

## PROGRAM OF THE 9<sup>th</sup> INTERNATIONAL SYMPOSIUM ON OPTICAL MATERIALS, IS-OM'9

### 26th June, Monday

**8:00 h** Registration

**9:00 h** Opening welcome

**9:30 h** Luisa BAUSÁ. Plenary

*Controlling the spatial coherence and subwavelength waveguiding of rare earth quantum emitters by plasmonic nanostructures*

**10:30 h** Coffee break

**11:15 h** Amina BENSALAH-LEDOUX. Invited

*Chirality at the molecular scale: materials and spectroscopy*

**11:40 h** ~~Ismail MEKKAOU. Oral~~ **CANCELLED**

~~*Fluorescence time decay of 1,2-Indanedione-arginine and applications*~~

**11:55 h** Natalia JURGA. Oral

*Designing photon upconversion nanoparticles showing luminescence in whole human blood*

**12:10 h** Akira YOSHIKAWA. Invited

*Crucible-free bulk crystal growth of oxide single crystals using OCCO method*

**12:35 h** Kacper PROKOP. Oral

*Structural and spectroscopic properties studies of perovskite-type cubic Nd<sup>3+</sup>-doped M<sub>3</sub>Y(PO<sub>4</sub>)<sub>3</sub> (M = Sr<sup>2+</sup> or Ba<sup>2+</sup>) solid-solution*

**12:50 h** Lukasz DUDA. Oral

*Organic dye-doped systems based on different matrices: properties and potential applications*

**13:05 h Lunch on-site**

**14:30 h** Kheirreddine LEBBOU. Invited

*Recent progress on GAGG (Ce,Mg) single crystal growth and their performance for high energy physics*

**14:55 h** Andrey TURSHATOV. Invited

*Tracer-based sorting with lanthanide-activated phosphors for plastics recycling*

**15:20 h** N. SARUKURA. Invited

*Spectral Imaging of cultural assets using newly developed fluoride ultraviolet optics*

**15:45 h** A. DIKSHIT. Oral **CANCELLED**

~~*TCAD assessment of hybrid perovskite solar cell incorporating NiOx as HTL and TiO2 as ETL*~~

**18:30 h. Welcome reception**

## **27th June, Tuesday**

**8:00 h** Registration

**9:00 h** Muhammad Ali BUTT. Invited

*HYPHa project - A voyage of developing a low-cost integrated photonic platform*

**9:25 h** Eva MIHÓKOVÁ. Invited

*Lead halide perovskite nanocomposites for fast timing detectors*

**9:50 h** Yuui YOKOTA. Invited

*High pressure annealing effects on optical and scintillation properties for Gd<sub>3</sub>(Ga,Al)<sub>5</sub>O<sub>12</sub>:Ce scintillator single crystal*

**10:15 h** Georges BOULON. Oral

*Investigations on the electric-dipole allowed  $4f^25d \rightarrow 4f^3$  broadband emission of Nd<sup>3+</sup>-doped 20Al(PO<sub>3</sub>)<sub>3</sub>-80LiF glass for potential VUV scintillator of neutron detection*

**10:30 h Coffee break**

**11:15 h** Rei SASAKI. Oral

*Growth and scintillation properties of LaCl<sub>3</sub>/6LiCl /SrCl<sub>2</sub> ternary eutectic for thermal neutron detection*

**11:30 h** Karol BARTOSIEWICZ. Oral

*Correlation between Sc concentration and Lu<sub>3</sub>(Al,Sc,Ga)<sub>5</sub>O<sub>12</sub>:Pr single crystal lattice distortion, atom distribution, Raman, luminescence, and scintillation properties*

**11:45 h** Christophe DUJARDIN. Oral

*Nanoporous scintillators for radioactive gas detection*

**12:00 h** Mohamed MEHNAOUI. Oral

Structural and optical properties of dysprosium-doped calcium-oxapatites  $\text{Ca}_{10-2x}\text{Dy}_x\text{Li}_x(\text{PO}_4)_6\text{O}_2$   
( $0 \leq x \leq 1$ )

**12:15 h** Melvin John EMPIZO. Oral

*Ce<sup>3+</sup> centers in scintillating lithium fluorophosphate glasses*

**12:30 h** Keito SHINOHARA. Oral

*Pr<sup>3+</sup> ion energy levels and decay times of scintillating fluoride glasses*

**12:45 h** Masao YOSHINO. Oral

*Growth, scintillation properties, pulse shape discrimination capability of (Ca,Sr)I<sub>2</sub>:Eu scintillator*

### **13:00 h Lunch on-site**

**14:30 h** Tomasz GRZYB. Oral

*The use of Er<sup>3+</sup> ions as sensitizers in upconverting nanoparticles: from synthesis to biological applications*

**14:45 h** Nicolás PAZOS-PEREZ. Oral

*Tuning the optical properties of gold nanostars*

**15:00 h** Dominika PRZYBYLSKA. Oral

*Core@shell structure with highly doped Nd<sup>3+</sup> sensitizing ions for temperature sensing and bioimaging*

**15:15 h** Agata SZCZESZAK. Oral

*Inorganic nanoparticles based on rare earth elements for advanced applications*

**15:30 h** Eugenio CANTELAR. Oral

*Er<sup>3+</sup>-doped CaF<sub>2</sub> nanocubes: Synthesis and optical characterization*

**15:45 h** Jakub PAWLOW. Oral

*Structural and spectroscopic properties of nano-crystalline Nd<sup>3+</sup>-doped GdPO<sub>4</sub> obtained by ionic liquid and oleic acid-assisted methods*

### **18:00 h. Excursion**

## 28th June, Wednesday

**9:00 h** Malgorzata GUZIK. Oral

New transparent optical ceramics based on isotropic and anisotropic oxide structures - challenges and perspectives

**9:15 h** Shekhar GUHA. Oral

*Anisotropic thermo-mechanical properties of BaGa<sub>2</sub>GeS(e)<sub>6</sub> crystals*

**9:30 h** Valentin PETROV. Plenary

*Acentric Barium chalcogenides for nonlinear optics in the mid-IR*

**10:30 h Coffee break**

**11:15 h** Maria Jesús PASCUAL. Invited

*Processing of rare-earth-doped nanostructured glass-ceramics for enhanced photoluminescence*

**11:40 h** I. LÓPEZ. Invited

*Second harmonic generation in femtosecond laser-induced damage structures in Nd:YAG crystals*

**12:05 h** Makoto NAKAJIMA. Invited

*Terahertz time domain ellipsometry and its application in wide-bandgap semiconductors characterization*

**12:30 h** Luis SCALVI. Oral

*Thin film deposition of organic-inorganic quinoline-tin dioxide pn-junction for optoelectronic devices*

**12:45 h** Masood GHOTBI. Invited

*BIBO: an effective nonlinear crystal for femtosecond optical parametric oscillators*

**13:10 h Lunch on-site**

**FREE TIME**

## 29th June, Thursday

**9:00 h** Ionut Gabriel BALASA. Invited

*Rare earth-diamond hybrid structures for optical quantum technologies*

**9:25 h** Laura MERCADE. Invited

*Silicon optomechanical crystal cavities for microwave signal processing and biosensing*

**9:50 h** Luca GUERRINI. Invited

*Chemosensing of low molecular weight biothiols via surface-enhanced Raman spectroscopy (SERS)*

**10:15 h** Hendrik SWART. Oral

*Laser-induced heating decimated luminescence nanothermometry using robust  $\text{LaOF:Yb}^{3+}, \text{Er}^{3+}$  upconversion nanophosphor*

### **10:30 h Coffee break**

**11:15 h** Víctor LAVÍN. Oral

*New strategies for efficient optical pressure & temperature sensors*

**11:30 h** Anastasia BABKINA. Oral

*Highly luminescent borogermanate glass with mixed perovskite  $\text{CsPb}(\text{Br}, \text{I})_3$  and  $(\text{Cs}, \text{Rb})\text{Pb}(\text{Br}, \text{I})_3$  nanocrystals: properties and applications*

**11:45 h** Anna KOZLOWSKA. Oral

*Tailoring the optical and photometric properties of light sources based on dual-layer ceramics*

**12:00 h** Yashashchandra DWIVEDI. Oral

*Optical modulation and humidity sensing performance of Tb:Ce complex inhibited polymeric nanofibres*

**12:15 h** Luis SCALVI. Oral

*Ultraviolet excitation of persistent photoconductivity, close to room temperature, in composites of reduced graphene oxide and tin dioxide*

**12:30 h** Yuriy ZORENKO. Oral

*Recent developments of composite scintillators and LED converters based on the epitaxial structures of oxide compounds*

**12:45 h** Ashutosh Kumar DIKSHIT. Oral **CANCELLED**

*Effect of ZnO Nanorods on Nontoxic Perovskite solar cell*

### **13:00 h Lunch on-site**

**14:30 h - 16:00 h POSTER SESSION**

**19:30 h. Gala dinner**

## 30th June, Friday

**9:00 h** Mamoru KITaura. Invited

*Local structures of Tm ions in  $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Eu,Tm}$  long persistent phosphorescence phosphor studied by X-ray fluorescence holography and positron annihilation lifetime spectroscopy*

**9:25 h** Kei KAMADA. Invited

*A novel  $\text{CeCl}_3/\text{NaCl}/\text{SrCl}_2$  ternary eutectic scintillator for fast and high resolution radiation imaging applications*

**9:50 h** Shunsuke KUROSAWA. Invited

*Luminescent Properties of Ce-doped Garnet Transparent Ceramics Prepared by the Spark Plasma Sintering Process*

**10:15 h** Yusuke URANO. Oral

*Scintillation Properties of Tl-doped  $\text{Cs}_3(\text{Cu, Li})_2\text{I}_5$  Crystals for Cosmic Dark Matter Search*

**10:30 h** Coffee break

**11:15 h** Daisuke MATSUKURA. Oral

*Demonstration of Dose Rate Monitoring System with Garnet-Type Scintillators*

**11:30 h** Sami SLIMI. Oral

*Structure and luminescence properties of  $\text{Dy}^{3+}$  doped  $\text{Li}_3\text{Ba}_2\text{Gd}_3(\text{WO}_4)_8$  tungstate for applications in wLEDs*

**11:45 h** Giulio GORNI. Oral

*Toward white light emission from Bi and V codoped borosilicate glasses upon UV excitation*

**12 h** Closing ceremony

## LIST OF POSTERS

1 *Dual green-red emission of Mn-doped Li<sub>2</sub>O-ZnO-GeO<sub>2</sub> glass-ceramics*

**Anastasiia Babkina**

2 *Localized-enhancement of 1L MoS<sub>2</sub> photoluminescence on ferroelectric domain walls*

