior is more evident for the second data series, with a forward threshold bias of about 5 V. When negatively polarized, the rectifying behavior is seen, with a reverse breakdown at about 8 V. When the TiO<sub>2</sub> is doped with rare-earth ions, the observed *pn*-junction may lead to a LED behavior. Results displayed in the inferior inset of fig. 1 reveals electroluminescence for Yb-doped TiO<sub>2</sub>/QD with a blue band and peak about 443 nm in good agreement with the diode-like behavior as observed in the superior inset [2].



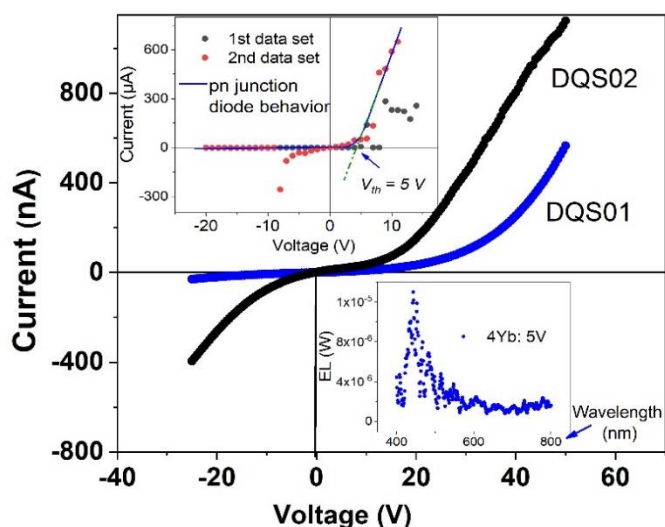


Figure 1:  $I_xV$  characteristics for a  $\text{SnO}_2/\text{DQ}$  device were the DQ is dissolved in acetone (DQS01) and THF (DQS02). Superior inset:  $I_xV$  for a  $\text{TiO}_2/\text{DQ}$  device. Inferior inset: electroluminescence optical power for a  $\text{TiO}_2/\text{DQ}$  where  $\text{TiO}_2$  layer is  $\text{Yb}^{3+}$ -doped. 5V applied bias.

$\text{TiO}_2$  thin films doped with  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  coupled to a D- $\pi$ -A quinoline derivative forms hybrid heterostructures, where structural analysis confirmed preservation of  $\text{TiO}_2$  anatase phase after doping, with slight modifications in preferential orientation and surface morphology. Optical absorption revealed characteristic intra-4f transitions of the lanthanides, indicating the introduction of localized states within the  $\text{TiO}_2$  bandgap. FTIR spectroscopy revealed clear evidence of interfacial chemical interaction through deprotonation of the quinoline carboxylic group and coordination to surface Ti sites. For  $\text{Er}^{3+}$  a well-defined bridging bidentate configuration was identified, indicating strong and organized anchoring of the organic layer. In contrast,  $\text{Yb}^{3+}$  exhibited a less defined coordination environment, suggesting a more heterogeneous interface. Photoluminescence measurements showed a blue shift from 500 to 483 nm upon heterostructure formation, evidencing modification of the excited-state electronic structure due to interfacial coupling. Electroluminescence is observed for all the doped systems which is in good agreement with the diode-like behavior shown in fig. 1 for  $\text{TiO}_2/\text{DQ}$  as well as  $\text{SnO}_2/\text{DQ}$ , even though the undoped  $\text{TiO}_2$  samples do not lead to interface light emission. The  $\text{Er}^{3+}$  heterostructure exhibited a lower turn-on voltage (5 V), associated with stronger interfacial coupling and facilitated charge injection, whereas  $\text{Yb}^{3+}$  devices required higher bias but showed improved emission stability under higher electric fields. These results demonstrate that rare-earth doping actively modulates interfacial coordination strength, which in turn governs excited-state dynamics. These findings point to the applicability of these hybrid structures in optoelectronic devices.

Acknowledgements: CNPq (process 303388/2022-6) and FAPESP (process 2022/12998-5 and 2025/04274-5)

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# EPITAXIAL RARE EARTH DOPED OXIDE THIN FILM ON DIAMOND

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Rare-earth (RE)-doped oxide thin films are key building blocks for quantum technologies, yet their integration into photonic devices remains hindered by substrate limitations. While conventional substrates (e.g., silicon) suffer from restricted optical transparency or immature photonic platforms (e.g., YSZ), diamond offers a compelling alternative, combining ultra-wide transparency and advanced photonic structuring capabilities. However, the stark lattice mismatch and chemical differences between oxides and diamond poses a fundamental challenge for epitaxial growth.

In this work, we demonstrate the first epitaxial growth of high-crystalline-quality RE-doped Y<sub>2</sub>O<sub>3</sub> thin films on diamond using Direct Liquid Injection Chemical Vapor Deposition (DLI-CVD). By optimizing growth parameters beyond previously reported conditions [3,4], we

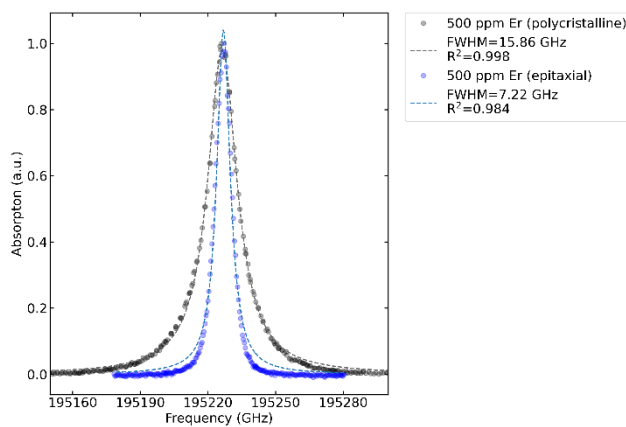


Figure 1 – Comparison of inhomogeneous linewidth for C<sub>2</sub> site of Er in polycrystalline (grey) VS epitaxial (blue) Y<sub>2</sub>O<sub>3</sub> film on diamond

achieve films with inhomogeneous linewidths for erbium 3 to 7 times narrower than their polycrystalline counterparts (Figure 1) and comparable to state-of-the-art silicon-based systems (~ 7 GHz at 10K [5]). High-resolution spectroscopy reveals Zeeman splitting in Er-doped films that closely matches theoretical predictions for a single-crystalline environment, confirming the epitaxial quality. Leveraging diamond's transparency, we extend these measurements to ytterbium and europium, paving the way for multi-species doping strategies.

These results establish RE-doped oxide/diamond hybrids as a versatile platform for quantum memories and microwave-to-optical transducers, bridging the gap between high-coherence RE ions and scalable photonic architectures.

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# MODULATION OF THE OPTICAL RESPONSE OF VANADIUM DIOXIDE IN MICROCAVITIES AND METAL/OXIDE STACKS

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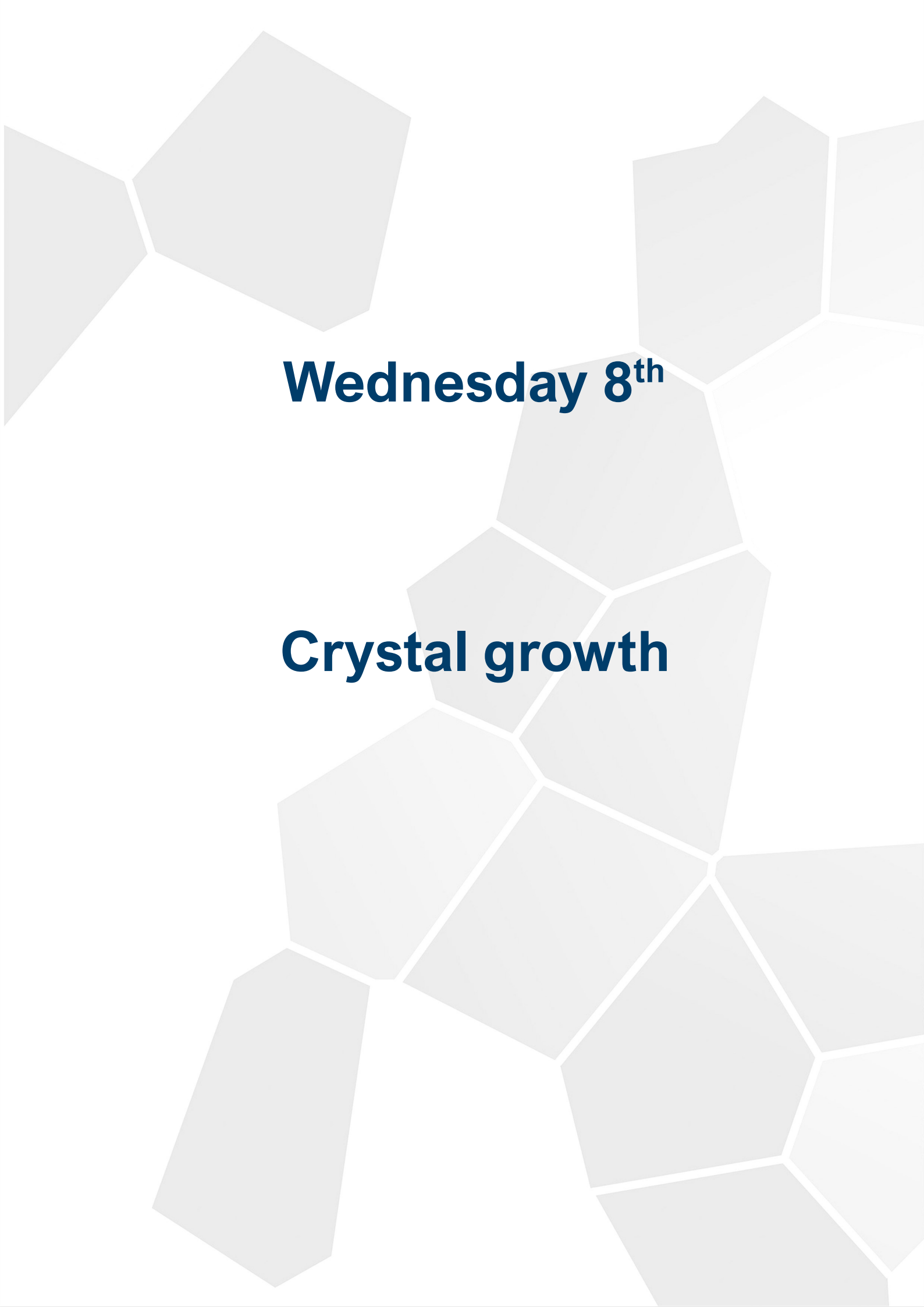
Vanadium dioxide ( $\text{VO}_2$ ) has emerged as a key material for advanced optical technologies due to its remarkable, reversible insulator–metal phase transition, which enables strong modulation of light with minimal thermal input. Building on these unique properties, vanadium-dioxide-based photonic devices show significant promise for applications ranging from smart windows to reconfigurable optical switches.

In this work, we introduce a microcavity architecture that incorporates a  $\text{VO}_2$  layer sandwiched between two photonic structures, each consisting of a random sequence of 32 alternating silicon dioxide and zirconium dioxide layers. The design explicitly accounts for the complex, temperature-dependent refractive index of  $\text{VO}_2$ , ensuring accurate modeling of its optical behavior. Our analysis demonstrates that even a temperature shift as small as one-degree Celsius produces measurable, though subtle, variations in the cavity's optical response. These small variations can be effectively captured through differential transmission measurements, which require only simple and low-cost optical instrumentation. As a result, the proposed microcavity operates not only as a compact and efficient temperature sensor but also as a highly sensitive photon detector, where absorbed photons induce a detectable thermal change in the  $\text{VO}_2$  layer.

We further investigate a gold/vanadium oxide bilayer system in which a pulsed laser interacts with the metal layer. A three-temperature model—tracking the dynamics of gold electrons, the gold lattice, and the vanadium oxide lattice—is used to estimate the heating transferred to the oxide and to identify the conditions under which its phase transition is triggered. The optical response of the bilayer is then analyzed using the transfer matrix method, revealing clear differences in light transmission between the unexcited and laser-excited states. Together, these results highlight the versatility of  $\text{VO}_2$ -based structures for sensitive, thermally driven photonic functionalities.

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**Wednesday 8<sup>th</sup>**

**Crystal growth**

# Ce:La-GPS Scintillator: Crystal Structure, Luminescence, and Processing Effects

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(La,Ce,Gd)<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> (Ce:La-GPS) is an oxide scintillator characterized by a high light yield (~46,000 ph./MeV), excellent energy resolution (4–5% FWHM at 662 keV), a relatively short decay time (~60 ns), and high chemical stability [1,2]. Its emission peaks are located around 380 nm, which matches well with the high quantum efficiency of photomultiplier tubes (PMTs). In addition, the scintillation output shows only a small degradation at elevated temperatures up to approximately 150 °C. Owing to these properties, Ce:La-GPS has been extensively investigated for resource exploration applications such as oil-well logging. In this presentation, we review the correlation between crystal structure and Ce<sup>3+</sup> luminescence in rare-earth pyrosilicate scintillators, focusing on studies conducted by the authors.

Rare-earth pyrosilicates RE<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> (RE: rare-earth elements) can exhibit multiple crystal structures (polymorphs) depending on the average ionic radius of the rare-earth cations and temperature [3]. The number of rare-earth sites and their coordination environments vary with crystal structure. Since Ce<sup>3+</sup> luminescence originates from 5d–4f transitions, the symmetry of the coordination polyhedron and the crystal field at the Ce<sup>3+</sup> site influence the splitting of the 4f to 5d absorption bands, emission wavelength, decay time components, and thermal quenching behavior [4].

Substitution at the rare-earth site allows the average ionic radius to be tuned, thereby enabling control of the stable phase and the local structure. Gd<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> (GPS) exhibits orthorhombic and triclinic phases and shows incongruent melting behavior during crystal growth from the melt [5]. To address this issue, heavy Ce doping (~10 mol% at the rare-earth site) has been employed to stabilize the pyrosilicate phase and facilitate melt growth. However, such high Ce concentrations can induce concentration quenching and optical losses due to self-absorption, resulting in reduced scintillation output.

Ce:La-GPS can be regarded as a material system developed to mitigate the structural instability and high-Ce-concentration requirements of Ce:Gd<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>. By introducing non-luminescent La<sup>3+</sup> as a structural stabilizer, stable single-crystal growth becomes possible. At compositions with ~25% La substitution, a monoclinic structure (P2<sub>1</sub>/c) is obtained, enabling a high light yield and excellent energy resolution while maintaining a relatively low Ce concentration of ~1 mol% [2].

The scintillation behavior of Ce:La-GPS depends strongly on both composition and processing conditions. The concentrations of Ce and La affect self-absorption and thermal quenching characteristics. Co-doping with divalent or tetravalent metal ions often results in a reduction in light yield accompanied by a slight shortening of the decay time. Crystal growth conditions influence the stress distribution during growth and may lead to crystal defects such as cracks. Furthermore, it has been found that thermal treatments and chemical etching can improve the light yield and energy resolution.

In this presentation, we discuss the structural diversity of RE<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> and the site selectivity of Ce<sup>3+</sup>, the influence of La and Ce concentrations on luminescence behavior, and the effects of processing parameters—including co-doping, thermal treatment, and surface treatment—on crystal quality and scintillation response. Challenges and perspectives for practical implementation are also discussed.

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# **Sapphire: an exceptional crystal at the heart of tomorrow's technologies**

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Sapphire (single-crystal  $\text{Al}_2\text{O}_3$ ) has established itself as a high-value material due to its exceptional physical, chemical, and optical properties. Its high hardness (9 on the Mohs scale), remarkable thermal stability, extended transparency from ultraviolet to infrared, and chemical resistance make it a crystal of choice for a wide range of advanced applications. It is used in fields as diverse as high-performance optics, rugged windows for extreme environments, substrates for power electronics and optoelectronics (LEDs, lasers), and components for the aerospace and defense sectors. In the field of photonics in particular, sapphire provides an ideal crystalline matrix for doping with active ions (such as  $\text{Ti}^{3+}$ ), paving the way for high-performance, stable, and efficient laser sources. Its high thermal conductivity and mechanical robustness also make it possible to envision high-power devices with excellent long-term reliability. These characteristics make sapphire a strategic material for the technologies of tomorrow. At the Institut Lumière Matière (iLM), sustained efforts have been made in recent years to master and optimize sapphire crystal growth. In close collaboration with RSA Le Rubis Company, this work has led to the development of high-quality growth processes, precisely controlling thermodynamic and structural parameters to obtain high-purity, homogeneous crystals suitable for the most demanding applications. These advances have helped strengthen sapphire's position as a key material in next-generation optical and electronic devices.

This research is also part of a long-standing scientific dynamic championed by Professor Georges Boulon, whose contribution to materials science and doped crystals was significant. His involvement in national and international collaborations, as well as his unwavering commitment to training young researchers, profoundly influenced the scientific community. His pioneering work, particularly on ytterbium (Yb)-doped crystals, opened up important new perspectives in the field of optics.

The ISOM10 conference, organized in his memory, thus provides a unique opportunity to highlight both the importance of sapphire as an exceptional functional material, the advances made in its crystal growth, and the scientific legacy of Professor Georges Boulon. Through the presentation of recent results and a monograph dedicated to this collaboration, the aim is also to underscore how crucial human and scientific interactions have been to the progress of this field.

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Xiaodong XU<sup>4</sup>, Abdeldjelil NEHARI<sup>1</sup>, Kheirreddine LEBBOU<sup>1</sup>**

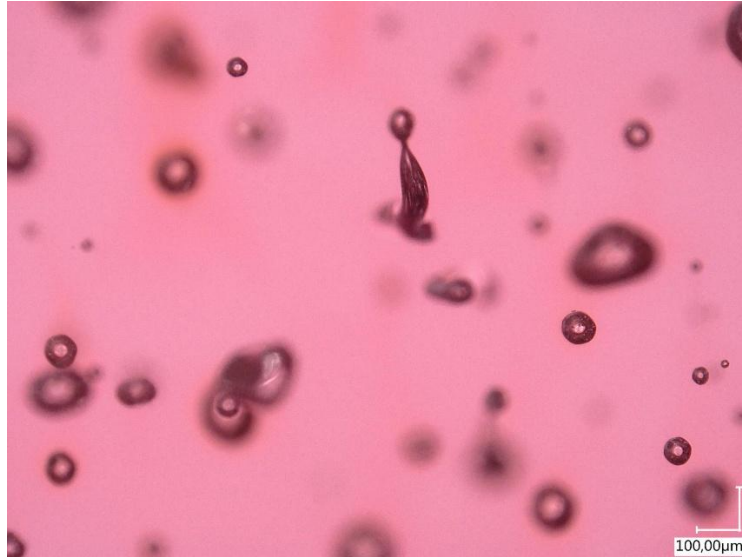
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Gas bubble inclusions remain one of the most critical defects limiting the structural integrity and optical performance of undoped and Ti-doped sapphire single crystals [1,2]. In Ti:sapphire, even micron-scale bubbles induce light scattering, degrade laser gain uniformity, and reduce damage thresholds, directly impacting high-power and ultrafast laser applications [3,4]. Bubble formation is strongly governed by the complex coupling between radiative heat transfer, melt convection, and crystal–melt interface dynamics in furnaces operating above 2000 °C. Understanding and predicting the thermofluidic conditions that promote gas entrapment therefore represents a central challenge in optical-grade sapphire growth. In this work, a comprehensive global finite element model of the entire growth system is developed to capture the full multiphysics behavior governing crystal quality. The model simultaneously incorporates conductive, convective, and surface-to-surface radiative heat transfer, as well as internal radiation within semitransparent sapphire, coupled with melt momentum transport and crystal–melt interface evolution [5,6]. The simulation resolves the complete furnace geometry, including heaters, crucible, melt, growing crystal, insulation, and surrounding gas domain, enabling accurate prediction of temperature fields, flow structures, and interface curvature. Particular emphasis is placed on bubble formation mechanisms. Numerical results show that radiatively driven thermal gradients strongly modify buoyancy-induced convection patterns, generating recirculation zones and local pressure conditions favorable to gas entrapment. The influence of heater configuration, thermal gradients, and cooling strategies on bubble capture probability is systematically analyzed. Model predictions are validated through experimental observations, including macroscopic crystal photographs and microstructural characterization. Micrographs confirm the correlation between simulated convection structures, thermal field non-uniformities, and the spatial distribution of bubbles within the crystal. This combined numerical–experimental approach provides a predictive tool for furnace optimization and defect mitigation, contributing to improved structural and optical quality in both undoped and Ti-doped sapphire crystals.



**Fig.** Micrographs of titanium–sapphire crystal showing bubbles with different shape and size.

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## THRESHOLD FOR BUBBLE INCORPORATION GROWTH RATE IN 250 MM DIAMETER TITANIUM DOPED SAPPHIRE SINGLECRYSTALS

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Session : **Crystal growth technologies (bulks, fibers)**

### ABSTRACT :

Titanium-doped sapphire ( $\text{Ti}:\alpha\text{-Al}_2\text{O}_3$ ), commonly known as Ti:sapphire, is a key material in modern optics and the basis of femtosecond and petawatt-class laser systems. Its wide tunable emission range (650–1100 nm), excellent transparency in the visible and near-infrared regions, and strong thermo-mechanical stability make it particularly well suited for high-performance laser applications [1]. Since its introduction in the 1980s at MIT Lincoln Laboratory, Ti:sapphire has played a central role in ultrafast laser development. Current research focuses on improving crystal growth techniques to obtain large, high-quality crystals with minimal defects, and homogeneous dopant distribution to achieve optical uniformity. Ti:sapphire is typically produced by melt growth methods, which yield crystals ranging in weight from a few grams up to a hundred kilograms. However, only a few techniques are used to produce large crystals, and these are often designed to improve crystal's quality. During growth, bubbles tend to form consistently, especially near the edge and the base of the crystal [2]. These bubbles alter the optical properties by causing light scattering and localized heating, which can lead to mechanical stress, crack formation, and a decrease in laser efficiency [3]. It is therefore essential to minimize bubble formation to improve the material quality. By comparing our numerical and experimental results with those of D. Song et al., we propose a critical threshold for bubble incorporation in titanium-doped sapphire single crystals, beyond which bubbles should be encapsulated during growth.

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#### **ACKNOWLEDGEMENTS :**

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The background of the slide features a collection of light gray, irregular geometric shapes, primarily pentagons and hexagons, scattered across a white background. These shapes are outlined in white and vary in size and orientation, creating a modern, crystalline aesthetic.

**Wednesday 8<sup>th</sup>**

**Luminescence (Organic)**

# INFRARED PHOTONIC SENSORS FOR WATER POLLUTANTS BASED ON CHALCOGENIDE GLASS THIN FILMS

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The detection of organic molecules in water demands sensors with high selectivity, stability and miniaturization. We present a chalcogenide-based mid-infrared (MIR) platform using evanescent wave spectroscopy. Chalcogenide thin films, synthesized by RF magnetron sputtering, were characterized and patterned for MIR integration. Surface functionalization enhances detection capabilities, offering a step forward in compact, cost-effective water monitoring sensors.

The detection of organic molecules in water is a critical scientific and environmental issue, especially given the growing global demand for clean water resources and the increasing presence of pollutants linked to industrial, agricultural, and pharmaceutical activities. Traditional analytical techniques, although accurate, often rely on centralized laboratory infrastructure and time-consuming protocols, which are unsuitable for real-time, on-site monitoring. To address this limitation, the development of miniaturized, portable optical sensors capable of in situ analysis has emerged as a strategic priority. Such sensors must ideally meet a stringent set of performance requirements, including high selectivity, large domain of sensitivity, robustness, limited power consumption, rapid response, and compatibility with complex aqueous environments. Mid-infrared (MIR) spectroscopy stands out as a particularly effective technique for this purpose, as it allows direct access to the fundamental vibrational modes of chemical bonds, thus enabling the unambiguous identification of a wide range of organic species through their unique spectral signatures. However, conventional MIR spectrometers remain too bulky and expensive for widespread deployment. In this context, integrated photonic platforms using waveguides and evanescent field-based sensing provide a promising solution, offering not only device miniaturization and real-time detection but also compatibility with multiplexed and multivariate sensing approaches. In these systems, the evanescent field generated by light confined within a waveguide extends into the surrounding medium, allowing direct interaction with target analytes at the transducer surface without requiring a free-space optical path through the liquid.

Among the materials suitable for MIR photonics, chalcogenide glasses have attracted significant attention due to their unique combination of physical and optical properties. These glasses, typically composed of chalcogen elements (such as sulphur, selenium, or tellurium) bonded with network formers like arsenic or germanium, exhibit a wide transmission window that extends deep into the MIR spectral range, beyond 6  $\mu\text{m}$ . Their inherently high refractive indices facilitate pronounced optical confinement within the waveguide structure. However, such strong confinement may concurrently reduce the penetration depth of the evanescent field into the surrounding medium, which can impose slight limitations on sensor sensitivity. However, due to the ability to tailor their refractive index through compositional adjustments, chalcogenide glasses can achieve an optimal balance between strong optical confinement and sufficient evanescent field penetration, rendering them suitable materials for the development of sensitive and compact mid-infrared (MIR) transducers. Additionally, their amorphous nature allows deposition as thin films on various substrates using scalable techniques such as RF

magnetron sputtering, and their fabrication into integrated photonic components is enabled by standard microfabrication techniques, including lithography and etching processes.

In this work, we employed GeSe<sub>2</sub>-based chalcogenide glasses, deliberately avoiding arsenic-containing compounds due to their potential toxicity and environmental concerns, to fabricate planar waveguide structures tailored for mid-infrared (MIR) sensing applications in aqueous environments. These films were deposited via RF sputtering under carefully controlled conditions to achieve uniform thickness and low optical loss. The morphological and topographic properties were characterized, while the optical performance was evaluated through spectroscopic ellipsometry and Fourier-transform infrared spectroscopy. The resulting films exhibited good uniformity and low surface roughness, both critical parameters that directly influence optical quality. Moreover, the measured propagation losses reflect the state-of-the-art performance. A rigorous design framework was employed to define the optimal geometric parameters of the waveguide structure, including film thickness, waveguide width, and effective refractive index, to maximize evanescent field penetration and ensure efficient interaction with dissolved analytes.

To translate these chalcogenide materials into functional sensing platforms devoted to water, we developed a complete fabrication and integration process suitable for device prototyping and eventual scaling. A critical step in the development was the surface functionalization of the waveguides to ensure chemical stability and improve analyte selectivity in aqueous media. To this end, a hydrophobic polymer coating was applied to the surface, enhancing resistance to water infiltration, limiting non-specific adsorption, and improving sensor longevity. This functionalization layer was carefully chosen to maintain transparency in the MIR region while preserving the interaction of the evanescent field with target organic compounds. The functionalized transducer ensures compatibility with microfluidic systems, enabling monitoring under real-world operating conditions. The transducer has been conceived as a reconfigurable and replaceable component, allowing adaptability to various sensing requirements. The platform will be specifically designed to accommodate, if required, arrays of quantum cascade lasers (QCLs) operating at multiple wavelengths, as well as a mid-infrared detector. This modular configuration supports robust and versatile analyte detection, while significantly reducing the system's overall footprint, an essential criterion for the development of compact and portable mid-infrared sensing solutions suitable for in situ deployment.

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## ACKNOWLEDGEMENTS

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## BORANIL-BASED MOLECULAR SWITCHES FOR THE DEVELOPMENT OF CHIROPTICAL MATERIALS

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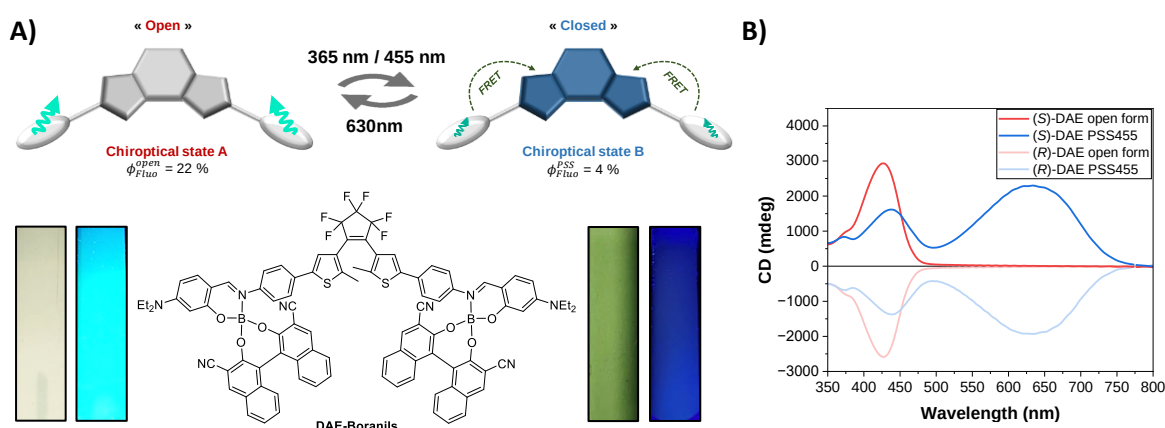
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Session: **Spectroscopy of luminescent materials, Thin films for optical applications**

### ABSTRACT

Constructing sophisticated luminescent dyes around a tetrahedral boron(III) center is a particular approach that has fuelled the creativity of chemists motivated by their use in organic electronics and applied photonics or as molecular probes in biomedical analysis, sensors and materials science.<sup>1</sup> We have recently described a very simple and efficient gram-scale synthetic pathway towards Boranils substituted directly on the boron center by 1,1'-bi-2-naphtol derivatives (BINOL).<sup>2</sup> These chiral dyes typically feature high molar absorption coefficient in the range of 35,000 to 90,000 M<sup>-1</sup>.cm<sup>-1</sup>, absorption dissymmetry factor ( $g_{\text{abs}}$ ) in the range of 2.5–5.5 × 10<sup>-4</sup> at the maximum wavelength of absorption of Boranils and Circularly Polarized Luminescence (CPL) brightness up to  $B_{\text{CPL}} = 5.4 \text{ M}^{-1}.\text{cm}^{-1}$ . Based on this new family of CPL emitters, we are currently developing supramolecular chiral soft-materials such as stimuli-responsive gels and liquid crystals.<sup>3,4</sup> As an illustration, we will describe molecular switches taking advantage of the control of energy transfer to a photochromic diarylethene (DAE) core to modulate chiroptical properties in liquid crystals thin films (**Fig. 1**).



**Fig. 1** (A) Schematic and structural representations and (B) chiroptical signatures of the DAE-boranils.

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# MAGNETO-PHOTONIC LOGIC IN A $\text{Dy}^{3+}$ SINGLE-MOLECULE MAGNET

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Lanthanide-based optical materials offer unique opportunities for integrating multiple functionalities within a single platform. In particular, the coexistence of luminescence and magnetism in  $\text{Dy}^{3+}$ -based single-molecule magnets (SMMs) provides a powerful framework for developing multifunctional photonic systems.[1,2]

In this presentation, we report the magnetic-field control of luminescence in a benchmark air-stable  $\text{Dy}^{3+}$  SMM,  $[\text{Dy}(\text{bbpen})\text{Cl}]$ , and demonstrate its application as a multifunctional optical material capable of simultaneous information processing and storage. Under UV excitation, the complex exhibits characteristic  $\text{Dy}^{3+}$  emission, which is strongly modulated by external magnetic fields up to 60 T. The magnetic field induces significant spectral reshaping, including intensity variations, energy shifts, and asymmetric broadening associated with Zeeman splitting of the 4f electronic states.

To quantitatively describe these effects, two independent photonic parameters were defined based on the emission spectra: a ratiometric intensity parameter ( $\phi$ ) and a dissymmetry factor ( $g_h$ ) derived from differential spectra analysis. These parameters provide robust optical readouts of the magneto-photonic response over a wide temperature range (2–300 K).

By combining optical excitation and magnetic field as external stimuli, the system operates as a dual-output molecular logic device. At low temperature, within the SMM regime, distinct logic functions are implemented in parallel, including OR and INHIBIT gates, while the intrinsic magnetic bistability enables information storage at the molecular scale. Importantly, temperature acts as a global reconfiguration parameter, switching the logic behavior without acting as a direct input.

This approach introduces a new paradigm for optical materials, in which fast, externally addressable stimuli such as photons and magnetic fields enable logic operations, while magnetic anisotropy provides non-volatile memory. These findings open new perspectives for magneto-photonic devices integrating sensing, processing, and storage functionalities within a single molecular system, extending recent advances in luminescent SMMs.[3].

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The background of the slide features a collection of light gray, irregular geometric shapes, primarily pentagons and hexagons, scattered across a white background. These shapes are separated by thin white lines, creating a mosaic-like effect. The shapes vary in size and orientation, with some appearing more prominent than others.

**Wednesday 8<sup>th</sup>**

**Fluorides for optics**



# Various Fluoride Materials For Optical Applications

**Nobuhiko SARUKURA**<sup>1,2,3</sup>, **Marilou CADATAL-RADUBAN**<sup>1,4</sup>, **Toshihiko SHIMIZU**<sup>1</sup>,  
**Tsuguo FUKUDA**<sup>2</sup>, and **Akira YOSHIKAWA**<sup>3,5,6</sup>

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Light sources in the ultraviolet (UV,  $\lambda = 400$  nm to 250 nm), deep ultraviolet (DUV,  $\lambda = 250$  nm to 190 nm) and vacuum ultraviolet (VUV,  $\lambda = 190$  nm to 100 nm) wavelength regions have numerous technologically important applications, including lithography, sterilization, and surface modification. Solid-state lasers in these short wavelength regions offer the promise of being more robust, easier to maintain, and more cost-efficient light sources compared to conventional excimer lasers, synchrotron radiation, and free electron lasers (FEL). Towards UV, DUV and VUV laser development, we have explored fluoride crystals such as lithium calcium aluminum fluoride (LiCaAlF) and lanthanum fluoride (LaF) as excellent solid-state laser host materials because of their extremely wide band gaps which make them transparent down to about 100 nm. Fluoride crystals have been successfully doped with trivalent rare-earth ions such as cerium ( $\text{Ce}^{3+}$ ) and neodymium ( $\text{Nd}^{3+}$ ), whose dipole-allowed interconfigurational 5d to 4f transitions result in broad fluorescence bandwidths that enable the development of short-pulse tunable solid-state UV lasers. Interconfigurational transitions also result in fast luminescence emission. We leverage these fast emissions to develop fast-response scintillators that detect high-energy radiation. In this talk, I will present our work on rare-earth ion-doped fluoride crystals for solid-state UV, DUV and VUV laser and scintillator development.

# DEVELOPMENT OF LARGE AND HIGH-QUALITY FLUORIDE SINGLE CRYSTALS FOR UV-IR OPTICAL APPLICATION

Hiroki SATO<sup>1,2</sup>

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Because of their unique properties such as wide range transparency and high laser durability, fluoride single crystals have long been investigated for various demanding UV and IR optical applications. Over the past decades, the rigorous and ever-changing demands of the optical industry significantly drove the advancement of fluoride crystal growth technologies. To meet the strict material requirements of the time, we extensively investigated the growth and optical characterization of high-quality complex fluoride single crystals using the Czochralski. This presentation will review our past efforts and progress in the growth of fluoride single crystals.