**Joan Javier Ronquillo Tutiven**

3 *Modelling of spectral response of electrically biased suspended graphene over variable trench depth*

**Kamila Leśniewska-Matys**

4 *Surface waveguides with modal shaping in Nd:YAG crystal for sensing applications: design and fabrication with femtosecond laser pulses*

**Víctor Arroyo Heras**

5 *Material aspects of Yb:CNGG lasers*

**Carlos Zaldo**

6 *Optical and Scintillation Properties of Pr<sup>3+</sup>-Doped (La, Y)<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> Single Crystals*

**Yuka Abe**

7 *Luminescence and scintillation properties of Tb,Ce co-doped (Gd,La)<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> for radiation imaging*

**Rikito Murakami**

8 *Crystal Growth and Optical Properties of Ce-doped (Gd, Y, Tb)<sub>3</sub>Ga<sub>3</sub>Al<sub>2</sub>O<sub>12</sub> Scintillators for X-ray Imaging*

**Kazuya Omuro**

9 *Excitonic luminescence in (Lu,Y)<sub>2</sub>SiO<sub>5</sub>:Ce<sup>3+</sup> single crystals*

**Vladimir Pankratov**

10 *Influence of swift heavy ions on structural and luminescent properties of several important optical and scintillator materials*

**Viktorija Pankratova**

11 *Optical and luminescence investigation of barium borate doped with Ce<sup>3+</sup> under ultraviolet (UV) excitation for scintillating glasses*

**Masahiro Yamashita**

12 *Optical thermometry properties of a novel quaternary tungstate Li<sub>3</sub>Ba<sub>2</sub>Gd<sub>3</sub>(WO<sub>4</sub>)<sub>8</sub>: Ho, Tm*

**Sami Slimi**

13 *New nanoprobe designs for bioimaging and contactless luminescence thermometry*

**Carlos Zaldo**

14 *Fabrication of surface relief gratings (SRGs) in hydrogen bonded polymer-dye complexes and their replication for security features*

**Łukasz Duda**

**15** Photoluminescence and Raman spectroscopy of  $Ce^{3+}$  doped  $Y_3Al_5O_{12}$  single crystalline films LPE grown onto  $Y_3Al_5O_{12}$  and  $Lu_3Al_5O_{12}$  substrates

**Anton Markovskiy**

**16** Optimization of photolithography process using negative tone resist towards obtaining high-quality photonic structures

**Jakub Pawłó**

**17** Fabrication of Mach-Zehnder interferometer structures based on low-cost  $SiO_2:TiO_2$  optical platform for integrated photonics applications

**Kacper Prokop**

**18** Transmission measurements of GaAsP layers grown from the vapour phase by heteroepitaxy

**Valentin Petrov**

**19** Second harmonic microscopy of femtosecond laser micro-modifications in BBO crystal

**Nuria Sevilla-Sierra**

**20** Application of hard metal (Al, Cu, Cr) masks for dry etching of sol-gel-derived silica-titania photonic structures

**Łukasz Duda**

~~**21** Structural and optical properties of  $nd^{3+}$  doped  $Sr_6Y(PO_4)_5$  phosphor-~~

~~**Abdesslem Badri** CANCELLED~~



	26 June	27 June	28 June	29 June	30 June	
	MONDAY	TUESDAY	WEDNESDAY	THURSDAY	FRIDAY	
8 h	registration	8 h	registration			
9 h	Opening welcome	9 h	A. BUTT / Invited	9 h	M. GUZIK / Oral	
9:30 h	Plenary: Prof. Luisa BAUSÁ	9:25 h	E. MIHÓKOVÁ / Invited	9:15 h	S. GUHA / Oral	
10:30 h	Coffee break	9:50 h	Y. YOKOTA / Invited	9:30 h	Plenary: Dr. Valentin PETROV	
11:15 h	A. BENSALAH-LEDOUX / Invited	10:15 h	G. BOULON / Oral	10:30 h	Coffee break	
11:40	I. MEKKAOU / Oral	10:30 h	Coffee break	11:15 h	M.J. PASCUAL / Invited	
11:55 h	N. JURGA / Oral	11:15 h	R. SASAKI / Oral	11:40 h	I. LÓPEZ / Invited	
12:10 h	A. YOSHIKAWA / Invited	11:30 h	K. BARTOSIEWICZ / Oral	12:05 h	M. NAKAJIMA / invited	
12:35 h	K. PROKOP / Oral	11:45 h	C. DUJARDIN / Oral	12:30 h	L. SCALVI / Oral	
12:50 h	L. DUDA / Oral	12 h	M. MEHNAOUI / Oral	12:45 h	M. GHOTBI / Invited	
13:05 h	Lunch on-site	12:15 h	M. EMPIZO / Oral	13:10 h	Lunch on-site	
14:30 h	K. LEBBOU / Invited	12:30 h	K. SHINOHARA / Oral		12:15 h	L. SCALVI / Oral
14:55 h	A. TURSHATOV / Invited	12:45 h	M. YOSHINO / Oral		12:30 h	Y. ZORENKO / Oral
15:20 h	N. SARUKURA / Invited	13 h	Lunch on-site		12:45 h	A. DIKSHIT / Oral
15:45 h	A. DIKSHIT / Oral	14:30 h	T. GRZYB / Oral		13 h	Lunch on-site
16 h	end	14:45 h	N. PAZOS-PEREZ / Oral		14:30 h	POSTER SESSION
		15:00 h	D. PRZYBYLSKA / Oral		16 h	end
		15:15 h	A. SZCZESZAK / Oral			
		15:30 h	E. CANTELAR / Oral			
18:30	WELCOME RECEPTION	15:45 h	J. PAWLOW / Oral		19:30 h	GALA DINNER
		16 h	end			
		18	EXCURSION			

# Ultraviolet excitation of persistent photoconductivity, close to room temperature, in composites of reduced graphene oxide and tin dioxide

André L. ALMEIDA,<sup>a,b)</sup> Lucas P. FONSECA,<sup>a)</sup> Lucas M. MARTINS,<sup>b)</sup> Luis V A SCALVI<sup>a)</sup>

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Reduced graphene oxide (rGO) is reported with high electrical conductivity, with bandgap tuned in the range of 0.02 to 2.8 eV [1]. SnO<sub>2</sub>/rGO devices deposited on Pt substrates constitute electrodes with the possibility of gas detection [2]. In this work, rGO is synthesized by the method of Abdolhosseinzadeh et al. [3], and is combined with SnO<sub>2</sub> forming a composite, which is deposited on borosilicate glass substrates by spin coating, exhibiting very good electrical current stability in air, on the order of nA. Surprisingly, when the film is placed in vacuum (about 10<sup>-5</sup> Torr), the current drops 2 orders of magnitude, decreasing slightly with lowering of temperature (in the range 150 – 300 K). It suggests that the material is preferentially adsorbing a reducing gas, which increases the amount of free electrons when exposed to air. Recently, the effect of ultraviolet light of a He-Cd laser (325nm) on this sort of film was reported, for similar samples but where the SnO<sub>2</sub> layer was slightly doped with 0.05at% of Er [4]. The general effect of the irradiating monochromatic light is to increase the conductivity about 6 orders of magnitude compared to the results in vacuum, changing from a current of 10 pA, to a current of the order of 20 μA, under application of a voltage of 40 V. This experiment when performed at temperatures below room temperature leads to the excitation with ultraviolet light to give rise to the phenomenon of persistent photoconductivity (PPC) even very close to room temperature. However, it is not clear the effect of the rare earth doping (Er<sup>3+</sup>) on the PPC phenomena since the observable luminescence is green, unlike the Er<sup>3+</sup> PL, preferentially in the near infrared. In this sense, we have built composites rGO/SnO<sub>2</sub> where the SnO<sub>2</sub> layer is not doped and the rGO proportion clearly affects the SnO<sub>2</sub> optical properties and the sample surface, as observed by optical transmittance and confocal microscopy images, leading to the presence of surface islands, for 3at% of rGO, which may contribute to optical confinement.

The strong response to ultraviolet light and the phenomenon of PPC indicates potential application in amplifiers, which could be adjusted by doping with rare-earth ions such as Eu<sup>3+</sup> and Er<sup>3+</sup>. The large difference in conductivity under light and in vacuum suggests application as sensors. Acknowledgements: FAPESP (Proc. 2018/09235-4 and 2022/08483-0)

## References:

- [1] Shen, Y.; Yang, S.; Zhou, P.; Sun, Q.; Wang, P.; Li, J.; Chen, L.; Wang, X.; Ding, S.; Zhang, D.W.; *Carbon*, Vol. 62, **2013**, 157–164.
- [2] C. Aydin, *J. Alloy Compd.*, Vol. 771, **2019**, 964-972.
- [3] Abdolhosseinzadeh, S.; Asgharzadeh, H.; Kim, H.S.; *Sci. Rep.-UK*, Vol. 5, **2015**, 1-7
- [4] Oliveira, L.S.; Fonseca, L. P.; Souza, R. D. ; Bueno, C. F.; Martins, L. M.; Scalvi, L. V.A.; *Current Appl. Phys.* Vol. 41, **2022**, 49–58

# Second harmonic generation in femtosecond laser-induced damage structures in Nd:YAG crystals

a) Ignacio Lopez-Quintas, a) Nuria Sevilla-Sierra, a) Javier R. Vázquez de Aldana

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Ultrashort laser pulses in the femtosecond regime are widely used for 3D nano- and micro-structuring of transparent solids, allowing for high-precision local modification of the material (i.e., inducing refractive index changes). These modifications, in the form of damage tracks, are used to inscribe waveguides and other optical active elements in crystals, which can be integrated in photonic devices [1]. While the process of second harmonic generation (SHG) takes place exclusively in non-centrosymmetric materials, such as nonlinear crystals, it is known that a breakage in the symmetry can lead to an enhancement of the nonlinear susceptibility. Furthermore, in the case of focused beams, phase shift effects can also influence the nonlinear response of the material. Under this framework, we have investigated the nonlinear response of a modified centrosymmetric material, which, due to this symmetry, is not expected to generate second harmonic radiation. For that purpose, we have inscribed different structures using femtosecond laser pulses in the bulk of a Nd:YAG crystal (cubic system) and the nonlinear response of the sample was investigated using second harmonic generation microscopy (SHGM) [2,3]. This is the first time, to the best of our knowledge, that this technique has been applied to the analysis of damage tracks produced in an isotropic (centrosymmetric) crystalline material. The second harmonic signal is generated exclusively in the damage tracks, enabling the acquisition of high-resolution 3D images of the structures. The reported results are relevant, not only for the potential extension of the SHGM technique to other isotropic materials, or for their prospective application in the fabrication of photonic devices, but also because this is the first demonstration of bulk SHG in a modified Nd:YAG crystal.

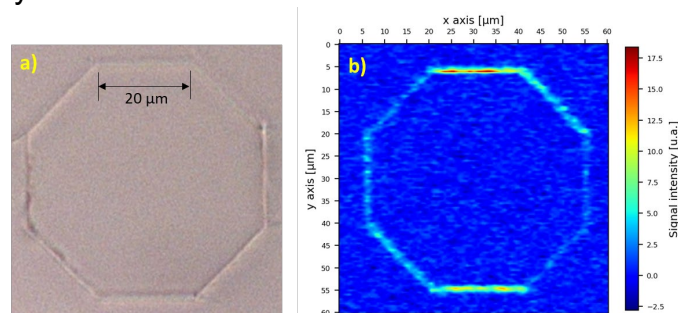


Figure 1. a) Optical image of the inscribed octagonal structure in the Nd:YAG crystal. Damage tracks are formed by focusing amplified NIR laser pulses in the crystal bulk. b) SHGM map of the structure obtained by focusing non-amplified 120 fs pulses at 800 nm. The SH signal (400 nm) is generated exclusively in the damage tracks.

## References:

- [1] Dong, N. et al., Femtosecond laser writing of multifunctional optical waveguides in a Nd:YVO<sub>4</sub><sup>+</sup> KTP hybrid system. *Optics Letters*, 36, **2011**, 975.
- [2] Aghigh A. et al., Second harmonic generation microscopy: a powerful tool for bio-imaging. *Biophysical Reviews*, 15, **2023**, 43-70.
- [3] Yokota, H. et al., Optical second harmonic microscopy as a tool of material diagnosis. *Physics Research International*, 2012, **2012**, 704634.

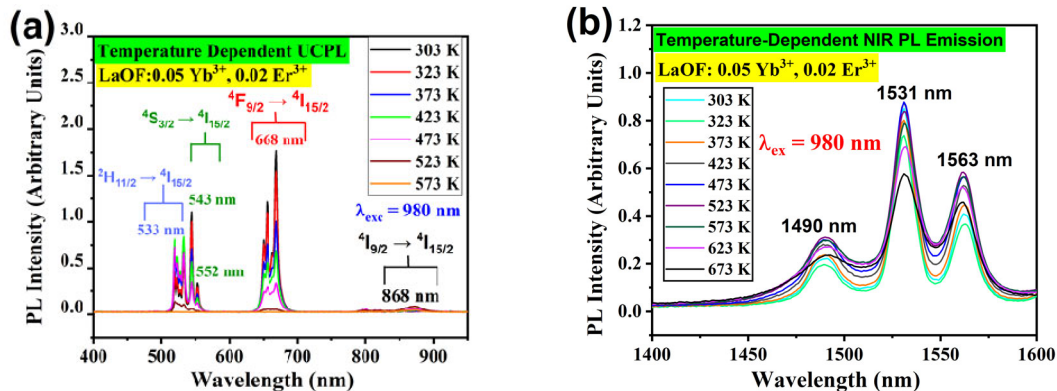
# Laser-induced heating decimated luminescence nanothermometry using robust LaOF:Yb<sup>3+</sup>, Er<sup>3+</sup> upconversion nanophosphor

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A microwave-assisted hydrothermal route was used to synthesize LaOF:0.05 Yb<sup>3+</sup>, x Er<sup>3+</sup> (0.001 ≤ x ≤ 0.05) upconversion nanoparticles (UCNPs). Luminescence nanothermometers based on LaOF:Yb<sup>3+</sup>,Er<sup>3+</sup> UCNPs were also investigated. Laser-induced heating is a bothersome factor that can lead to the degradation of several temperature-sensing probes. One way to eliminate this influence on the thermal readouts is to identify the critical point of the laser power that produces undesirable effects on the probe and operate the laser excitation source at safe levels below this point. Unfortunately, most luminescent probes must be pumped by lasers operating at alarming power levels that can either disintegrate the probe or produce counterfactual results. The fluorescence intensity ratio (FIR) of the UCNPs was recorded using the visible (red) and near-infrared (NIR) regions, Fig 1(a) and (b), at different temperatures. The impact of laser-heating on the UCNPs was prevented by identifying the optimal operating conditions of the laser that could be used to record the FIRs without compromising the integrity of the UCNPs. The behaviour of the UCNPs against the laser exposure time and power was analyzed to recognize the critical point of the laser power, below which laser-heating of the UCNPs was negligible. In this scenario, LaOF: Yb<sup>3+</sup>, Er<sup>3+</sup> UCNPs proved to be a highly sensitive and durable temperature sensing probe that can operate efficiently at low laser powers. Up to power densities below 18 W/cm<sup>2</sup>, the laser-induced heating was easily nullified from the thermal readouts of this temperature sensor, thus, preventing the need for temperature calibrations in the measurements. The LaOF: Yb<sup>3+</sup>, Er<sup>3+</sup> UCNPs demonstrated consistent thermal readouts with impeccable accuracies at low laser power density (6.91 W/cm<sup>2</sup>). These UCNPs exhibited remarkable durability and reusability over multiple thermal cycles. The impressive relative and absolute sensitivities, and noteworthy temperature resolution of the LaOF:Yb<sup>3+</sup>,Er<sup>3+</sup> UCNPs indicates their potential for luminescence nanothermometry applications. This approach can be perceived as a benchmark for testing luminescent materials using nanothermometry.



**Fig. 1:** Temperature-dependent PL spectra of LaOF:0.05 Yb<sup>3+</sup>,0.02 Er<sup>3+</sup> UCNPs excited with a 980 nm diode laser: (a) UCPL, (b) NIR PL

## Material aspects of Yb:CNGG lasers

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Recently, 31 fs laser pulses have been achieved by Kerr lens mode-locking of a 5 at% Yb doped  $\text{Ca}_3(\text{NbGa})_5\text{O}_{12}$  single crystal garnet, hereafter Yb:CNGG. [1] This achievement is associated with the occupancy of the octahedral (16a) and tetrahedral (24d) crystalline sites of the garnet simultaneously by  $\text{Nb}^{5+}$  and  $\text{Ga}^{3+}$ , what creates a great crystalline disorder nearby the dodecahedral  $\text{Yb}^{3+}$  (24c, also  $\text{Ca}^{2+}$  site) cation, thus its fluorescence is broadened as needed for short pulse laser operation.

CNGG melts at  $\approx 1450$  °C, i.e. much lower than YAG (m.p. 1940 °C), what eases its crystal growth. Platinum crucibles and air atmosphere can be used for the Czochralski growth of large crystal sizes. [2] The favorable crystal growth properties along with crystal isotropy and a significant thermal conductivity,  $\kappa = 3.6\text{--}4.4$  W/mK, [2] made of Yb:CNGG a firm candidate for developing ultrashort pulsed laser devices, but CNGG melts congruently only for off-stoichiometry compositions,  $\text{Ca}_3\text{Nb}_{1.5+1.5x}\text{Ga}_{3.5-2.5x}\square_x\text{O}_{12}$ , where  $x=0.11$  to 0.14 stands for the cationic vacancy composition. [3] The Nb/Ga occupancy factor ratios for the two (16a and 24d) sites are sensitive to the starting melt composition, Ga evaporation from the melt, as well as to the incorporation of other cations used as crystal modifiers (for instance  $\text{Li}^+$ ). To fully understand the  $\text{Yb}^{3+}$  spectroscopy in CNGG and maximize the fluorescence bandwidth a crystallographic model in terms of charge compensation and occupation sites is required.

In this work we study the occupation sites in the CNGG lattice of several foreign cations with charge ranging from I to IV and ionic radius similar to  $\text{Nb}^{5+}$  and  $\text{Ga}^{3+}$ , namely  $\text{Li}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ti}^{4+}$  and  $\text{Ge}^{4+}$ . Several experimental techniques including X-ray absorption spectroscopy, X-ray and neutron diffraction single crystal refinements and nuclear magnetic resonance are used to determine the sites of the foreign cations incorporated upon Czochralski growth of CNGG single crystals. It is shown that the incorporation of cations with increasing electric charge in the tetrahedral sites of the garnet lattice displaces the  ${}^2F_{5/2}(0') \leftrightarrow {}^2F_{7/2}(0)$   $\text{Yb}^{3+}$  transition to larger energy.

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# The use of Er<sup>3+</sup> ions as sensitizers in upconverting nanoparticles: from synthesis to biological applications

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Upconversion (UC) is one of the most studied phenomena in materials science—converting the near-infrared (NIR) wavelength to visible or ultraviolet results in many advanced applications. Upconverting nanoparticles (UCNPs) can be used in nanomedicine to detect and treat cancer, in analytical applications such as luminescent labels, temperature sensors, or anti-counterfeiting.

Typically, Yb<sup>3+</sup> ions act as NIR sensitizers in UCNPs which results from the properties of the Yb<sup>3+</sup> ion, i.e., its simple electronic structure and high absorption of radiation at 975 nm wavelength. Excitation with different wavelengths can also result in intense UC [1]. Er<sup>3+</sup> ions absorb effectively at about 1480-1550 nm, giving emission in the visible range up to NIR [1]. In addition, UCNPs heavily doped with Er<sup>3+</sup> ions can undergo self-sensitization, which improves the emission intensity. In core@shell UCNPs, the emission can be as effective as in the case of Yb<sup>3+</sup>-doped systems. However, due to excitation at a wavelength of around 1535 nm, Er<sup>3+</sup>-doped UCNPs offer more emission bands in the first biological window, which is crucial for biomedical applications. These bands can be utilized for ratiometric temperature sensors [2]. Moreover, the laser radiation with wavelength at around 1535 nm is less scattered in blood than 975 nm used in most of the studied UCNPs, making such UCNPs promising for medical applications. Additionally, by co-doping with various lanthanide ions, such as Tm<sup>3+</sup> or Ho<sup>3+</sup> ions, it is possible to improve the spectroscopic properties of UCNPs based on the absorption of Er<sup>3+</sup>. Moreover, security labels based on the Er<sup>3+</sup> technology are promising in anti-counterfeit applications, an alternative to the best-known solutions [3].