Historically, during the developmental phase of 157-nm projection lithography and F<sub>2</sub> laser systems, discovering highly transparent and durable optical materials was a critical challenge. We identified colquiriite-type LiCaAlF<sub>6</sub> (LiCAF) as a promising candidate. By precisely modifying the crystal growth conditions, we successfully established the growth technology for inclusion-free LiCAF single crystals up to 4 inches in diameter. These crystals demonstrated over 95% transmittance at 157 nm, vanished birefringence around 152 nm, and exceptional resistance to X-ray induced radiation damage by Mg doping<sup>1</sup>.

Subsequently, as the semiconductor industry temporarily pursued high-index materials for 193-nm immersion lithography to increase the numerical aperture, we systematically investigated cubic fluoride compounds<sup>2</sup>. We successfully grew BaLiF<sub>3</sub> single crystals up to 150 mm in diameter, achieving a high refractive index of 1.64 at 193 nm with excellent internal transmittance of 99.2%/cm. Although the industrial roadmap ultimately shifted away from these lithography applications, the profound insights gained during these developmental phases dramatically advanced our capabilities in growing complex fluoride crystals.

Concurrent with the developments for lithography, we also explored the potential of fluoride materials for advanced solid-state lasers. In the ultraviolet region, we developed highly efficient lasers utilizing Ce<sup>3+</sup>-doped fluorides such as Ce:LiCAF. In the infrared region, we successfully grew 1- to 3-inch Tm, Ho-codoped LiYF<sub>4</sub> and LiLuF<sub>4</sub> single crystals for 2-μm eye-safe lasers<sup>3</sup>, achieving excellent output energies through a novel quasi-end-pumping technique.

Unlike oxide materials, fluorides possess exceptionally high transmittance across a wide spectrum from the ultraviolet to the infrared region. Because of this unique advantage, fluoride single crystals will undoubtedly be utilized in various fields in the future.

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# Fluoride Optical Materials and Lens Systems for Deep Ultraviolet Photonics

**Toshihiko SHIMIZU<sup>1</sup>, Yugo AKABE<sup>1</sup>, Marilou CADATAL-RADUBAN<sup>2</sup>, Yuki MINAMI<sup>1</sup>, Keito SHINOHARA<sup>1</sup>, Kohei YAMANOI<sup>1</sup>, Nobuhiko SARUKURA<sup>1</sup>, Motosuke KIYOHARA<sup>3</sup>, Kazuya TAKAHASHI<sup>4</sup>, Tsuguo FUKUDA<sup>4</sup>**

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Optical systems in the deep ultraviolet (DUV) region are required for applications such as ultraviolet spectroscopy and atmospheric monitoring. The performance of such systems is strongly influenced by the availability of optical materials that remain transparent at wavelengths below 300 nm and exhibit suitable refractive-index dispersion for lens design. However, the number of materials satisfying these conditions is limited.

Fluoride crystals are among the most widely used materials for ultraviolet optics because of their wide band gaps and good transmission at short wavelengths. Calcium fluoride (CaF<sub>2</sub>), magnesium fluoride (MgF<sub>2</sub>), and lithium calcium aluminum fluoride (LiCaAlF<sub>6</sub>) have therefore been used in various ultraviolet optical components such as lenses, windows, and prisms. In particular, LiCaAlF<sub>6</sub> has attracted interest for deep-ultraviolet optical systems because its dispersion properties allow the design of achromatic lens combinations.

Deep-ultraviolet optical techniques are applied in several fields including ultraviolet absorption spectroscopy and environmental sensing. For example, molecular absorption bands in this wavelength region enable the detection of atmospheric gases such as SO<sub>2</sub> and NO<sub>2</sub>, and ultraviolet imaging techniques are also used for environmental monitoring and combustion diagnostics.

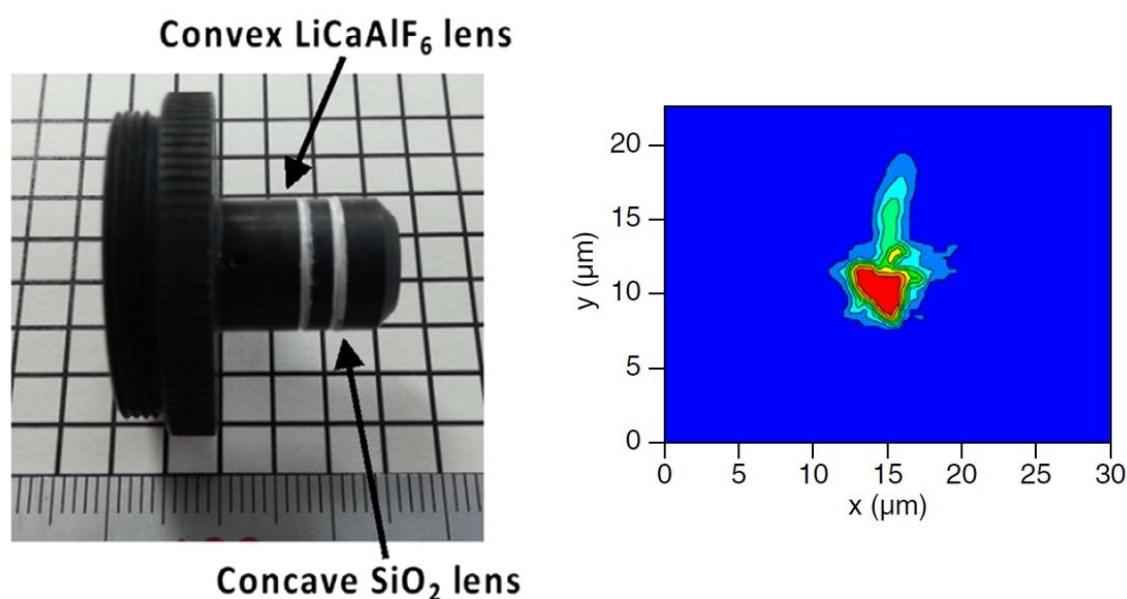
The performance of optical systems in the deep ultraviolet region is strongly influenced by the dispersion characteristics of the available materials. Because the number of transparent materials in this wavelength range is limited, optical design often requires careful combinations of several fluoride crystals in order to control chromatic aberration. In this context, accurate knowledge of refractive index dispersion and ultraviolet transmission is essential for practical optical design. Systematic studies of fluoride optical materials therefore play an important role in expanding the design flexibility of DUV optical systems.

Using these materials, we have investigated several optical systems operating in the DUV region. One example is an achromatic objective lens designed using a combination of wide-bandgap materials including LiCaAlF<sub>6</sub>. By selecting materials with appropriate dispersion characteristics, chromatic aberration can be significantly reduced even at short wavelengths. The fabricated lens shows improved imaging performance compared with conventional ultraviolet optical designs.

We have also developed compact imaging optics for ultraviolet monitoring. In particular, a compact wide-angle lens was designed for atmospheric SO<sub>2</sub> detection around 300 nm. The optical configuration uses ultraviolet-transparent materials such as CaF<sub>2</sub>, sapphire, and synthetic quartz in order to obtain a compact lens system with corrected aberrations. The optical performance of the lens, including focal shift, chromatic aberration, spot size, and modulation transfer function, was evaluated through both optical simulations and experimental measurements.

Substitution of Sr in the  $\text{CaF}_2$  lattice is expected to modify the refractive index dispersion, which may provide additional flexibility for ultraviolet optical design. Single crystals of  $\text{CaSrF}_2$  grown by the cone-die Czochralski method are therefore being investigated, and their optical properties in the ultraviolet region are currently under evaluation.

The results presented here suggest that progress in ultraviolet optical systems depends strongly on the availability of suitable fluoride materials together with appropriate optical design. Mixed fluoride crystals such as  $\text{CaSrF}_2$  may therefore become useful candidates for future deep-ultraviolet optical components.



**Fig.** Photograph of the prototype objective lens consisting of a  $\text{LiCaAlF}_6$ - $\text{SiO}_2$  doublet and focused image of a 212 nm wavelength laser pulse at the focal point of the prototype objective lens with an NA of 0.2

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# **Thursday 9<sup>th</sup>**

## **Weekly summary**

# Fluoride Crystals For Lithography Applications

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Fluoride single crystals play a critical role in ultraviolet (UV) and vacuum ultraviolet (VUV) optical systems due to their wide transparency range, low absorption, and excellent radiation resistance. As optical technologies continue to advance, particularly in high-power laser systems and semiconductor lithography, there is increasing demand for large, high-quality fluoride crystals with improved mechanical stability and optical performance. In this work, we investigate the growth and characteristics of fluoride crystals grown using the Czochralski (CZ) method. Particular attention is given to mixed fluorides such as  $\text{Ca}_{1-x}\text{Sr}_x\text{F}_2$ , which offer opportunities to tailor physical and optical properties between those of  $\text{CaF}_2$  and  $\text{SrF}_2$  through compositional control. Crystal growth experiments were conducted under controlled thermal conditions to evaluate compositional uniformity, crystallinity, and scalability toward large-diameter boules. Czochralski technique using Cone-shape Die (CD-CZ method) enables improved diameter control and stable crystal growth, leading to the growth of large-sized single crystals. Structural and compositional analyses reveal good homogeneity and high crystalline quality across the grown crystals. The potential of these materials for large-aperture optical components is discussed, with emphasis on applications requiring high optical quality and dimensional stability, including next-generation lithography optics. These results highlight the promise of mixed fluoride crystals as versatile optical materials and demonstrate pathways toward scalable production of large, high-quality crystals for demanding UV optical applications.

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**Thursday 9<sup>th</sup>**

# **Persistent Luminescence**

# Development of biophotonic glass-based materials with persistent luminescence for in situ activation of photoswitchable drugs

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Bioactive glasses have been extensively used in tissue engineering for the regeneration, repair, and replacement of damaged tissues. This is due to their ability to release therapeutic ions and to form an apatite layer when dissolved in physiological fluids [1]. Phosphate glasses have been materials of interest as bioactive glasses as they can be engineered to exhibit higher solubility and ion release compared to silica-based glasses [2]. Phosphate bioactive glasses are unique materials with fully resorbable characteristics, making them favorable for hard and soft tissue engineering. Their composition can be easily tailored so the glasses possess controlled ion release, congruent dissolution, and resistance to crystallization, making them suitable for processing fibers as well as 3D porous scaffolds [3]. If designed with luminescent properties, such biophotonic materials can promote osteogenesis and angiogenesis while emitting in the same time light which can be used for imaging or on-demand drug release control.

Persistent luminescent materials have been of great importance as they emit light for hours once the excitation source, responsible for charging it, is removed [4]. This persistent luminescence, also called afterglow, is a consequence of energy storage in the material during excitation. Among the known PeL materials, the  $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+},\text{Dy}^{3+}$  phosphor is remarkable for its characteristic green emission and long decay time after UV charging. Since its discovery [5], efforts have been focused on developing new PeL materials, including PeL glasses [6]. Such materials have emerged as promising materials. Despite their advantages, the primary limitation of PeL phosphors in biomedical applications is their dependence on UV or blue light for charging, which is toxic to cells and restricts their use in deep-tissue applications since short wavelength radiation does not penetrate biological tissues effectively. As a result, these phosphors must be pre-charged before implantation, limiting their practicality and total light output. Recent studies have investigated the potential of near-infrared (NIR) light (650–1000 nm) to charge the PeL phosphors, to broaden their applicability. Unlike ultraviolet (UV) light, NIR light penetrates more deeply into biological tissues, enabling advanced in vivo applications such as bioimaging, disease tracking, and therapeutic monitoring. A promising strategy involves incorporating upconversion ion pairs, such as  $\text{Yb}^{3+}$ ,  $\text{Tm}^{3+}$ , alongside PeL phosphors [7].

This presentation introduces a methodology for designing biophotonic glass-based materials capable of long-lasting green emission under near-infrared excitation. The approach relies on combining  $\text{Tm}^{3+}/\text{Yb}^{3+}$  codoping with  $\text{SrAl}_2\text{O}_4\text{:Eu,Dy}$  persistent phosphors to achieve efficient NIR-to-visible energy storage and release. We will highlight recent advances in the fabrication of NIR-rechargeable persistent luminescent fibers and porous scaffolds, emphasizing their potential for biomedical applications. Particular attention will be given to the challenges associated with incorporating crystalline phosphors into glass matrices, as well as the processing constraints encountered during fiber drawing and composite 3D printing. Together, these insights outline a pathway toward multifunctional, rechargeable photonic materials with tailored structural and optical properties.

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# CHROMIUM DOPED MATERIALS; AN OLD STORY TOWARDS NEW APPLICATIONS... FOCUS ON PERSISTENT LUMINESCENCE

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Professor Georges Boulon was a pioneer in the work on  $\text{Cr}^{3+}$  doped materials [1-4] and towards this trivalent  $\text{Cr}^{3+}$  cation a long collaboration was established between Lyon and Paris research laboratories to analyse the optical properties of glass, glass ceramics [3] and crystals such as hexaaluminate [4], garnets and others mixed oxides materials elaborated in the two cities. At that time, the main application was the study of new Lasers hosts in the deep red and near infrared ranges. Later,  $\text{Cr}^{2+}$  and  $\text{Cr}^{4+}$  were also investigated for their interesting properties. More recently, persistent luminescence (PersL) based on  $\text{Cr}^{3+}$  doped zinc gallate host was developed [5]. Nanosize persistent luminescent materials require perfect materials with high fluorescence intensity and careful control of the defects. PersL can last for few minutes to hours after the removal of the excitation source, and PersL is controlled by a slow liberation of trapped charge carriers by simple thermal deexcitation process. This concept was proposed for the development of new optical imaging modalities [5]. Lot of parameters of these nanoprobes can be adjusted, such as surface functionalization, composition by using for instance  $\text{Sn}^{4+}$  as dopant to improve the intensity (Fig.1 left), or wavelength of the optical stimulation/emission to favor multiple challenging biomedical applications. Bioimaging applications can be tuned when using probes emitting in BW-I and BW-II (Fig.1 center) [6]. New applications of the persistent luminescence nanophosphors include *optical sensors in nanothermometry or biological markers*. A novel *in-vitro* strategy for biomolecule detection is introduced, leveraging the dose-dependent enhancement of persistent luminescence signal upon exposure to hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) [7] (Fig.1 right). The development of sensitive, rapid, and user-friendly  $\text{H}_2\text{O}_2$  sensors is of great biomedical significance. A comprehensive analysis of material structure, surface chemistry and spectroscopic and electrochemical properties is proposed.

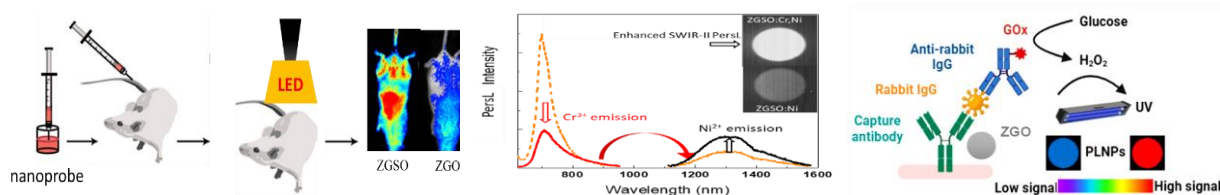


Fig.1. Persist. Lum. NPs with optimized: composition (left), dopant for SWIR bioimaging (center), and  $\text{H}_2\text{O}_2$  nanosensors (right)

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# DUAL EMISSION PHOSPHORS WITH PERSISTENT LUMINESCENCE FOR NEUTROMORPHIC OPTICAL COMPUTING

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Artificial intelligence is increasingly present in scientific, technological, and societal contexts, but its rapid expansion is placing severe pressure on current computing hardware. Conventional von Neumann architectures, in which memory and processing units are physically separated, suffer from bottlenecks in data transfer, latency, bandwidth, scalability, and energy consumption. These limitations become particularly critical for machine-learning workloads, where large datasets and high-dimensional models require repeated memory access and intensive matrix operations. As electronic scaling approaches practical and physical limits, alternative hardware paradigms are needed to process information more efficiently, especially by bringing memory and computation closer together and by exploiting physical processes as part of the computation itself [1].

The increasing interest in photonic and neuromorphic hardware has therefore opened new opportunities for luminescent materials whose excited-state dynamics can be exploited beyond conventional sensing or display applications [2]. Systems displaying excitation-dependent emission, spectral overlap between emissive channels, intersystem crossing, persistent phosphorescence, and energy-transfer-mediated population redistribution offer a direct physical route to encode, transform, and retain information in the optical domain [3,4]. In this context, hybrid photonic-digital architectures benefit from the intrinsic complexity of luminescent materials: radiative and non-radiative pathways, donor-acceptor interactions, and long-lived excited states can generate enriched optical representations before digital processing. Rather than acting only as emitters or transducers, these materials can therefore operate as active photonic layers for information processing, bridging luminescence physics, optical computing, and neuromorphic hardware.

In this work, the luminescent materials selection was guided by the need to combine efficient and stable luminescence with photophysical complexity, simple processing, and compatibility with low-cost optical excitation and readout. As one example, carbon dots embedded in a boron oxide matrix provide chemically tunable absorption and emission through surface functionalization, allowing different emissive centres to contribute across the UV-visible spectral range [3]. When combined in a multicomponent photonic layer, these centres generate complex emission spectra arising from the superposition of radiative pathways and

coupled non-radiative processes. As a second example, lamellar carbon-based materials are incorporated into a rigid boron-based lamellar matrix (HNA@BA) to promote intersystem crossing, suppress non-radiative relaxation, and stabilize triplet excitons [4]. The lamellar organization further provides nanoscale confinement, making it suitable for interlamellar energy transfer and persistent phosphorescence. In both examples, the material selection is therefore not only aimed at producing bright emission, but at engineering excited-state dynamics that can be used as a physical computing resource. These two material platforms illustrate complementary ways in which luminescence can be transformed into computation.

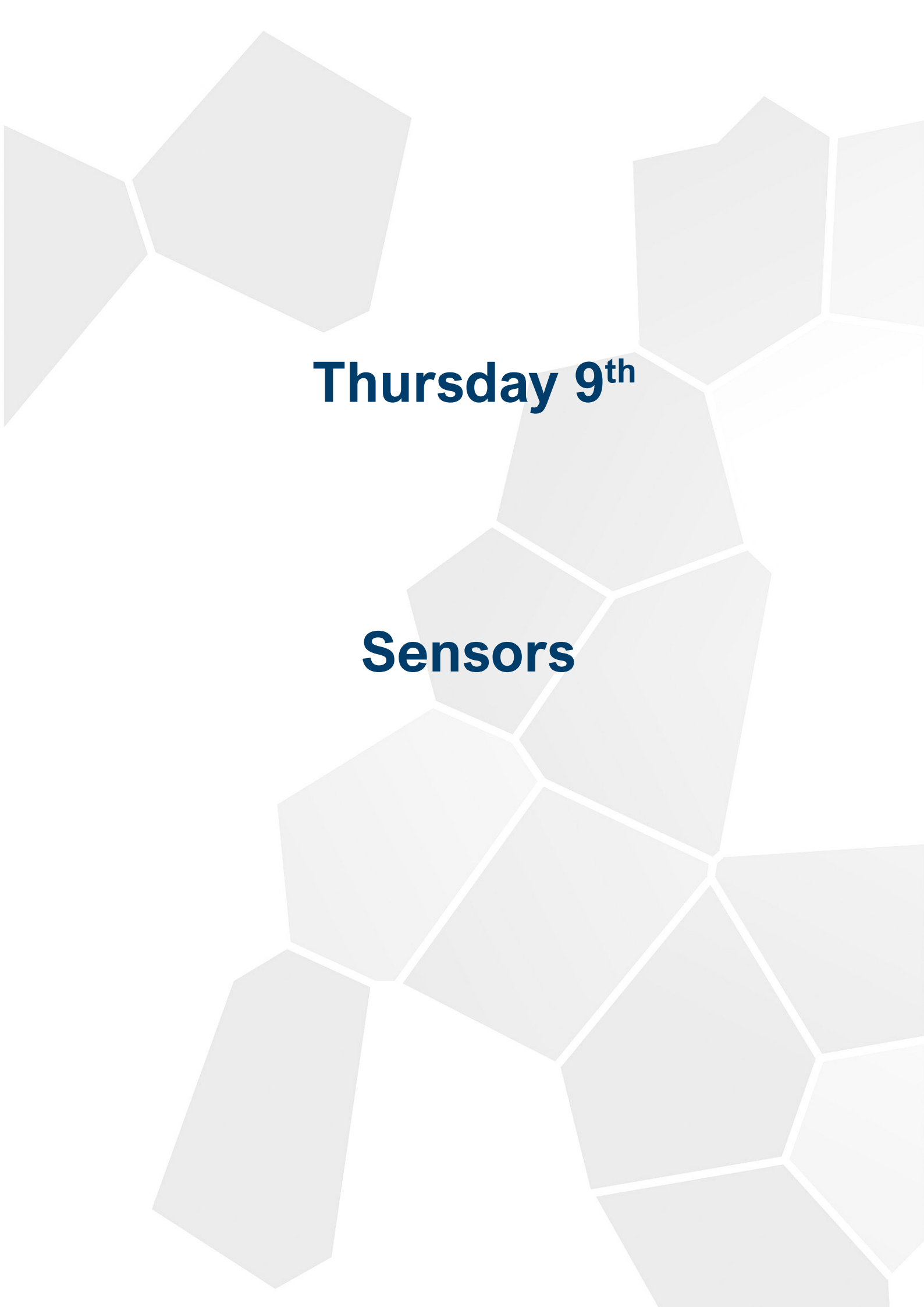
In the carbon dots photonic layer, numerical inputs are encoded through multi-wavelength LED excitation and converted into complex emission spectra, which are then processed by a Gaussian-process model. The resulting photonic-digital architectures outperform the corresponding digital-only model, reaching  $r^2 = 0.90$  and  $0.84$  during training and  $r^2 = 0.85$  and  $0.87$  during testing for the optical and neuromorphic implementations, respectively. In the HNA@BA photonic layer, the key functionality arises from dual fluorescence–phosphorescence emission and excitation-history-dependent photoactivation. The spectral overlap between the short-lived fluorescence channel and the long-lived phosphorescence channel gives an overlap integral of approximately  $4.56 \times 10^{11} \text{ erg}^{-1}$ , supporting efficient population transfer from singlet-related emissive states to triplet-related phosphorescent states. Using experimentally measured lifetimes within a combined Förster–Dexter framework, the energy-transfer rate was estimated to be approximately  $2.3 \times 10^7 \text{ s}^{-1}$ , with a characteristic donor–acceptor distance of about  $0.55 \text{ nm}$ . This sub-nanometre distance is consistent with the interlamellar spacing inferred from the lamellar morphology and indicates that short-range Dexter-type exchange interactions dominate, with a smaller Förster dipole–dipole contribution. These calculations establish a direct link between nanoscale structural organization and macroscopic optical memory, showing that interlamellar energy transfer underpins persistent phosphorescence, synaptic-like potentiation, and the transition from short- to long-term optical memory. When integrated into a hybrid photonic–digital neural architecture, these temporally separated optical channels enable MNIST classification with approximately 94% accuracy, including a smartphone-compatible implementation with comparable performance.

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## Acknowledgments

*This work was developed within the scope of the projects PhotonAI, Cutting-edge Photonic-Digital Hybrid Architecture for Next-Generation (2024.14411.PEX), CICECO Aveiro Institute of Materials, UID/50011/2025 (DOI 10.54499/UID/50011/2025) & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020), and Instituto de Telecomunicações, UID/50008/2025 (DOI 10.54499/UID/50008/2025)&LA/P/0109/2020 (DOI 10.54499/LA/P/0109/2020) financed by national funds through the FCT/MCTES (PIDDAC), and, when eligible, co-funded by EU funds. DOI 10.54499/CEECINST/00058/2021/CP2816/CT0004).*

The background features a collection of light gray, irregular geometric shapes, primarily pentagons and hexagons, scattered across a white field. These shapes are separated by thin white lines, creating a fragmented, crystalline effect. The shapes vary in size and orientation, with some appearing more prominent than others.

**Thursday 9<sup>th</sup>**

**Sensors**

# Feeling the Heat: Super-Resolved Hyperspectral Thermal Mapping with Upconversion Nanoparticles and Silver Nanowire Networks

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Light, matter, and heat are inseparable at the nanoscale, yet experimental tools have long treated them as independent variables. As plasmonic and transparent optoelectronic architectures become increasingly complex, their performance and stability are governed not only by their optical response but also by how and where electromagnetic energy is converted into heat. Accurate hotspot thermometry is particularly critical for detecting localized overheating, optimizing energy efficiency, and ensuring reliable device operation.<sup>1</sup>

Techniques for mapping nanoscale hotspots can be broadly divided into scanning and wide-field approaches. Scanning methods such as scanning thermal microscopy and fibre-optic thermometry provide high spatial precision through point-by-point measurements. However, their raster-based acquisition and probe-sample thermal interactions can limit their applicability in complex or dynamic systems. In contrast, wide-field optical methods based on luminescence thermometry, particularly those employing rare-earth-doped upconversion nanoparticles (UCNPs), enable rapid temperature readout over extended areas with submicron spatial resolution and broad operational ranges. When combined with hyperspectral microscopy, in which a full emission spectrum is recorded at each pixel, UCNPs enable quantitative thermometry with enhanced signal-to-noise ratio and the potential for sub-diffraction spatial resolution.

In this lecture, we will present a hyperspectral luminescence thermometry platform for quantitative mapping of heat dissipation in plasmonic nanostructures. By integrating UCNPs with electrically percolated silver nanowire (AgNWs) networks, we create optically addressable electrothermal systems in which heat generation, plasmonic field enhancement, and luminescent thermometry are intrinsically coupled.<sup>1,2</sup> Plasmonic junction hotspots strongly amplify multiphoton upconversion processes, revealing the interplay between the local electromagnetic density of states and nonlinear emission. However, this enhancement also introduces artifacts in conventional ratiometric thermometry, producing artificial thermal gradients.<sup>3</sup> However, an essential question remained unresolved: whether these electromagnetic hotspots corresponded to genuine local temperature increases.

To address this challenge, we developed ultrasmall (<10 nm) anti-thermal-quenching UCNPs whose emission intensity increases with temperature, enabling high signal-to-noise, pixel-resolved thermal mapping with sub-diffraction effective resolution. This approach allows direct visualization of conductive pathways, inactive AgNWs, and steep nanoscale thermal gradients in operating devices. Temperature gradients of  $8 \pm 1 \text{ K} \cdot \mu\text{m}^{-1}$  are resolved with an effective spatial resolution of  $\sim 88 \text{ nm}$ , surpassing the optical diffraction limit. Importantly, these measurements demonstrate that regions of enhanced electromagnetic fields are not necessarily

accompanied by local temperature increases, enabling experimental discrimination between plasmonic field hotspots and true thermal hotspots.

More broadly, hyperspectral upconversion thermometry provides a powerful framework for simultaneously probing light, heat, and nanoscale structure, opening new opportunities for the thermally informed design of advanced plasmonic, optoelectronic, and energy-conversion materials.

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# OPTICAL SPECTROSCOPIC METHODS FOR DETECTION OF INORGANIC NUTRIENTS IN WATER

**Anna JUSZA<sup>1,2</sup>, Jerzy KALWAS<sup>1,3</sup>, Aleksandra BIENIEK-KACZOREK<sup>1</sup>, Paweł BORTNOWSKI<sup>1</sup>, Łukasz KOZŁOWSKI<sup>1</sup>, Michał KOZUBAL<sup>1</sup>, Agata DANISZEWSKA<sup>1</sup>, Filip ŁABAJ<sup>3</sup>, Krzysztof ANDERS<sup>1,2,3</sup>, Stanisław STOPIŃSKI<sup>1,2,3</sup>, Edyta KIEDRZYŃSKA<sup>4</sup>, Natalia MATWIEJ<sup>4</sup>, Ryszard PIRAMIDOWICZ<sup>1,2,3</sup>**

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The progressive eutrophication of surface waters remains one of the most pressing environmental challenges in Europe and worldwide. Excessive inputs of inorganic nutrients - primarily nitrates ( $\text{NO}_3^-$ ), nitrites ( $\text{NO}_2^-$ ), phosphates ( $\text{PO}_4^{3-}$ ), and ammonium ( $\text{NH}_4^+$ ) - drive harmful algal blooms, including toxic cyanobacteria, reduce light penetration, disturb aquatic food webs, and promote the formation of hypoxic and anoxic zones. The Baltic Sea is a particularly critical example, hosting the world's largest annual maximum hypoxic zone among coastal seas. Despite well-established regulatory frameworks, effective mitigation is hindered by the limited temporal resolution of conventional monitoring strategies and the absence of autonomous in-situ analytical tools capable of continuous operation.

Traditional determination of inorganic nutrients relies on laboratory spectrophotometric (colorimetric) assays and chromatographic techniques, including ion chromatography. Although these methods provide high accuracy and low detection limits, they require sample collection and transport, skilled personnel, complex instrumentation, and chemical reagents. Consequently, monitoring is performed only periodically, preventing the detection of rapid concentration fluctuations associated with rainfall events, agricultural runoff, or accidental discharges. There is therefore a clear demand for compact, field-deployable sensing platforms enabling real-time analysis.

Optical spectroscopy offers a compelling alternative due to its non-destructive character and suitability for miniaturization and integration. This work presents an overview of optical spectroscopic approaches for detecting inorganic nutrients in water, with particular emphasis on techniques operating in the ultraviolet (UV) and mid-infrared (mid-IR) spectral regions. Both direct absorption-based methods and evanescent-field techniques are discussed, highlighting their physical principles, analytical performance, and material-related challenges relevant to photonic sensor design.

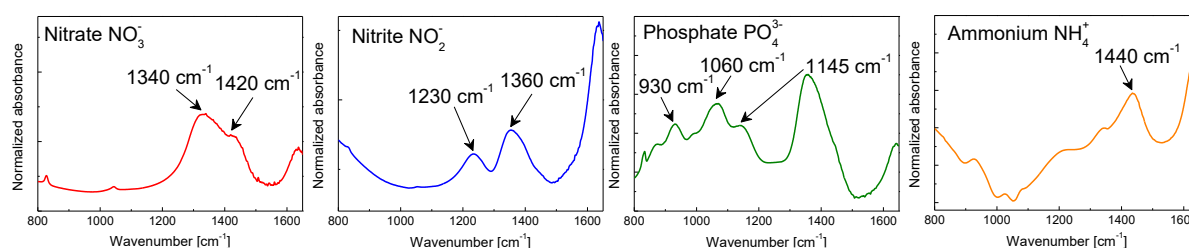
In the UV domain, transmission spectroscopy enables direct detection of nitrates and nitrites through their characteristic electronic transitions. Compact systems based on light-emitting diodes (LEDs) provide a cost-effective and scalable solution for wavelength-selective interrogation, facilitating integration into autonomous probes. Nevertheless, spectral overlap and interference from dissolved organic matter require careful calibration procedures and advanced signal processing to ensure robust quantification.

In the mid-infrared range (3–11  $\mu\text{m}$ ), attenuated total reflection (ATR) spectroscopy grants access to fundamental vibrational modes of nitrate, nitrite, phosphate, and ammonium ions. A horizontal ATR (HATR) configuration employing a multi-reflection ZnSe crystal enhances the interaction between the evanescent field and the analyte, thereby improving sensitivity while maintaining a compact geometry. The selection of appropriate ATR materials – ensuring chemical resistance, mechanical stability, and broad spectral transparency – is crucial for the development of durable sensors intended for aqueous environments.



The long-term objective of our research is the realization of a prototype photonic system for remote and continuous monitoring of selected water quality parameters. The proposed architecture combines UV transmission spectroscopy with mid-IR FTIR-ATR measurements, exploiting complementary detection mechanisms: electronic transitions in the UV and fundamental vibrational modes in the mid-IR. This dual-modality approach enhances selectivity and enables cross-validation within a unified sensing platform.

A compact laboratory demonstrator based on discrete UV LEDs was constructed and optimized with respect to optical path length, stray light suppression, and detector sensitivity. Complementary measurements were performed using a multi-reflection horizontal ZnSe ATR cell integrated into an FTIR setup. The obtained spectra (showed in Fig. 1) exhibit well-defined absorption features corresponding to the characteristic vibrational bands of the investigated ions, confirming the suitability of mid-IR evanescent-field spectroscopy for quantitative aqueous analysis.



**Fig. 1** FTIR-ATR absorbance spectra of nitrate, nitrite, phosphate and ammonium ions with characteristic bands indicated.

The combined implementation of UV transmission and mid-IR ATR spectroscopy demonstrates the feasibility of a multi-modal photonic sensing architecture capable of reliable nutrient quantification. This approach constitutes a significant step toward integrated, autonomous systems for long-term environmental monitoring in natural aquatic ecosystems.

**Acknowledgments:** This work has received support from the National Centre for Research and Development through project FOSMO (HYDROSTRATEG1/000E/2022).

# Multilayer Optical Sensor for High-Energy Radiation Detection

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Conventional radiation sensors rely on a two-step process in which high-energy radiation (such as vacuum ultraviolet radiation, x-rays, or gamma rays) is first absorbed by a luminescent material (scintillator) that converts the radiation into UV or visible light. This light is subsequently detected by a separate photodetector, which transforms it into electrical signals for analysis. While effective, this approach requires two distinct components, limiting opportunities for sensor miniaturization and cost reduction. In this work, we present a hybrid radiation sensor that integrates scintillator and photodetector functionalities into a single device. The design involves coating the surface of a scintillator (Ce:YAP or Gd<sup>3+</sup>-doped borosilicate glass) with a titanium dioxide (TiO<sub>2</sub>) photoconductive semiconductor thin film. Aluminum electrodes are then applied to enable measurement of photocurrent generated when the TiO<sub>2</sub> film absorbs light emitted by the scintillator. This configuration allows the conversion of high-energy radiation into electrical signals, removing the need for a separate photodetector [1]. Testing with a vacuum ultraviolet source emitting at 160 nm demonstrates that the hybrid device produces a current approximately four orders of magnitude greater under irradiation compared to background levels. Further investigations reveal that thermal treatment during or after TiO<sub>2</sub> deposition enhances film crystallinity and optical quality, leading to improved detector performance [2,3]. Detection of 45 keV x-rays using a Ce:YAP/TiO<sub>2</sub> hybrid sensor will also be presented. This hybrid sensor concept offers a pathway toward more compact, economical, and integrated radiation sensors. Such advances hold promises for applications ranging from medical imaging and security screening to scientific instrumentation requiring sensitive and reliable radiation detection.

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# **Spatial Multiplex Immunofluorescence in Head & Neck Tumours**

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Spatial proteomics has emerged as a transformative tool for decoding the complex tissue architecture of head and neck tumours. By enabling high-dimensional, in situ characterisation of protein expression at single-cell and subcellular resolution, these technologies provide critical insights into immune phenotypes, tumour heterogeneity, and cell–cell interactions that are not accessible through conventional bulk or dissociative approaches. They allow precise spatial mapping uncovering spatially resolved biomarkers associated with disease progression and therapeutic response.

Among these approaches, multiplex immunofluorescence (mIF) has become a particularly powerful and clinically adaptable platform. mIF enables the simultaneous detection of multiple protein markers within a single tissue section while preserving spatial context, allowing detailed characterisation of cellular phenotypes, functional states, and cell–cell interactions within the tumour microenvironment. Recent advances in cyclic and iterative staining technologies, have significantly expanded the number of detectable markers and improved signal sensitivity and reproducibility.

Despite these advances, the clinical implementation of multiplex spatial proteomics remains limited. Standardisation of staining protocols, image acquisition, and data analysis pipelines - together with the development of scalable, interoperable analytical framework, will be essential to fully realise the potential of multiplex immunofluorescence–based spatial proteomics in precision medicine.