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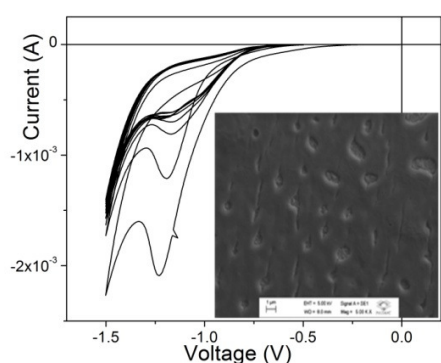
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# Thin film deposition of organic-inorganic quinoline-tin dioxide p-n junction for optoelectronic devices

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Quinolinic derivatives have been applied in organic optoelectronics, generating efficient layers concerning electron transport. The quinolinic nucleus has in its central structure an aromatic azaheterocycle with a benzene ring fused at positions 2 and 3 of a pyridine ring, which gives them a strong electron-acceptor characteristic. On the other hand, SnO<sub>2</sub> is an oxide semiconductor used as transparent electrodes in many optoelectronic systems [1]. The n-type electrical conductivity of SnO<sub>2</sub> is linked to interstitial tin ions and oxygen vacancies, which act as donors in the matrix. Layers of SnO<sub>2</sub> and quinoline derivatives combined as a hybrid structure leads to the formation of an optically excitable p-n junction. One of the great challenges is the deposition of quinolines in the form of films, with high homogeneity of the quinoline layer on SnO<sub>2</sub>. Thus, the performance of systems deposited by electrodeposition and drop-casting are compared. The quinoline was synthesized according to the literature [2], with N,N-diethyl-p-phenylenediamine and 4-formylbenzoic acid forming a Schiff base, which reacts with phenylacetylene to give the quinoline derivative. The reaction occurs under stirring and reflux, over 4 days, with a hydrochloric acid 0.5 M solution as a catalyst. The quinoline is extracted and recrystallized. For electrical characterization of hybrid structures, devices are built with metallic contacts of Sn or In, deposited by resistive evaporation, allowing evaluation both parallel and perpendicular to the direction of deposition. Cyclic voltammetry for quinoline electrodeposition (fig. 1) shows a reduction peak that decreases for each cycle, which probably means protonation of quinoline ring and indicates film



deposition, confirmed by the SEM (inset fig 1). When deposited by drop casting, with annealing after each layer at 50°C for 10 min on a hot plate, and 20 min in the oven, the best solvent is acetone, adhering effectively to fluorine-doped tin dioxide (FTO) and also to silica. They present characteristic peaks of optical absorption [3]. Previous heating of the substrate (70°C) leads to increased transparency. Acknowledgements: FAPESP (Proc. 2018/09235-4, 2022/08483-0 and 2022/12998-5)

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# HYPHa project - A voyage of developing a low-cost integrated photonic platform

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HYPHa project is a joint venture to develop a low-cost integrated photonics platform based on silica-titania materials deposited *via* a sol-gel method and a dip-coating procedure. The dip-coating technique is cost-effective and makes it possible to produce a high-quality and low-loss silica-titania thin-films on a glass or buffered silicon substrates [1]. Fabrication techniques such as reactive ion etching (RIE), wet-chemical etching, and nanoimprint lithography (NIL) are being researched to structure silica-titania layers. Currently, the development of the silica-titania platform is realized, and some successful results related to structuration are being demonstrated. Additionally, several photonic components such as ring resonator, subwavelength grating waveguide, 1D-photonic crystal waveguide, reverse rib waveguide, and demultiplexer systems are being numerically investigated [2-4]. We believe that with the success of such a photonic platform, the integrated photonics industry will be revolutionized in terms of performance and fabrication cost.

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# Demonstration of Dose Rate Monitoring System with Garnet-Type Scintillators

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For the decommissioning of Fukushima Daiichi Nuclear Plants, the real-time dose-rate monitor under the high dose-rate situation is required to remove the debris remaining inside the plants. To realize such monitoring system, we have proposed a dose monitor consisting of a scintillator, optical fiber and CCD spectrometer (Fig. 1), and scintillation photons are read with the CCD spectrometer under the lower dose condition [1]. Since optical fiber is planned to use with a length of over 100 m, suppression of the photon loss through the fiber is necessary. Also, some noises originating from the optical fiber such as luminescence and Cherenkov photons with dominant emission bands of less than 550 nm must be separated from the scintillator light [2, 3]. Therefore, longer emission wavelength (goal: 650-1000 nm) and higher light output compared to that of conventional material (Cr-doped  $\alpha$ - $\text{Al}_2\text{O}_3$ ) are required for the scintillator.

We focused on Nd-doped  $\text{Y}_3\text{Al}_5\text{O}_{12}$  (Nd:YAG) crystals, which is known as a laser material with infra-red emission. The Nd:YAG single crystals doped with different Nd concentrations were grown by the micro-pulling down method[4], and the optical properties of the crystals were investigated. Each sample showed an emission wavelength of approximately 880 nm originating from 4f-4f transition ( $^4\text{F}_{3/2}$  to  $^4\text{I}_{9/2}$ ) of  $\text{Nd}^{3+}$  by X-ray excitation.

We succeeded in showing a dynamic range (approximately 1-700 Gy/h) for the monitoring system coupled with a 20 m-long optical fiber under high dose rate conditions. Figure 2 shows the calibration curve for signal intensity of emission spectra as a function of dose rate. After the irradiation, we checked the afterglow, and 1%-level of the maximum of intensity during the irradiation was observed after approximately 18 sec of irradiation off including the moving time for the source return (~25 sec). This results shows afterglow was negligible, and Nd:YAG was found to have good properties for the system.

In this paper, we show the detail results of optical and scintillation properties of Nd:YAG and discuss the feasibility to use this system in the Plants.

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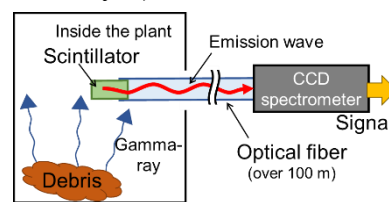


Fig. 1 Schematic view of the radiation dose monitoring system

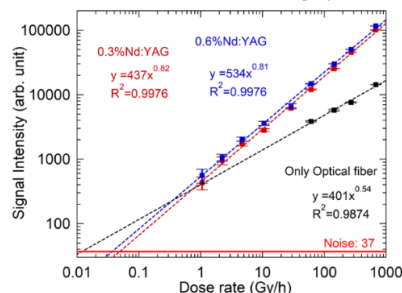


Fig. 2 Calibration curve for signal intensity of emission spectra (integration range: 800-980 nm) as a function of dose rate

# Chemosensing of low molecular weight biothiols via surface-enhanced Raman spectroscopy (SERS)

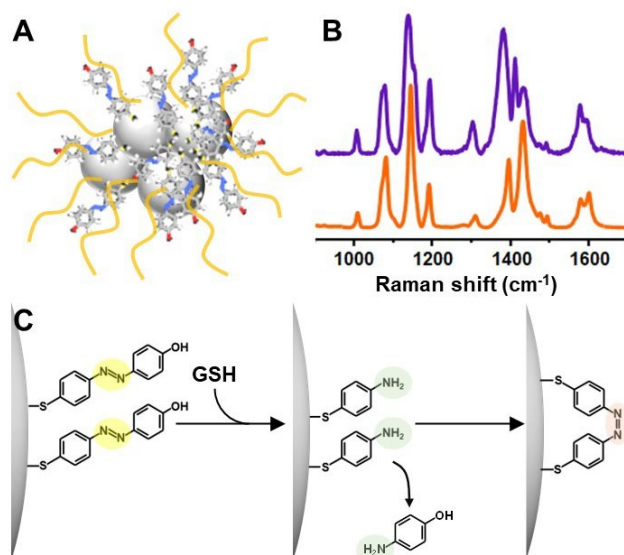
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Low molecular weight thiols (biothiols) are highly active compounds extensively involved in human physiology and whose abnormal levels have been associated with multiple diseases.[1] To overcome the intrinsic limitations of conventional analytical approaches, major efforts have been devoted in recent years to developing new nanosensing methods for the low cost and fast quantification of this class of analytes in minimally pre-treated samples.

To this end, we designed a novel strategy for engineering a highly efficient surface-enhanced Raman scattering (SERS) platform for the dynamic sensing of biothiols.[2] SERS combines Raman spectroscopy with nanotechnology into an ultrasensitive and highly specific analytical tool.[3] Colloidally stable silver nanoparticle clusters equipped with a specifically designed azobenzene derivative (AzoProbe) were generated as highly SERS active substrates.[2] These aggregates were further encapsulated by thiol-containing polyethylene glycol (PEG-SH) to afford high colloidal stability in complex biological media. In the presence of small biothiols (e.g., glutathione: GSH), breakage of the AzoProbe diazo bond causes drastic spectral changes that can be quantitatively correlated with the biothiol content, with a limit of detection of ca. 5 nM for GSH. An identical response was observed for other

low molecular weight thiols, while larger macromolecules with free thiol groups (e.g., bovine serum albumin) do not produce distinguishable spectral alterations.[2] This indicates the suitability of the SERS sensing platform for the selective quantification of small biothiols in biofluids.



**Figure 1.** (A) Schematic of a colloidal stable silver nanoparticle cluster modified with the AzoProbe molecular sensor and PEG-SH. (B) SERS spectra of clusters before (purple) and after (orange) mixing with GSH. (C) Outline of the proposed molecular mechanism for detection.

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## Recent developments of composite scintillators and LED converters based on the epitaxial structures of oxide compounds

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This report presents the review of our latest achievements in the development of multilayered composite luminescent materials based on the single crystalline films (SCFs) and single crystals (SCs) of garnet, perovskite and orthosilicate compounds using the liquid-phase epitaxy (LPE) growth method for application in the environmental radiation monitoring, microimaging techniques and industrial lighting.

We created **multilayered composite scintillators** of phoswich-type (phosphor sandwich) based on SCFs and SCs of different compounds for simultaneous registration of different types of ionizing radiations in mixed high energy photon and particle fluxes [1]. Such composite scintillators consist from *three-layer epitaxial structures* containing two SCF scintillators grown „step-by-step” using the LPE method onto substrates from SC scintillators. Films and crystal parts of composite scintillators were fabricated from efficient scintillation materials with differing scintillation decay achieved by different types of dopants and various host compositions [1].

We show results of fabrication of new types composite scintillators, based on the film and crystals of  $\text{Ce}^{3+}$  doped  $\text{R}_3\text{B}_5\text{O}_{12}$  ( $\text{R}=\text{Lu}, \text{Y}, \text{Gd}, \text{Tb}$ ;  $\text{B}=\text{Al}, \text{Ga}$ ) garnets,  $\text{Ce}^{3+}$  and  $\text{Pr}^{3+}$  doped  $(\text{Lu}, \text{Y}, \text{Gd})\text{AlO}_3$  perovskites and  $\text{Ce}^{3+}$  and  $\text{Bi}^{3+}$  doped  $(\text{Lu}, \text{Y}, \text{Gd})_2\text{SiO}_5$  orthosilicates using LPE method as well as their luminescent and scintillation properties. The application-minded tests of these prototypes of three layered composite scintillators for simultaneous registration of  $\alpha$ - and  $\beta$ -particles and  $\gamma$ -quanta were performed, and further analyzed to optimize their scintillation figure-of merit.

The report presents also the brief review of developments of **multilayered composite** converters for WLED based on the SCFs of  $(\text{Gd}, \text{Lu}, \text{Tb})_3\text{Al}_5\text{O}_{12}:\text{Ce}$  garnets, grown by the LPE method onto undoped and  $\text{Ce}^{3+}$  doped YAG and LuAG SC substrates [2]. The results of their luminescent and photo-conversion properties (color coordinates, color rendering index, luminous efficacy) are also presented.

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# Scintillation Properties of Tl-doped $\text{Cs}_3(\text{Cu}, \text{Li})_2\text{I}_5$ Crystals for Cosmic Dark Matter Search

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## Abstract

The search for cosmic dark matter (DM) is an important issue in modern physics. Weakly interacting massive particles (WIMPs) are considered to be the most promising candidate for DM [1], and WIMPs only interact via gravity and weak interaction. WIMPs are expected to detect via the low energy nuclear recoil associated with rare scattering of WIMP on target nuclei, while the mass of WIMPs is predicted to have the order of GeV~TeV, roughly. The scintillation materials used in DM search must have high light output, high energy resolution, and chemical stability. Moreover, large Stokes shift samples have the advantage to maintain the light output when we use large-size scintillation crystals to suppress self-absorption. Since NaI(Tl) scintillators have a high light output of 40,000 photons/MeV [2], this scintillator is used as conventional material for WIMPs search. However, NaI(Tl) is hard to handle due to hygroscopicity.

We focused on the halide scintillator  $\text{Cs}_3\text{Cu}_2\text{I}_5$  (CCI). In previous studies, CCI crystals were reported to have high light output (98,200 photons/MeV) and energy resolution (3.3 % at 662 keV) [3,4]. In addition, CCI is a chemically stable crystal with low hygroscopicity. Although the mass of DM is unidentified, doping  $\text{Cs}_3\text{Cu}_2\text{I}_5$  with Li is expected to improve sensitivity to the DM with various masses of Li, Cs, Cu, and I. Thus,  $\text{Cs}_3(\text{Cu}, \text{Li})_2\text{I}_5$  crystals were grown by the Bridgeman method, and scintillation properties were evaluated.

Scintillation decay of  $\text{Cs}_3(\text{Cu}, \text{Li})_2\text{I}_5$  was evaluated to be  $758 \pm 7$  ns with a photomultiplier tube, and its energy resolution was estimated to be  $\sim 6.9$  % (FWHM, 662 keV). The non-proportional response (NPR) value for  $\text{Cs}_3(\text{Cu}, \text{Li})_2\text{I}_5$  showed in Fig. 2. Compared to Li-free CCI, the emission wavelength was not changed by doping Li, while the excitation wavelength was blue-shifted from 360 to 334 nm. Thus, the Stokes shift was confirmed to be broadening.

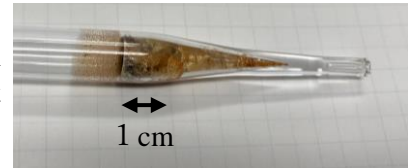


Fig.1 Grown  $\text{Cs}_3(\text{Cu}, \text{Li})_2\text{I}_5$  crystal in the ampoule

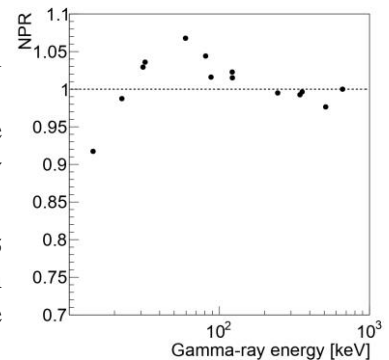


Fig.2 NPR behavior as a function of gamma-ray energy

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# Acentric Barium chalcogenides for nonlinear optics in the mid-IR

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The number of non-oxide nonlinear crystals for frequency conversion in the mid-IR (3–30  $\mu\text{m}$ ) part of the spectrum is limited and only few of them are commercially available [1]. In the last decade there have been substantial efforts and progress in the development of new Ba chalcogenide compounds with improved properties compared to the classical I-III-VI<sub>2</sub> chalcopyrites AgGaS<sub>2</sub> (AGS) and AgGaSe<sub>2</sub> (AGSe) with tetragonal  $\bar{4}2m$  symmetry which represent the benchmarks for frequency down-conversion of solid-state laser systems operating near 1  $\mu\text{m}$  (Nd- or Yb-lasers) and near 1.5  $\mu\text{m}$  (Er-lasers).

In this presentation I will review the main properties, including transmission, dispersion, birefringence, nonlinear coefficients, thermo-optic coefficients, etc., of five such non-centrosymmetric Ba crystals that have been characterized recently using large size single crystalline samples of high optical quality. These chalcogenide crystals have been grown by the vertical Bridgman-Stockbarger method. They include the orthorhombic ( $mm2$ ) BaGa<sub>4</sub>S<sub>7</sub> (BGS), the monoclinic ( $m$ ) BaGa<sub>4</sub>Se<sub>7</sub> (BGSe), the trigonal (3) BaGa<sub>2</sub>GeS<sub>6</sub> (BGGs) and BaGa<sub>2</sub>GeSe<sub>6</sub> (BGGSe), and the hexagonal ( $6mm$ ) Ba<sub>2</sub>Ga<sub>8</sub>GeS<sub>16</sub> (B2GGS). In almost all their characteristics, including thermo-mechanical properties such as expansion, conductivity and hardness, as well as their anisotropy, these new nonlinear materials seem to be superior compared to the corresponding sulphide (AGS) and selenide (AGSe) chalcopyrites. Based on the larger bandgaps, the same is expected for their damage resistivity in different temporal regimes. In addition, these new materials do not require post-growth annealing procedures and the polished surface is chemically stable. The main difficulties so far have originated from the low-symmetry of the trigonal and monoclinic compounds, which complicates the characterization and the orientation of elements for nonlinear frequency conversion.

All of the Ba chalcogenide crystals possess the phase-matching capability to cover parts of the mid-IR spectral range by down-conversion of 1.064  $\mu\text{m}$  laser radiation, show clear transparency and are free of two-photon absorption (TPA) at this pump wavelength. The selenides transmit up to  $\sim 18$   $\mu\text{m}$ , with clear transparency at 10.6  $\mu\text{m}$ . The main applications of these nonlinear crystals will be in frequency down-conversion of advanced all-solid-state laser sources operating in the near-IR between 1 and 3  $\mu\text{m}$  [1] but also for harmonics generation of CO<sub>2</sub> gas lasers (selenides only). The sulphides might prove unique for pumping near 1  $\mu\text{m}$  while for pump wavelengths near 2  $\mu\text{m}$  and beyond, the selenides possess a much longer mid-IR cut-off limit compared to the widely used II-IV-V<sub>2</sub> chalcopyrite ZnGeP<sub>2</sub> [1].

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# Correlation between Sc concentration and Lu<sub>3</sub>(Al,Sc,Ga)<sub>5</sub>O<sub>12</sub>:Pr single crystal lattice distortion, atom distribution, Raman, luminescence, and scintillation properties

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Pr<sup>3+</sup> doped Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> (LuAG:Pr) single crystal belongs to the family of high performance complex oxides scintillators. Pr<sup>3+</sup> centers offer high quantum efficiency and fast response (~20 ns decay time) in the 310 nm emission band [1]. However, the LuAG host lattice contains electron traps related to antisite defects and oxygen vacancies, which significantly reduce the yield of scintillation light and slow down the kinetics of scintillation decay. The balanced substitution of Al for Ga atoms in LuAG:Pr crystals successfully deactivates trapping processes associated with trapping centers, consequently accelerating the scintillation response, but a slight decrease of the light yield is observed as well. The admixing with Sc<sup>3+</sup> ions can improve scintillation characteristics due to spectral overlap of the Sc-related emission (Sc-trapped exciton) centered around 275 nm with the 4*f*→5*d*<sub>1</sub> absorption band of Pr<sup>3+</sup> ions [2]. However, the incorporation of large Sc atoms into the Lu<sub>3</sub>Al<sub>2.5</sub>Ga<sub>2.5</sub>O<sub>12</sub>:Pr crystal lattice can lead to lattice distortion and trigger the global structural rearrangements. This research discusses in details the response of the Lu<sub>3</sub>Al<sub>2.5</sub>Ga<sub>2.5</sub>O<sub>12</sub>:Pr crystal lattice to the incorporation of a large Sc substitute and the consequences on the crystal growth process, the host lattice perturbation, atom segregation, Raman, optical, luminescence, and scintillation properties. The EDS elemental mapping revealed an apparent change in the radial distribution of atoms. Raman spectroscopy verified the correlation between the concentration of Sc atoms and the degree of distortion of the crystal lattice. The distortion of the crystal structures was also reflected in the high-resolution photoluminescence (PL) emission spectra and PL mapping. The scintillation properties gradually deteriorated with increasing concentration of Sc atoms.

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# Investigations on the electric-dipole allowed $4f^2 5d \rightarrow 4f^3$ broadband emission of $\text{Nd}^{3+}$ -doped $20\text{Al}(\text{PO}_3)_3\text{-}80\text{LiF}$ glass for potential VUV scintillator of neutron detection

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Research efforts are geared towards the design and development of potential scintillator materials. Large-area and high-quality crystals that are required for most radiation detection applications are difficult to produce because of the restrictions by their crystal growth technologies including high production costs and slow growth processes. The complex fluorophosphate glass,  $20\text{Al}(\text{PO}_3)_3\text{-}80\text{LiF}$  (APLF) which is more stable to moisture than other metaphosphates and easier to synthesize than a crystal has been developed by the Institute of Laser Engineering, Osaka University. APLF glass has a high lithium (Li) content of  $31.6 \text{ mmol cm}^{-3}$  essential in enhancing the detector sensitivity to low-energy (270 keV) fast neutrons.

Among rare earth ion dopants, neodymium ( $\text{Nd}^{3+}$ ) is a well-known optical activator of laser materials for which the  $\text{Nd}^{3+}$  transitions are largely analyzed in the  $4f^3$  configuration, but rarely in the  $4f^2 5d$  configuration, which lies in the VUV region. The most important property of these glasses is that they exhibit electric-dipole allowed interconfigurational  $4f^2 5d \rightarrow 4f^3$  ( $^4\text{I}_{9/2}$ ) broadband emissions with a maximum at 187 nm (VUV) and a decay time of  $\sim 5.0$  ns, faster than  $\text{Pr}^{3+}$  or  $\text{Ce}^{3+}$ -doped APLF glasses [1-2]. Consequently, the  $\text{Nd}^{3+}$ -doped APLF glass can be ranked as one of the advanced potential scintillator materials in time-of-flight (TOF) detectors for high-counting-rate fast neutron detection [3].