# BODIPY-based fluorescent pH sensors: synthesis, properties and theoretical insights

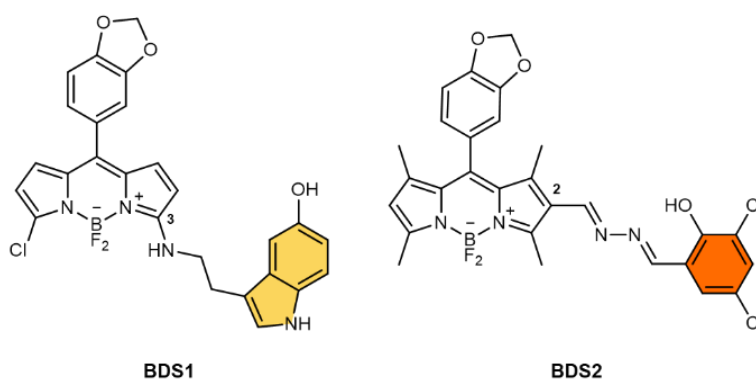
Patrycja PIĘKOŚ<sup>1</sup>, Nurgul TURSINOVA<sup>1</sup>, Jerzy SOKOLNICKI<sup>1</sup>, Maria JERZYKIEWICZ<sup>1</sup>, Wim DEHAEN<sup>2</sup>, Aleksander FILAROWSKI<sup>1</sup>

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Fluorescent BODIPY dyes are widely recognized for their strong absorption, high fluorescence quantum yield and remarkable photostability, which make them attractive platforms for the development of responsive fluorescent systems.<sup>1,2</sup>

In this work, two BODIPY-based dyes, designed as pH-responsive fluorescent probes, are presented. These dyes incorporate a benzodioxole fragment in *meso*-position as well as different functional substituents capable of modulating the electronic structure and the protonation behaviour of the chromophore, namely serotonin (**BDS1**)<sup>3</sup> and an *o*-hydroxy Schiff base (**BDS2**).<sup>4</sup> (Figure 1).



**Fig. 1.** Molecular structures of the BODIPY dyes (**BDS1** and **BDS2**) with colour-highlighted rings of the substituents: (1) serotonin and (2) *o*-hydroxy Schiff base.

The studied dyes were synthesized and characterized by NMR spectroscopy and mass spectrometry (MS). Their optical properties were investigated using UV–Vis absorption and fluorescence spectroscopy in solvents of varying polarity as well as under different pH conditions.

**BDS1** exhibits typical spectral features of the BODIPY core in non-polar media, while the increasing solvent polarity results in subtle shifts in absorption and the appearance of additional bands in highly polar environments, indicating the presence of different molecular forms and aggregation effects. The spectral behavior also shows a pronounced dependence on the protonation state of the substituent, reflected in changes of absorption and emission bands during the entire range of pH changes, thus, confirming the dyes' effectiveness as a pH sensor in the analyzed environments.

In contrast to **BDS1**, **BDS2** is characterized by pronounced negative solvatochromism, accompanied by changes in fluorescence intensity with significant spectral response, observed only under very low pH conditions.

DFT and TD-DFT calculations were performed, showing good agreement with the experimental data and providing a deep insight into conformational preferences, electronic transitions, and the role of non-covalent interactions.

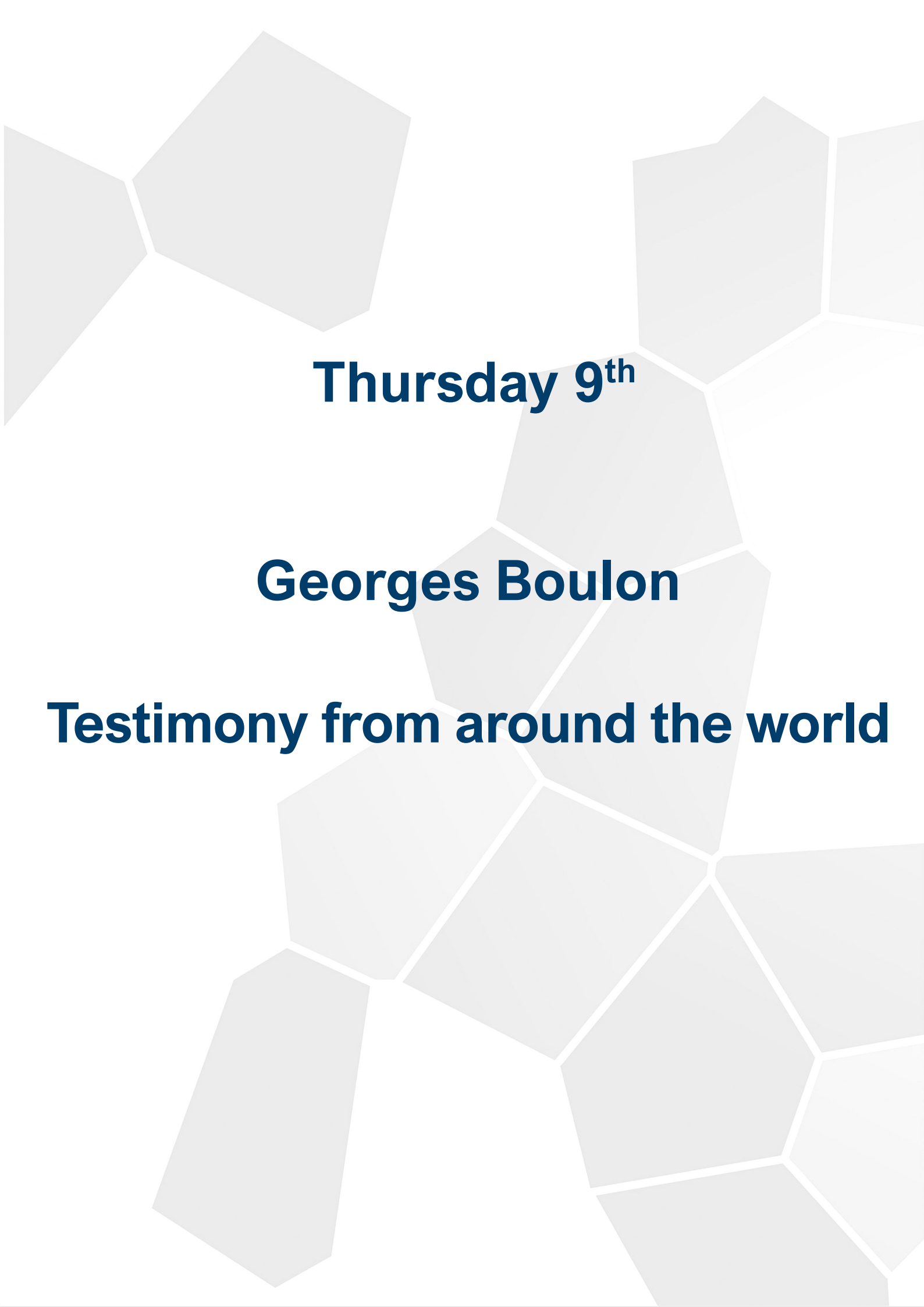
The combined experimental and theoretical analysis highlights how structural modifications of the BODIPY core affect the photophysical response of the studied dyes and their pH-sensing behaviour in different environments. These results demonstrate the potential of these systems as versatile fluorescent probes, and the observed effects are promising for the design of future functional BODIPY-based sensors.

#### ACKNOWLEDGMENTS

*The authors gratefully acknowledge the Wrocław Centre for Networking and Supercomputing (WCSS) for computational facilities.*

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The background of the slide is white, featuring several large, light gray, irregular geometric shapes that resemble facets of a crystal or pieces of a mosaic. These shapes are scattered across the page, with some overlapping. The text is centered over these shapes.

**Thursday 9<sup>th</sup>**

**Georges Boulon**

**Testimony from around the world**

## THANK YOU GEORGES

**Marie-France JOUBERT**

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It is with emotion that I will deliver this tribute to my colleague and friend Georges Boulon.

As he had wished during his higher education, Georges would become teacher and researcher in the university. He was recruited as a teaching assistant in 1966, became senior lecturer in 1971 and promoted professor in 1981, where he would climb all the ranks and steps.

Georges taught at all levels of the University Claude Bernard Lyon 1, mainly in the disciplines of atomic physics, physical optics, quantum optics, nonlinear optics, materials for optics and lasers. He also taught at other Lyon institutions such as engineering schools and at the higher normal school ENS. His lectures were very popular with students; the lecture halls were full with him, even in engineering schools. He also taught and presented numerous educational lectures on luminescence and laser materials in international summer schools or as a visiting professor in various universities (USA, Europe, Brazil, Japan, China).

Georges was a passionate researcher. His research focused primarily on the growth and structural as well as optical characterizations of inorganic crystals containing luminescent ions; often, with his team and collaborators, he studied these materials with a view to their potential application as solid-state lasers. His contribution to the advancement of knowledge in this field is extraordinary, as evidenced by the number of his productions. He was recognized worldwide and chaired many international conferences, including the International Conference of Luminescence (ICL), the largest international conference in the field, which he successfully organized in Lyon in July 2008 (650 participants). Thanks to his remarkable activities, his exceptional work ethic, and his interpersonal skills (always attentive, patient, and understanding), Georges has developed numerous collaborations in France and abroad, particularly in the USA, then in Spain, Italy, Poland, Russia, Israel, Brazil, China, and Japan, where he has spent considerable time. Georges hosted researchers at the laboratory and he traveled a lot abroad.

Highly sought after to take on collective responsibilities, he has always been willing and has never spared his time or energy in this area. He received several scientific awards and was Doctor Honoris Causa of 3 universities: the Autonomous University of Madrid, the University of Wroclaw and the Rovira I Virgili University of Tarragona. He has been awarded the rank of Chevalier in the order of the Academic Palms as well as rank of Chevalier in the National Order of Merit.

As for the Academy of Sciences, Letters and Arts of Lyon, Georges Boulon was elected on December 7, 2010, to seat 8, section 1 of the Sciences class. He was always very diligent in attending the academy's meetings. He enjoyed meeting up with his colleagues and friends there and felt at home. He was elected Vice-President for the year 2021 and President of the Academy for the year 2022. Not only was he a very courteous and always attentive President, but we should highlight his excellent year as President during which the Academy organized three exceptional events outside its premises and was involved in the publication of the book 'Physics in Lyon. A gallery of portraits since Ampère' as part of the celebration of the 150<sup>th</sup> anniversary of the French Physical Society.

Our colleague and friend Georges was a scientist of international stature. He taught us and gave us a lot, and we owe him a great deal. Many of his colleagues, students and friends honored his memory via

different ways. It is very important to emphasize that in his professional life and in the Academy, it was not only science that mattered to him, there were also human relationships and friendship.

Thank you to the organizers of his 10th anniversary edition of ISOM, a conference he co-founded 30 years ago, to take this opportunity to pay tribute to him.

Georges, we pay you a sincere, profound, and grateful tribute.

Thank you.



*Fig. 1 Memories of Georges*



# **The memory of cooperation on luminescent glasses between Prof.Boulon and SIOM, China**

Lili Hu

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Abstract: My research field is luminescent and laser glasses doped by rare earth ions and bismuth ion. Prof.Boulon was elegant and distinguished scholar in luminescent material field with open and kind mind. He was very interested at Chinese culture and was ready to help Chinese colleagues. He was the visiting professor of our Institute since 2012. My research team had more than 20 years cooperation with Prof.George Boulon. Prof.Boulon had given us many advices and helps in the fundamental research of luminescence glasses. We had made 25 co-published papers since 2005. I will share the cooperation experience between my research group and Prof.Boulon as well as Prof.Guzik in past 20 years by the time. Here I attached some photos of Prof.Boulon taken in Shanghai visit and with my group members.



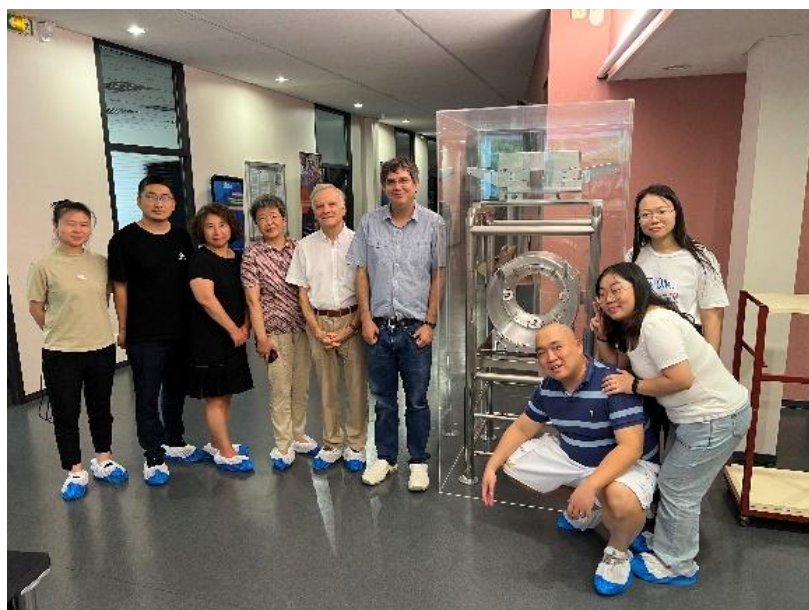
The appointment ceremony of Prof.G.Boulon as visiting professor of Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences in 2012



Prof.G.Boulon gave a lecture in Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences in 2012



Prof.G.Boulon visited Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences in 2019



Prof.G.Boulon hosted visiting Chinese colleagues in Lyon Univ. 1, France in Sept.2023

# GEORGES BOULON AND RUSSIAN OPTICAL COMMUNITY

Marina POPOVA

<sup>1</sup> *Institute of Spectroscopy of the Russian Academy of Sciences, Department of Condensed Matter Spectroscopy, Troitsk, Moscow, Russia*

Georges Boulon has defended his Diplôme d'Etudes Approfondies "Spectronomy" on July 1966, then his thesis of Doctorat 3ème cycle "Photoluminescence properties of the Bi<sup>3+</sup> ion in alkaline earth antimonates" on March 1, 1968 and his PhD thesis (Doctorat d'Etat ès-Sciences Physiques) "Photoluminescence process and dynamics of excited states of Bi<sup>3+</sup> ions in sesquioxides (Y,Sc,Gd) and orthovanadates (Y,Sc,Gd)" on June 1, 1970 at the Physical Chemistry of Luminescent Materials Laboratory of the University of Lyon (Supervisors: Dr. Françoise Gaume and Pr. Daniel Curie).

George Boulon's student years, like my own, coincided with the beginning of the laser era: in 1960, the first laser (the Maiman's ruby laser) was created, and in 1964, Charles Townes (Columbia University), Nicolay Basov and Aleksandr Prokhorov (Lebedev Physical Institute of the USSR Academy of Sciences) were awarded the Nobel Prize in Physics "for fundamental work in the field of quantum electronics, which has led to the construction of oscillators and amplifiers based on the maser-laser principle". At that time, whilst a student at the Moscow Institute of Physics and Technology, I worked in the Luminescence Laboratory of the Lebedev Physical Institute under the supervision of Prof. M.D. Galanin and Dr. A.M. Leontovich. There, I was a member of the research group that conducted the first studies of the ruby laser in the USSR and defended my PhD thesis "Dynamics of ruby laser" in 1968.

In August 1972, the International Conference on Luminescence was held in Leningrad, USSR. Georges Boulon and Daniel Curie have presented a talk "Luminescence processes in Bi<sup>3+</sup> centers", and I was appointed as a French translator for D. Curie. It is worth noting that Bi<sup>3+</sup> ions have attracted great attention of E.M. Dianov, collaborator of A.M. Prokhorov at the Lebedev Institute and head of the Centre of Fiber Optics there, in connection with fiber optics.

Intensive work on laser research, the creation of new ones, and the search for effective laser media has unfolded worldwide. Georges Boulon's work has earned a prominent place in this field. In the USSR, and then in Russia, such research was conducted in the General Physics Institute RAS (I.A. Shcherbakov, V.V. Osiko, Yu.K. Voron'ko, A.A. Sobol, B.I. Denker, T.T. Basiev), the Institute of Crystallography RAS (A.A. Kaminskii, Kh. S. Bagdasarov), Vavilov State Optical Institute (P.P. Feofilov), Ioffe Physical-Technical Institute RAS (A.A. Kaplyanskii, S.P. Feofilov), Moscow State University (B.V. Mill) and many other places. Georges Boulon was aware of all of this work and cited it in his articles, just as Russian researchers cited his work. In the 1990s, Georges collaborated fruitfully with Alexandr Kaminskii and published 10 joint articles with him and his colleagues. Three of them are cited below. Georges Boulon was a regular participant in the Feofilov Symposia on the Spectroscopy of Crystals Doped with Rare Earth and Transition Metal Ions, held in various cities across Russia. His invited lectures invariably attracted great interest from the audience.

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# LOCATION AND ENVIRONMENT OF TRIVALENT RARE EARTH IONS IN LITHIUM NIOBATE CRYSTALS

**José García SOLE**

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Professor Georges Boulon has played an outstanding role in the research and development on new optical materials. One of the main subjects that we faced together is the study of the local structure of optically active ions in different crystalline materials, which finally determine the most relevant applications of any optical material. As a relevant example of our joint scientific trajectory I will show how, using optical techniques and Rutherford Back Scattering, we determined the site location and non-equivalent environments of trivalent lanthanide ions in Lithium Niobate crystals. These crystals have a large variety of applications in laser physics, non-linear optics, optical communications and optical memories. This joint research marked strong friendship a fruitful and large cooperation between the Laboratory of Luminescence Materials (University of Lyon), headed by him for a large period, and the Department of Materials (Universidad Autónoma de Madrid, UAM), which was culminated with the recognition of Georges as Doctor Honoris Causa by the UAM by 2009 (see photos bellow).



# Georges Boulon: a life devoted to Luminescence

Marco BETTINELLI

<sup>1</sup> *Luminescent Materials Laboratory, Univ. Verona, Verona, Italy*

Professor Georges Boulon has been a real scientific pioneer and a source of continuous inspiration for researchers in our field. His highly original and creative work has been crucial for the development of the modern science of luminescent materials.

I have met Georges for the first time in the early '90s at a conference in Poland, and since then we have discussed very frequently during numerous scientific meetings.

His contributions to the development of inorganic luminescent materials are very numerous and influential. In my opinion, especially important are the ones related to the following topics:

- 1) Advances in the synthesis and spectroscopy of novel laser crystals, transparent ceramics and glasses
- 2) Investigation of energy transfer and quenching processes involving  $\text{Ln}^{3+}$  ions
- 3) Spectroscopy of the  $\text{Bi}^{3+}$  and  $\text{Yb}^{3+}$  ions

Our collaboration has led to the publication of two joint scientific papers:

- Hreniak, D., Stręk, W., Speghini, A., Bettinelli, M., Boulon, G., Guyot, Y., Infrared induced red luminescence of  $\text{Eu}^{3+}$ -doped polycrystalline  $\text{LiNbO}_3$ , (2006) *Applied Physics Letters*, 88 (16), art. no. 161118.

- Kaminska, A., Kozanecki, A., Ramírez, M.O., Bausá, L.E., Boulon, G., Bettinelli, M., Boćkowski, M., Suchocki, A., Spectroscopic study of radiative intra-configurational  $4f \rightarrow 4f$  transitions in  $\text{Yb}^{3+}$ -doped materials using high hydrostatic pressure (2016) *Journal of Luminescence*, 169, pp. 507–515.

Georges was an extremely kind and nice person, always available for help and explanations to colleagues and young researchers. He also possessed a special personal charisma. Our scientific community will miss him immensely.

**Fig. 1** In the pictures, Georges Boulon is portrayed with Renata Reisfeld (left), and with the participants of a meeting in Erice organized by Rino Di Bartolo (right).



# REMEMBERING GEORGES BOULON: A PERSONAL AND SCIENTIFIC REFLECTION

ALOK M. SRIVASTAVA

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*Srivastaam@outlook.com*

Professor Georges Boulon's research spanned an extraordinary range of topics—from rare-earth and transition-metal luminescent materials to nonlinear crystals, glasses, and transparent ceramics. Rather than attempt to cover all he accomplished, I want to acknowledge the two areas that shaped my own research path.

As a doctoral student in the 1980s, his studies on  $\text{Bi}^{3+}$  luminescence left a deep impression on me. His careful temperature-dependent measurements revealed the key role of the metastable  $^3\text{P}_0$  level, and that insight guided much of my early thinking. Later, his work on  $3d^3$  ions such as  $\text{Mn}^{4+}$  and  $\text{Cr}^{3+}$ , in crystals, glasses, and glass ceramics, helped me understand how subtle structural changes influence optical behavior.

I cannot clearly recall whether I met Georges before 1996, but in 1996 I met him at the Erice Workshops held at the Ettore Majorana Centre for Scientific Culture in Erice, Sicily. That encounter marked the beginning of a long and meaningful scientific and personal relationship that continued from 1996 to 2018. At the 2016 workshop, I gave a talk on the luminescence of  $\text{Bi}^{3+}$  in solids. I told the audience that I was quite nervous, knowing that Georges Boulon, one of the pioneers in the luminescence of  $\text{Bi}^{3+}$ , was sitting in the lecture hall. True to his generous nature, Georges, both a wonderful person and an exceptional scientist, was warm and appreciative of the talk.

Over the years, he extended many opportunities to me. He invited me to deliver a plenary lecture at ICL 2008 in Lyon. When he became Editor-in-Chief of Optical Materials, he asked me to join the journal as an Associate Editor. And most significantly, at the 2014 Erice workshop, Georges and Małgorzata Guzik (Margot) offered me the chance to lead Optical Materials as its Editor-in-Chief. I was deeply humbled that Georges saw me in that role, and I will always remain grateful to him for giving me the opportunity to guide the journal.

With Georges's passing, we have lost an extraordinary scientist and a truly remarkable human being. He will be remembered for his cheerful spirit, his wide-ranging scientific contributions, and his lasting impact on our community.





*Fig 1. Memories of Georges Boulon*

## A TRIBUTE TO AND MEMORIES WITH GEORGES BOULON, FROM BRAZIL

**OSCAR MANOEL LOUREIRO MALTA**

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Georges Boulon is a renowned researcher, widely recognized for his pioneering contributions to the field of optical spectroscopy of materials doped with rare-earth and transition metal ions. Throughout his career, he was associated with the CNRS (Centre National de la Recherche Scientifique), where he conducted highly impactful research on luminescence processes and energy transfer in solids in the Université Claude Bernard in Lyon. It is worth emphasizing that he was a great friend and visited Brazil to participate in ICL 2017 in João Pessoa. However, earlier he visited the State University of Maringá and the State University UNESP in Araraquara, motivating many Brazilian students. His work has been fundamental to advancing photonic materials, particularly in applications such as solid-state lasers, optical devices, and light-conversion technologies. With extensive, highly cited scientific output, Georges Boulon is regarded as an international reference in the field, having trained generations of researchers and collaborated with numerous groups worldwide.



*With Georges*

# Optical Crystals: Materials Design, Crystal Growth from the Melt, and Structural and Spectroscopic Characterization

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<sup>4</sup> Institute of Physics, Czech Academy of Sciences, Prague, Czech Republic; <sup>5</sup> Université Claude Bernard Lyon 1, UMR 5620 CNRS, Villeurbanne, France (corresponding author: akira.yoshikawa.d8@tohoku.ac.jp)

Throughout the history of civilization, major advances have been inseparable from the discovery of new materials and from our ability to enhance their purity, reduce structural imperfections, and control defects. Optical crystals are no exception. Their development requires a subtle interplay of crystal chemistry, phase equilibria, thermodynamics, and solid-state physics and chemistry, together with a precise understanding of luminescent centers and spectroscopic behavior. In this presentation, I will discuss the development of novel optical crystal materials through an integrated approach combining materials design, crystal growth from the melt, and structural and spectroscopic characterization.

Representative examples include rare-earth-doped garnets, fluorides, pyrophosphates, niobates, and oxyapatites. Particular emphasis will be placed on the complementary roles of the micro-pulling-down and Czochralski methods. The former is a powerful and rapid technique for compositional screening and proof-of-concept crystal growth, whereas the latter remains indispensable for the preparation of high-quality bulk crystals suitable for detailed characterization and practical implementation. Through these examples, I shall highlight how the intimate relationship between composition, growth conditions, crystalline perfection, and spectroscopic functionality can guide the rational design of advanced optical crystals [1-4].

In pursuing these studies, I had the privilege of being guided by Prof. Boulon, who was a formative figure in my scientific life. From the very beginning of my career, he mentored me with extraordinary breadth of knowledge, unwavering intellectual rigor, and profound respect for experimental fact. Without my collaboration with Prof. Boulon, I would not, after moving from the field of superconductivity to that of optical crystals, have been able to obtain results worthy of early publication. Thanks to his guidance and generous support, I was able to establish my own scientific path. He was always available for discussion, and his wise advice illuminated the way forward. The scientific and human lessons I received from him remain among the most precious treasures of my academic life.



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# GEORGES BOULON: AN OUTSTANDING SCIENTIFIC MENTOR AND AN EXCEPTIONAL PERSON – A TRIBUTE FROM POLAND

Malgorzata GUZIK <sup>1,2</sup>

<sup>1</sup> *University of Wrocław, Faculty of Chemistry, Wrocław, Poland*

<sup>2</sup> *Łukasiewicz Research Network – PORT Polish Center for Technology Development, Wrocław, Poland*  
(corresponding author: malgorzata.guzik@uwr.edu.pl)

This lecture is dedicated to the memory of Professor Georges Boulon and his long-standing collaboration with Polish researchers, as well as to the enduring scientific and personal legacy he left behind. For more than three decades, he maintained close collaborations with researchers from Poland, especially from Wrocław, *i.e.*, from the University of Wrocław and from the Polish Academy of Sciences, inspiring generations of young scientists through his knowledge, openness, kindness, and enthusiasm for science.

For us, he was much more than an internationally renowned authority in luminescence, laser materials, and optical spectroscopy. He was our dear friend, a trusted scientific partner, and a person whose presence always brought wisdom, warmth, and genuine kindness. Every visit by Professor Boulon to Wrocław and every opportunity to meet him at international conferences were inspiring occasions, eagerly anticipated by us, our students, and young researchers. He had a rare gift for making people feel valued, encouraging them to think boldly and to pursue scientific excellence with passion and integrity.

His scientific achievements are universally recognised and have profoundly influenced the development of optical materials and luminescence research worldwide. Yet those who had the privilege of knowing him personally will remember above all his generosity, humility, intellectual curiosity, and sincere interest in other people. These qualities made him not only a great scientist but also an exceptional human being. He loved being with and talking to young people and had excellent relationships with them. It kept him young. No one ever felt the doctoral student-professor barrier, because you treated everyone as a partner. He was firmly convinced that women have a place in teaching and scientific research, and you always supported and defended them when necessary. He believed that each of us could be the next Marie Skłodowska-Curie. This is also what made him exceptional.

The University of Wrocław was deeply honoured to confer upon Professor Georges Boulon the title of Doctor Honoris Causa. This distinction symbolised our admiration for his outstanding scientific accomplishments, but equally our gratitude for the lasting friendship he offered to our University. He became a member of our academic family, and we have always regarded him as one of us. Many scientific collaborations initiated or inspired by Professor Boulon continue today. His ideas live on in many research projects, more than one hundred publications with Polish researchers, and, above all, in the people whom he mentored and inspired. His legacy is not measured solely by scientific discoveries, but also by the countless friendships he built across borders and generations.

Although his passing has left a great void, his spirit remains present wherever curiosity, collaboration, and kindness guide scientific endeavour. His life reminds us that the greatest scientists are remembered not only for what they discovered, but also for how they inspired others.



The memory of this distinguished scientist, extraordinary mentor, and cherished friend will remain with us forever. As we remember him today, let us carry with us the joy and privilege of having known him, and the pride of having crossed paths with such an exceptional person.

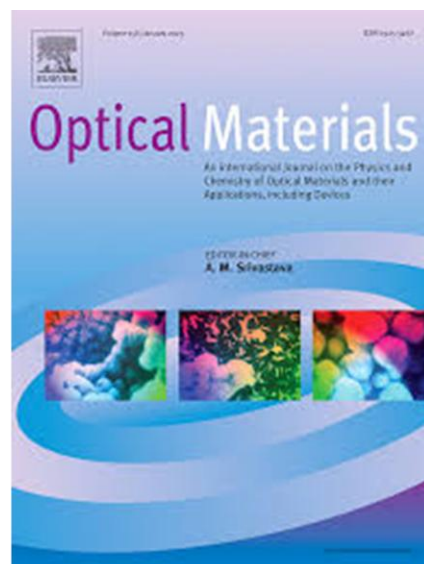


**Figure 1** Excited States of Transition Elements and Workshop on Luminescence, ESTE2010, September 4-9, 2010, Piechowice & Wrocław, Poland



**Figure 2** Professor Georges Boulon receiving the Honorary Doctorate (Doctor Honoris Causa) from the University of Wrocław, November 15, 2010.





**Figure 3** Professor Georges Boulon, Editor-in-Chief of *Optical Materials*, together with his team: Joanna Cybińska, Małgorzata Guzik, and Dariusz Hreniak.



**Figure 4** Visit to Wrocław on the occasion of the Symposium on Advanced Technologies and Materials (ATAM 2024), held at PORT in Wrocław on June 5–7, 2024.

The background features several light gray, irregular geometric shapes, primarily pentagons and hexagons, scattered across a white field. These shapes are semi-transparent and overlap each other, creating a layered, crystalline effect. The shapes are more concentrated in the upper and lower portions of the frame, leaving the center relatively clear for the text.

# Friday 10<sup>th</sup>

## Weekly summary



**Friday 10<sup>th</sup>**

# **Transparent Ceramics I**



# EVOLUTION OF LASER CERAMICS: FROM HOMOGENEOUS MATERIALS TO MULTILAYER AND WAVEGUIDE STRUCTURES

Laura ESPOSITO<sup>1</sup>, Jan HOSTAŠA<sup>1</sup>, Francesco PICELLI<sup>1</sup>, Guido TOCI<sup>2</sup>

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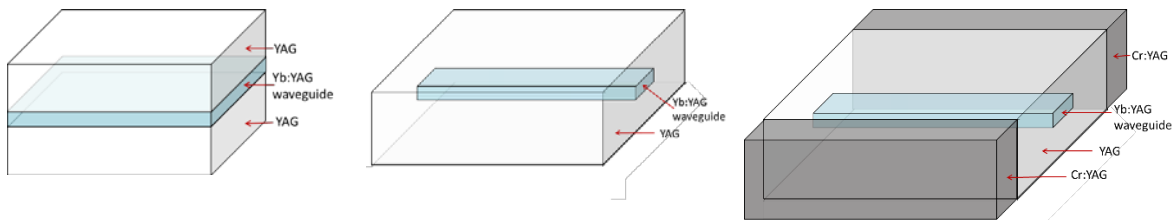
Over the past three decades, laser ceramic technologies have advanced significantly, evolving to meet increasingly stringent performance requirements [1].

Research has progressed from the understanding of key phenomena, such as the role of the sintering aids and powder characteristics on the transparency of ceramics, the distribution of active ions in the microstructure, or the spectroscopic properties of single-doped and co-doped compositions, to the design and fabrication of sophisticated multicomponent architectures [2, 3].

These advanced structures, often guided by modeling and simulation, are specifically engineered to mitigate thermal stresses arising during laser operation [4].

This presentation pays particular attention to Yb<sup>3+</sup>-doped materials [5]. It will provide an overview of this evolution, with emphasis on the most recent results obtained in laser waveguide development. Namely, an innovative approach for the production of modelled planar laser waveguides will be illustrated.

The adopted approach combines two shaping techniques tape casting and powder pressing, which, when integrated, enable the fabrication of complex two-dimensional architectures [6]. This methodology has been applied to the production of the structures resulting from the modelling and illustrated in the figure below: Yb:YAG laser waveguides embedded in undoped YAG, with Cr<sup>4+</sup>:YAG as absorbing regions. The guiding effect is due to the higher refractive index of the doped Yb:YAG compared to the pure YAG.



**Fig. 1** Schematic of a planar waveguide (a), channel waveguide (b), and a channel waveguide with Cr<sup>4+</sup>:YAG cladding (c).

In a planar waveguide (Fig. 1.a) the guiding region consists of a flat Yb:YAG layer embedded within an undoped YAG volume, thus having a lower refractive index.

In a channel (2D) waveguide (Fig. 1.b) the guiding region is a rectangular Yb:YAG channel fully surrounded by undoped YAG.

In Fig. 1.c the channel waveguide is cladded with Cr<sup>4+</sup>-doped YAG as absorbers to suppress the amplified spontaneous emission (ASE).

The various processing steps will be presented, and the results obtained under different experimental conditions will be reported.

The authors gratefully acknowledge the support from the Italian Ministry of Defence under PNRM, Contract No. 8731 of 04/12/2019 (CeMiLAP<sup>2</sup>).

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# YB-DOPED CERAMICS FOR LASER APPLICATIONS: FROM PIONEERING STUDIES TO HIGH EFFICIENCY COMPOSITE MATERIALS

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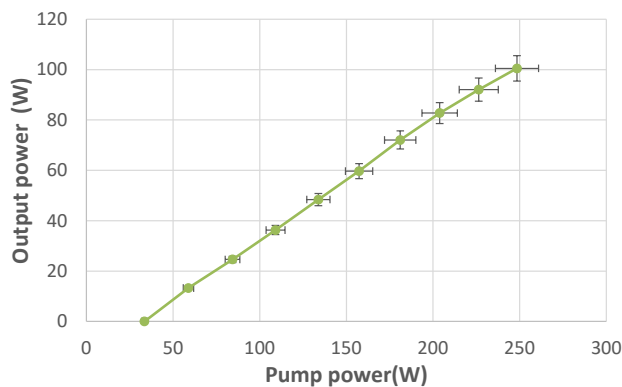
Since their first appearance in the late nineties, transparent ceramics for laser applications have shown a significant evolution, from the first examples of transparent materials up to state of the art realization that feature composite structures with non-uniform doping distribution, capable to achieve high laser emission efficiency and output power.

This presentation will first retrace some of the pioneering studies to which Prof. G. Boulon gave an outstanding contribution, in cooperation with the researchers of the Italian National Research Council (CNR), on subjects such as Nd and Yb-doped sesquioxide ceramics<sup>1</sup>.

Then the subject will shift to the most recent achievements obtained at CNR, where in the framework of several national programs<sup>2,3</sup> we developed YAG–Yb:YAG multimode active waveguides for laser applications. Some designs also include Cr:YAG absorbing regions, introduced to suppress unwanted amplified spontaneous emission (ASE).

The guiding structure was realized by embedding a thin strip composed of Yb<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and Y<sub>2</sub>O<sub>3</sub> powders into a bulk matrix of pressed Y<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> powders.

The aim of these waveguide lasers is to provide an active medium architecture suitable for an efficient pump power coupling, and control of the temperature gradients via an efficient removal of the heat generated during laser action.



**Fig. 1 Left: Output power vs. pump power obtained from a YAG/Yb:YAG ceramic waveguide. Right: picture of the waveguide input (the area shown in the picture is 2.42 x 1.82 mm)**

These waveguides were tested in a high-power laser setup, achieving a maximum output power exceeding 100 W in *quasi*-CW emission conditions, under semiconductor laser pumping. The slope efficiency was as high as 46 %.

In the presentation, we will describe the design of the waveguides, their optical properties, and how these structures were integrated in the laser source. The architecture of the laser setup and its emission properties will also be described in details.

The authors gratefully acknowledge the support from the Italian Ministry of Defence under PNRM, Contract No. 8731 of 04/12/2019 (CeMiLAP<sup>2</sup>).

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# ELABORATION OF HIGHLY TRANSPARENT RARE-EARTH SESQUIOXIDE CERAMICS FOR LASER APPLICATIONS

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Currently, the most widely used material in solid-state lasers is single-crystalline neodymium-doped yttrium aluminum garnet (Nd:YAG), primarily operated at a laser wavelength of 1.06  $\mu\text{m}$ . For high-power laser systems, gain media with high thermal conductivity are generally preferred in order to efficiently dissipate the heat generated during laser operation. Extensive studies have demonstrated that rare-earth sesquioxides exhibit significantly higher thermal conductivity than YAG, and can be used as efficient amplifier media in solid-state lasers [1]. Nevertheless, their production in the form of single-crystals is very expensive and remains limited to small pieces < 1 cm due to their high melting temperature superior to 2400°C, and high-temperature phase transitions in some cases.

In recent years, advances in ceramic processing technologies have enabled the large-scale fabrication of these materials in the form of transparent polycrystalline components with tailored compositions, such as  $\text{Sc}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ , or  $\text{Lu}_2\text{O}_3$  doped with various luminescent ions including  $\text{Ho}^{3+}$ ,  $\text{Yb}^{3+}$ , and  $\text{Nd}^{3+}$ , depending on the targeted laser wavelength [2-4]. More recently some studies have also highlighted the interest in developing magneto-optical transparent ceramics like  $\text{Ho}_2\text{O}_3$ ,  $\text{Tb}_2\text{O}_3$  or  $\text{Tb}_{1-x}\text{Lu}_x\text{O}_3$  as Faraday rotators in high power lasers [5]. As a result, ceramic technology offers several major advantages for the production of innovative solid-state laser materials, including the capability for high-volume production of components in a wide range of sizes, as well as the fabrication of new compositions that are hardly achievable using current single-crystal growth techniques.

This work focuses on the fabrication and characterization of transparent ceramics mainly based on  $\text{Lu}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  doped with luminescent ions such as  $\text{Eu}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Ho}^{3+}$ ,  $\text{Dy}^{3+}$  and  $\text{Tm}^{3+}$ .

A first research axis addressed the powder synthesis stage. The objective was to demonstrate the feasibility of producing pure, highly reactive nanopowders capable of achieving full densification during sintering. The selected synthesis route was aqueous precipitation, a method widely used for industrial-scale powder production. This technique offers several advantages: it is cost-effective, relatively fast, scalable to larger quantities, and readily adaptable to a wide range of compositions. Using this approach, nanopowders of  $\text{Lu}_2\text{O}_3$ ,  $\text{LuScO}_3$ ,  $\text{LuGdO}_3$ , and  $\text{LuYO}_3$  were successfully synthesized. The resulting particles exhibited isotropic grain morphology, crystallized in a cubic bixbyite-type structure, and had particle sizes ranging from 30 nm to 80 nm.

Subsequently, several experiments were conducted to shape these powders among other ones and sinter them in order to obtain transparent ceramics. In particular, three sintering techniques were compared: conventional vacuum sintering (secondary vacuum), flash sintering by Spark Plasma Sintering (SPS), and Hot Isostatic Pressing (HIP). The optical quality of the resulting ceramics was found to be strongly influenced by processing parameters, especially the chemical

composition of the powders, the nature of sintering additives, as well as the sintering temperatures and pressures, as illustrated in Figure 1.

One of the key challenges identified concerns the use of SPS. This technique offers the significant advantage of producing dense and transparent samples within a very short time (< 1 hour). However, it also presents notable drawbacks, including contamination from the graphite die used during sintering and potential hydroxide/carbonate contamination coming from the initial nanopowders. Such impurities are incompatible with their intended use as laser gain media and therefore require dedicated studies aimed at their elimination.

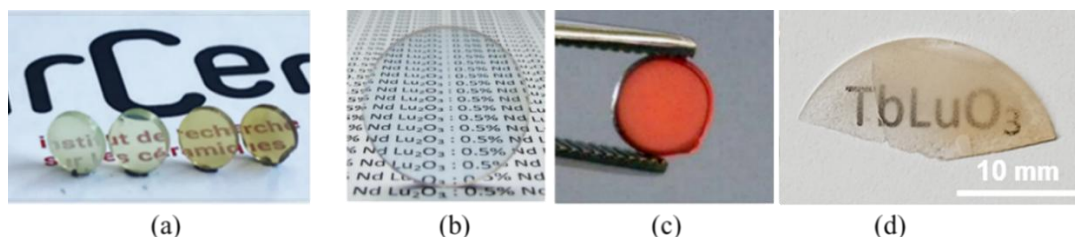


Figure 1: Macrographs of  $\text{Lu}_2\text{O}_3$ -based ceramic samples:  $\text{Lu}_2\text{O}_3:\text{Ho}$  fabricated by Spark Plasma Sintering (SPS) (1 at.% to 10 at.% from left to right) (a);  $\text{Lu}_2\text{O}_3:1 \text{ at.}\% \text{ Nd}$  fabricated by SPS (b);  $\text{Lu}_2\text{O}_3:\text{Eu}$  fabricated by conventional vacuum sintering (sample excited under UV illumination) (c); and  $\text{TbLuO}_3$  fabricated by conventional sintering under argon (d).

After more than 20 years of development, the research conducted at IRCER demonstrates that it is possible to fabricate transparent ceramics belonging to the rare-earth sesquioxide family. Compared with other sintering techniques, Spark Plasma Sintering (SPS) appears to be a particularly promising approach. However, key challenges remain, notably the complete elimination of residual porosity and the prevention of contamination by impurities such as carbon. Addressing these issues is essential before these materials can be reliably implemented in laser systems.

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# TRANSPARENT LITHIUM CERAMICS AS A SUITABLE MATRIX FOR THERMAL NEUTRON DETECTION

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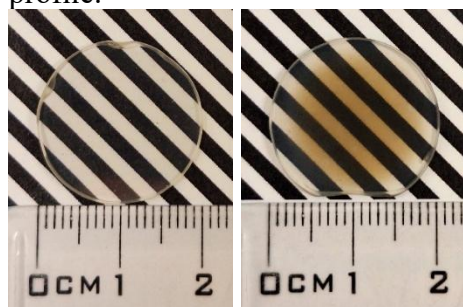
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A potential thermal neutron detecting solid material should possess several properties to be applicable. It should contain nuclei with a high neutron-capture efficiency while maintaining relatively low density to differentiate thermal neutrons from the gamma radiation background. The high-energy products of the neutron capture need to be converted into visible radiation to be detected, so the material should also be scintillating (either intrinsically or via doping) and this radiation needs to be led to a detector so the material should be as transparent as possible. Using suitable preparation methods, lithium-based aluminium oxide can be seen as such a potential material.

Pseudobinary system  $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3$  contains three stoichiometric phases:  $\text{Li}_5\text{AlO}_4$ ,  $\text{LiAlO}_2$  and  $\text{LiAl}_5\text{O}_8$ . The latter stands out thanks to its cubic spinel-like structure which makes it highly interesting to be processed by means of advanced sintering methods, such as Spark Plasma Sintering (SPS). SPS is a suitable alternative technique when transparent (or just highly dense) materials are required but single crystals are grown with difficulty for some reason. In the case of lithium aluminates, this reason is increased volatility of lithium which disrupts the stoichiometry of the melt.

In this work, the SPS preparation of highly transparent undoped  $\text{LiAl}_5\text{O}_8$  ceramics is presented. First, the powder precursor was synthesized via either solid-state reaction or Pechini polyesterification. The preparation method was one of the parameters evaluated, the other being annealing temperature to produce single-phase and properly crystalline precursor powder.

Second, the optimization of the SPS process followed, which is always a more complex and challenging part of transparent ceramics development because of a multi-parameter character of the method. Besides the sintering temperature and its dwell time, heating and cooling profiles have to be optimized. In the case of  $\text{LiAl}_5\text{O}_8$  ceramics, we first had to suppress significant abnormal grain growth resulting in non-uniform microstructure, thus causing lower transparency of samples. Then, due to extensive cracking of the SPS-prepared pellets (otherwise highly transparent), further optimization was needed, namely the adjustment of the cooling profile.



**Fig.** Selected samples of SPS-processed crack-free  $\text{LiAl}_5\text{O}_8$  ceramics from the final stage of SPS optimization.

Phase composition and microstructure of both precursor powders and SPS samples was evaluated by X-ray powder diffraction and SEM/TEM, respectively. The transparency of the sintered  $\text{LiAl}_5\text{O}_8$  pellets was assessed using in-line transmittance spectra measurement in the UV–vis spectral range. Finally, X-ray excited radioluminescence spectra and also luminescence spectra along with PL decay were measured.

Finally, it is worth noting that no sintering agent, usually used to achieve high transparency, was used. The optimized, crack-free samples reached over 80% transmittance at 500 nm. Such good optical parameters together with optical isotropic behavior make this transparent ceramic material a candidate for activator doping applicable not only in the detection of thermal neutrons but also in other luminescence applications.



The background of the slide is composed of numerous light gray, irregular polygons of various shapes and sizes, some of which are outlined in white, creating a fragmented, crystalline effect.

**Friday 10<sup>th</sup>**

# **Transparent Ceramics II**

# Giant Micro-photonics for Tiny Integrated Lasers

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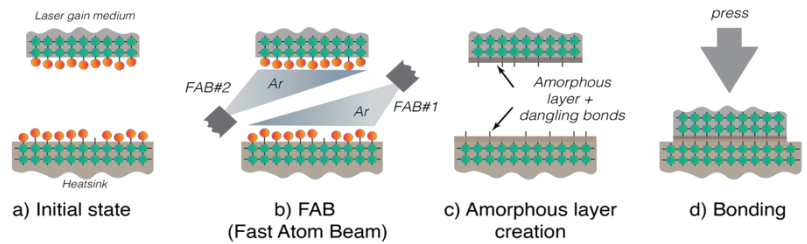
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## 1. Introduction

Extreme light-matter experiments have been driven by large-scale, high-brightness power lasers, enabling breakthroughs in fields such as gravitational wave sensing, laser ignition, and particle acceleration. However, their massive size remains an obstacle for both practical applications and fundamental verifications. Downsizing these systems is essential for fostering innovation [1]. At the RIKEN SPring-8 Center, we are developing compact electron accelerators for X-ray free-electron lasers (XFEL) by leveraging laser-plasma acceleration (LPA) and THz-wave dielectric acceleration (THz-DLA). These are powered by Tiny Integrated Lasers (TILA) based on micro solid-state photonics—a platform for ubiquitous power lasers that integrates ceramics-based laser technology, quasi-phase-matching (QPM) nonlinear optics, and inter-layer assisted surface-activated bonding (il-SAB) at room-temperature. These cutting-edge, high-performance lasers are poised to unlock new industrial frontiers, including laser ignition, laser peening for infrastructure maintenance, long-distance laser-induced breakdown spectroscopy (LIBS), and laser processing with palm-top devices.

## 2. DFC-Concept and discussion

The maximum extractable power  $P_{ex}$  from typical solid-state lasers is limited by the catastrophic damage threshold as  $P_{ex} \approx R_T \cdot L / \chi$ , where  $L$  is the length of the laser gain medium and  $\chi$  is the heating parameter defined as the heat deposited per unit of stored energy. It is clear that the maximum extractable power is directly proportional to the thermal shock parameter  $R_T$ , which is roughly proportional to the thermal conductivity  $\kappa$ . For instance, while the National Ignition Facility (NIF) has demonstrated laser ignition with 4 MJ pulse energy, it suffers from a poor repetition rate (a few shots per day) because its glass-based gain media have a low  $\kappa$  of  $<1 \text{ W/mK}$ . Notably, crystalline RE:YAG exhibits a value of  $\sim 10 \text{ W/mK}$ , which is an order of magnitude higher than that of typical high-energy laser glasses. Consequently, advanced architectures using such crystalline media have been explored, with extremely high output energies of 100 J at a 10 Hz repetition rate already demonstrated. To overcome the material power limits imposed by  $\kappa$ , we utilize our il-SAB method (Fig. 1). This process enables the room-temperature direct bonding of heterogeneous materials—such as laser media and transparent heat sinks (e.g., sapphire or the



other high- $\kappa$  materials)—without thermal strain. By leveraging this bonding, our Distributed Face Cooling (DFC) concept realizes a monolithic, laser-ion gradual-doping-level multi-disc structure. This architecture ensures homogeneous temperature and gain distributions within the chip, which is essential for high-density laser operation. To enable extreme power scaling, the quality of the bonded interface is paramount. In a non-bonded DFC chip, Fresnel reflections at the sapphire and Nd:YAG air-interfaces would result in a prohibitive total loss exceeding 64%. Our il-SAB process achieves an atomic-level diffusion that suppresses these reflections, resulting in a remarkably low measured round-trip cavity loss of only 0.51% with a DFC chip (composed of five sapphire and four Nd:YAG plates). This value is nearly twice the theoretical limit of interface loss 0.2%, demonstrating an exceptionally high-quality optical bonding [2]. Furthermore, the il-SAB interface exhibits a laser-induced damage threshold (LIDT) exceeding 100 J/cm<sup>2</sup>, equivalent to bulk materials [3]. Additionally, considering the effective thermal conductivity ( $\kappa_{eff}$ ) of the DFC chip (Fig. 2), increasing the sapphire thickness ratio allows  $\kappa_{eff}$  to approach bulk sapphire levels of  $\kappa_1=36$  W/mK (Fig. 3) [4]. These results indicate that the DFC structure successfully breaks through the inherent limits of conventional laser gain media, paving the way for extremely high-power, compact lasers such as TILA.

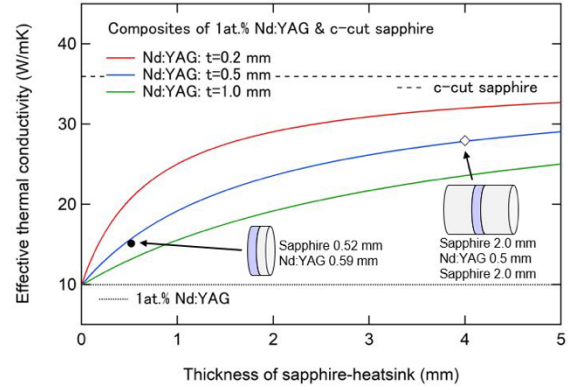
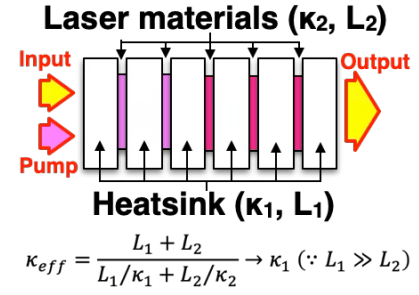
### 3. Conclusion

The successful fabrication of the DFC-Nd:YAG/sapphire PowerChip for extremely high-density, tiny integrated lasers has been demonstrated, achieving a performance of 5 J, 8.4 GW in a TILA-module at room temperature [5],[6]. We have also realized a single TILA-chip system delivering >100 MW and 30 mJ. Furthermore, the application of single-crystal il-SAB enhances the surface damage thresholds of ceramics, making them suitable for high-power, attosecond-class ultrashort pulses. Consequently, TILA promises to provide extremely high-brightness, compact lasers for both of LPA and THz-DLA as XFEL drivers, diverse industrial and space applications including quantum computing and fusion science [7],[8].

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# SINTERING OF TRANSPARENT $\text{Y}_2\text{O}_3$ CERAMICS FOR IR LASERS

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Yttria ( $\text{Y}_2\text{O}_3$ ) is a material with good mechanical and thermal properties, high thermal and chemical stability, along with a wide range of transparency. It also has a low phonon energy, lower than that of glasses or that of YAG [1], which allows the radiative transitions of rare earth dopants at longer wavelengths. Alas, due to its very high melting point ( $T_m > 2400\text{ °C}$ ) and phase transitions, the growth of  $\text{Y}_2\text{O}_3$  single crystals is very challenging. This, increases the interest in the fabrication of polycrystalline  $\text{Y}_2\text{O}_3$  by ceramic methods. Still, due to its high melting point, achieving transparency of  $\text{Y}_2\text{O}_3$  typically requires high sintering temperatures or post-HIP treatments.

In this study, our objective was to produce transparent yttria ceramics with limited grain growth at reduced sintering temperatures. Process-wise, we studied two different sintering approaches:

1. pressureless sintering under high vacuum;
2. pressure-assisted spark plasma sintering.

We studied the effect of the introduction of  $\text{ZrO}_2$  as a sintering aid that can hinder grain growth, while maintaining a single-phase system. The tested amount of  $\text{ZrO}_2$  ranged from 0 to 15 mol.% [2] and we analyzed its influence on the microstructure and the mechanical and thermal properties. The effect of the introduction of rare earth dopants on the optical quality was also assessed.

Both sintering approaches yielded ceramics with uniform microstructures and good mechanical properties. The optimal  $\text{ZrO}_2$  amount differed for the two sintering methods: lower for SPS (3 mol.% [3]) compared to a wide range from 3 mol.% up to 15 mol.%, for samples sintered under vacuum.

The results pave the way for low-cost, novel, low-phonon-active transparent ceramics with high application potential in infrared solid-state lasers.

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# ADVANCED TAG MAGNETO-OPTICAL CERAMICS FOR HIGH POWER FARADAY ISOLATORS

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The Faraday isolator is an important component of laser systems and it is mainly used to isolate the reverse light and prevent unwanted feedback between different parts of the laser systems. Faraday isolators have great significance for laser amplification and the stability of laser systems. Nowadays, high power is an important developing trend of laser systems, and the demand for magneto-optical isolators is also increasing with the increase of the laser power. Currently, the most widely used magneto-optical material in visible to near infrared wavelength band is  $\text{Tb}_3\text{Ga}_5\text{O}_{12}$  (TGG) single crystals, which has good comprehensive performance and has been occupied the major market. However, it is reported that the performance of TGG crystals at high power is not sufficient, and TGG cannot meet the demand for compact Faraday isolators. Hence, researchers are looking for new magneto-optical materials with higher Verdet constant and better thermal-optical performance. The Verdet constant of  $\text{Tb}_3\text{Al}_5\text{O}_{12}$  (TAG) magneto-optical ceramics is higher than that of commercial TGG single crystals, which is beneficial for the miniaturization of magneto-optical devices and systems, and has application prospects in high-power Faraday optical isolators. In this work, the microstructure, composition control and properties of TAG ceramics were mainly investigated.

# TRANSPARENT NANO-STRUCTURED CERAMICS FABRICATED BY HIGH PRESSURE SPARK PLASMA SINTERING

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MEILLE<sup>5</sup>, Laurent GREMILLARD<sup>5</sup>, Alexandre MAITRE<sup>4</sup>, Sandrine COTTRINO<sup>5</sup>**

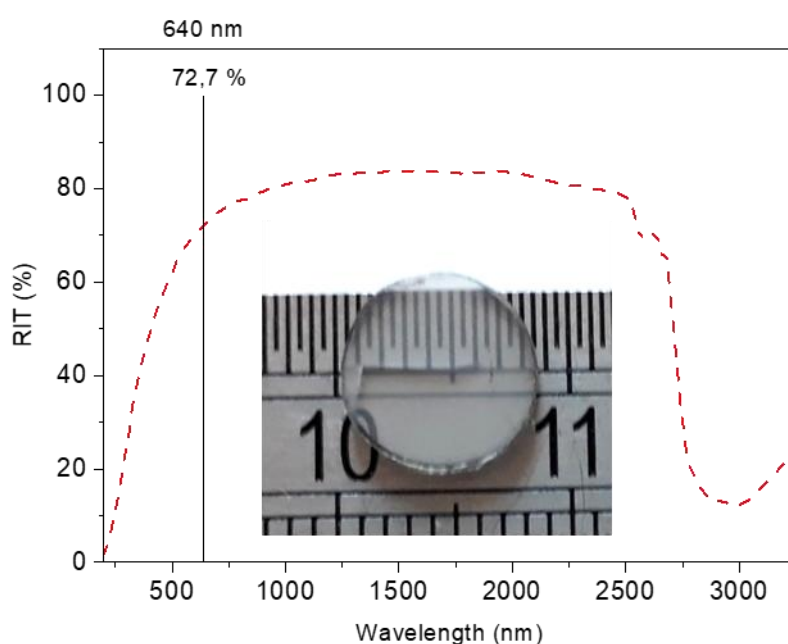
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Transparent ceramics have great potential for applications in lasers, optical systems, armor windows, nuclear technologies and electro-optical devices. Among them, magnesium aluminate spinel ( $\text{MgAl}_2\text{O}_4$ ) is a promising material for use in harsh environments, thanks to its high melting point (2135°C), superior hardness, excellent chemical and thermal stability, outstanding optical properties and low coefficient of thermal expansion. Owing to its isotropic cubic crystal structure, spinel exhibits optical transparency from the ultraviolet (near-UV) to the mid-infrared range (0.4 to 6  $\mu\text{m}$ ), even in its polycrystalline form. Nevertheless, spinel is a hard-to-sinter material. In a pressureless sintering process, densification cannot exceed 90% without the addition of sintering aids, which is insufficient to achieve transparency. Polycrystalline alumina is another widely used engineering ceramic. However,  $\alpha\text{-Al}_2\text{O}_3$  is birefringent as its crystal structure is hexagonal (space group  $R\bar{3}c$ ). Hence, high transparency in the visible domain can only be obtained with very low residual porosity ( $< 0.1\%$ ) and mean grain sizes smaller than the wavelength of incident light to limit scattering losses.

Spark Plasma Sintering (SPS), a pressure-assisted sintering technique with a pulsed current heating, has been widely used in order to produce ultrafine transparent  $\text{Al}_2\text{O}_3$  and  $\text{MgAl}_2\text{O}_4$  ceramics. The very high heating and cooling rates of the SPS process enable rapid powder consolidation while effectively limiting grain growth. However, conventional SPS, operating under uniaxial pressures below 100 MPa, still requires temperatures of at least 1200 °C to fully densify alumina or spinel nanopowders. Under these conditions, grain growth remains significant, with grain sizes increasing by at least a factor of five, which prevents the fabrication of ceramics with grain sizes below 200 nm. Since the application of high pressure is known to reduce the sintering temperature, we have developed a High-Pressure Spark Plasma Sintering (HP-SPS) device combining a Paris-Edinburgh press with a pulsed current generator. This system is capable of reaching pressures up to 10 GPa and temperatures as high as 2300 °C [1]. Alumina and spinel nanopowders with various grain size ranging from 25 to 120 nm have been consolidated by HP-SPS at pressures up to 5 GPa. High-pressure compaction was shown to produce dense green bodies with fine, uniformly distributed porosity, thereby enhancing sintering efficiency. In particular, applying a pressure of 1.5 GPa during SPS lowered the sintering temperature by approximately 500 °C, enabling the production of fully dense, transparent ceramics with limited grain coarsening [2]. This enables preservation of extremely fine nanostructures, down to 50 nm, and fabrication of transparent oxide ceramics combining excellent optical and mechanical properties. Real in-line transmittance values at 640 nm

reached 72% for alumina and 80% for spinel, approaching the theoretical values 86 and 87%, respectively. These ultrafine nanostructured ceramics exhibit significantly enhanced hardness. Spinel ceramics with mean grain sizes between 50 and 75 nm display a Vickers hardness (HV0.3) close to 19 GPa, compared with approximately 15 GPa for ceramics with grain sizes around 550 nm. Similarly, alumina ceramics with a mean grain size of 70 nm reach a Vickers hardness (HV0.1) of nearly 25 GPa, exceeding that of monocrystalline sapphire (22 GPa). This improvement arises from Hall–Petch strengthening, whereby grain size reduction limits dislocation accumulation within individual grains and increases grain boundary density, thereby hindering dislocation motion.



**Fig 1.** RIT measurement and image of a 0.8 mm thick polycrystalline alumina HP-SPS-processed at 1,2 GPa and 900°C.

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# POSTERS

**Weekly summary**



# SLICA COATING OF PbS and PbS-CdS QUANTUM DOT FOR OPTOELECTRONICS

**Miguel DOSIL <sup>1</sup>, Raphaël FAUST <sup>2</sup>, Mariona DALMASES <sup>1</sup>, Marta MARTOS <sup>1</sup>,  
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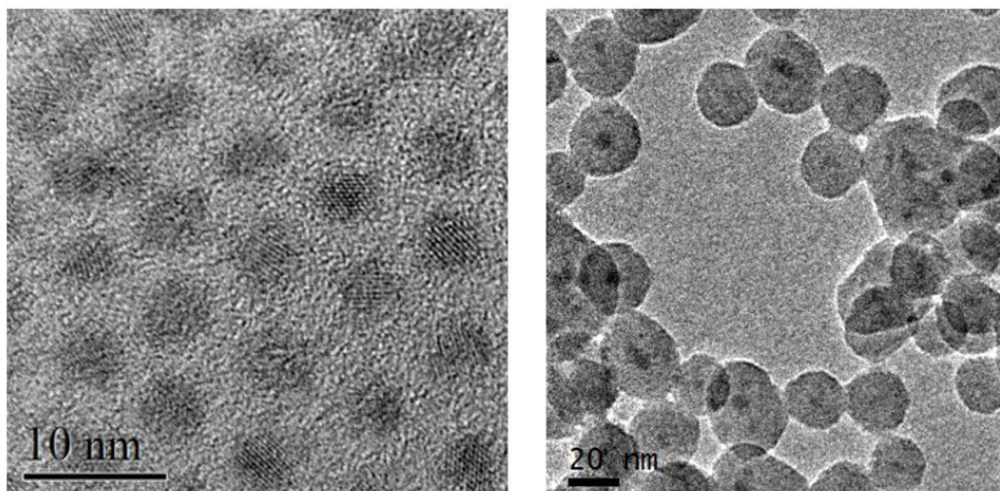
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Quantum electrodynamics has advanced significantly in recent decades, driven by applications in quantum information processing and quantum sensing [1-3]. Semiconductor quantum dots (QDs) are promising candidates for single-photon sources. However, achieving high purity, efficiency, and photon indistinguishability remains a central challenge.

Quantum dots are semiconductor nanocrystals whose optical properties resemble those of single atoms due to quantum confinement at the nanometer scale. As solid-state emitters, they can be integrated into photonic nanostructures such as plasmonic nanoantennas and photonic crystals [2]. Colloidal QDs offer additional advantages for single-photon emission, including solution-processability, narrow and tunable photoluminescence (PL) wavelengths, high quantum yields, and compatibility with diverse substrates [1].

In this work, we present a strategy to develop near-infrared single-photon emitters based on colloidal QDs. PbS and core-shell PbS-CdS nanocrystals are employed as model systems (Fig. 1). A silica coating is introduced to prevent aggregation and protect against moisture and oxygen, with the goal of preserving and enhancing the photoluminescence (PL) quantum yield. The key challenges are to retain the intrinsic PL properties after silica encapsulation and to ensure single-QD occupancy per silica nanoparticle. Additionally, because the QDs are only few nanometers in diameter, shell growth increases particle size, facilitating handling and integration into electronic and photonic devices.

Different synthesis strategies to coat the quantum dots will be presented together with a complete study of the photoluminescent properties both in colloidal suspension as well as a film.



**Fig. 1** TEM image of PbS quantum dots absorbing at around 1300 nm (left), and core-shell PbS-SiO<sub>2</sub> nanoparticles stable in ethanol (right).

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# Fast and artifact-free measurements of circularly polarized luminescence (CPL)

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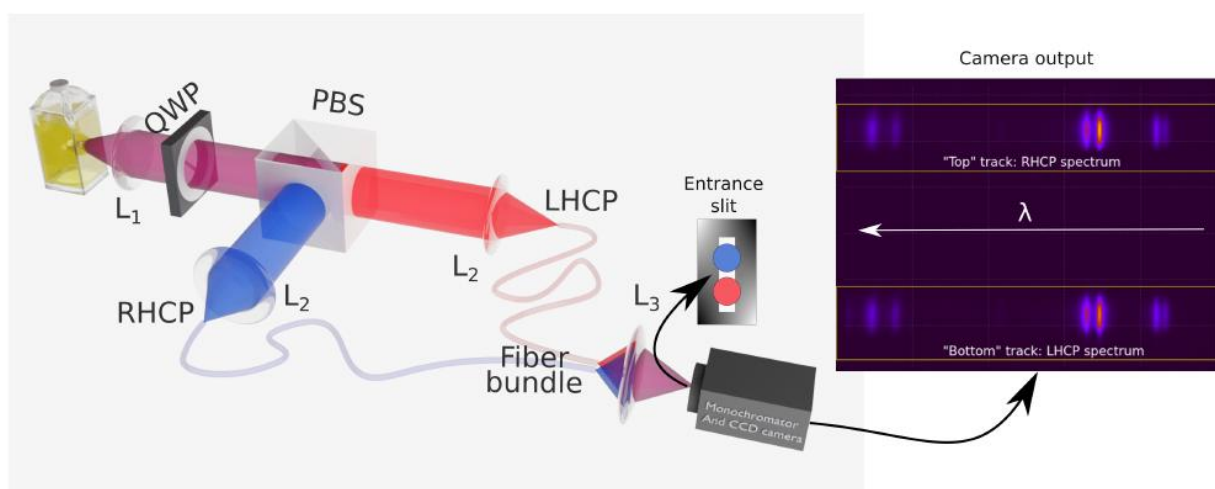
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The interactions between circularly polarized light and chiral materials are unequal for left-handed and right-handed circular polarizations and are revealed by different phenomena such as optical rotation (refractive index difference), electronic circular dichroism (ECD) (UVVIS absorption difference) or vibrational circular dichroism (IR absorption difference) [1]. The luminescence from chiral luminophores is also asymmetric in term of handedness which lead to the Circular Polarized Luminescence  $CPL = \Delta I = I_L - I_R$ , corresponding to the difference between the left-handed circular (LHCP) polarization and the right-handed circular polarization (RHCP) of luminescence [2].

CPL is a fast growing research field as a complementary chiroptical tool to the conventional circular dichroism, for the structure analyzes of chiral materials. Besides, the synthesis of systems with high CPL brightness, quantified by the dissymmetry factor  $g_{lum} = 2(I_L - I_R)/(I_L + I_R)$ , makes it a valuable alternative for the detection of chiral environmental probes or for applications in future displays and photonic technologies [3-10]. Current CPL spectrometers, based on time modulation of polarization, cannot use a spectral camera. This results in long acquisition times due to wavelength-by-wavelength scanning.

Here we present a new spectrometer that overcomes this limitation by spatially separating the two circular polarizations emitted by the chiral system before their spectral dispersion on a camera (see figure bellow). In this way, the acquisition times are divided by 1000 compared to the usual techniques. Moreover, thanks to a rigorous Mueller analysis of our setup, we show that, by combining spatial and temporal separation through two switchable circular polarization encoding arms, accurate CPL spectra are recorded without the need of tedious calibrations [11]. Indeed all the first order artifacts arising from residual imperfections in the optical components self-compensate except for samples mixing linear and circular anisotropies. This aspect is fundamental in chiroptical studies, as signals - from a few 0.01% to a few % - can easily be masked or even confused with instrumental biases.

Thanks to our device, studies on the coupling between chirality and the generation of molecular magnets, the induction of chirality of organic ligands to rare earths or the development of chiral biological probes have been carried out and are presented. More generally, these developments enable fundamental studies on chiral interactions via luminescence, studies that have so far been limited by prohibitive acquisition times.



Schematic diagram of a PLC optical bench based on the spatial separation of right- and left-handed circular polarizations and their simultaneous detection using a CCD camera. The two spots are horizontally diffracted by the grating giving on the CCD camera the top/bottom spectrum coming from the top/bottom spots and thus related to the LHCP and RHCP emission. Here, the image is recorded from an  $\text{Eu}^{3+}$  chiral complex.

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# Characterizing the Extinction Cross-Section of Laser-Generated Plasma in Gold Nanoparticle Fragmentation

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Laser fragmentation in liquids has attracted growing attention in laser-based synthesis because it allows the generation of narrow, monomodal particle size distributions [1]. It is also increasingly employed in combination with photochemical processes to produce alloys, including high-entropy alloys [2]. However, the plasma generated during laser fragmentation remains poorly characterized, even though it may serve as a source of reactive oxygen species (ROS) and solvated electrons capable of initiating chemical reactions.

In this work, we investigate the mechanisms of fragmentation induced by nanosecond laser pulses. Our goal is to determine the extinction cross-section of the plasma generated during the fragmentation of gold nanoparticles. A notable aspect of nanosecond-pulse excitation is that the plasma forms on a timescale shorter than the pulse duration, causing the newly formed plasma to absorb a portion of the incident laser energy. Nevertheless, the role of this plasma in the overall energy distribution is still not well understood, even though plasma shielding is a recognized phenomenon in laser ablation in liquids.

We developed an experimental setup and a corresponding model to evaluate the extinction cross-section of laser-generated plasma following the fragmentation of gold nanoparticles, using pristine particles with diameters of 20, 50, 100, and 200 nm. In fragmentation experiments with the third harmonic of a Nd:YAG laser (355 nm, 5 ns), monitoring the time-dependent transmitted pulse energy through the colloidal solution allowed us to track the evolution of fragmentation events.

After complete fragmentation of the pristine particles, the size distribution of the resulting particles reveals a monodisperse population, with a mean size of 4 nm (standard deviation < 1 nm), independent of the applied fluence over the range from a few J/cm<sup>2</sup> to ~38 J/cm<sup>2</sup>, and also of the particle size in the pristine solution. The monodisperse distribution indicates that the fragmentation process is a single-step event [3]. As the solution is continuously composed of two particle populations, namely pristine particles and fragmented particles, it is therefore possible to deduce, from the temporal evolution of the pump attenuation into the colloid solution during fragmentation, the contribution of the plasma to pump extinction. It appears that the extinction cross-section of the laser-generated plasma is much larger than the absorption cross-section of the particles in the pristine solution, confirming that a significant portion of the pulse energy is absorbed by the plasma when using nanosecond sources for laser ablation or fragmentation in liquids. From our modeling, we can also characterize a time evolution of the fragmentation probability, i.e., an increase in fragmentation probability (decrease of the fragmentation threshold) as the solution is continuously illuminated. We interpret this as the accumulation of “defects” in the illuminated particles without them undergoing fragmentation.

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# **A HYBRID ANTI-COUNTERFEITING MARKER WITH A DUAL OPTICAL SIGNATURE PRODUCED USING THE SOL-GEL METHOD**

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The development of new optical security and authentication components to address the growing problem of product and document counterfeiting is of increasing interest for many industrial sectors. Indeed, virtually all products can be counterfeited, including luxury goods, everyday consumer products, and industrial items. In response to this issue, the French government, through the Directorate General of Customs and Indirect Duties, launched a national anti-counterfeiting action plan in February 2021 [1].

One of the key challenges is the design of secure marking solutions that remain cost-effective while considering the value of the protected product. Security markings are commonly classified into three levels, from level 1 to level 3. Level 1 is the overt level, the level 2 is the covert one. Level 3 markers, referred to as expert-level markers, are the most sophisticated, both in terms of their design and the advanced detection techniques required for their identification.