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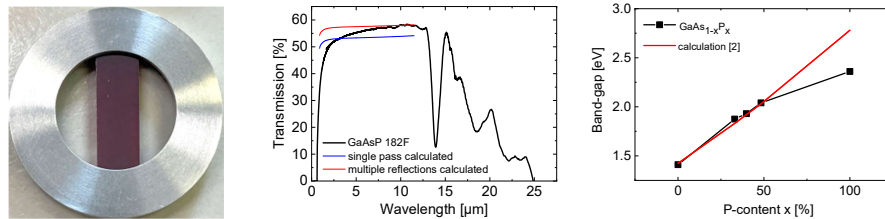
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# Transmission measurements of GaAsP layers grown from the vapour phase by heteroepitaxy

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The acentric cubic semiconductors GaAs and GaP are attractive materials for nonlinear frequency conversion in the mid-IR due to their high second-order nonlinearity, thermal conductivity, and optical quality when grown from the vapour phase. Fabricated by epitaxy on orientation-patterned (OP) templates, they can be quasi-phase matched for efficient three-wave interactions without spatial walk-off. Tailoring of their properties by growing mixed ternary compounds by heteroepitaxy will enable pumping of nonlinear frequency down converters by Er-fiber laser systems at 1.56  $\mu\text{m}$  and idler wavelengths beyond the mid-IR limit of GaP. The chosen substrates are GaAs wafers due to their much lower price and higher quality compared to GaP. The fabrication, crystalline structure, quality and homogeneity of ternary  $\text{GaAs}_{1-x}\text{P}_x$  layers have been widely studied by various techniques [1], however, optical properties have not been well assessed from transmission measurements. Millimeter-thick samples of  $\text{GaAs}_{1-x}\text{P}_x$  with sufficient aperture do not exist. Here we present transmission measurements with 167-322  $\mu\text{m}$  thick layers of GaAsP with different composition [1].



**Fig. 1.** 295- $\mu\text{m}$  thick  $\text{GaAs}_{0.517}\text{P}_{0.483}$  (left), the measured/calculated transmission (middle), and estimated band-gap for the five compositions of  $\text{GaAs}_{1-x}\text{P}_x$  (symbols) with calculated dependence of the direct band-gap following [2] (right).

Unpatterned layers with  $x=0\%$ , 33%, 39.8%, 48.3%, and 100% were grown, separated from the substrate and chemically polished to a roughness of 0.8 nm. Their actual thickness was derived from observed interference fringes. Figure 1 shows the transmission for  $x=48.3\%$ . At 10  $\mu\text{m}$  it amounts to 58% which coincides with the value calculated accounting for multiple reflections. This sample presents the worst case of increasing residual losses towards the band-gap. The estimated band-gaps are shown in Fig. 1 together with the empirical relation  $1.424 + 1.172x + 0.186x^2$  for the direct band-gap compiled in [2], where 1.424 eV stand for the GaAs. Note that GaP with a direct band-gap at 2.78 eV, has an indirect band-gap at 2.23 eV. A strong absorption band is seen around 13.3  $\mu\text{m}$  in GaP and at 19.1  $\mu\text{m}$  in GaAs. The band at 13.3  $\mu\text{m}$  is present in all samples except pure GaAs. The parasitic absorption band in the 2-4  $\mu\text{m}$  range known for pure GaP, is absent in the ternary compounds.

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# Lead halide perovskite nanocomposites for fast timing detectors

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Lead halide perovskite nanocrystals of the formula CsPbX<sub>3</sub> (X=Cl,Br,I) have recently attracted attention as potential time taggers in scintillating heterostructures [1] intended for new generation of detectors requiring fast timing [2]. Such detectors are desirable in the time-of-flight (TOF) techniques in medical imaging as well as high energy physics. Cesium lead halide nanoparticles feature favourable properties, in particular, ultrafast scintillation decays [3] thanks to quantum confinement effect. However, they suffer from poor chemical stability and low stopping power for ionizing radiation. The first drawback can be overcome by incorporation of nanocrystals in the polymer matrix. The second can be helped by combination of such nanocomposite with the standard bulk scintillator in resulting heterostructure.

In this work we study synthesis, structural and optical characteristics including the timing performance of CsPbBr<sub>3</sub> and CsPb(Br/Cl)<sub>3</sub> nanocrystals embedded in polystyrene matrix. We focus on nanocomposites with high nanocrystal loading. Favourable luminescent properties of nanocrystals can be compromised by agglomeration of nanoparticles in the process of nanocomposite preparation. To limit this effect we use advanced polymerization techniques and copolymerizable ligands. We measure scintillation characteristics of prepared nanocomposites, especially scintillation decays. Their time resolution is also assessed using a novel setup [4] with low energy pulsed X-ray excitation where the signal is detected by the analog silicon photomultiplier. Prepared nanocomposites feature more than twofold better time resolution with respect to the LYSO:Ce crystal currently used in the TOF positron emission tomography.

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## New strategies for efficient optical pressure & temperature sensors

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The control of extreme conditions of pressure (P) and/or temperature (T) is the subject of multidisciplinary studies involving physics, chemistry, materials science, biology or geology, as well as of enormous interest in many industrial processes. High P conditions can be induced in a solid with the help of a diamond anvil cell, whereas low/high T only needs a more conventional cryostat or furnace, respectively. P-T determination is a key issue requiring calibrated standards, and indirect, in situ pressure and/or temperature calibrations can be performed by taking advantage of the high sensitivity to P and/or T changes of some rare earth emission lines. In this work, we present different rare earth ions in materials and nanomaterials that have been successfully tested as optical P- and/or T- sensors.

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# Tuning the optical properties of gold nanostars

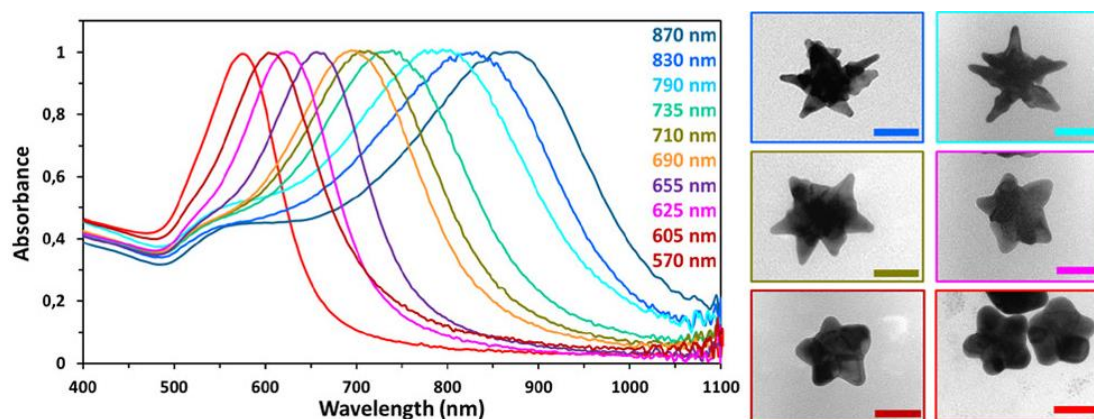
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During the last years, the controlled synthesis of Au nanoparticles (NPs) has attracted the interest of many research groups. Thus, a remarkable success in the development of Au NPs has been achieved. Nowadays, it is possible to prepare quite homogeneous with a la carte dimensions structures like spheres, cubes, rods, decahedra or octahedra and therefore, controlling their optical properties. Among all possible morphologies, spiked NPs are one of the most efficient plasmonic structures for a wide variety of applications ranging from sensing and imaging to photothermal treatments. However, despite all the advances made in the synthesis of plasmonic nanostructures, there is still a lack of tunability in the optical properties of spiked NPs. Therefore, the ability to concentrate large electromagnetic fields at the apexes of the NSt tips upon illumination was till now restricted to concrete wavelengths and so were also, their possible applications.

In the presented work we demonstrate the possibility of tuning the concentration of the electromagnetic fields at the apexes of the NSt tips by an optimized bottom-up approach that allows the preparation of highly homogeneous plasmonic nanostars (NSt) with a la carte optical properties. Produced Au NSt as shown in Figure 1, exhibit absorbance maximums that can be tuned from the visible to the infrared. [1]

Furthermore, the effect of the plasmon tunability on the optical enhancing properties of the synthesized structures was effectively tested for sensing using surface-enhanced Raman scattering spectroscopy (SERS) with visible and NIR lasers.



**Figure 1.** Normalized UV-vis spectra of different Au NSt solutions with plasmon resonances ranging from the visible to the infrared (left). TEM images of Au NSt corresponding to selected UV-vis spectra (right).

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# Anisotropic thermo-mechanical properties of BaGa<sub>2</sub>GeS(e)<sub>6</sub> crystals

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The quaternary chalcogenides BaGa<sub>2</sub>GeS<sub>6</sub> (BGGs) and BaGa<sub>2</sub>GeSe<sub>6</sub> (BGGSe) (point group 3) are viable alternatives to the well-established chalcopyrite (point group  $\bar{4}2m$ ) mid-IR nonlinear optical crystals AgGaS<sub>2</sub> (AGS) and AgGaSe<sub>2</sub> (AGSe) [1]. Most of their optical properties are now well documented [1]. Here we study the anisotropic thermal expansion, thermal conductivity, hardness and Young's modulus of BGGs and BGGSe.

The thermal expansion was evaluated using powdered samples and X-ray diffraction in the 200-430 K temperature range. The temperature  $T$  dependence for the two lattice constants  $a$  and  $c$  was fitted with a quadratic law and the relative thermal expansion coefficient  $\alpha$  was obtained as a linear fit  $A + B \cdot T$ . The coefficients  $A$  and  $B$  and the room temperature (RT) values of  $\alpha$  are summarized in Table 1. The anisotropy of the thermal expansion defined as  $\alpha_a - \alpha_c$  is roughly 2-3 times smaller compared to AGS and AGSe, respectively, with both coefficients  $\alpha$  being positive without the anomalous behaviour typical for AGS and AGSe.

The thermal diffusivity ( $\kappa$ ) and specific heat capacity ( $c_p$ ) of BGGs and BGGSe were measured in a contactless way over a temperature range from 184 to 473 K by the flash analysis technique. For both crystals the anisotropy of the calculated thermal conductivity  $k$  (Table 1) is rather low (< 20%). Compared with RT values known from the literature on AGS and AGSe, BGGs and BGGSe show roughly 30% lower thermal conductivity, respectively.