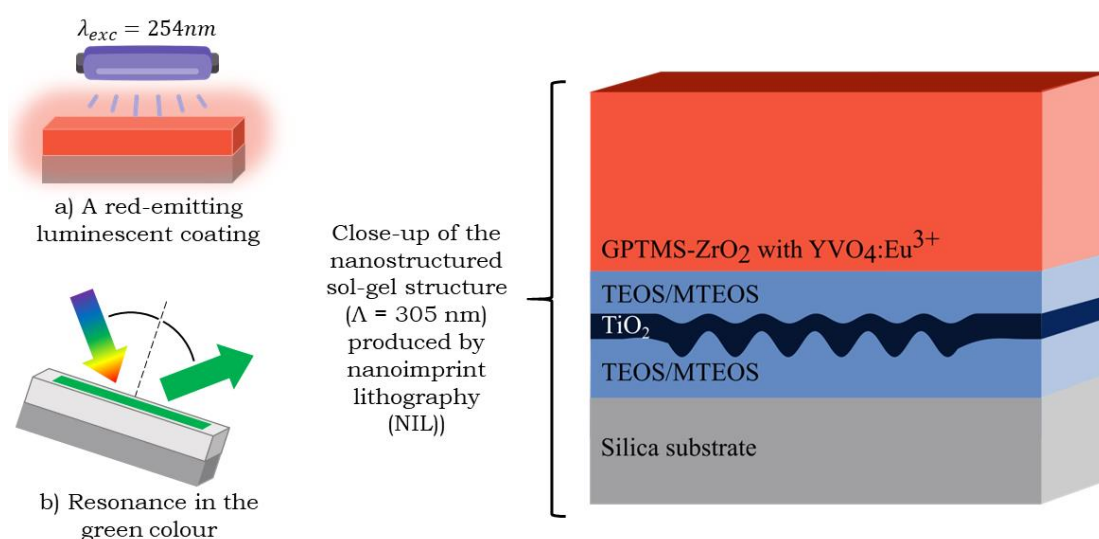
Protection against counterfeiting requires the development of optical markers that are difficult to replicate and that provide multiple levels of verification. In this context, we propose a hybrid device combining a guided-mode resonant grating (GMR) [2] and a luminescent coating (LC), enabling a response with a dual optical signature.

The proposed multilayer architecture will be presented in detail, from the preparation of the sol-gel layers and their structural integration to the characterization of the optical properties and the demonstration of the resulting dual optical signature. This multilayer strategy significantly increases the structural complexity of the device and enhances the overall security level of the optical marking.

Numerical tools, including modeling and simulation, were used to combine optical effects of different physical origins, namely optical resonances and luminescence. Based on the simulation results, structures were designed to exhibit a resonance in the green wavelength range.

The complete architecture is fabricated using a sol–gel process based on a mild chemistry approach compatible with large-scale replication techniques. First, a TEOS/MTEOS-based sol–gel layer was deposited on a quartz substrate, stabilized, and microstructured using nanoimprint lithography (NIL). Then a thin film of high-refractive-index  $\text{TiO}_2$  is deposited to form the waveguide of the resonant grating and to produce a selective spectral response. Finally, a luminescent coating [3], consisting of a sol–gel hybrid matrix incorporating  $\text{YVO}_4\text{:Eu}^{3+}$  nanocrystals, is then deposited as the top layer. This layer provides both mechanical protection of the resonant array and a characteristic emission centered on the  $\text{Eu}^{3+}$  transitions.

After each fabrication step, the coatings were characterized in terms of thickness, refractive index, surface roughness, and microstructure profile. Optical transmission and reflection measurements were performed and compared with spectra obtained from simulations. Finally, the luminescence of the active coating was measured to assess the influence of the resonant structure on the  $\text{Eu}^{3+}$  emission.



**Fig.** Schematic representation of the multilayer architecture for our anti-counterfeiting marker with dual optical signature: a) and b).

## ACKNOWLEDGEMENTS

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# MICROWAVE-DRIVEN HYDROTHERMAL SYNTHESIS OF $\text{Eu}^{3+}$ -DOPED La/Al OXIDES: STRUCTURE AND OPTICAL PROPERTIES

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Lanthanum aluminate-based materials are of growing interest due to their favourable optical properties and thermal stability. These features make them promising candidates for use in advanced photonic devices, sensors, and modern lighting technologies. The incorporation of  $\text{Eu}^{3+}$  ions into these matrices improves their luminescent properties, making them attractive for applications as luminophore materials used in displays and bioimaging. An important aspect in obtaining these materials with controlled composition, morphology, and emission characteristics is the fine-tuning of the synthesis conditions.

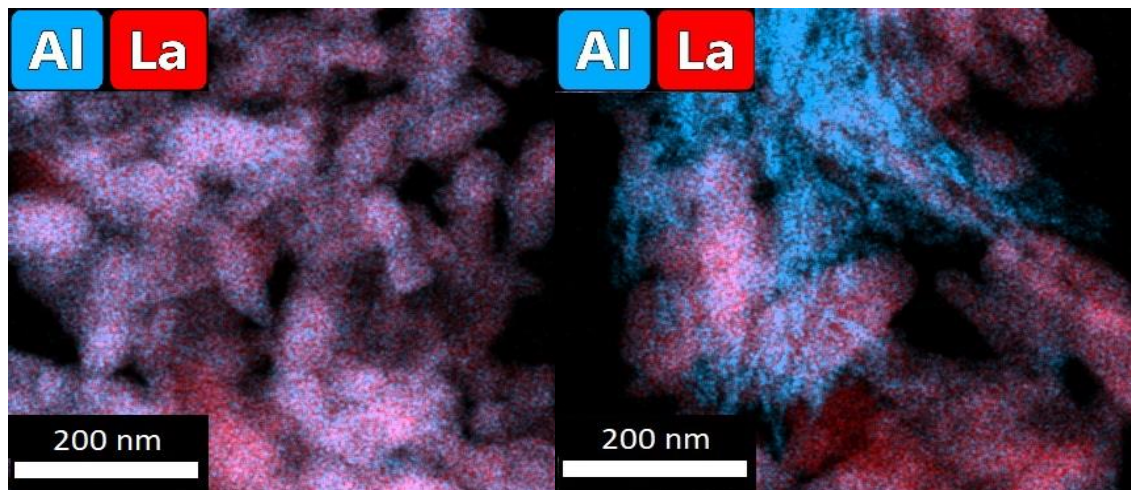
The aim of the work was to determine the influence of synthesis conditions on the phase composition, microstructure, and luminescent properties of nanocrystalline lanthanum and aluminum oxide systems doped with  $\text{Eu}^{3+}$  ions, obtained by microwave-driven hydrothermal technique. Two series of powders with molar ratios of La/Al = 1:1 (corresponding to perowskites), and 3:5 (corresponding to garnets) were studied, obtained in the pH range of 11-14 and then calcined at 1000 °C. Structural and optical properties of the obtained powders were determined using thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG), X-ray diffraction (XRD), scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), Raman spectroscopy, and photoluminescence (PL) measurements at room temperature and at 19 K.

TGA allowed us to determine the temperature stability range of the materials and select calcination conditions ensuring their complete crystallization. XRD revealed the presence of two main crystalline phases, whose relative proportions depend on the synthesis conditions, in particular on the pH of the reaction mixture. It was demonstrated that changing the process parameters allows control of the phase composition of the obtained powders. SEM confirmed the nanocrystalline nature of the materials and the possibility of adjusting the grain size by modifying the synthesis conditions. EDX and TEM revealed differences in the homogeneity of



element distribution between the tested series. Raman spectra confirmed the dominant structure. PL allowed the identification of characteristic emission transitions of  $\text{Eu}^{3+}$  ions.

The results obtained prove that microwave-assisted hydrothermal synthesis enables effective control of both the structure and optical properties of La-Al-O materials, making this method promising in the context of applications in photonics and optoelectronics.



**Fig.** HAADF images of samples obtained by the hydrothermal method with calcination at 1000 °C for (a) La-Al-3O (Series 1), and (b) 3La-5Al-12O (Series 2).

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# EPITAXIAL GROWTH OF $\text{KTiOAsO}_4$ BY PULSED LASER DEPOSITION FOR NONLINEAR FREQUENCY CONVERSION

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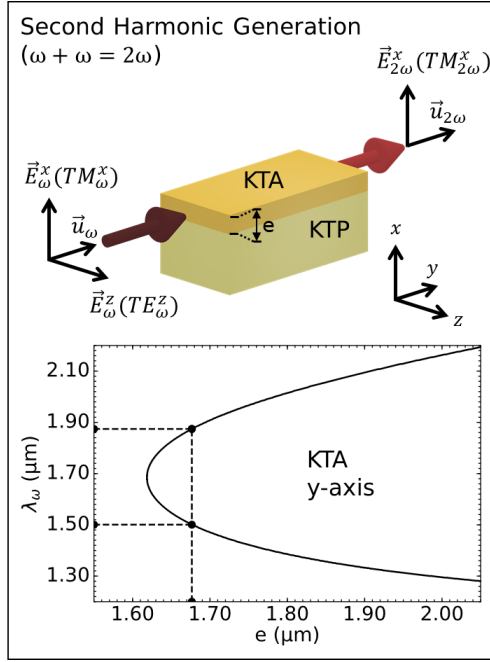
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Second-harmonic generation (SHG) ( $\omega + \omega \rightarrow 2\omega$ ) as well as the inverse process of photon pair generation ( $2\omega \rightarrow \omega + \omega$ ) require pump laser intensities of several hundred  $\text{MW cm}^{-2}$ . Micrometer-sized crystalline waveguides allow such interactions to be achieved at relatively low energies by taking advantage of the confinement of light [1]. The materials selected to achieve these phenomena in the present work are from the titanyl phosphate family. The chosen architecture is a micrometric layer of  $\text{KTiOAsO}_4$  (KTA) grown on a  $\text{KTiOPO}_4$  (KTP) substrate forming a planar waveguide. These two isostructural materials have a low lattice parameter mismatch (around 2 %), making it possible to achieve high-quality epitaxial growth [2]. The refractive index of KTA being higher than that of KTP ( $\Delta n \approx 0.043$  at 1500 nm), this couple of materials could allow light to be guided in the deposited layer.

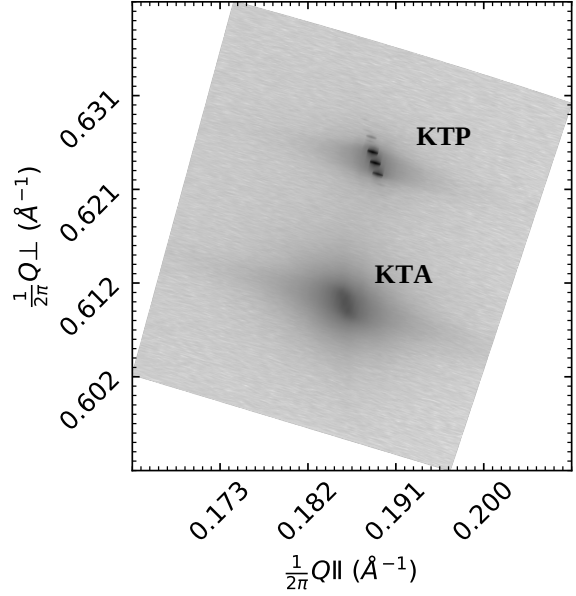
Considering the materials used and the geometry of the device we want to study only two fabrication techniques can be used: liquid phase epitaxy (LPE) and pulsed laser deposition (PLD). However, it has been shown that growth of  $\text{KTiOAs}_x\text{P}_{1-x}\text{O}_4/\text{KTiOPO}_4$  by LPE forms cracked of scaled films for mismatches over 1%, which is not compatible with our goal of growing KTA over KTP [3]. Therefore, the technique we chose is pulsed laser deposition (PLD), a technique that allows nonlinear complex oxides layer of optical quality to be grown [4].

PLD consists in the ablation by a pulsed high energy laser of a material of the layer's desired composition. The ablation forms a plasma plume which condenses on the substrate. An epitaxial layer is then obtained by heating of the substrate during the deposition or by annealing later on. Deposition of materials from the titanyl phosphate family on KTP by pulsed laser deposition has already been reported [5, 6].

At first, we will show that considering the geometry of our system, waveguiding and birefringence phase-matching is possible for layers of high thickness:  $1.68 \mu\text{m}$  (fig. 1). Then we will show that the growth is well oriented for layers with a thickness up to  $100 \text{ nm}$  after deposition under 32 mTorr of oxygen and a laser fluence of  $0.8 \text{ J cm}^{-2}$  forming epitaxial layers (Fig. 2). And that after annealing at  $700^\circ\text{C}$  for 14h, the crystal state is improved as well as the surface. Finally, we will present the advances of this research on the increase of the layer's thickness to achieve waveguiding and SHG at telecom wavelengths (i.e.  $\sim 1.5 \mu\text{m}$ ).



**Fig. 1** Geometry of the waveguide studied with polarization states suited for birefringence phase-matched second-harmonic generation (top) and phase-matching curve given the fundamental wavelength ( $\lambda_\omega$ ) and the corresponding layer thickness (bottom).



**Fig. 2** Reciprocal space map of the (802) reflection of the substrate and layer after annealing showing the oriented growth and the relaxed state of the layer after annealing.

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# RARE EARTH MATERIAL FOR OPTICAL GAIN IN INTEGRATED PHOTONICS

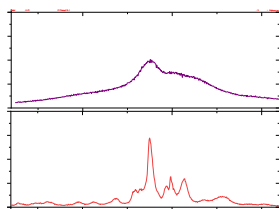
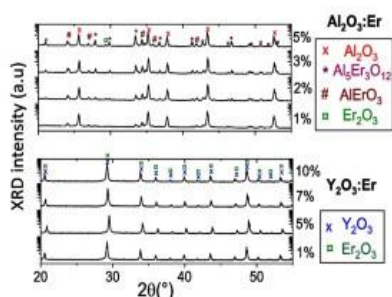
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The mid-InfraRed (mid-IR, 2–14  $\mu\text{m}$ ) region is essential for chemical and biological sensing due to molecular absorption bands from fundamental vibrational and rotational transitions [1]. Although, conventional mid-IR systems are bulky and expensive. Integrated photonics offers a route toward compact, scalable platforms with on-chip sources and amplifiers [1–2], yet efficient integrated mid-IR light sources remain a major challenge. Rare-earth (RE) ions enable IR and mid-IR emission via intra-4f transitions, characterized by narrow linewidths, thermal stability, and chemical robustness [2–4]. Among typical dopants ( $\text{Er}^{3+}$ ,  $\text{Yb}^{3+}$ ,  $\text{Ho}^{3+}$ ),  $\text{Dy}^{3+}$  provides broadband tunable emission in the  $\sim 2.8\text{--}3.4\ \mu\text{m}$  range ( ${}^6\text{H}_{13/2} \rightarrow {}^6\text{H}_{15/2}$ ), making it a strong candidate for compact mid-IR lasers.



This work focuses on RE-doped  $\text{Al}_2\text{O}_3$  grown by pulsed laser deposition (PLD). Alumina was chosen for its wide transparency (UV–mid-IR), low optical losses, and high rare-earth solubility, while sapphire substrates ensure high crystallinity and thermal robustness

[2]. Previous work on  $\text{Er}^{3+}\text{-Al}_2\text{O}_3$  and  $\text{Er}^{3+}\text{-Y}_2\text{O}_3$  microstructures (Fig.1) confirmed crystalline phase formation and efficient RE incorporation through XRD and

photoluminescence (PL) measurements [5,6]. Extending this platform to a  $\text{Dy}^{3+}$ -based integrated photonic chip fabricated by PLD is a promising direction for mid-IR applications. Indeed, the demonstrated performance of  $\text{Dy}^{3+}$ -doped fiber lasers featuring continuous tunability, high slope efficiency, and output powers suitable for trace gas detection and other sensing applications strongly supports the potential for translating these favorable properties into integrated photonic architectures [4].

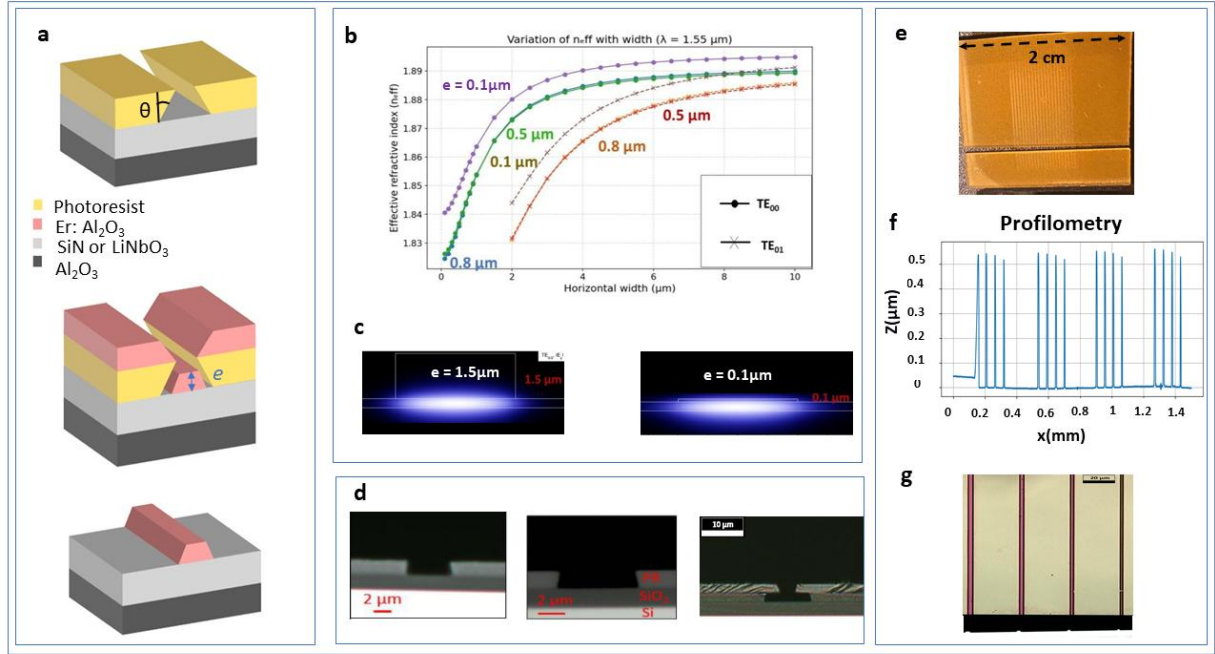


Fig.2.(a) Process flow for rare-earth-doped microstructure fabrication (b) and (c) Simulation results showing the variation of effective refractive index as a function of horizontal width of the waveguide (top) and coupling of thickness corresponding to 1.5  $\mu\text{m}$  and 0.1  $\mu\text{m}$  (bottom), (d) images shows the horizontal under-cut obtained after lithography using single layer and double layer approaches, (e,f,g) fabricated sample, profilometry result and microscopic images

The integration strategy toward rare-earth-doped micro-emitters and waveguide-based mid-IR amplifiers is illustrated in Fig. 2. The fabrication sequence (Fig. 2a) combines lithography, pulsed laser deposition (PLD), and lift-off processing to define RE:Al<sub>2</sub>O<sub>3</sub> microstructures on sapphire substrates. Numerical simulations (Fig. 2b–c) show how effective refractive index depends on waveguide width and film thickness, revealing that a  $\sim 4 \mu\text{m}$  alumina width ensures optimal mode confinement. Lithographic optimization (Fig. 2d) demonstrates precise undercut control using single- and double-layer resist; the double-layer process is preferred for reliable lift-off. Fabricated straight waveguides (Fig. 2e) confirm structural integrity, while profilometry (Fig. 2f) and microscopic imaging (Fig. 2g) validate film thickness, uniformity, and well-defined geometries compatible with integrated photonic architectures with waveguide losses currently under investigation.

Together, these results demonstrate a complete pathway from waveguide design and process optimization to material deposition and microfabrication, positioning Dy<sup>3+</sup>:Al<sub>2</sub>O<sub>3</sub> as a promising platform for compact mid-IR optical gain in integrated photonics.

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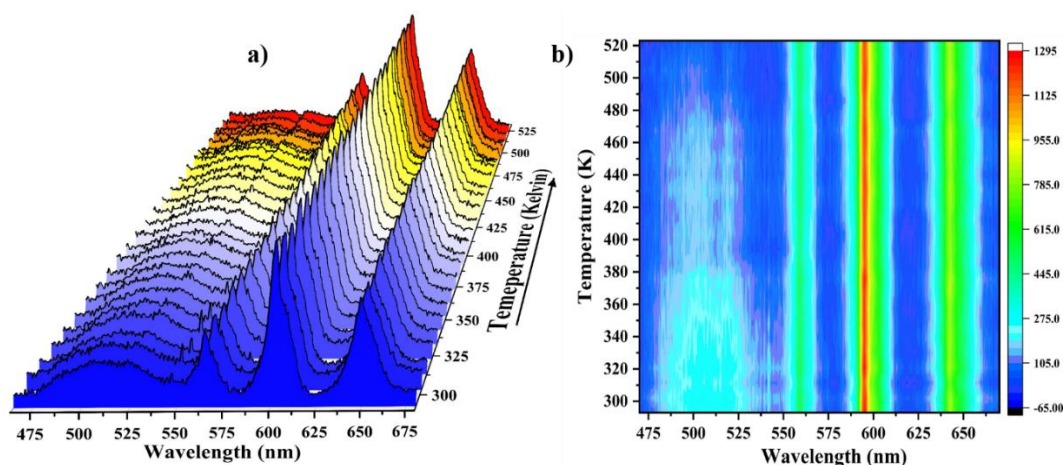
# APPLICATION OF $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}:\text{Sm}^{3+}$ COMPOSITES FOR STAND-OFF THERMOMETRY AND MULTICOLOUR EMISSION

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Strontium aluminate ( $\text{SrAl}_2\text{O}_4$ ) doped with  $\text{Eu}^{2+}$  and  $\text{Dy}^{3+}$  emits bright green light and shows long-lasting luminescence, but its use is restricted by environmental sensitivity. Embedding it in glass improves stability and adds multifunctionality. We fabricate  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$  borotellurite glass composite while glass was doped with  $\text{Sm}^{3+}$  ions which yield dual-channel luminescence (dominant green emission ( $\text{Eu}^{2+}$ ) and orange-red emission ( $\text{Sm}^{3+}$ )). Further, the composite's bandgap ( $\sim 3.95$  eV) was found to be higher than that of the glass ( $\sim 3.91$  eV), confirming a slight widening of the bandgap upon phosphor integration. Structural investigations confirmed homogeneous dispersion of phosphor crystallites within the amorphous glass host. Importantly, temperature-dependent luminescence demonstrated the feasibility of luminescence intensity ratio ( $\text{Eu}^{2+}$  (600 nm)/ $\text{Sm}^{3+}$  (646 nm)) based optical thermometry reveal absolute sensitivity  $\sim 0.0051$  and  $0.0049$  across a temperature range of 293-523 K (Fig. 1). The EPR spectrum shows a marked reduction in  $\text{Eu}^{2+}$  signals in the composite, with only weak resonances, indicating partial passivation of oxygen vacancies. Time-resolved emission spectroscopy demonstrates an increased transition probability in the composite, as evidenced by a substantial decrease in lifetime from 4.5 ns for the  $\text{Eu}^{2+}$  ion in  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$  to 1.1 ns in the composite.



**Fig.1** a) Temperature-dependent emission spectra of SrBT-10 composite measured from 293K-523K b) corresponding 2D contour plot, and histogram of integrated emission intensity of  $\text{Eu}^{2+}$  (520 nm) with c)  $\text{Sm}^{3+}$  (563 nm) d) with  $\text{Sm}^{3+}$  (600 nm) and e) with  $\text{Sm}^{3+}$  (646 nm) respectively.

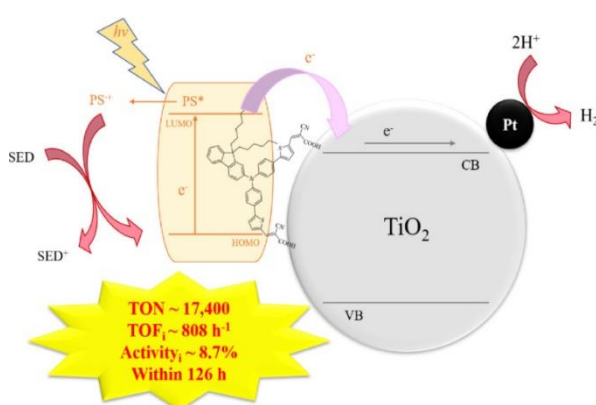
# High-Performance Photocatalytic Hydrogen Generation Using Robust Dianchoring Photosensitizers

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A novel series of donor–donor– $\pi$ –acceptor (D–D– $\pi$ –A) 9,9'-dihexylfluorene-based dianchoring organic dyes, each featuring distinct bridging electron-donating moieties, have been synthesized and characterized. Their performances in photocatalytic hydrogen evolution (PHE) were evaluated, taking into account of their photophysical and electrochemical attributes. Remarkably,



(Z)-3-(5-(4-((4-(5-((E)-2-carboxy-2-cyanovinyl)thiophen-2-yl)phenyl)(9,9-dihexyl-9H-fluoren-2-yl)amino)phenyl)thiophen-2-yl)-2-cyanoacrylic acid achieved an active and robust H<sub>2</sub> generation system with a turnover number (TON) of up to 17 400 in 126 h, with a production of 1090  $\mu$ mol (26.3 mL) of hydrogen. The initial turnover frequency (TOF<sub>i</sub>), initial activity (activity<sub>i</sub>), and initial apparent quantum yield (AQY<sub>i</sub>) were 808 h<sup>-1</sup>, 505 mmol g<sup>-1</sup> h<sup>-1</sup>, and 8.65%, respectively, under visible light irradiation in water. This photosensitizer is considered one of the most effective and durable systems for photocatalytic hydrogen production that attached to molecular Pt–TiO<sub>2</sub>, as stated out in the literature using organic dyes under visible light, when compared the TOF and TON values. The experimental results demonstrated that the dianchoring dyes with bridging units could significantly enhance PHE performance, maintaining justifiable durability over prolonged irradiation. [1-3]

A series of novel dibranched dianchoring dyes D–D(– $\pi$ –A)<sub>2</sub> (D1 – D4) with 9,9'-dihexylfluorene as the common electron donor and different electron-rich moieties centers connected to two  $\pi$ -bridges with anchoring groups were developed. D3M was also prepared

as a monoanchoring analogue for comparisons. This design, with various substituents and combinations, facilitates the investigation of the structural properties essential for studying the performance of PHE, such as the HOMO–LUMO gap and absorbance. The three components system (organic-PS/TiO<sub>2</sub>/Pt) using these dianchoring organic dyes as photosensitizers exhibited impressive performance of hydrogen production in aqueous solution containing 0.8 M ascorbic acid at a pH of 4.0, under the irradiation of both blue and green light. The results surpassed the capabilities of the blank TiO<sub>2</sub> – Pt system, and notably sustaining such efficiency over an exceptionally extended period of irradiation time. Among the donor moieties conjugated with 9,9' -dihexylfluorene at their N atom (except triphenylamine and N-phenylcarbazole), the most remarkable one was the diphenylamine conjugated dye (D3), generating 1090 μmol (26.3 mL) hydrogen with up to 17 400 of turnover number (TON) in 126 h. The initial turnover frequency (TOFi) was 808 h<sup>-1</sup>, the initial activity (activity<sub>i</sub>) was 505 mmol g<sup>-1</sup>h<sup>-1</sup>, and the initial apparent quantum yield (AQY<sub>i</sub>) was 8.65%, under visible light irradiation in water. The stability of D3 was also notable as it remained active in generating hydrogen over 126 h under blue light and 189 h under green light. The presence of the D-D(-π-A)<sub>2</sub> structure and the π-extended fluorene could potentially enhance stability and durability, while also reducing charge recombination in the organic photosensitizers used in the photocatalytic hydrogen evolution system.<sup>[1,4,5]</sup>

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# ENGINEERING HIGH CIRCULAR BIREFRINGENCE IN CHIRAL POLYMERS: A MOLECULAR ROUTE TO OPTICAL APPLICATIONS

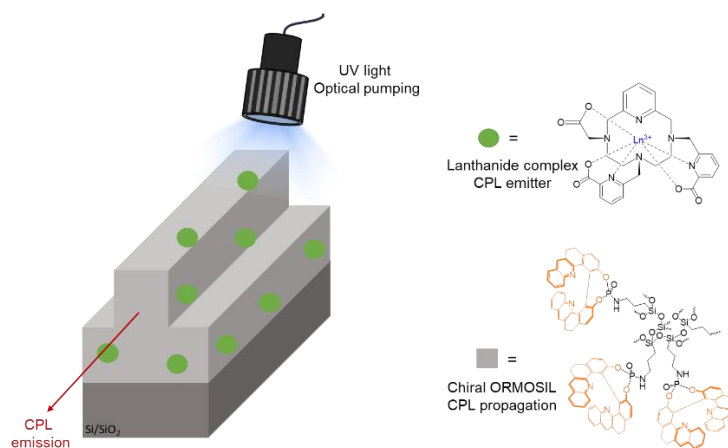
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The generation and manipulation of circularly polarized light underlie many modern technologies, ranging from medical diagnostics to advanced display systems. Despite their potential, current circularly polarized luminescence (CPL) sources rely on bulky optical setups that induce significant light losses.<sup>[1]-[3]</sup> This project aims to bypass these constraints through the development of an integrated device that generates CPL within the laser cavity.

Polymeric materials must be engineered to exhibit high circular birefringence (i.e., optical rotation), enabling efficient propagation of circularly polarized light within waveguides. The polymer matrices will be functionalized with chiral lanthanide complexes, to provide an internal source of CPL emission. While waveguides constructed from 1,1'-Binaphthol (BINOL) derivatives have been successfully produced, the current materials do not provide sufficient circular birefringence for the targeted applications.<sup>[4]</sup>

Chiral ORMOSIL (Organically Modified Silica) precursors with enhanced optical rotation are currently being investigated through the synthesis of helicoidal molecules.<sup>[5]-[6]</sup> Chiral polymer thin films are produced through sol-gel polymerization, the process is being refined in order to obtain high-quality optical waveguides.



**Fig.** Schematic representation of generation of CPL in chiral ORMOSIL waveguide

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# NIR TO VISIBLE UP-CONVERSION NANOMATERIALS BASED LUMINESCENT SOLAR CONCENTRATOR FOR SMART WINDOW PHOTONIC DEVICE

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This study integrates upconverting nanoparticles into luminescent solar concentrators to convert near infrared into visible sunlight efficiently. Fluoride host NaYF<sub>4</sub> co-doped with Er<sup>3+</sup> and Yb<sup>3+</sup> was synthesized and characterized optically. The near infrared radiations are converted into visible using up conversion process and partially waveguided to edges where small size efficient solar cells are stacked for power generation and partially visible light is transmitted into the rooms for illumination purpose. The device is developed for transparent building integrated photovoltaics device.

## 1. Introduction

The Pervoskites, dye sensitized, organic or inorganic solar cells can primarily harvest photons within the visible region while only partially covers the near infrared spectral profile of sunlight. The limited ability of solar cells to absorb NIR photons reduces their overall energy conversion efficiency. To address this limitation, strategies such as advanced optical coatings, Luminescent solar Concentrator (LSCs), and photon Upconversion (UC) materials has been explored [1-5]. Photon Upconversion is a promising approach that transforms low-energy NIR photons into higher-energy visible photons, using antistokes shifts. The UC process uses sensitizer ions (materials selected from Lanthanoid series) to absorb NIR light and transfer energy to activator ions, which emit shorter-wavelength photons. This energy transfer occurs via mechanisms such as Excited State Absorption (ESA), Energy Transfer Upconversion (ETU), enabling efficient conversion of photon wavelengths. LSCs are optical devices that absorb and emit light via total internal reflection (TIR) [6], directing it to the edges, where photovoltaic cells can be mounted for electricity generation [7]. These concentrators have various benefits, including the ability to operate in diffuse lighting conditions, making them excellent for building-integrated photovoltaic (BIPV) systems [7]. In this study, nanoparticles of NaYF<sub>4</sub> ω-doped with Er<sup>3+</sup> and Yb<sup>3+</sup> were successfully synthesized using a hydrothermal process. The as-synthesized materials were subjected to comprehensive characterization, including structural, morphological, and optical analyses, to confirm their crystalline phase, particle uniformity, and upconversion luminescence properties. Following synthesis and characterization, the nanoparticles were embedded into a transparent polymer matrix to fabricate luminescent solar concentrator (LSC) slabs. These slabs can be directly integrated with silicon solar cells to harvest near-infrared photons and re-emit them as visible photons, thereby improving photovoltaic efficiency for building integrated application as smart window.

## 1.2 Synthesis of NaYF<sub>4</sub>: Yb<sup>3+</sup> (5%), Er<sup>3+</sup> (2.5%) and LSC Development

Yb<sup>3+</sup>, and Er<sup>3+</sup> co-doped yttrium fluoride (NaYF<sub>4</sub>) nanoparticles were synthesized via a microemulsion-assisted hydrothermal method. To characterize the produced material in-depth, we embedded the RE-doped phosphor into a UV-curable optical-grade acrylate resin, chosen for its high transparency (> 90% in the 350-900 nm range) and refractive index (n ≈ 1.52). The optical clarity of the resin minimizes scattering and absorption losses, enabling efficient light trapping and guiding through total internal reflection within the slab. We were able to assess their optical properties, such as TIR and edge emission characteristics, in a solid-state form (LSC slab). For the incorporation of the Upconversion material into the resin matrix, the phosphor was added proportionally to the resin (0.3 wt.% of the material in the resin matrix).

### 1.3 Results and Conclusion

Figure 1 shows the UC spectra of  $\text{Yb}^{3+}$  and  $\text{Er}^{3+}$  co-doped  $\text{NaYF}_4$  nanoparticles under 980 nm LASER excitation that arises primarily through an ETU mechanism between  $\text{Yb}^{3+}$  sensitizers and  $\text{Er}^{3+}$  activators. The variation in spectra underscores  $\text{NaYF}_4$ 's efficiency as an Upconversion host, owing to its low phonon energy, which minimizes non-radiative losses. Figure 2(A, B, and C) represents the UC spectra of  $\text{NaYF}_4$  co-doped with 2.5%  $\text{Er}^{3+}$  constant and varying 5, 10, and 15 %  $\text{Yb}^{3+}$ , respectively, under varying excitation power (From 0.3 to 1.3 W) and Figure 2 (D) shows the PL of 15% Yb with 2.5%  $\text{Er}^{3+}$  under varying excitation power (From 0.3 to 1.3 W). The spectra show distinct emission bands in the visible range, especially between 640 nm and 680 nm.  $\text{Er}^{3+}$  ions cause these bands to be sensitized by  $\text{Yb}^{3+}$  ions, resulting in Upconversion emission. Upon 980 nm stimulation,  $\text{Yb}^{3+}$  ions absorb infrared photons and transfer energy to  $\text{Er}^{3+}$  ions via non-radiative transfer.

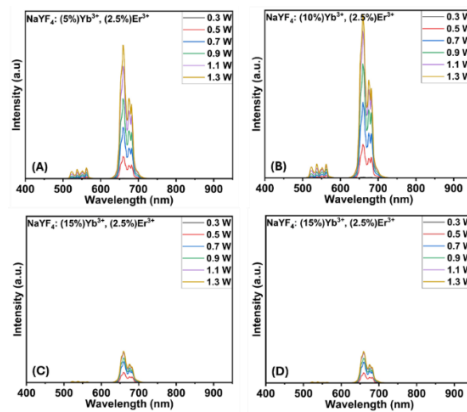


Figure 1. UC spectra of  $\text{NaYF}_4$  codoped with 2.5%  $\text{Er}^{3+}$  and varying concentrations of  $\text{Yb}^{3+}$  under 980 nm LASER excitation (A) 5%  $\text{Yb}^{3+}$ , (B) 10%  $\text{Yb}^{3+}$  and, (C) 15%  $\text{Yb}^{3+}$ , and (D) comparison for 5%  $\text{Yb}^{3+}$ , 10%  $\text{Yb}^{3+}$  and, 15%  $\text{Yb}^{3+}$

The results suggested that  $\text{NaYF}_4$ -based UC materials are particularly promising for improving solar energy conversion by converting NIR photons into visible light highlighting the potential of  $\text{NaYF}_4$ -based upconverting nanoparticles, specifically in building-integrated photovoltaics (BIPV). The device is developed based on LSC and results are promising for BIPV application.

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# EXPLORING A NOVEL TELLURATE GARNET $\text{Li}_3\text{Y}_3\text{Te}_2\text{O}_{12}$ HOST FOR TRANSPARENT OPTICAL CERAMICS

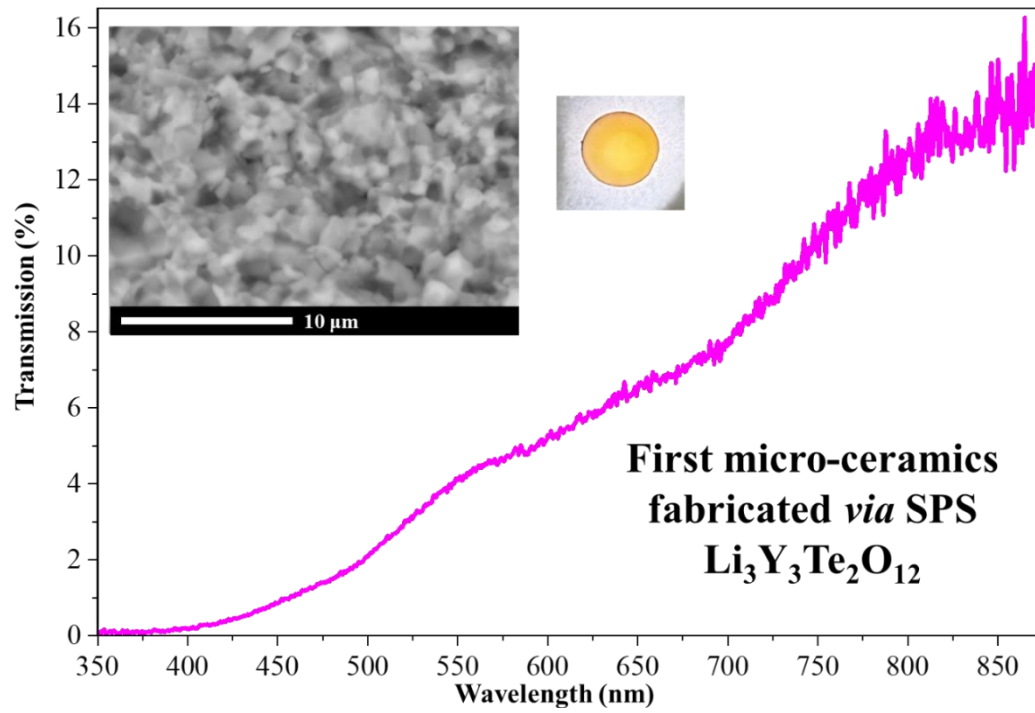
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Research on advanced optical materials for a broad range of photonic applications continues to grow rapidly, driven by the increasing demand for materials with improved optical performance. In particular, rare-earth-ion-doped ceramics have attracted significant attention due to their potential in laser, scintillation, and luminescent technologies. Among the available host matrices, garnet-type structures are especially attractive because they combine excellent optical transparency with high chemical and thermal stability and allow efficient incorporation of rare-earth activators.

In this work, we investigate the cubic tellurate garnet  $\text{Li}_3\text{Y}_3\text{Te}_2\text{O}_{12}$ , a promising yet underexplored candidate for rare-earth-doped optical ceramics, despite its close structural relationship to well-established garnet materials. Un-doped as well as  $\text{Nd}^{3+}$ ,  $\text{Yb}^{3+}$ , and  $\text{Eu}^{3+}$ -doped micro-crystalline powders were synthesized using an optimized solid-state reaction method. Their crystal structure and morphology were systematically investigated. The  $\text{Li}_3\text{Y}_3\text{Te}_2\text{O}_{12}$  crystallizes in the cubic crystal system with the space group of Ia – 3d (No. 230), which is a huge advantage in the pursuit of obtaining them in the form of sintered transparent ceramics. Thermogravimetric and differential thermal (TG-DTA) analyses were carried out to evaluate the thermal stability of the material and to optimize the ceramic processing conditions. In addition, the spectroscopic properties of  $\text{RE}^{3+}$ -doped powders were investigated at both room and cryogenic temperatures.

Within the framework of this study, the synthesized  $\text{Li}_3\text{Y}_3\text{Te}_2\text{O}_{12}$  micro-powders were consolidated into ceramic bodies using Spark Plasma Sintering (SPS). The effects of annealing temperature and dwell time on densification and microstructural evolution were systematically investigated. X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses confirmed the retention of the cubic garnet structure and the formation of dense ceramic microstructures. The optical quality of the obtained ceramics was further evaluated by total forward transmission (TFT) measurements, which revealed transmission values of approximately 15% at 850 nm, as presented in the Figure. Conducted studies demonstrated that  $\text{Li}_3\text{Y}_3\text{Te}_2\text{O}_{12}$  is a highly promising material for optical applications and indicate that further optimization of the sintering process may enable the development of efficient tellurate-based transparent optical ceramics.



**Fig.** Photographs of  $\text{Li}_3\text{Y}_3\text{Te}_2\text{O}_{12}$  ceramics fabricated by the SPS technique under indirect illumination, corresponding SEM micrographs, and TFT spectra of un-doped sintered ceramic body.

# STRUCTURAL AND OPTICAL PROPERTIES OF EU-DOPED $\text{BaGa}_2\text{O}_4$ SYNTHESIZED BY ENERGY-EFFICIENT MICROWAVE HYDROTHERMAL SYNTHESIS

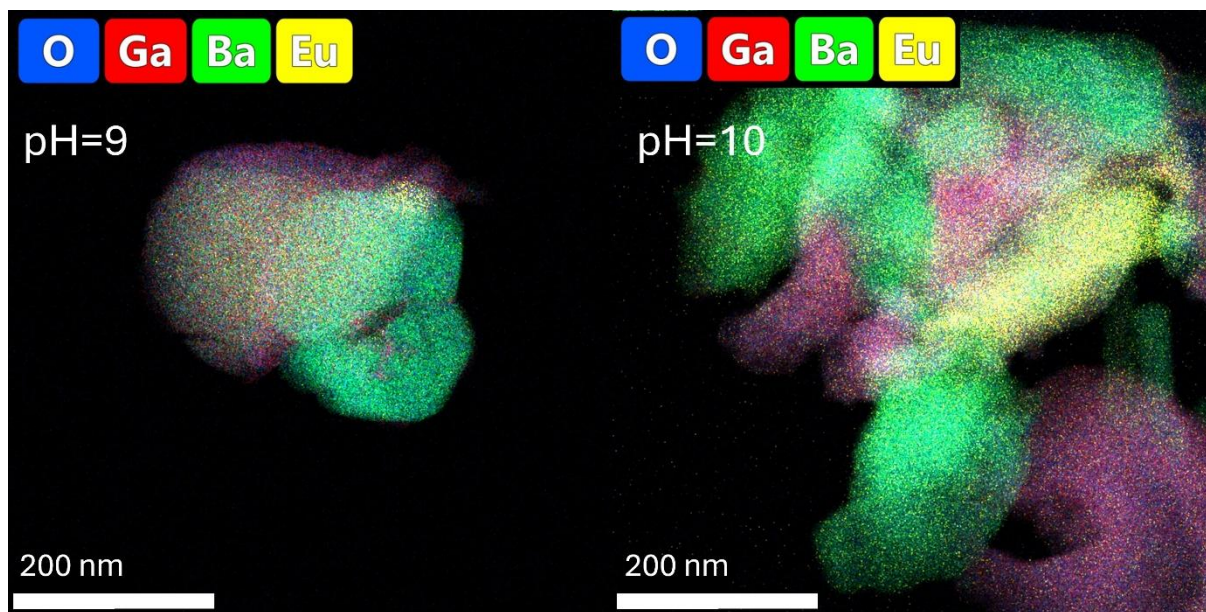
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This study presents a comprehensive analysis of the influence of synthesis parameters on the structural and optical properties of  $\text{BaGa}_2\text{O}_4\text{:Eu}$  powders obtained by microwave-driven hydrothermal synthesis. Interest in this type of material stems from its potential application in light sources, optoelectronic components, and energy conversion technologies, where chemical stability, structural durability, and high luminescence efficiency are of key importance.

Particular attention was paid to the role of the pH of the reaction environment as one of the most important factors determining the course of crystallization and the final microstructure of the material. Controlling the pH of the solution affects not only the phase composition and degree of crystallinity of the obtained powders, but also the morphology of the particles, their size and the uniformity of the distribution of europium admixture in the crystal lattice. The developed synthesis method is characterized by a significant reduction in reaction time compared to classical crystal growth techniques. The use of microwave heating enables uniform and rapid energy delivery to the entire volume of the reaction solution. Optimization of the composition of precursor solutions and precise pH control have made it possible to obtain single-phase structures.

The structural characteristics of the obtained material were determined using X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). XRD analysis enabled unambiguous identification of phases, while Raman spectroscopy provided additional information on the local structure ordering, crystal lattice symmetry, and the presence of possible structural defects. SEM and TEM allowed for detailed assessment of morphology, grain size, and degree of agglomeration. The analysis of optical properties was carried out based on photoluminescence (PL) and photoluminescence excitation (PLE) spectra, which allowed for a comprehensive assessment of the influence of the structure and local environment of the rare-earth ion.



**Fig. caption (Times10 italic)** HAADF images of samples obtained by microwave-driven hydrothermal synthesis (pH=9 – left, pH=10 – right).

The combined structural and spectroscopic investigations provided a coherent understanding of the structure-property relations in Eu-doped BaGa<sub>2</sub>O<sub>4</sub>. They demonstrated that precise control of synthesis conditions, particularly pH, is crucial for tailoring its luminescent properties for optoelectronic applications.

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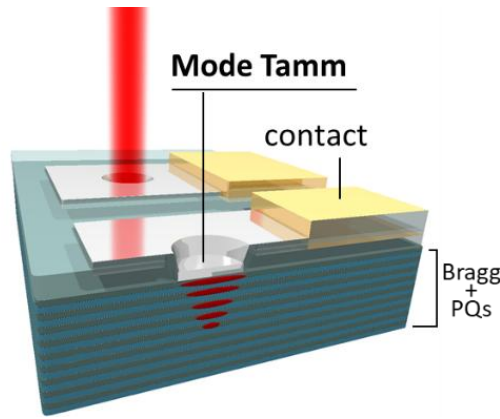


# ELECTRICALLY INJECTED TAMM LASER DIODES

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We present the realization of a new type of laser diode based on surface-confined Tamm plasmon modes, offering an innovative approach for the design of optoelectronic sources that combine high optical performance with technological flexibility. Tamm plasmon modes are electromagnetic modes localized at the interface between a distributed Bragg reflector (DBR) and a metallic layer<sup>1</sup>, merging key features of optical cavity modes and surface plasmons. In this approach, optical confinement is achieved through the lateral structuring of the metallic layer<sup>2</sup>, which enables both efficient mode confinement and the realization of complex laser source geometries<sup>3</sup>. Importantly, the Tamm laser mode can be engineered and shaped without modifying the underlying DBR, providing additional freedom in device design and fabrication.



**Fig.** Schematic diagram of a Tamm mode diode)

Based on these principles, we demonstrate an electrically injected Tamm laser based on the integration of a silver microdisk with a GaAs/AlAs DBR embedding InGaAs quantum wells positioned at the maxima of the mode electric field. The metallic microdisk serves as a localized electrical contact, enabling efficient current injection into the active region. Under electrical injection and cryogenic operation (95 K), the device exhibits clear laser behavior, with a maximum emitted power of 200  $\mu$ W at 906 nm. Spectral measurements reveal the onset of optical gain and clear mode confinement, ultimately leading to lasing characterized by pronounced spectral and angular narrowing<sup>4</sup>. Dispersion imaging further corroborates these results, confirming lasing from the fundamental confined Tamm mode.



These results establish Tamm plasmon lasers as a promising platform for compact, integrable, and potentially reconfigurable light sources. The metallic patch plays a dual role by simultaneously providing optical mode confinement and electrical injection. The ability to control the optical mode—and therefore the laser emission—through metal patterning alone offers a powerful route for network engineering of coupled laser architectures, enabling the design of arrays of coupled lasers with collective emission properties. This approach provides exceptional flexibility in tailoring the spatial, spectral, and polarization properties of the emitted light, opening promising perspectives for the realization of advanced light sources, including lasers emitting complex polarization states, such as optical vortices, achieved through metal nanostructuring.

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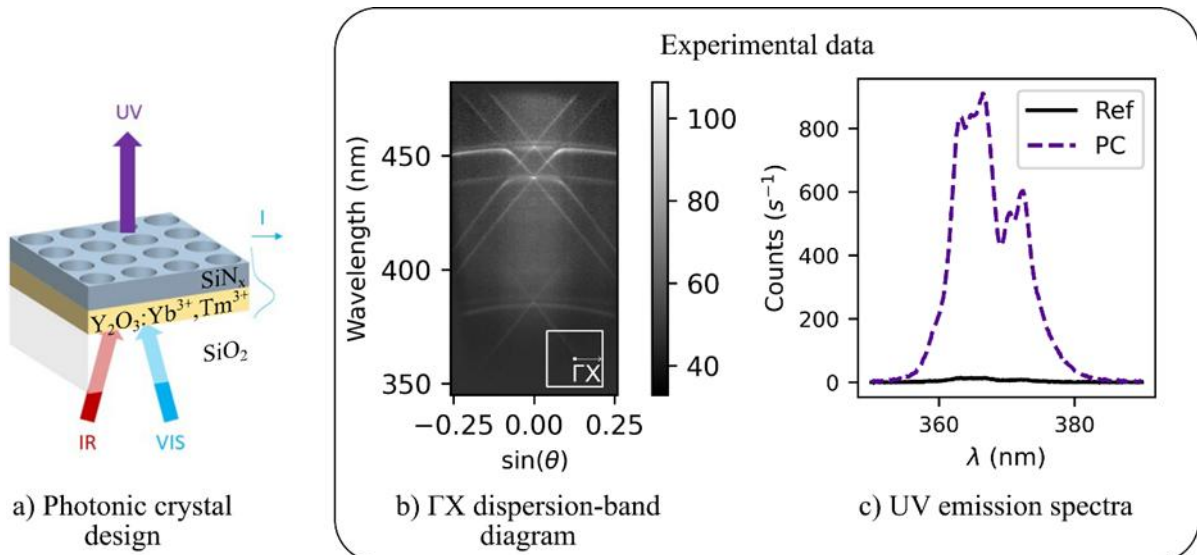
# UV UPCONVERSION ASSISTED PHOTONIC CRYSTALS

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Upconverting the solar spectrum to ultra-violet is interesting for photocatalysis of solar-fuels. Near infra-red and visible parts of the solar spectrum can be upconverted with lanthanides, however with a limited efficiency due to their low absorption cross-sections. We have designed, fabricated and characterized photonic crystal slabs enhancing multicolor upconversion process from near infra-red and visible to ultra-violet in  $\text{Yb}^{3+}$  -  $\text{Tm}^{3+}$  co-doped system, through excited-state absorption mechanism.

A few years back we demonstrated the possibility to convert part of the solar spectrum into UV photons useful for classic photocatalysts like  $\text{TiO}_2$  [1,2] or  $\text{SrTiO}_3$ . However, the energy conversion efficiency is limited by lanthanides low absorption cross-section. Here we present an all-dielectric photonic crystal slab composed of a patterned non-stoichiometric silicon nitride ( $\text{SiN}_x$ ) and  $\text{Y}_2\text{O}_3:\text{Yb}^{3+},\text{Tm}^{3+}$  thin film on a fused silica wafer to assist the excited-state absorption and the UV extraction with guided mode resonances, resulting in a substantial enhancement of the upconversion luminescence, higher than 20-fold.



**Fig. :** a - Schematic of the photonic crystal slab. b -  $\Gamma$ X dispersion-band diagram of a photonic crystal slab measured by Fourier reflectance imaging,  $\theta$  referring to the incident polar angle. c - UV emission of the photonic crystal (violet dashed line), denoted as PC, is compared to that of the unpatterned reference (black continuous line), under the following excitation conditions: 447 nm ( $18.2 \text{ kW/cm}^2$ ) + 990 nm ( $966.5 \text{ kW/cm}^2$ ).

A schematic of our photonic crystal slab is presented in the upper figure. It consists of a  $\text{Y}_2\text{O}_3:\text{Yb}^{3+},\text{Tm}^{3+}$  thin film and a  $\text{SiN}_x$  layer patterned as a hole square lattice, whose lattice parameter stands in the 240-280 nm range, which is challenging from a fabrication point of view. Materials have been optimized to avoid parasitic absorption losses and doping concentration quenching. The structure was designed to promote the excited-state absorption  $^3\text{F}_4 \rightarrow ^1\text{D}_2$  in  $\text{Tm}^{3+}$  with a guided mode resonance at the  $\Gamma$ -point ( $\theta=0^\circ$ ), as shown on the measured dispersion band-diagram presented Figure b. The latest increase the local photonic density of state at 447 nm, and so the absorption cross-section. UV light emission at 368 nm from  $^1\text{D}_2 \rightarrow ^3\text{H}_6$  spontaneous emission is also affected by a guided mode resonance, enhancing its extraction from the structure. As a result, the UV upconversion luminescence is significantly increased, as shown Figure c. The contributions of both modes to the overall enhancement were optically characterized varying the excitation conditions. Different excitation regimes have also been studied to confirm the dominance of the upconversion mechanism via excited-state absorption under solar-like excitation condition.

We acknowledge the funding from Agence Nationale de la Recherche through the grant number ANR-22-CE09-0036

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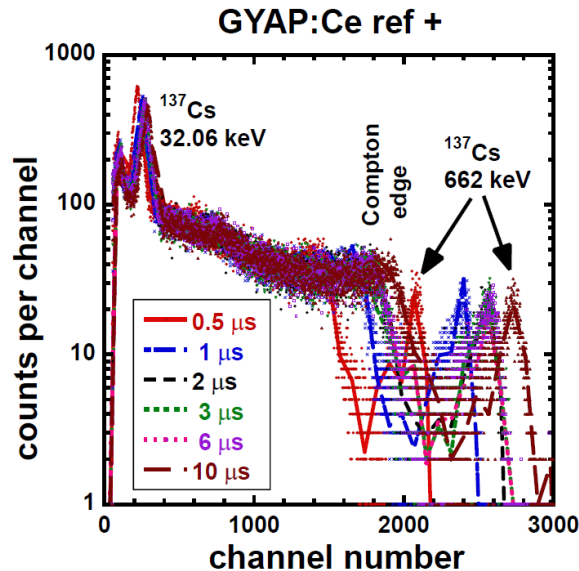
# FROM YAP:Ce TO GYAP:Ce MULTICOMPONENT PEROVSKITES

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The YAlO<sub>3</sub>:Ce (YAP:Ce) scintillating crystal has been known for over 50 years. The first paper on the subject, titled “Optical spectra of Ce<sup>3+</sup> and Ce<sup>3+</sup>-sensitized fluorescence in YAlO<sub>3</sub>”, was published by M. J. Weber in 1973 [1]. Towards the end of the 20th century, we investigated the spectroscopic properties of Ce<sup>3+</sup> impurities in YAP:Ce, as well as those of Cr<sup>3+</sup> and Nd<sup>3+</sup> impurities. This included studying energy transfer processes between them and multisite positions, in cooperation with G. Boulon [2,3].

Large YAP:Ce crystals have recently been prepared, as well as multicomponent analogues GYAP:Ce recently also [4,5]. The GYAP:Ce crystals were grown using the Czochralski method [4,5] and the prepared crystal ingots are approximately 45 mm in diameter and 170 mm in length. GYAP:Ce crystals can contain various amounts of Gd and Y (composition: Ce<sub>x</sub>Gd<sub>y</sub>Y<sub>1-x-y</sub>AP) with the optimal Gd/Y ratio being between 0.4 and 0.6 [5]. Samples for scintillation measurements, measuring 10 mm in diameter and 1 mm in thickness were cut from the as-grown crystal ingots. I will also present a detailed description of the measurements taken to



**Fig. 1** Pulse height spectra of the GYAP:Ce ref + crystal under excitation by 662 keV  $\gamma$ -ray quanta from the <sup>137</sup>Cs radioisotope at RT for various shaping times

analyze the scintillation response of the crystals, including light yield, energy resolution and the non-proportionality of the light yield, as well as scintillation decay. These measurements will be taken using a hybrid photomultiplier (HPMT) [6].

The detailed scintillation response and properties of the newly developed multicomponent GYAP:Ce crystals [4,5] were investigated using gamma rays in the 8–1300 keV energy range (light yield, energy resolution, non-proportionality, and scintillation decay). The pulse height spectra of the GYAP:Ce ref+ crystal at an energy of 662 keV ( $^{137}\text{Ce}$  radioisotope) are displayed in Fig. 1.

These studies also include a comparison of the scintillating properties of GYAP:Ce multicomponent crystals with those of the YAP:Ce crystals. GYAP:Ce crystals exhibit a higher light yield of up to 30000 photons per MeV compared to 23000 photons per MeV for YAP:Ce crystals. The energy resolutions are approximately 4–5% at 662 keV for YAP:Ce and 5–9% for GYAP:Ce crystals, respectively. The non-proportionality of the GYAP:Ce crystals reach ~70–80% at an energy of 10 keV, whereas that of the YAP:Ce crystals reach ~85%. The 1/e scintillating decay time is 49 ns for the YAP:Ce crystals and 60-100 ns for the GYAP:Ce crystals.

The detailed conclusions regarding the scintillating properties of GYAP:Ce crystals have been published in *Optical Materials*, a special issue dedicated to the memory of Georges Boulon, published in June 2026 [7].

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# **Zn<sup>2+</sup> - and Yb<sup>3+</sup>-DOPED MONOCLINIC MgWO<sub>4</sub> CRYSTALS FOR BROADBAND LASERS**

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The rapid development of next-generation photonic technologies places increasing demands on gain media with broad emission bandwidths, enabling tunable solid-state lasers and ultrafast operation. In this context, monoclinic magnesium monotungstate (MgWO<sub>4</sub>) has emerged as an excellent laser host due to its strong optical anisotropy and relatively high thermal conductivity ( $\kappa \sim 8.7 \text{ W m}^{-1} \text{ K}^{-1}$ ). When doped with rare-earth (RE) ions, the dopants substitute for the divalent Mg<sup>2+</sup> ions at the low-symmetry sites, where the mismatch in ionic radii distorts the local crystal field, inducing significant Stark splitting of the ground states and inherently broad emission spectra [1]. These properties have enabled remarkable ultrafast laser performance such as the first demonstration of sub-100 fs pulse generation from a mode-locked 2  $\mu\text{m}$  solid-state laser using a Tm<sup>3+</sup>:MgWO<sub>4</sub> crystal [2], and more recently, pulses as short as 32 fs from diode-pumped Yb<sup>3+</sup>:MgWO<sub>4</sub> via Kerr-lens mode-locking [3]. However, incorporating RE<sup>3+</sup> ions into the MgWO<sub>4</sub> lattice is also challenging, including relatively low segregation coefficients during crystal growth.

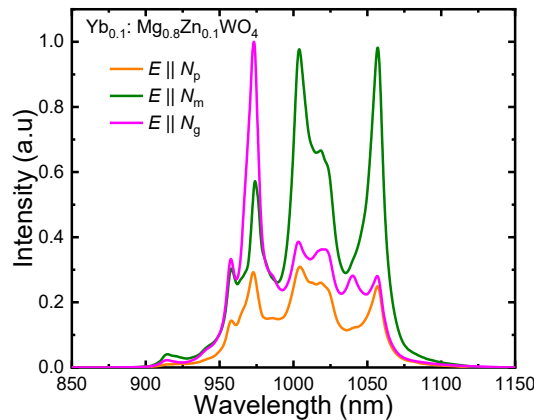
Beyond intrinsic structural properties, compositional and structural perturbations are known to enhance the gain bandwidth of laser crystals. Controlled disorder introduced through cation substitution modifies the local crystal field, leading to increased inhomogeneous broadening and enhanced Stark-level splitting. Inspired by disordered crystal families such as CNGG and CALGO, where mixed cation occupancy creates multiple non-equivalent rare-earth sites and broadened emission profiles, similar strategies can be extended to monotungstate systems. In particular, substitution within the divalent cation sublattice provides an effective route to tailor the local environment of RE<sup>3+</sup> ions while preserving the anisotropic framework of the host. Motivated by these considerations, this work investigates the modification of MgWO<sub>4</sub> through partial substitution of Mg<sup>2+</sup> with Zn<sup>2+</sup>. We report the growth and spectroscopic characterization of a novel Yb<sup>3+</sup>-doped mixed monotungstate crystal, Yb<sub>0.1</sub>:Mg<sub>0.8</sub>Zn<sub>0.1</sub>WO<sub>4</sub>. This substitutional approach is expected to enhance inhomogeneous broadening, improve dopant segregation behavior, and support the development of broadband anisotropic gain media for tunable and ultrafast laser applications.

Single crystals of the Yb<sup>3+</sup>-doped mixed monotungstate (Yb<sub>0.1</sub>:Mg<sub>0.8</sub>Zn<sub>0.1</sub>WO<sub>4</sub>) were grown using the Top-Seeded Solution Growth (TSSG) method. A solute-to-solvent molar ratio of K<sub>2</sub>W<sub>2</sub>O<sub>7</sub>/MgWO<sub>4</sub> = 70/30 was employed. The starting materials, K<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>O, MgO and WO<sub>3</sub>, as well as ZnO and Yb<sub>2</sub>O<sub>3</sub> were mixed in the appropriate ratios to achieve 10 at.% doping levels for Zn and Yb relative to the Mg cations.

The mixture was loaded into a conical platinum crucible and placed in a vertical tubular furnace with an axial temperature gradient of 4 °C/cm (bottom hotter than the surface). The solution was maintained 50 °C above the saturation temperature for 9 h to ensure homogenization. Crystal growth was initiated using a *b*-oriented MgWO<sub>4</sub> seed, followed by controlled cooling of 40 °C at a rate of 0.2 °C/h, with continuous rotation at 60 rpm. The crystal was then extracted and cooled to room temperature at a rate of 35 °C/h.

The preliminary as-grown crystals were transparent with a slightly pink coloration. Although further optimization of the growth conditions is required to improve crystalline quality, the obtained samples exhibited sufficient optical quality for detailed spectroscopic investigations.

Polarized room-temperature optical absorption and luminescence spectra of the Yb<sup>3+</sup>-doped MgZnWO<sub>4</sub> crystal were measured to assess the impact of Zn<sup>2+</sup> substitution. The absorption spectra confirm that the strong polarization-dependent anisotropy of the monoclinic wolframite structure is preserved. Likewise, the luminescence (<sup>2</sup>F<sub>5/2</sub> → <sup>2</sup>F<sub>7/2</sub>) retains the inherently broad emission profile of MgWO<sub>4</sub>. Although the initial strategy aimed to enhance inhomogeneous broadening through compositional disorder in the divalent cation sublattice, the preliminary results with 10 at.% Zn<sup>2+</sup> substitution do not indicate a significant spectral broadening beyond that of the parent host. This means that the introduced structural perturbation is accommodated by the lattice without significantly modifying the local crystal-field distribution. Higher Zn (i.e. 20%) content is currently under investigation.



**Fig.** Polarized luminescence spectra of the Yb<sup>3+</sup>-doped Mg<sub>0.8</sub>Zn<sub>0.1</sub>WO<sub>4</sub> crystal.

Nevertheless, the present results provide a clear proof of concept, demonstrating that mixed monotungstate crystals can be grown while preserving both the strong optical anisotropy and the broad emission bands of Yb<sup>3+</sup>:MgWO<sub>4</sub>, which are essential for sub-100 fs pulse generation. Further compositional optimization, including alternative cation substitutions (e.g., Cu<sup>2+</sup>), will be pursued to enhance Stark-level splitting and enable broader emission spectra.

In summary, we have successfully grown a Zn<sup>2+</sup>- and Yb<sup>3+</sup>-doped MgWO<sub>4</sub> crystal by the TSSG method for the first time, to the best of our knowledge. Spectroscopic characterization reveals that this 10 at.% Zn<sup>2+</sup> modification maintains both the strong optical anisotropy and the inherently broad emission profile characteristic of the parent MgWO<sub>4</sub> host. These results provide a clear proof of concept, demonstrating that mixed monotungstate crystals can be engineered without compromising their key spectroscopic properties.

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# INTEGRATION OF Er-DOPED $\text{Al}_2\text{O}_3$ WAVEGUIDES FABRICATED BY PULSED LASER DEPOSITION FOR ON-CHIP PHOTONIC APPLICATIONS

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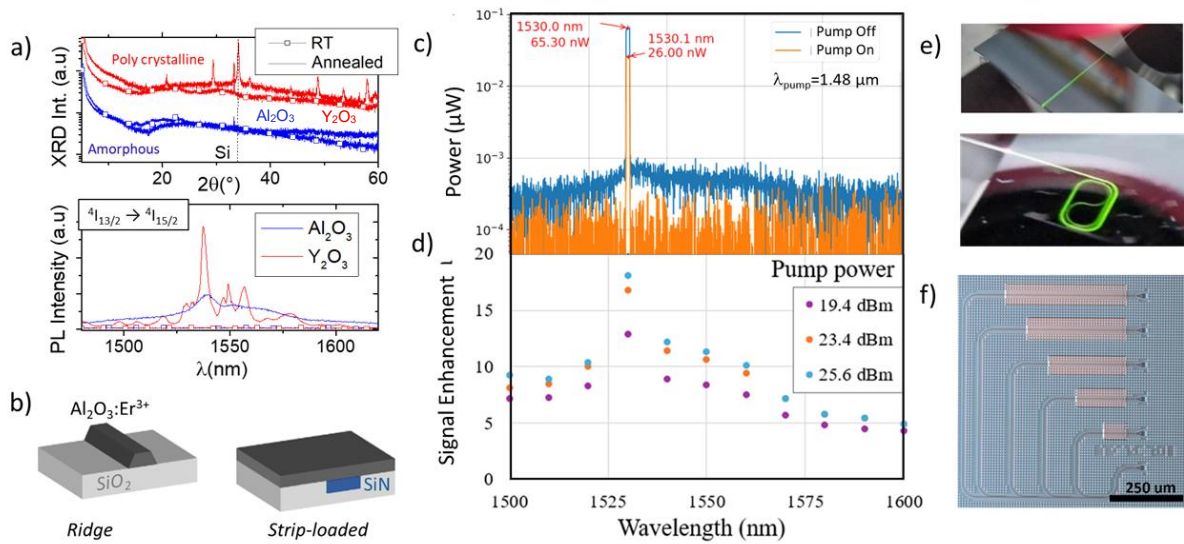
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Integrated optics represents a significant advancement in photonic technologies, aiming to miniaturize conventional optical setups by integrating multiple components on a single chip. Among the key components in such systems are optical amplifiers and integrated lasers, which rely on achieving optical gain [1, 2]. One effective approach for realizing optical gain in integrated photonic systems is through the use of rare-earth doped materials. Due to their unique electronic configurations, rare-earth ions exhibit sharp optical transitions and strong luminescence, enabling efficient light emission at specific wavelengths. When these dopant ions are embedded in a low-loss host matrix, net optical gain can be achieved if the signal enhancement provided by the dopants exceeds the intrinsic propagation losses of the waveguide [3]. For that purpose, alumina is particularly well suitable for integrated photonics as it offers high transparency in the relevant wavelength range and exhibits low optical losses. However, its chemical resistance presents challenges for device fabrication [4, 5]. The standard fabrication procedure of such optical components typically involves material deposition, patterning, and etching steps. However, etching alumina leads to degradation of the waveguide profiles resulting in increased scattering losses which affects the device performance. To overcome this limitation, we propose a novel fabrication approach based on lithography patterning, pulsed laser deposition of erbium-doped alumina and a subsequent lift-off process. This approach avoids alumina etching issues and enables direct room-temperature deposition [6]. With this method, we recently demonstrated low-loss alumina waveguides without doping [7].

In our study, we focus on the fabrication of integrated optical amplifiers-based on erbium-doped oxide materials. Figure 1-a presents the X-Ray Diffraction (XRD) and the photoluminescence of layers and micro-strips made with doped  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  hosts [8]. A broader emission is clearly observed in alumina host due to its amorphous structure, while  $\text{Y}_2\text{O}_3$  is polycrystalline. We then focus our work on alumina since it is more suitable for low-loss light propagation. We fabricated two types of waveguides architectures (Figure 1-b): ridge waveguides, in which the erbium-doped alumina constitutes the guiding core, and strip-loaded structures, where thin doped alumina layers are deposited on top of silicon nitride waveguides.





**Fig.1** (a) Erbium doped oxide photoluminescence and XRD [6]; (b) waveguide designs; (c, d) Signal amplification for e) erbium doped alumina waveguide; (f) Integration of erbium doped alumina thin film on a photonic chip

For the ridge waveguides, Figure 1-c presents an example of the gain measurement. Upon excitation with a 1.48  $\mu\text{m}$  pump laser, a signal enhancement is observed at 1.53  $\mu\text{m}$ . Two waveguide samples were investigated, with erbium doping concentrations of 3 at.% and 1.5 at.%. For the 3 at.% concentration, the losses outweigh the signal enhancement, resulting in no net gain. In contrast, for the 1.5 at.% waveguide, the signal enhancement reaches a factor of 18 at a wavelength of 1.53  $\mu\text{m}$  for a 1.6 cm propagation length (Figure 1d). Considering our measured propagation losses, this result corresponds to the first potential demonstration of net optical gain in alumina ridge waveguide fabricated without any etching process. Additional samples currently under investigation are shown in Figure 1-e, presenting also upconversion phenomena (work in progress).

For the integration of thin films on a photonic chip (i.e strip-loaded design presented in Figure 1-b), a localized 100 nm erbium-doped alumina thin film was deposited on top of a SiN strip-loading layer, and subsequently annealed at 650  $^{\circ}\text{C}$ . The chip integrates straight waveguides, ring resonators, and spiral structures. The process yielded successful localized film deposition in most of the microstructures (Figure 1-f).

These results highlight the high potential of pulsed laser deposited erbium-doped alumina combined with lift-off processing as a promising method for integrated optical amplifiers.