**Table 1.** Thermal expansion, thermal conductivity, hardness and Young's modulus of BGGs and BGGSe.

	BGGs		BGGSe	
	$a$	$c$	$a$	$c$
$A$ [ppm/K]	16.7	8.38	20.4	8.43
$B$ [ppm/K <sup>2</sup> ]	-0.0153	-0.00481	-0.0273	-0.0153
$\alpha$ at RT [ppm/K]	12.1 ± 1	6.93 ± 0.4	12.2 ± 1	3.84 ± 0.4
$c_p$ at RT [J/gK]	0.40 ± 0.01		0.27 ± 0.008	
$k$ at RT [W/mK]	0.91 ± 0.03	1.10 ± 0.03	0.63 ± 0.02	0.76 ± 0.02
Hardness $H_{IT}$ [GPa]	4.99 ± 0.08	4.66 ± 0.05	4.10 ± 0.04	4.25 ± 0.07
Hardness VHN [kg/mm <sup>2</sup> ]	463	432	380	394
Young's modulus $E_{IT}$ [GPa]	65.1 ± 0.5	71.3 ± 0.5	53.5 ± 0.1	61.1 ± 0.5

The hardness and Young's modulus were obtained from nanindentation tests using a Berkovich tip. The averaged (over 10 runs) RT results for the  $a$ -cut and  $c$ -cut plates are summarized in Table 1. The hardness of BGGs is ~40% higher than AGS and that of BGGSe ~70% higher than AGSe, comparing with microhardness results from the literature.

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# New nanoprobe designs for bioimaging and contactless luminescence thermometry

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A new direction in bioimaging utilizes hierarchically built exogenous nanoprobe enabling two or even more imaging modalities. The combination of photoluminescence (PL) and magnetic resonance (MR) imaging in a single nanoprobe provides simultaneously high sensitivity and spatial resolution, compensating the individual weaknesses of both imaging modalities. To address the challenge of proposing new nanoprobe for dual NIR-excited PL and MR imaging modalities, this work evaluates a series of trivalent lanthanide (Ln)-doped nanoparticles and core-shell nanostructures based on the scheelite-like NaGd(WO<sub>4</sub>)<sub>2</sub> host. This host doped with Er<sup>3+</sup> demonstrated excellent ratiometric thermal sensitivity in the temperature range of interest for biomedical applications ( $\approx 42$  °C), [1, 2] but the used Er<sup>3+</sup> green emissions are strongly scattered by human tissues, thus these emissions fall outside of the biomedical transparency windows (BW).

In currently studied nanoprobe, T<sub>1</sub>- and T<sub>2</sub>-MRI contrasts are delivered by Gd<sup>3+</sup> (at 1.5 T) and Ho<sup>3+</sup> (from 3 to 11.7 T), respectively, which are properly distributed in the core-shell nanostructure to avoid interactions between them. Dual contrast T<sub>2</sub>/T<sub>1</sub> is possible at magnetic fields from 3 to 7 T. Besides, efficient Tm<sup>3+</sup> and Ho<sup>3+</sup> emissions for imaging under Yb<sup>3+</sup> ( $\approx 980$  nm) NIR-excitation or Nd<sup>3+</sup> in a surface Yb<sup>3+</sup>-Nd<sup>3+</sup> codoped layer for efficient NIR-excitation at  $\approx 803$  nm allow for simultaneous deep tissue imaging and thermometry within I-II- III- and IV-BWs. Details of the synthesis procedure to obtain well-individualized and monodisperse-sized nanoparticles and core-shell nanostructures, as well as results of their PL properties, MR contrast imaging, ratiometric thermal sensitivity and cytotoxicity are presented.

## Acknowledgments

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# Processing of rare-earth-doped nanostructured glass-ceramics for enhanced photoluminescence

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The growing field of photonics demands the design of new rare-earth (RE)-based optical materials for their use in efficient optical telecommunications, solid-state lasers and other applications. Transparent oxyfluoride glass-ceramics (GCs) combine the transparency and both mechanical and chemical resistance of aluminosilicate glasses with the low phonon energy and facile incorporation of RE ions in the fluoride crystals. The incorporation of RE ions in the crystalline phases enhances the optical emission intensity, a major property of these materials [1]. Moreover, the additional presence of metallic nanoparticles (Ag, Au, Pt) in the RE-doped glass-ceramics can further enhance the luminescent response.

By the other hand, transparent GC materials have also been obtained by spark plasma sintering (SPS) [2]. This approach combines thermal action with simultaneous compression of the material to reach full densification and high homogeneity in a short time [3]. The structural, mechanical, and optical properties have been characterized and compared with GCs of the same composition prepared by melt-quenching followed by conventional heat treatment. The results confirm the suitability of the SPS processing for the preparation of highly dense and transparent oxyfluoride glass-ceramics containing nanocrystals.

These materials are suitable for the preparation of preforms as precursors for the drawing of optical fibers and as substrates for waveguides written using laser radiation and some examples of the materials preparation and its possible applications will be provided in this presentation.

*Keywords: oxyfluoride glass-ceramics; transparent; rare earths, metallic nanoparticles, spark plasma sintering*

## Acknowledgment

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# Localized-enhancement of 1L MoS<sub>2</sub> photoluminescence on ferroelectric domain walls

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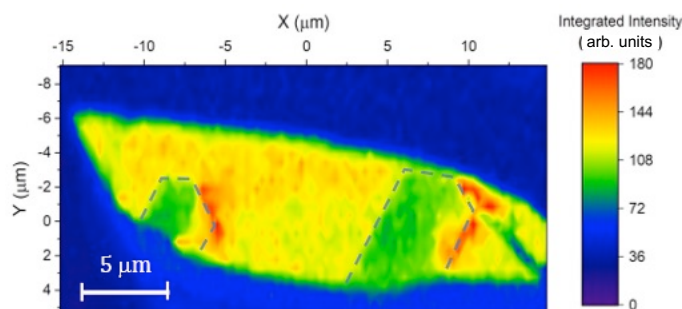
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Two-dimensional (2D) Transition Metal Dichalcogenides (TMDs) are an interesting class of materials with promising properties for the next generation of optoelectronic devices. Their atomic thickness nature offers a unique opportunity to engineer their properties by means of the surrounding environment. In this context, ferroelectric crystals as substrates for TMDs provide a means for electrostatic doping due to the remnant polarization, avoiding complex doping strategies that hinder fabrication processes of devices.

In this work we analyze the effects of integrating a (1L) monolayer MoS<sub>2</sub> on LiNbO<sub>3</sub> (LN), one of the most versatile and attractive current platforms for integrated photonics. We demonstrate, ferroelectric-induced electrostatic doping in monolayer 1L MoS<sub>2</sub> when deposited on a LN crystal with hexagonal domains of alternating polarity. The MoS<sub>2</sub> doping is optically probed by spatially resolved scanning micro-photoluminescence ( $\mu$ -PL) at low and room temperature. The results show the presence of p- and n-doped regions in MoS<sub>2</sub> depending on the polarization of the ferroelectric domain, as revealed by the different contributions of exciton and trion quasiparticles to the PL spectrum. Additionally, the  $\mu$ -PL of 1L MoS<sub>2</sub> is analyzed on the vicinities of the ferroelectric domain walls, where the lateral MoS<sub>2</sub> p-n homojunctions are located. A significant enhancement of the MoS<sub>2</sub> exciton PL is systematically observed on alternating domain walls. This result can be explained by the exciton dissociation at the depletion region on a first wall (p-n homojunction), which induces a long-term local carrier accumulation and electron-hole recombination in an adjacent p-n homojunction, resulting in the MoS<sub>2</sub> PL enhancement.

These results open new avenues for the optical control ultra-thin p-n-lateral homojunctions in 2D materials integrated on relevant optoelectronic platforms.



**Figure 1.** Image of the spatial variation of the 1L MoS<sub>2</sub> PL showing the exciton-dominant region (p type in yellow) and the trion-dominant region (n type in green). The emission enhancement (red) is observed on the vicinities of alternating ferroelectric domain walls.

# High pressure annealing effects on optical and scintillation properties for $\text{Gd}_3(\text{Ga,Al})_5\text{O}_{12}:\text{Ce}$ scintillator single crystal

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Garnet-type scintillator single crystals have been developed for various radiation detectors in various devices for medical, environmental and physics measurement fields.  $\text{Gd}_3(\text{Ga,Al})_5\text{O}_{12}:\text{Ce}$  [GGAG:Ce] scintillator single crystals indicate relatively high light yield, great energy resolution and fast decay time under  $\gamma$ -ray irradiation[1]. However, GGAG:Ce single crystal has oxygen defects in the as-grown single crystal because oxygen defect can generate during the crystal growth under inert or reduction atmosphere [2]. In the previous report [3], crystal growth under oxygen atmosphere by the Floating Zone method affected the scintillation properties of GGAG:Ce scintillator single crystals and their improvement could be observed[3]. In this study, as-grown GGAG:Ce single crystal under inert atmosphere was annealed at high pressure under oxygen atmosphere using the hot isostatic pressing (HIP) equipment to compensate the oxygen defects and the scintillation properties were investigated.

A plate-shaped specimen was prepared from the GGAG:Ce bulk single crystal grown by the Czochralski method under inert atmosphere and it was annealed at 1500°C and 200 MPa for 30 hours under Ar+20%O<sub>2</sub> atmosphere. Optical and scintillation properties of the GGAG:Ce single crystal before and after the HIP annealing were evaluated. Transmittance and photoluminescence spectra, pulse-height spectra and decay curves under  $\gamma$ -ray irradiation were measured.

Emission spectra of GGAG:Ce single crystal under 445 nm excitation before and after the HIP annealing are shown in Fig. 1. An emission peak originated from 5d-4f transition of  $\text{Ce}^{3+}$  ion was observed around 550 nm for both spectra. On the other hand, the emission peak shifted toward longer wavelength by the HIP annealing from 535 to 550 nm, suggesting that the crystal field around  $\text{Ce}^{3+}$  ion was changed by the HIP annealing. Details of other optical and scintillation properties will be reported.

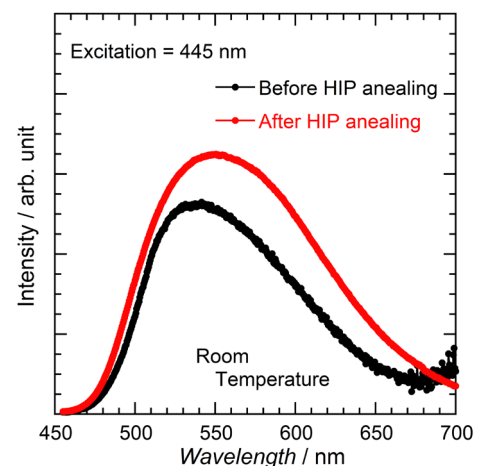


Fig.1 Emission spectra of GGAG:Ce before and after the HIP annealing.