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# Synthesis, structure, ionic conductivity and optical properties of Dy<sup>3+</sup> doped Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>O oxyapatites

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Apatites with the general formula M<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>X<sub>2</sub> (M is a divalent cation and X is a halide) have a considerable flexibility in their elemental composition. The apatite lattice has two sites M(I) and M(II) available for cations localized in the 4(f) and 6(h) positions, respectively. This study describes the structure, electrical and luminescent properties of Dy<sup>3+</sup> doped Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>O (0 ≤ x ≤ 1) oxyapatites. The materials were prepared via conventional solid-state reaction. The effects of synthesis parameters, Dy<sup>3+</sup> concentration and charge compensator Li<sup>+</sup> co-doping on the structural and vibrational properties of samples were investigated. The ionic conductivity of the samples was measured using the complex impedance spectroscopy.

The results showed that the double substitution of dysprosium and lithium in calcium oxyapatite was effective and well-crystallized single-phase apatites were successively obtained. Moreover, the chemical stability and the structure containing large tunnels enhance the diffusion of the ion charge carrier, resulting in significant ionic conductivity. According to the Dy<sup>3+</sup> emission spectra, two different cation sites have been identified in this apatite structure. Two emission bands of the Dy<sup>3+</sup> ion is observed, the blue band (460–500 nm) corresponding to the <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>15/2</sub> transition and the yellow band (550–600 nm) due to the <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>13/2</sub> transition. The overlap between the emission band of one site and the excitation band of the other site corresponds to an energy transfer phenomenon. Both blue and yellow emissions would constitute the white light.

Correlations between the structural data, the electrical and the luminescence results are discussed.

# Study of the energy transfer occurring in nanoscintillator-photosensitizer platform for X-PDT applications.

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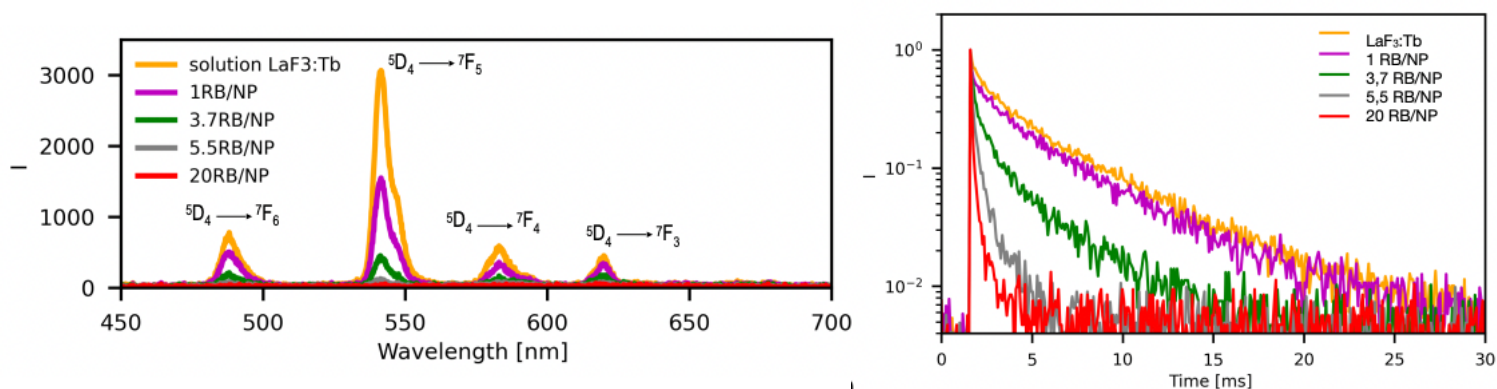
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Photodynamic therapy (PDT) is a well-established cancer treatment approach. This process involves a photosensitizer (PS), molecular oxygen, and visible light, which work together to generate cytotoxic reactive oxygen species (ROS) that can destroy cancer cells. However, the visible light range typically used (550–700 nm) has limited tissue penetration, rendering conventional PDT ineffective for treating deep tumors. To overcome this issue, alternative strategies utilize the deep penetration of X-rays to generate ROS : X-ray-induced photodynamic therapy (X-PDT). In this approach, nanoscintillators (ScNP) serve as energy convertors. X-rays are producing excitations within the ScNP, which in turn are transferring their energies to PS grafted onto the ScNP surface that ultimately produces cytotoxic singlet oxygen from the surrounding molecular oxygen. [1]

This study investigates the ET mechanism between LaF<sub>3</sub>:Tb nanoscintillators and rose bengal (RB), an efficient X-PDT platform. ET between ScNPs and PS can proceed via two distinct pathways: (i) non-radiative transfer, which occurs over very short distances, (ii) radiative transfer, which operates at longer ranges. Key challenges in optimizing this system include synthesizing ultra-small ScNPs, achieving short and stable covalent grafting of PS molecules, and precisely controlling the PS-to-ScNP ratio to ensure efficient, reproducible energy transfer. Spectroscopic measurements are used in order to study and quantify the involved processes.

The results of this study show that both energy transfer occur as the emissions and the decays of terbium decrease as shown in figure 1.



**Fig1:** Emission of terbium under X rays (left) and decay of terbium under X rays (right) for LaF<sub>3</sub>:Tb without RB and with 1-20 RB/NP.

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# Surface-modified rare earth fluoride nanoparticles: applications for cancer imaging and therapy.

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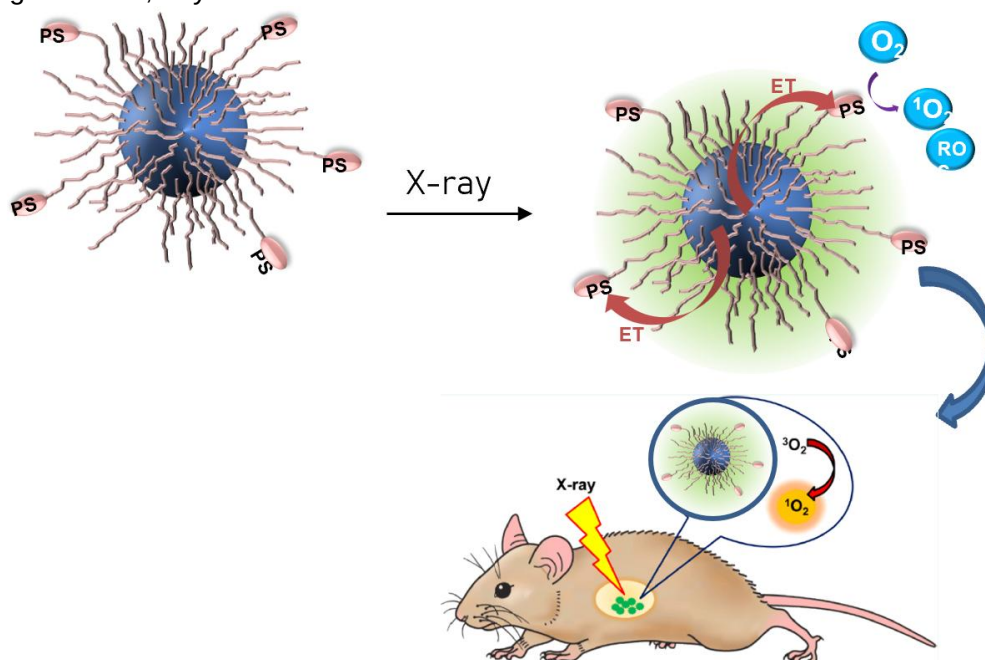
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Photodynamic Therapy (PDT) is among the strategies for cancer treatment at clinical level. PDT is based on the uptake of a photosensitizer (PS) which, upon excitation by light in a wavelength in the NIR, reacts with oxygen and generates reactive oxygen species (ROS - radicals, singlet oxygen), able to kill cancer cells directly and/or damage tumor microvessels.. However, PDT suffers from a limited use due to the shallow tissue penetration of light and is thus limited when deep tissues are concerned. To overcome that drawback, X-rays activated Photodynamic Therapy (XPDT) appears as a promising approach and reach deeper tumors by exploiting the high tissue penetration of X-rays. The mechanism of X-PDT is based on the conversion of X-ray photons into visible light capable of efficiently exciting photosensitizers. This conversion can be achieved using nanoscintillators (NS), able to transfer the emission to adjacent photosensitizers.

In the present work, the design of nanoprobes capable of generating ROS under low energy X-rays irradiation will be described. [1] Here, the X-ray doses will come from a Spectral Photon Counting CT (SPCCT), a new imaging modality based on conventional CT but using energy-resolving detectors. The spectral information enables material separation and provides additional contrast with clinically relevant information. A key feature of spectral CT is K-edge imaging, which allows selective and quantitative detection of elements such as iodine, gold, bismuth, gadolinium, or ytterbium.



**Fig.** Schematic illustration of the operating mechanism of specific nanoprobes.

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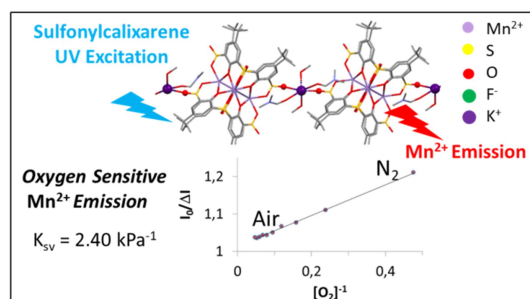
# MANGANESE II SULFONYLCALIXARENE COMPLEX- BASED MATERIALS FOR OXYGEN SENSING

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Oxygen is essential for respiration and provides the energy necessary for many physiological processes. Detecting oxygen content is important in many fields, such as analytical chemistry, environmental monitoring, and medical diagnostics.<sup>1</sup> Traditional oxygen monitoring processes, such as amperometry and conductimetry techniques have some limits: continuous measurements are difficult and response times are limited.<sup>2,3</sup> In contrast, the optical method is sensitive, non-invasive and fast. One way to measure it is to use photoluminescence measurements of some metal complexes.<sup>4</sup> The process is based on the collision between molecular oxygen and the excited electronic state of the complex, and involves a decrease in intensity and decay time. Complexes based on Mn<sup>2+</sup> ions and sulfonfylcalixarene macrocycle (ThiaSO<sub>2</sub>) are currently being studied as oxygen sensors (Figure).<sup>5-6</sup> The anionic complex [Mn<sub>4</sub>(ThiaSO<sub>2</sub>)<sub>2</sub>F]<sup>-</sup> exhibits oxygen-sensitive photoluminescent properties. A counter anion, the potassium (K<sup>+</sup>) cations, is used to obtain large crystals consisting of assemblies of anionic tetranuclear complexes, using a solvothermal process. The transformation of crystals into smaller particles leads to a structural and textural reorganization that significantly improves oxygen reactivity. Photoluminescence measurements are performed under controlled oxygen concentration and very good sensitivity to

oxygen is observed in particles, highlighting the considerable impact of structure and texture on luminescent properties. Particle shaping tests are performed in different polymer matrices which show that the supported particles have retained their properties and that the oxygen response dynamics are very fast.



**Fig.** Representation of the sulfonfylcalixarene Mn<sup>2+</sup> system and luminescence intensity versus  $[O_2]^{-1}$ .

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# COUPLED THERMAL-OPTICAL ANALYSIS OF PICOSECOND SHG IN CsLiB<sub>6</sub>O<sub>10</sub>

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High-power deep-ultraviolet (DUV) light sources based on second-harmonic generation (SHG) in CsLiB<sub>6</sub>O<sub>10</sub> (CLBO) crystals are used for a wide range of laser processing applications. However, under high-power DUV generation, absorption of the generated DUV light induces significant self-heating, which shifts the phase-matching condition and consequently degrades the conversion performance. This thermal effect becomes particularly critical in the DUV region, where both linear and nonlinear absorption are non-negligible [1]. Previous study has experimentally measured the temperature rise of CLBO crystal surfaces during high-power SHG and clarified that self-heating caused by DUV light leads to thermal dephasing [2].

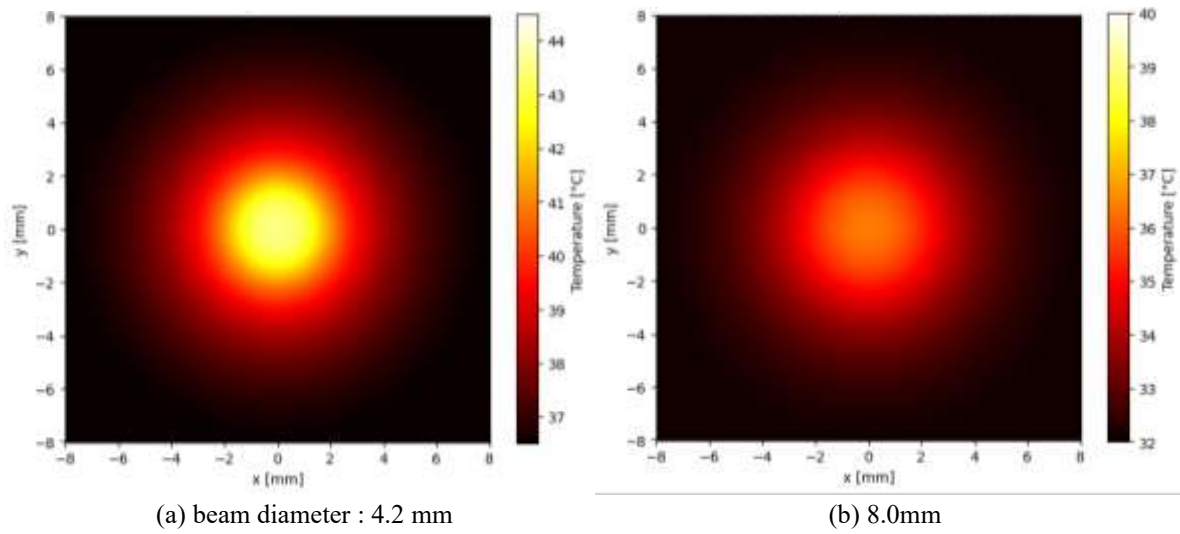
In this study, we performed numerical simulations of picosecond SHG in CLBO crystal, referring to all experimental conditions reported in the previous study [2]. The model couples nonlinear coupled-wave propagation, absorption-induced heat generation, and heat conduction by updating the phase-matching condition. The calculation conditions were as follows: The CLBO crystal was modeled with orientation angles ( $\theta$ ,  $\phi$ ) = (61.5°, 45.0°) and a cylindrical geometry (radius 8 mm, length 16 mm). The fundamental light source was assumed to be a 532 nm picosecond laser (pulse width 11 ps, repetition rate 600 kHz) with beam diameters of 4.2 and 8.0 mm (1/e<sup>2</sup>). The SH wave at 266 nm was generated via type-I phase-matching at an ambient temperature of 25°C under natural convection. The 532 nm input power was adjusted to keep the 266 nm output power at 20 W approximately constant during the simulation, consistent with the experimental procedure in the previous study. All absorbed DUV energy was assumed to be converted into heat and to diffuse throughout the crystal. Since absorption-induced heating caused thermal dephasing during SHG, the phase-matching angle  $\theta$  was periodically optimized (every 2 s during the first 60 s and every 30 s thereafter).

Figure 1(a, b) shows the simulated temperature distributions at the crystal output face after 240 s of SHG with periodic phase-matching angle adjustment (every 2 s during the first 60 s and every 30 s thereafter). The fundamental beam diameter (1/e<sup>2</sup>) is 4.2 mm in (a) and 8.0 mm in (b). The temperature differences between center and edge are approximately 6°C in (a) and 4°C in (b), which are of the same order as the previous study [2], and the surface temperature gradient is reduced for the larger beam diameter.

These calculations provide a useful framework for quantitatively evaluating the dynamic coupled effects of optical and thermal physics in frequency-conversion. This framework will support the practical design and optimization of robust frequency-conversion systems.



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**Fig.1** Simulated temperature distributions at the CLBO crystal output face after 240 s of SHG for two fundamental beam diameters: (a) 4.2 mm; (b) 8.0 mm.

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# SYNTHESIS, STRUCTURAL AND LUMINESCENCE PROPERTIES OF NEW HIGH ENTROPY PEROVSKITES $(\text{La}_{1/3}\text{Gd}_{1/3}\text{Y}_{1/3})_{1-x}\text{M}_x\text{AlO}_{3-\delta}:\text{Mn}^{4+}$ ( $M = \text{Ca}, \text{Sr}$ )

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High-entropy oxides exhibit high structural stability due to configurational entropy, which stabilises single-phase solid solutions containing multiple cations at the same crystallographic sites. Their tunable structural, electronic, and other application-relevant functional properties make them promising materials for catalysis, functional ceramics, and optical technologies [1].

High-entropy perovskites with nominal composition  $(\text{La}_{1/3}\text{Gd}_{1/3}\text{Y}_{1/3})_{1-x}\text{M}_x\text{AlO}_{3-\delta}:0.001\text{Mn}^{4+}$  ( $x = 0, 0.05, 0.1$ ;  $M = \text{Ca}, \text{Sr}$ ) were synthesised by sol-gel and solid-state reaction methods. The water solutions of the corresponding metal nitrates and citric acid were mixed and then evaporated at 80 °C. Obtained gel calcined at 300 °C and 450 °C. The sequential heat treatment of the prepared sols was performed at 800, 900, 1000, 1100 °C for 4h, and 1300 and 1500 °C for 5h. The solid-state synthesis was done starting from simple oxides in the form of micropowders. The starting powders in the appropriate proportions were thoroughly ground in an agate mortar and synthesised at 1300, 1500 and 1600 °C with an intermediate grinding. Additionally, in order to study the effect of reducing annealing, the samples were annealed in a high vacuum at 1000 °C for 2 hours.

DTA/TG analysis of  $(\text{La}_{1/3}\text{Gd}_{1/3}\text{Y}_{1/3})\text{AlO}_3:\text{Mn}^{4+}$  gel shows that the main weight losses are due to the decomposition of metal nitrates and the combustion of organic components, while the crystallisation process occurs up to 1000 °C. Thorough analysis of the XRD patterns after each annealing stage confirms that a single-phase perovskite structure of  $(\text{La}_{1/3}\text{Gd}_{1/3}\text{Y}_{1/3})_{1-x}\text{M}_x\text{AlO}_{3-\delta}:\text{Mn}^{4+}$  ( $x = 0, 0.05, 0.1$ ;  $M = \text{Ca}, \text{Sr}$ ) can be obtained via the sol-gel method after heat treatment at 1000 °C. It should be noted that in the case of the unsubstituted  $(\text{La}_{1/3}\text{Gd}_{1/3}\text{Y}_{1/3})\text{AlO}_3:\text{Mn}^{4+}$  material, the perovskite phase is already formed at 800 °C, whereas the desired crystal phase in the Ca- and Sr-containing perovskites appears only after annealing at temperatures above 900 °C. The Rietveld refinement of the crystal structures for the five high-entropy rare-earth (R) aluminates was performed in orthorhombic space group *Pbnm*. The obtained lattice parameters are in good agreement with the literature for the constituent stoichiometric and oxygen-deficient  $\text{RAlO}_3$  compounds [2].

The photoluminescence (PL) and photoluminescence excitation (PLE) studies of the materials obtained both by the sol-gel and the solid-state reaction techniques revealed a characteristic signal of  $\text{Mn}^{4+}$  ions emitting in the red spectral range at about 700 nm.

The studied materials revealed a thermally stimulated luminescence (TSL) after UV or even visible light exposure, similar to what was observed previously for  $\text{Y}_{1-x}\text{Gd}_x\text{AlO}_3:\text{Mn}^{4+}$  and  $\text{Gd}_{1-x}\text{La}_x\text{AlO}_3:\text{Mn}^{4+}$  phosphors [3]. It was also confirmed that the materials synthesised by the solid-state reaction technique have much higher radiation storage ability with respect to the sol-gel synthesised materials, which is evident in higher TSL and persistent luminescence (PersL) intensity. Analysis of the luminescence behaviour revealed that both the chemical composition and the synthesis conditions influence the formation and stability of charge trapping centers. In particular, the substitution of divalent cations ( $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ) and the annealing procedures determined the density and depth of traps, which in turn affected the



intensity and duration of the luminescent emission. These findings provide insight into how synthesis parameters and cation distribution govern the energy storage and release processes in Mn<sup>4+</sup>-doped high-entropy perovskites, offering a clearer understanding of the relationship between structural features and luminescent properties.

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# HIGH-POWER LASER TESTING OF YAG–YB:YAG MULTIMODE ACTIVE CERAMIC WAVEGUIDES

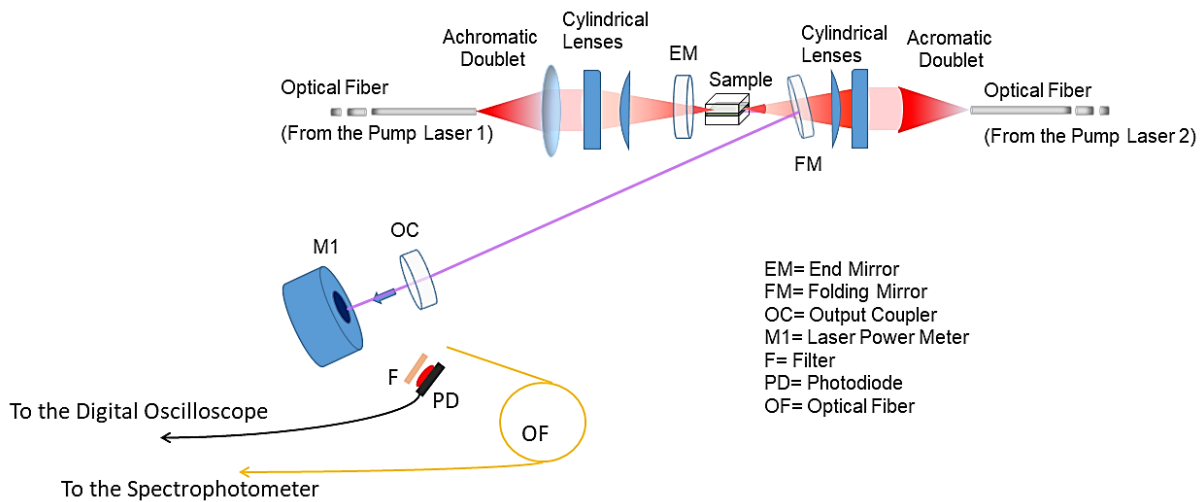
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We developed YAG–Yb:YAG multimode active waveguides for laser applications<sup>1</sup>. Some designs also include Cr:YAG absorbing regions, introduced to suppress unwanted amplified spontaneous emission (ASE). The set-up employed for the laser tests of these waveguides is shown in Figure 1. The active medium was pumped by two fiber-coupled diode lasers, each delivering a maximum output power of up to 130 W at 930 nm. The output fiber had a core diameter of 105  $\mu\text{m}$  and a numerical aperture of 0.22. The beam emerging from each fiber was re-imaged onto the waveguide input facet by means of an optical system composed of a re-collimating doublet and two cylindrical lenses for astigmatic refocusing, thus generating an elliptical focal spot.



**Fig. 1** Experimental setup used for the characterization of laser emission from the ceramic samples.

The focal spot size and their divergence were set as to match the size and angular acceptance of the waveguides. Spot dimensions and divergence were measured using a CCD-based laser beam diagnostic system.

The pump diodes were operated in quasi-continuous-wave (QCW) mode, with adjustable repetition rate and duty cycle, by suitable modulation of the driving current. The operating temperature of the pump sources was controlled by a thermoelectric cooling system, which was in turn water-cooled. Both pump lasers were adjusted to deliver the same output power in order to ensure symmetric pumping of the sample and an even distribution of the thermal load between the two ends.

The ceramic waveguide prototype was housed between two flat copper cooling plates. A 250  $\mu\text{m}$  thick indium foil was inserted between the copper surfaces and the sample faces. Owing to

its high malleability, indium ensured uniform pressure distribution on the sample faces and improved thermal contact. Heat removal was achieved by circulation of water cooled to 15 °C. The sample holder was mounted on a five-axis positioning stage, providing three translational degrees of freedom, parallel and perpendicular to the cavity axis, and two rotational adjustments about axes orthogonal to the optical axis. All movements were controlled by micrometric screws, enabling accurate optimization of sample positioning and cavity alignment. The tested waveguides achieved a maximum output power exceeding 100 W in *quasi*-CW emission conditions. The slope efficiency was as high as 46%.

The authors gratefully acknowledge the support from the Italian Ministry of Defence under PNRM, Contract No. 8731 of 04/12/2019 (CeMiLAP<sup>2</sup>).

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# STRATEGIES FOR LUMINESCENCE TUNING OF Ce:GAGG CERAMICS: Ga:Al RATIO AND SINTERING AIDS.

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We produced transparent ceramics of cerium-doped gadolinium aluminium gallium garnet (Ce:GAGG) with different Ga:Al ratio and with the use of sintering additives to evaluate the effect on sintering behaviour and luminescent properties.

Scintillating materials are fundamental in detectors for ionizing radiation and high-energy particles [1]. They convert the high energy of the incoming particles into low-energy UV or visible photons. Single-crystal rare-earth-doped garnets are already used in detectors for medical instruments and, due to their fast time-response, can be used in time-of-flight positron emission tomography (TOF-PET) and X-ray computerized tomography (CT). Transparent ceramics are a suitable alternative to single crystals since they combine the scintillating and thermomechanical properties of single crystals with optical homogeneity and the ease of fabrication typical of ceramic materials [2].

We produced Ce-doped GAGG with Ga:Al ratio 3:2, 4:1 and 5:0 (GGG) by ball milling of high-purity oxide powders of gadolinium, aluminium, gallium and cerium weighed to the desired stoichiometry. Silicon and magnesium oxides were used as sintering aids, along with a test without sintering aids. The densification takes place in two steps: a reactive sintering in air to obtain the garnet phase and a subsequent hot isostatic pressing treatment (HIP) to reach full density and transparency. To show the effect of the Ga:Al ratio and sintering aids, the samples were characterized for microstructure and luminescent properties. Microstructure was characterized by SEM and optical microscope. The investigated luminescent properties are radioluminescence spectra under soft X-rays excitation, radioluminescence response under prolonged exposure to X-ray irradiation up to a dose of around 2 Gy, and afterglow decays in the second-to-minutes time scale. UV-visible transmittance spectra were also recorded.

The variation of Ga:Al ratio induces shifts in the optimal sintering temperature as well as in the optical properties. On the other hand, the use of sintering aids can influence the microstructure and optical quality, but also the occurrence and the duration of the afterglow. The work assesses the different contributions of these effects in order to propose suitable materials for specific applications.

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# EXPLORING THE POTENTIAL OF Nd<sup>3+</sup>-DOPED PEROVSKITE-TYPE CUBIC BaLaLiTeO<sub>6</sub> AND BaLaNaTeO<sub>6</sub> FOR TRANSPARENT CERAMICS

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Yannick GUYOT<sup>4</sup>, Sandrine COTTRINO<sup>5</sup>, Martyna ZIĘCIAK<sup>1</sup>,  
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Tellurate-based materials are attracting increased interest as host lattices for optical applications due to their high rare-earth (RE<sup>3+</sup>) solubility, low phonon energies (~ 600 - 700 cm<sup>-1</sup>), and a wide transparency window extending into the mid-infrared region (~ 6 μm). Cubic perovskite-type tellurates are particularly promising for fabrication of transparent and translucent ceramics owing to their high crystallographic symmetry and structural flexibility.

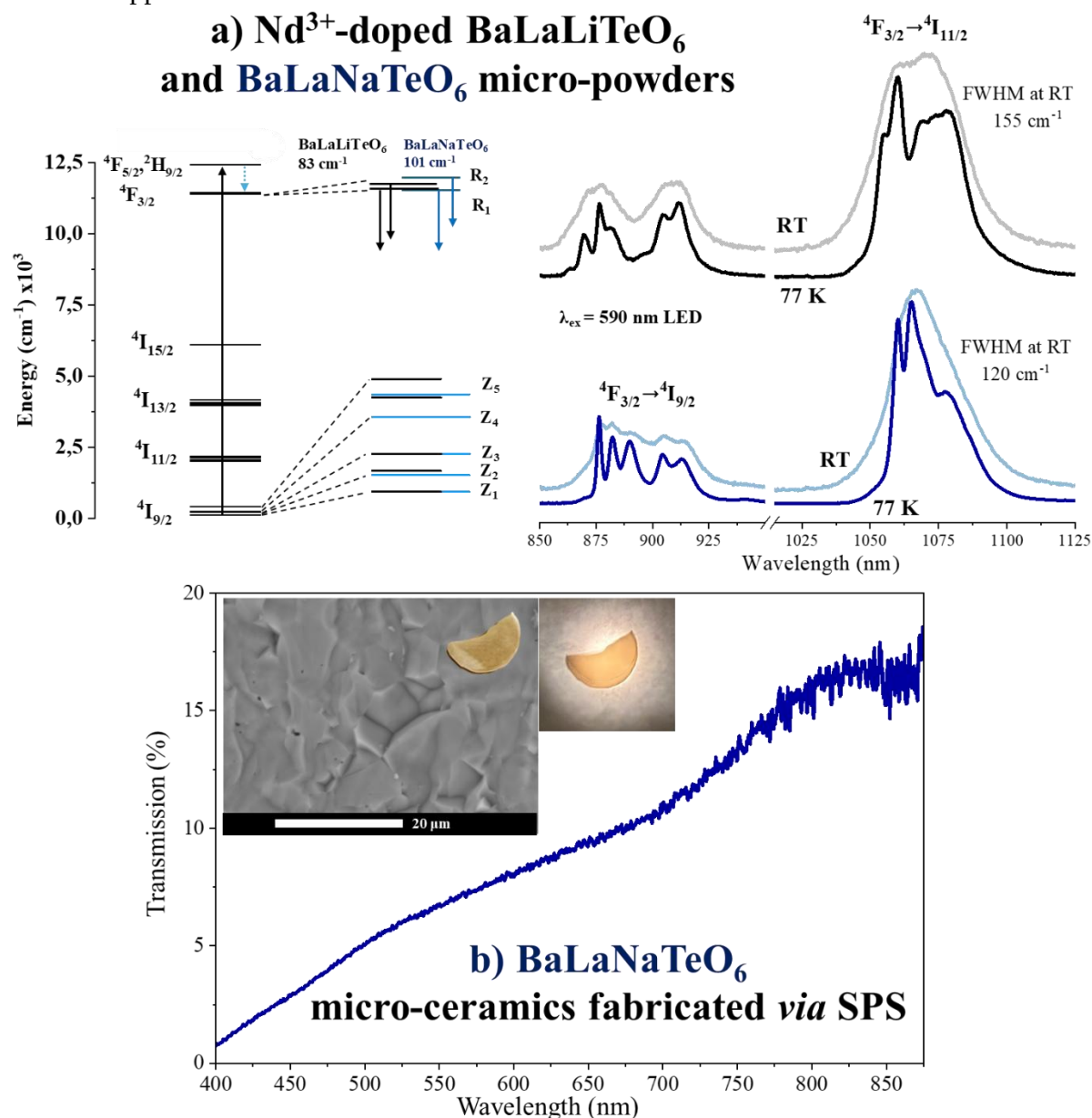
In this work, Nd<sup>3+</sup>-doped BaLaLiTeO<sub>6</sub> (BLLT) and BaLaNaTeO<sub>6</sub> (BLNT) were synthesized *via* an optimized solid-state reaction method and systematically investigated with respect to their structural, spectroscopic, luminescence, and ceramic-processing properties. For the first time, the crystal structures of BLLT, BLNT, and fully substituted BaNdLiTeO<sub>6</sub> were solved using micro-scale single-crystal X-ray diffraction, confirming their cubic double perovskite symmetry. Powder X-ray diffraction further confirmed the formation of phase-pure cubic structures across a wide range of Nd<sup>3+</sup> concentrations.

Low-temperature absorption and emission spectroscopy revealed pronounced differences in the local environments of Nd<sup>3+</sup> ions in the two hosts. BLNT exhibits narrower absorption and emission bands with well-resolved Stark components, indicating a more ordered activator environment. In contrast, BLLT shows broader spectral features consistent with increased structural disorder. Site-selective excitation experiments confirmed non-homogeneous Nd<sup>3+</sup> distributions in both systems. In BLLT, excitation-dependent spectral changes are dominated by band broadening with modest shifts of peak positions. In BLNT, such changes remain weak at low Nd<sup>3+</sup> concentrations (1 - 10%), whereas additional emission lines appear only at higher concentrations (≥20%), suggesting activation of a second Nd<sup>3+</sup> site with distinct symmetry. Luminescence decay measurements of the <sup>4</sup>F<sub>3/2</sub> level indicate concentration quenching in both materials, with a faster onset and more pronounced non-exponential behaviour in BLLT. BLNT shows a longer mono-exponential decay at low to intermediate Nd<sup>3+</sup> concentrations, with a decay time of 241 μs compared to 227 μs for BLLT at 1% Nd<sup>3+</sup>.

For the first time for these compositions, phase-pure micro-powders were densified into translucent ceramics using the Spark Plasma Sintering (SPS) technique to evaluate their potential for transparent ceramics fabrication. For the comparative studies, additional ceramics were also prepared by uniaxial pressing followed by conventional sintering. Thermal analysis was employed to optimize sintering conditions, while X-ray diffraction and scanning electron microscopy confirmed the formation of well-crystallized cubic phases and dense micro-structures. Importantly, BLNT was successfully densified into partially translucent ceramics, with optical transmission reaching approximately 17%.

These results demonstrate that Na<sup>+</sup> substitution enhances structural order, improves spectroscopic performance, and facilitates ceramics densification, positioning Nd<sup>3+</sup>-doped

BLNT as a promising material for near-infrared luminescent translucent and transparent ceramics applications.



**Fig.** (a) Energy-level diagram of  $\text{Nd}^{3+}$  ions in BLNT and BLNT micro-powders (left), together with emission spectra of both tellurate hosts recorded at room temperature and 77 K under broadband LED excitation. (b) Photographs of BLNT ceramics fabricated by the SPS technique under indirect illumination, along with corresponding SEM micrographs and Total Forward Transmission spectra of the sintered ceramic body.

# Unearthing the Real-Time Excited State Dynamics from Antenna to Rare Earth Ions Using Ultrafast Transient Absorption

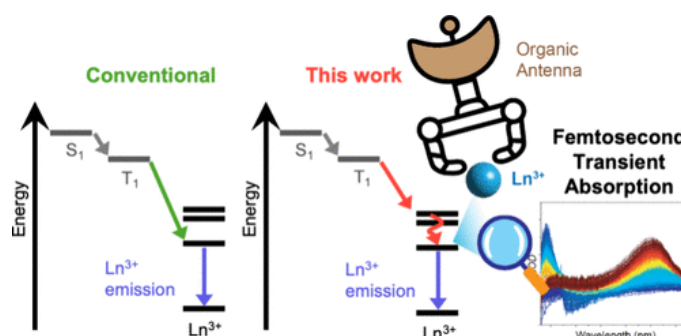
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The conventional energy transfer pathway in organic lanthanide complexes is purported to be from the excited singlet state of the chromophore to the triplet state and subsequently directly to the emitting state of the trivalent lanthanide ion.

With the aid of the antenna effect, luminescence from trivalent lanthanide ions can be harvested despite the weak absorption coefficient of  $\text{Ln}^{3+}$ .<sup>[1,2]</sup> To elucidate the excited dynamics in lanthanide complexes, which occur within the ultrafast time scale of picoseconds to nanoseconds, a spectroscopic technique capable of investigating this range is necessary. Femtosecond transient absorption spectroscopy (fs-TAS) can be employed to investigate the excited state properties of organic lanthanide complexes.<sup>[3-5]</sup>



In this work, we found that the energy transfer occurs from the triplet state to the nearest energy level, instead of directly to the emitting state of the lanthanide ion. The triplet decay rate for different lanthanide ions follows an energy gap law from the triplet level to the receiving level of the lanthanide ion. Three different categories of complexes were synthesized and inspected using different techniques, demonstrating the universality of our findings. This work renews the insights to conventional findings, highlighting the importance of the energy gap between the triplet state and the nearest lanthanide energy level in optimization of light harvesting. The rationale of ligand design of chromophores should be reconsidered, leading to various applications of lanthanide complexes with enhanced quantum yield and brightness.

*This work was supported by Innovation and Technology Fund - Partnership Research Programme (ITF-PRP) (PRP/040/23FX)*

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# ENHANCING LIGHT EXTRACTION IN $\text{YVO}_4\text{:Eu}^{3+}$ NANOCRYSTAL-BASED LUMINESCENT COATING USING METALLIC NANOPARTICLES

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Luminescent coatings based on nanophosphors have attracted significant interest in both academic and industrial circles, particularly for their potential applications in solid-state lighting, high-resolution displays, and anti-counterfeiting technologies<sup>1</sup>. These materials are highly valued for their exceptional photoluminescent properties, such as high quantum yields, chemical stability, and tunable emission spectra, which make them ideal candidates for next-generation optoelectronic devices. However, a persistent challenge in their practical implementation is the efficient extraction of emitted light. Total internal reflection (TIR) and waveguiding effects within the coating matrix often trap a substantial fraction of generated photons, thereby limiting the overall luminous efficacy and restricting device performance.

In this study, we address this challenge by investigating the angular emission properties and light extraction efficiency of luminescent coatings based on  $\text{YVO}_4\text{:Eu}^{3+}$  nanocrystals (NCs). We focus on two distinct types of NCs: spherical NCs with a diameter of 340 nm and rice grain-shaped NCs measuring 18 nm in length and 10 nm in width. These NCs were synthesized using hydrothermal methods to ensure high crystallinity and uniform doping of  $\text{Eu}^{3+}$  ions, and were subsequently embedded within a transparent organo-silicate hybrid matrix for achieving luminescent coatings of about 2 micrometers. The resulting composite forms a bright, red-emitting luminescent coating characterized by high homogeneity (see inset Figure 1b), excellent mechanical stability, and optical transparency, making it suitable for a wide range of applications<sup>2</sup>.

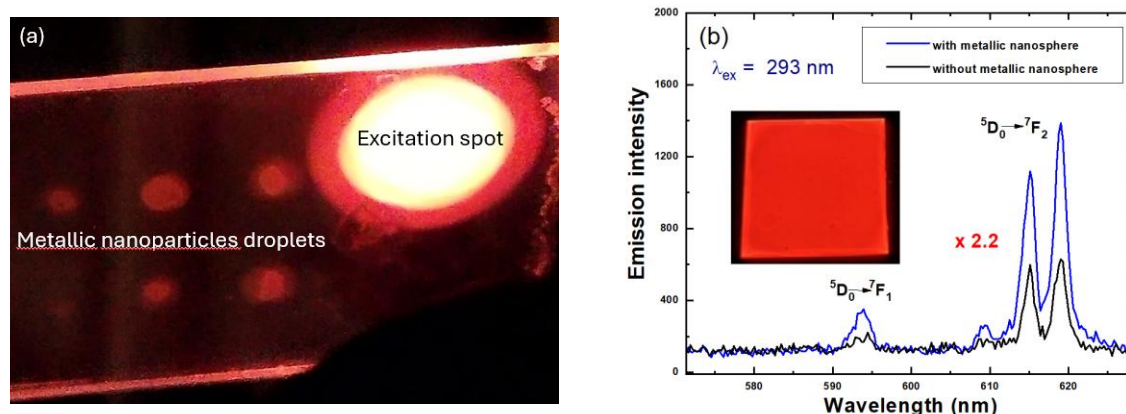
To characterize the angular distribution of emission, we employed two complementary techniques: angle-resolved photoluminescence (ARPL) and Fourier imaging. ARPL enables wide-angle measurements of emission intensity, covering the range from the front of the sample (0°) to its edge (90°). Fourier imaging, while limited to a smaller angular range (0° to 60°), offers higher angular resolution and the ability to probe micrometer-scale areas, providing detailed insights into local emission behavior.

Our results reveal that coatings based on small rice grain-shaped NCs (18×10 nm) exhibit significant photon leakage at the edges (Figure 1a), a behavior attributed to their subwavelength size, which minimizes scattering. In contrast, those embedding large spherical NCs (340 nm) display a strongly anisotropic emission profile, with pronounced intensity peaks at 10° and 60°. This phenomenon occurs because the size of these NCs is comparable to the effective

wavelength (defined as the ratio of the emitted wavelength to the refractive index of the matrix). At this scale, the NCs act as effective photonic scatterers, reducing TIR and redirecting photons toward specific angles. Our Finite-Difference Time-Domain (FDTD) simulations confirm these experimental observations and further suggest that inter-particle distance plays a critical role in determining the extraction angles.

To further optimize light extraction, we explored the integration of 100 nm gold nanospheres deposited by drop casting directly onto the luminescent coating. This modification resulted in a 2.2-fold increase in red photon emission (Figure 1b), attributed to the additional scattering centers provided by the metallic nanoparticles, which further reduce waveguiding losses. We study the influence of the droplet size and the metallic nanoparticles concentration on the light extraction (Figure 1a). We observed that the transition from enhancement to quenching is highly sensitive to the density of the metallic nanospheres. At low densities, scattering effects dominate, leading to increased emission. Beyond a critical density, absorption losses begin to quench the luminescence, highlighting the need for precise control over nanoparticle distribution.

In conclusion, this study demonstrates that the size and morphology of  $\text{YVO}_4:\text{Eu}^{3+}$  nanocrystals, combined with the strategic use of metallic nanoparticles, can significantly enhance light extraction and enable control over angular emission in luminescent coatings. By harnessing photonic scattering, we achieved a 2.2-fold increase in red photon emission while gaining the ability to tailor emission directionality. These findings present a simple yet effective method to control the light emission properties of luminescent coatings, offering promising avenues for the development of advanced optoelectronic devices. Future work will focus on optimizing nanoparticle distribution for large-scale industrial applications.



**Figure 1** (a) Image of the luminescent coating with metallic nanoparticles excited with a 280 nm LED. (b) Emission intensity spectra of luminescent coating under 294 nm excitation source with and without metallic nanospheres. Inset: picture of the luminescent coating under 254 nm excitation source.

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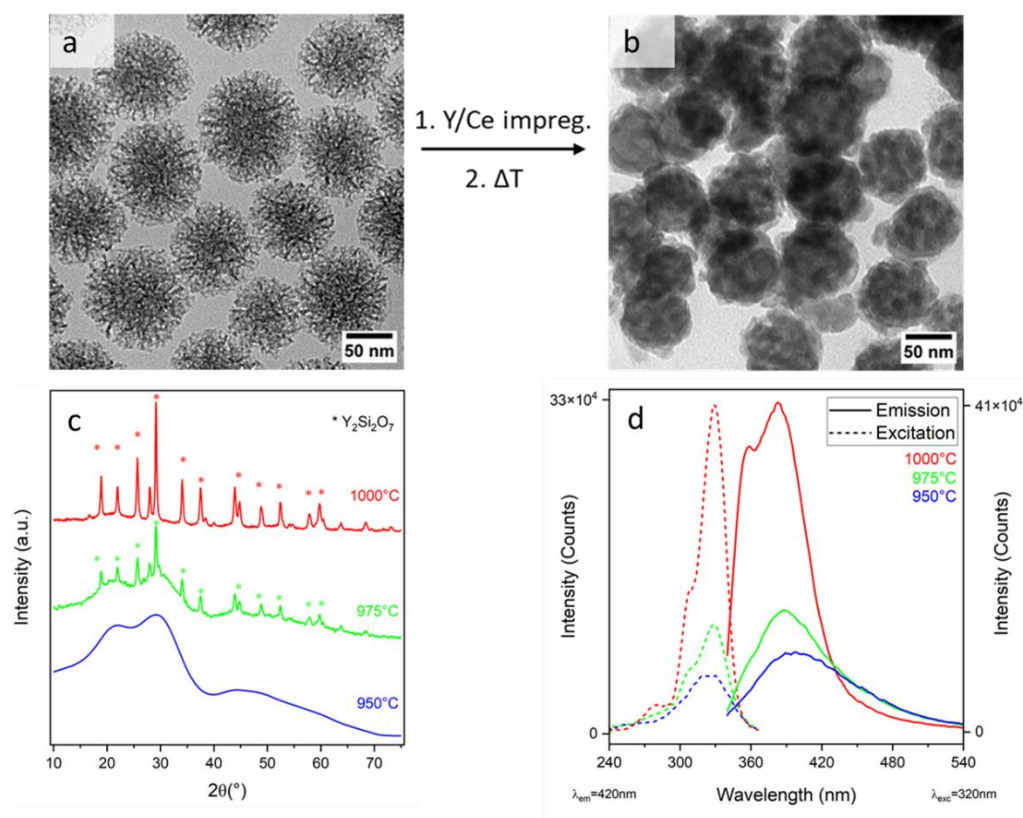
# **Ce-doped Yttrium Silicate Nanoscintillators via Reactive Nanocasting Synthesis for X-ray Photodynamic Therapy.**

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Scintillating materials, capable of converting high-energy ionizing radiation, such as X-rays, into UV–visible photons, are already widely used in medical imaging technologies and are increasingly being studied for otherwise inaccessible biological environments. At the nanoscale, scintillator nanoparticles further enable X-ray-induced photodynamic therapy (X-PDT), an emerging cancer treatment strategy. In X-PDT, X-rays are locally downconverted into light that activates a photosensitizer to generate cytotoxic reactive oxygen species. This approach addresses a fundamental limitation of conventional photodynamic therapy (PDT) that suffers from restricted penetration depth in tissues of externally applied light<sup>1</sup>. In this context, rare-earth-doped silicates are particularly attractive due to their efficient radiative transitions and tunable emission properties. Among those, cerium-doped  $\text{Y}_2\text{Si}_2\text{O}_7$  (YPS:Ce) offers broadband UV-blue emission with short decay times thanks to the  $\text{Ce}^{3+}$  5d–4f parity-allowed transitions<sup>2</sup>. This emission overlaps well with the Soret absorption band of porphyrin-based photosensitizers, making YPS:Ce nanoscintillators a promising candidate for X-PDT.

In this contribution, we are reporting on an innovative reactive nanocasting approach for the synthesis of YPS:Ce nanoscintillators suitable for biological applications. Mesoporous silica nanoparticles (MSNs) with stellate morphology and large porosity, are first synthesized to serve as both template and silica source. These template nanoparticles are subsequently impregnated with ionic yttrium and cerium precursors, followed by thermal treatment to induce formation and crystallization of the silicate phase while preserving nanoscale morphology. A range of synthesis parameters have been investigated, including yttrium loading, precursor solvent and concentration, as well as drying conditions, annealing temperature, and dwell time, among others. The impact of these parameters was systematically evaluated in terms of material crystallinity and photoluminescence efficiency in order to optimize the material for X-ray-based applications while maintaining good colloidal stability. This new nanocasting approach hence provides a versatile route to engineer rare-earth-doped optical nanomaterials for radiation-activated therapeutic applications.



**Fig. Ce-doped yttrium silicate synthesis and characterization:** TEM images of a) pristine MSN, and b) the nanoparticles after loading with Y/Ce precursors and thermal treatment. c) XRD patterns, and d) excitation and emission spectra of nanoparticles annealed at 950, 975 and 1000°C.

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# Growth and Optical Properties of Tm<sup>3+</sup>-Doped (Lu,Y,Sc)<sub>2</sub>O<sub>3</sub> and (Lu,Gd,Sc)<sub>2</sub>O<sub>3</sub> Single Crystals

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Masao YOSHINO<sup>2,3)</sup>, Rikito MURAKAMI<sup>2,3)</sup>, Kei KAMADA<sup>3,4)</sup>, Yuui YOKOTA<sup>2,4)</sup>  
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**1. Introduction** Optical thermometry is a promising technique for non-contact temperature measurement in extreme environments. While (Lu,Y,Sc)<sub>2</sub>O<sub>3</sub> single crystals doped with Eu<sup>3+</sup>, Pr<sup>3+</sup> and Tb<sup>3+</sup> have demonstrated great potential as an element of the optical thermometry [1,2], further extension of the operating temperature range and enhancement of sensitivity remain challenges for practical applications. In addition, blackbody radiation interferes with measurement accuracy at high temperatures, making short-wavelength (e.g., blue) emission desirable. To reduce interference from blackbody radiation, we focused on blue-emitting Tm<sup>3+</sup>. In this study, Tm-doped (Lu,Y,Sc)<sub>2</sub>O<sub>3</sub> (Tm:(Lu,Y,Sc)<sub>2</sub>O<sub>3</sub>) and (Lu,Gd,Sc)<sub>2</sub>O<sub>3</sub> (Tm:(Lu,Gd,Sc)<sub>2</sub>O<sub>3</sub>) single crystals were grown and characterized to evaluate their thermometric potential as novel optical materials.

**2. Materials and Methods** The crystals were grown by the micro-pulling-down ( $\mu$ -PD) method using a W crucible [3]. Sc<sub>2</sub>O<sub>3</sub> powder with a purity of 99.9%, and Y<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub> and Tm<sub>2</sub>O<sub>3</sub> powders with a purity of more than 99.99% were prepared as starting materials. The crystal structures were analysed by powder X-ray diffraction. After cutting and mirror polishing to 1 mm thickness, photoluminescence (PL) spectra were measured, and the optical properties were investigated.

**3. Results** Figure 1 shows the (Tm<sub>0.01</sub>Lu<sub>0.24</sub>Y<sub>0.25</sub>Sc<sub>0.50</sub>)<sub>2</sub>O<sub>3</sub> single crystal grown by the  $\mu$ -PD method. Several emission peaks corresponding to Tm<sup>3+</sup> 4f-4f transitions were observed in the PL spectrum, as shown in Fig. 2. We identified these emission peaks as <sup>1</sup>I<sub>6</sub>-<sup>3</sup>H<sub>6</sub>, <sup>1</sup>D<sub>2</sub>-<sup>3</sup>H<sub>6</sub>, <sup>1</sup>D<sub>2</sub>-<sup>3</sup>F<sub>4</sub>, <sup>1</sup>G<sub>4</sub>-<sup>3</sup>H<sub>6</sub> and <sup>1</sup>G<sub>4</sub>-<sup>3</sup>F<sub>4</sub> transitions. Details of the growth and optical properties of Tm:(Lu,Gd,Sc)<sub>2</sub>O<sub>3</sub> as well as Tm:(Lu,Y,Sc)<sub>2</sub>O<sub>3</sub> single crystals will be presented at this conference.

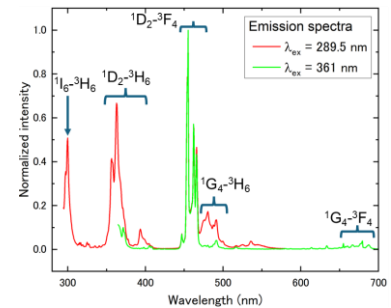
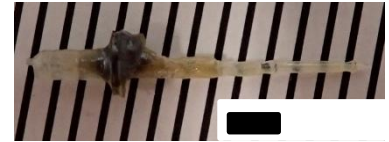


Fig. 2 PL emission spectra of Tm:(Lu,Y,Sc)<sub>2</sub>O<sub>3</sub>.

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# PREPARATION AND LUMINESCENCE CHARACTERIZATION OF TRANSITION-METAL-DOPED $\text{LiAl}_5\text{O}_8$

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Lithium aluminate spinel,  $\text{LiAl}_5\text{O}_8$ , is a promising host for the development of scintillators for thermal neutron detection. The focus on thermal neutrons is based on the ability of the  $^6\text{Li}$  isotope to convert neutrons via a neutron capture reaction into high-energy tritium and helium ions, which subsequently excite the emission of low-energy radiation (light) in the scintillation material along their ionization track. The  $\text{LiAl}_5\text{O}_8$  matrix itself does not exhibit any meaningful luminescent properties and therefore must be doped with suitable activator ions, such as transition metal or lanthanide ions. The preparation of  $\text{LiAl}_5\text{O}_8$  in the form of highly transparent single crystals is problematic due to lithium evaporation from the melt during crystal growth. However, the optically isotropic cubic structure of  $\text{LiAl}_5\text{O}_8$  allows this material to be prepared in the form of transparent ceramics, where the issue with lithium evaporation at high temperatures can be mitigated thanks to much lower processing temperatures. The preparation of pure  $\text{LiAl}_5\text{O}_8$  in the form of transparent ceramics has already been described in the literature, but the preparation of doped  $\text{LiAl}_5\text{O}_8$  transparent ceramics that would exhibit luminescence has not yet been achieved.

This work investigates potential transition metal activators for the  $\text{LiAl}_5\text{O}_8$  host for subsequent development of doped  $\text{LiAl}_5\text{O}_8$  transparent ceramics. Specifically, the preparation and luminescence characterization of  $\text{LiAl}_5\text{O}_8$  doped with  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cu}^+$ , and  $\text{V}^{4+}$  ions were carried out. The doped  $\text{LiAl}_5\text{O}_8$  samples were prepared in the form of bulk ceramics via powder synthesis by Pechini polyesterification, followed by powder compaction by uniaxial pressing and pressureless sintering of the green bodies in air or in a reducing atmosphere (due to the multivalent nature of the investigated activators). Among the studied dopants,  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  ions were readily stabilized in the  $\text{LiAl}_5\text{O}_8$  host and exhibited intense luminescence, whereas luminescence associated with  $\text{Cu}^+$  and  $\text{V}^{4+}$  ions could not be achieved.

# TIOPRONIN-CAPPED Ag<sub>2</sub>S QUANTUM DOTS: SYNTHESIS, OPTIMIZATION AND OPTICAL PROPERTIES

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We report the synthesis, optimization and comprehensive characterization of aqueous colloidal silver sulfide quantum dots (Ag<sub>2</sub>S QDs) capped with tiopronin (TP), a ligand not previously explored for Ag<sub>2</sub>S QDs. Systematic optimization of synthesis parameters, including temperature, reaction time, pH, precursor stoichiometry, and purification procedure, enabled the preparation of Ag<sub>2</sub>S/TP QDs with enhanced near-infrared (NIR) emission properties. Particular attention was paid to achieving relatively high quantum yield (QY = 0.49%) and prolonged fluorescence lifetimes ( $\tau_{\text{avg}} = 13.6$  ns), which remain key limitations of low-cytotoxicity NIR nanomaterials intended for bioimaging applications.<sup>1</sup>

FT-IR spectroscopy confirmed the attachment of TP molecules to the surface of Ag<sub>2</sub>S QDs while X-ray diffraction (XRD) measurements verified the crystalline Ag<sub>2</sub>S structure. Interestingly, absorption spectra and XRD patterns revealed the formation of metallic silver species in the presence of TP, which may contribute to partial fluorescence quenching.

Furthermore, femtosecond Z-scan measurements performed over a broad spectral range (650 – 1600 nm), demonstrated pronounced two-photon absorption (2PA), with a maximum two-photon absorption cross-section ( $\sigma_2$ ) of  $1159 \pm 414$  GM at an excitation wavelength of 800 nm. These findings demonstrate the potential of TP-stabilized Ag<sub>2</sub>S QDs as attractive NIR probes for both conventional single-photon diagnostics and two-photon fluorescence microscopy (TPFM).

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# Growth and characterization of colored Co, Cr, Ho, Eu -doped YAG single crystals

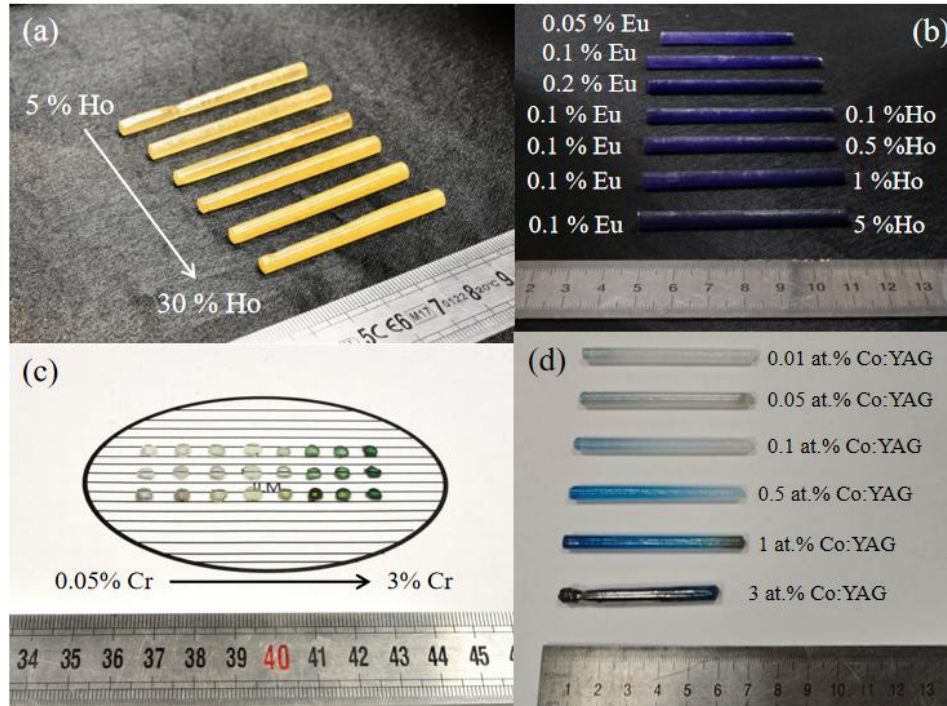
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Yttrium aluminum garnet (YAG,  $\text{Y}_3\text{Al}_5\text{O}_{12}$ ) garnet doped with rare earth ( $\text{RE}^{3+}$ ) and specific ions is the most famous kind of oxide crystals widely used as the active medium for a large wide of application [1]. The dopant, triply ionized typically replaces a small fraction of the yttrium ions in the host crystal structure of the yttrium aluminum garnet. It is the dopant ion which provides the wanted activity in the crystal. In our laboratory,  $\text{Y}_3\text{Al}_5\text{O}_{12}$  (YAG) single crystals doped with various ions (including  $\text{Ho}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Co}^{3+}$  ions) were successfully grown by the micro-pulling-down ( $\mu$ -PD) method. The micro-pulling-down method enables the growth of high-quality crystals, while featuring significant advantages in energy conservation and cost reduction [2]. Figure 1 presents YAG crystals with various dopants and different colors. The employment of molybdenum (Mo) crucibles and graphite thermal isolation significantly lowers the cost of crystal growth process. Comprehensive characterizations were conducted at room temperature using X-ray diffraction (XRD), absorption spectroscopy, fluorescence spectroscopy, fluorescence decay lifetime, and excitation spectroscopy. Optical microscopy revealed that while the internal quality of the crystals remained consistently high, with increasing doping concentration, the crystals edge quality gradually deteriorated, accompanied by a significant increase in defects such bubbles and cracks. The XRD analysis showed that the lattice parameters changed slightly with the concentration of doped ions which can be attributed to the differences in ionic radii between the dopants and the substituted  $\text{Y}^{3+}$  ions. Regardless of the doping concentration or dopant type, no impurities or secondary phases were observed, and the material remained a single crystal even at high doping levels ( $>2\text{mol}\%$ ). This confirms that  $\text{Y}^{3+}$  sites in the YAG lattice can be effectively substituted by the selected dopant ions even under highly doped conditions, indicating that the YAG crystals maintain excellent physicochemical stability upon doping. All selected dopant ions exhibited significant absorption peaks in the visible light region. In addition to the visible range, the absorption peak of Co:YAG in the 1400-1600 nm, corresponds to the  $^4\text{A}_2$  to  $^4\text{T}_1$  energy levels. Ho:YAG have a strong absorption peak in the 1900-1950 nm, corresponding to the  $^5\text{I}_8$  to  $^5\text{I}_7$  energy levels. Furthermore, the color variation trends of the samples with different dopants were mapped in the CIE chromaticity diagram. These results collectively demonstrate that the color of YAG crystals can be precisely tuned and stabilized by controlling the dopant type and concentration, rendering this material a highly promising candidate for high-quality synthetic gemstone applications. Therefore, the Cr, Co, Ho, Eu:YAG crystals may be a potentially jewelry and luxury serious candidate.





**Fig.**  $Y_3Al_5O_{12}$  crystals doped with different ions: (a) Ho:YAG, (b) Ho,Eu:YAG, (c) Cr:YAG, (d) Co:YAG.

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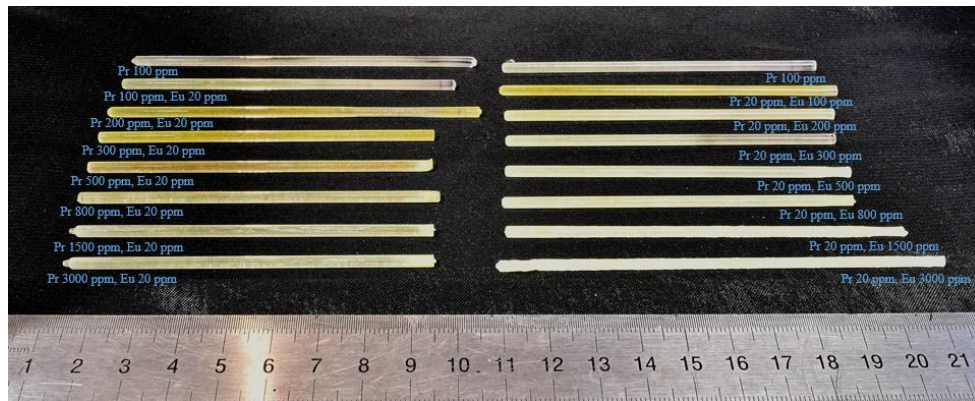
## **$\mu$ -PD crystal growth of Pr, Eu-doped sapphire rods and characterization**

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Sapphire ( $\text{Al}_2\text{O}_3$ ) remains one of the most important host materials for advanced optical applications owing to its excellent thermal stability, chemical inertness, high mechanical strength, and broad transparency window from the UV to the IR region [1]. Incorporation of rare-earth ( $\text{RE}^{3+}$ ) ions into the corundum lattice offers a promising pathway toward novel luminescent, specific coloration, and laser-active media, where controlled dopant concentration and defect minimization are critical to achieving efficient optical performance [2-3]. In this work, we systematically investigate the micro-pulling-down ( $\mu$ -PD) growth of Pr, Eu co-doped  $\text{Al}_2\text{O}_3$  rods using a molybdenum crucible under an argon atmosphere. The  $\mu$ -PD technique enables rapid prototyping of single-crystal rods with precise diameter control and efficient compositional screening, while maintaining a stable solid–liquid interface through accurate thermal management [4-5]. Growth parameters were optimized, and a pulling rate of  $0.25 \text{ mm} \cdot \text{min}^{-1}$  was identified as optimal for preserving interface stability and minimizing structural defects. To evaluate the influence of precursor purity on structural quality, different undoped sapphire crystals were independently grown from different starting materials. The optimal raw material, determined by crystallographic and optical assessment, was subsequently selected as the host matrix for Pr, Eu co-doping. The doping matrix comprised a baseline composition (100 ppm Pr, 100 ppm Eu) and two cross-concentration series: in each series, one dopant was fixed at 20 ppm while the second was varied systematically (100, 200, 300, 500, 800, 1500, and 3000 ppm). Comprehensive characterization at room temperature included X-ray diffraction (XRD), scanning electron microscopy (SEM), optical transmittance, absorption spectroscopy, fluorescence excitation and emission spectroscopy, and fluorescence lifetime measurements. The optimized undoped sapphire exhibited excellent crystalline quality, with XRD patterns fully matching the reference  $\alpha$ - $\text{Al}_2\text{O}_3$  phase, no observable cracks or bubbles under optical microscopy, and a VIS–IR transmittance of 86%. Moderate Pr, Eu co-doping resulted in active luminescence, confirming successful incorporation of RE ions into the lattice. However, critical concentration thresholds were identified. At extreme Pr loading (3000 ppm Pr, 20 ppm Eu), complete quenching of emission under UV excitation was observed, indicating concentration quenching effects. Conversely, excessive Eu doping (20 ppm Pr, 3000 ppm Eu) significantly destabilized the growth process, requiring continuous power adjustments and yielding small-diameter boules with rough surface morphology and degraded crystalline quality. These findings highlight the delicate balance between dopant concentration, crystal growth stability, and optical performance in RE-doped sapphire systems.



**Fig.** Photograph of the Pr, Eu co-doped sapphire crystals

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# Polarimetry to study reversible tuning of molecular conformation through elastomer stretching

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The polarization of light is a fundamental vector of information that allows probing the symmetry of the object with which it interacts. Chiral objects interact differently with left- and right-handed circular polarized light leading to the optical activity effects among which are Circular Dichroism (CD) and Circularly Polarized Luminescence (CPL). These (CD and CPL) signals are the optical fingerprints of chiral molecules as they are very sensitive to the 3D molecular geometrical structure (i.e. the conformation). However, such effects are very small - with relative response differences for the left-right-handed circular polarization in the order of  $10^{-4} - 10^{-2}$ , depending on the chiral molecule. Therefore, chiroptical measurements are mostly done with molecules in solution in order to avoid any other linear birefringences/dichroisms that overwhelm the chiroptical effects of interest. Indeed, these linear phenomena influence chiroptical signals which are then dominated by them, becoming the sources of difficult-to-predict, even false results and controversy[1, 2, 3, 4].

In this work, we report on the possibility at reversible tuning of the molecular conformation of chiral probes by cross-linking within a 3D polymer architecture and applying a macroscopic unidirectional stretching force onto the material[5]. The main challenge, in this case, is the measurement of the conformational changes of the chiral molecules through the polymer network, which is by far not an easy task. As the elastomer is stretched, polymer chains unfold and align themselves - this modifies not only the true chiroptical responses of the (chiral) molecules but also induces linear contributions, LD and LB of the material, which are much higher ( $\times 10^3$ ) than the chiral signals.

Thanks to a homemade Mueller spectropolarimeter, combined with a dedicated sample holder permitting smart sample/optical component configurations, we were able to properly measure each optical element, extract the real CD signal (corrected from the dominating linear contributions) and link it to the conformational change of the chiral molecule under stretch.

Where CD informs us about the conformation's variation in the fundamental state, CPL can reveal it in the excited state. Since the luminescence efficiency of a given organic molecule is lower than one, related CPL signal is generally weaker than CD and thus more difficult to measure. It is even more so in the presence of the linear effects and artefacts related to the optical alignment. Therefore, we used the developed CPL setup based on the combination of space separation of (left- and right- circularly polarized) luminescence and CCD[6] and adapted it to the specific case of stretched sample with high linear effects to access the true CPL signals.

By investigating specially designed mechano-sensitive chiral probes, we address the ability of soft-mechanochemistry [7, 8] to manipulate molecular conformation through the stretching of a 3D elastomer in a reversible way.

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## FROM FISH WASTE TO OPTICAL MATERIALS: TRANSPARENT HYDROXYAPATITE CERAMICS OBTAINED *via* SPS

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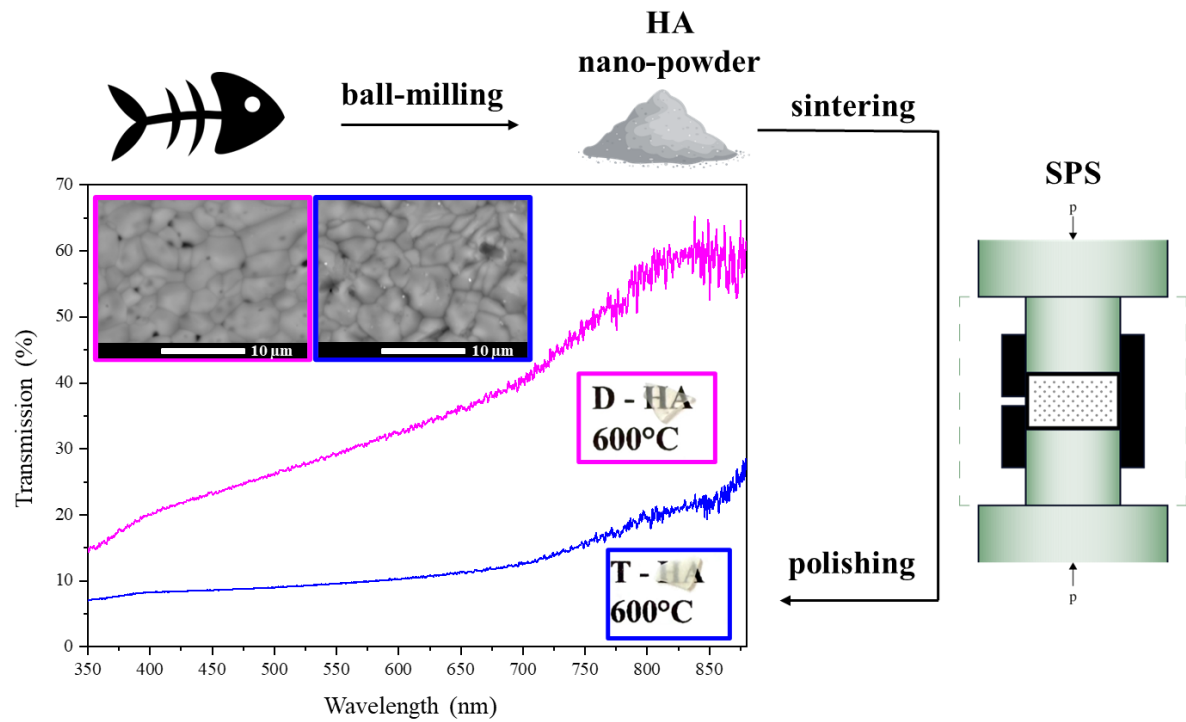
The objective of this study was to develop hydroxyapatite (HA) derived from biomass as a novel material suitable for transparent ceramics applications. The material is intended to combine high optical transparency with excellent mechanical durability, also enabling functionality as a laser source, scintillator, or phosphor when doped with rare-earth ions. Because hexagonal HA exhibits anisotropic properties, achieving precise control over the homogeneity and particle size of the starting powder is crucial for obtaining high-quality transparent ceramics [1, 2].

This study focused on producing homogeneous, good-quality HA powder from the bones of Dorada and Tilapia fish, and evaluating how the properties of the initial nano-powders affect the quality of the final sintered ceramics.

Nano-scale materials were prepared through a combination of thermal treatment and mechanical top-down processing. Laboratory-made HA, synthesized *via* a hydrothermal method, served as a reference material for comparative studies.

All initial powders were characterized using X-ray diffraction, inductively coupled plasma spectroscopy (ICP), FT-IR, and microscopic techniques (SEM and TEM). Translucent micro-crystalline ceramics were successfully fabricated by Spark Plasma Sintering (SPS) using the three types of HA nano-powders described above, and subsequently comprehensively characterized to assess their phase purity, microstructure, and optical transmittance using total forward transmission (TFT) measurement. This study represents the initial step toward the development of translucent HA ceramics derived from fish bones, which, when doped with rare-earth ions, may offer strong potential for laser applications.

The results of this study demonstrate that the quality of initial HA powder strongly affects the quality of sintered ceramics. To further enhance the performance of these ceramics, future research should focus on optimizing the SPS parameters, which are expected to play a crucial role in improving densification, transparency, and overall functional properties.



**Figure** Fabrication scheme of HA translucent ceramics developed from Dorada and Tilapia bones and their properties characterization, including TFT measurements and SEM imaging.

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