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# Nanoporous scintillators for radioactive gas detection

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

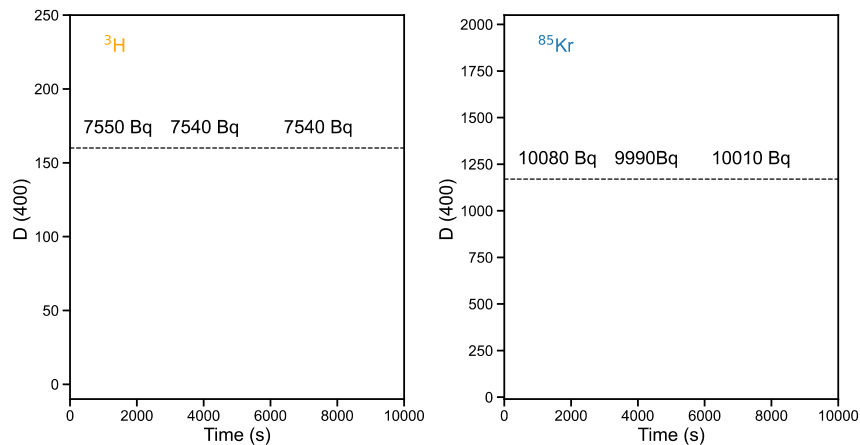


Figure 1: Typical measurements and their reproducibility for  $^3\text{H}$  and  $^{85}\text{Kr}$  detection. D(400) corresponds to the number of double coincidences measured in 400ns.

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# Controlling the spatial coherence and subwavelength waveguiding of rare earth quantum emitters by plasmonic nanostructures

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

Here, we show the capability of inducing directionality and spatial coherence in the emission of Nd<sup>3+</sup> ions distributed into a solid-state platform in the absence of photonic cavity [1]. To that end, we have used a plasmonic chain formed by closely-spaced Ag nanoparticles, which transforms the incoherent emission from Nd<sup>3+</sup> ions into spatially coherent light. In addition, we demonstrate the possibility of ultra-long-range waveguiding Nd<sup>3+</sup> fluorescence by means of the plasmonic chain. Namely, sub-diffraction fluorescence waveguiding is demonstrated over several tens of microns in the technologically relevant NIR spectral range of 900–1100 nm. The spatial coherence and the long-range energy transport originate from the coherent near-field coupling of the Nd<sup>3+</sup> emitters with the plasmon mode of the chain and the low dissipative losses displayed by this mode.

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

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# Core@shell structure with highly doped Nd<sup>3+</sup> sensitizing ions for temperature sensing and bioimaging

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In recent years there has been a notable rise in interest in multifunctional materials, especially those at the nanoscale [1-3]. In this area, upconverting nanoparticles (UCNPs), capable of converting radiation from the infrared (lower energy) to visible or ultraviolet light (higher energy), are particularly promising. Those materials have some crucial advantages, especially significant for biomedical applications, like negligible autofluorescence, large anti-Stokes shift, deep penetration into tissue, reduced photodamage of the cells and the possibility to use inexpensive continuous lasers [4-5]. The upconversion phenomenon has been observed for various metal ions and organic compounds, among which it is most often described for rare earth ions (RE). However, to achieve efficient emission, UCNPs should be adequately designed, e.g., choosing a matrix characterized by low phonon energy, appropriate sensitizer and activator and their concentration, and using core@shell structure, which is helpful, especially for a higher concentration of activator and sensitizer ions [6]. In the presented study, core@shell structures with a high concentration of Nd<sup>3+</sup> in a shell to achieve effective emission under 808 nm excitation wavelength were synthesized. The morphology, optical properties and thermal sensitivity were investigated. The obtained results are very promising and make the presented UCNPs pioneering in multifunctional materials for bioimaging and temperature sensing.

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# Scintillation properties of composite scintillators based on doped orthosilicate compounds

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The single crystals (SC) of Ce<sup>3+</sup> doped A<sub>2</sub>SiO<sub>5</sub> (A = Lu, Y) orthosilicates have been developed as promising scintillators for positron emission tomography (PET) due to their desirable properties such as high density, fast decay time and high light output [1]. Meanwhile, apart from their applications in crystal form, these orthosilicates also attract attention regarding the development of single crystalline film (SCF) scintillating screens for microtomography using the liquid phase epitaxy (LPE) method [2].

Recently, we developed various types of the doubly- and three-layered composite scintillators (CS), based on the SCFs of Ce<sup>3+</sup> and Pr<sup>3+</sup> doped (Y, Lu)AG simple garnets and Ce<sup>3+</sup> doped (Y,Lu,Tb,Gd)<sub>3</sub>(Al,Ga)<sub>5</sub>O<sub>12</sub> mixed garnets, grown using the LPE method onto heavy LuAG:R (R=Pr,Ce,Sc) and GAGG:Ce substrates [3, 4]. The results of our current researches show that the epitaxial structures of orthosilicates can be also considered as promising composite scintillators for simultaneous detection of α-, β-particles and γ-rays.

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

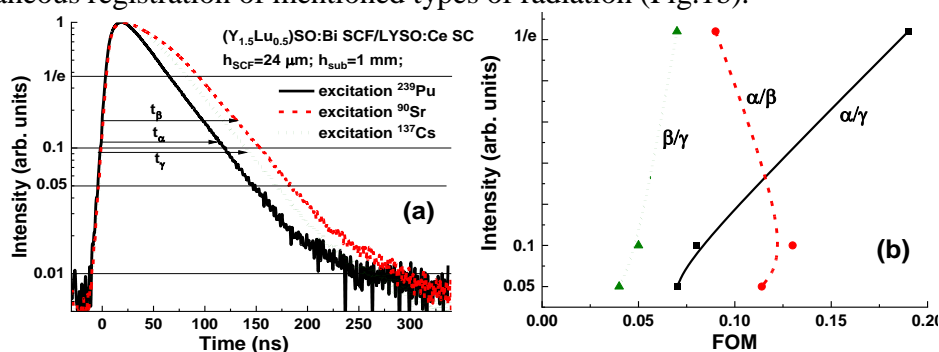


Fig.1. (a) - separation of the scintillation decay curves of (Y<sub>1.5</sub>Lu<sub>0.5</sub>)SO:Bi SCF/LYSO:Ce SC composite scintillators under excitation by α- (<sup>241</sup>Am) and β- (<sup>90</sup>Sr) particles and γ-quanta (<sup>123</sup>Cs). (b) -scintillation intensity decay and FOM values of this composite under registration of the mentioned types of radiation.

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# Second harmonic microscopy of femtosecond laser micro-modifications in BBO crystal

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Second harmonic generation microscopy (SHGM) is a microscopy technique based on the non-linear interaction of an intense fundamental beam (i.e., a femtosecond laser) with a sample. As a result, a signal with double the frequency of the incident beam is generated and registered while the sample is scanned. The so-generated images provide information with high spatial resolution about the second-order susceptibility of the sample, thus allowing to gain insight into its microscopic structure. It has been successfully applied to the analysis of biological samples [1], being also very useful in materials science [2].

On the other hand, femtosecond lasers have consolidated as excellent tools with unique properties for 3D micro-structuring of transparent dielectrics, enabling the direct writing (DW) of photonic devices in almost any optical material: the focused laser inside the target produces a localized damage track modifying the refractive index. This mechanism allows the fabrication of miniaturized efficient photonic devices [3].

In this work, we analyze by SHGM the damage tracks created inside a  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> (BBO) crystal. BBO is one of the most widely used nonlinear crystals for SHG with ultrashort pulses due to its high optical nonlinearity, wide range of transparency and physical robustness. In addition, it possesses 3m structure and has the possibility to phase-match the SHG process in a large spectral window, ensuring efficient conversion. We present a detailed study of the damage tracks inscribed with different irradiation conditions and geometries, demonstrating that, under certain conditions, the SHG process in the damage tracks may exhibit a local enhancement. This effect is observed both in phase-matching as in anti-phase-matching conditions, suggesting that the effective non-linear coefficient is enhanced by the high-intensity laser modification.

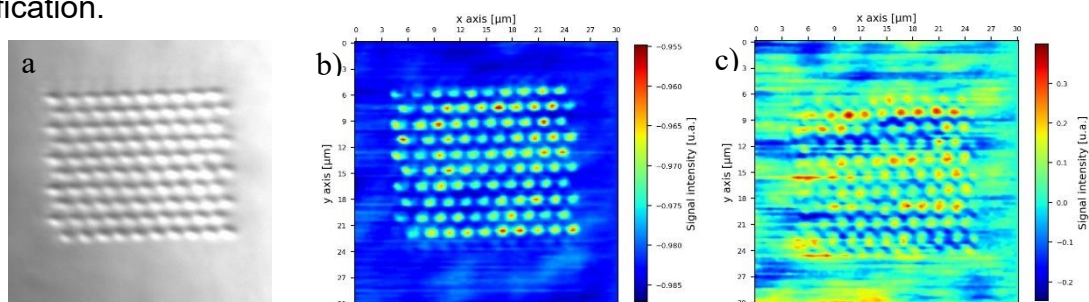


Figure 1: a) Optical image of an array processed with fs laser pulses inside a BBO crystal. b) SHGM image in phase-matching conditions. c) SHGM image in anti-phase-matching conditions.

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# Designing photon upconversion nanoparticles showing luminescence in whole human blood

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Finding the highly luminescent nanoparticles which can be excited in the range of first, second, or third biological windows is very important [1]. The near-infrared excitation provides low photodamage of biological materials, autofluorescence reduction, and deeper light penetration depth than in the case of UV and visible light [2]. Therefore, much attention has been paid to obtain up-converting nanoparticles (UCNPs) doped with lanthanide ions, which show intense luminescence even in biological fluids [3]. Nowadays, many blood experiments are carried on to determine, e.g., light penetration depth and the presence of analytes which are the markers for some diseases [4].

The main goal of our research was to determine the whole human blood penetration depth based on the luminescence of multi-mode NIR laser-excited UCNPs. The high-quality core/shell materials with hexagonal phases were obtained using precipitation in high-boiling-point solvents and then transferred to the water by acid treatment [5]. The different rare earth ions were used as light sensitizers: Yb<sup>3+</sup> ions for 975 nm, Er<sup>3+</sup> for 808, 975, and 1532 nm, or Tm<sup>3+</sup> for 1208 nm covering the optical transparency windows, important for medicine. We registered the emissions of ligand-free UCNPs in the water and whole human blood at different sample depths. The effect of light absorption and scattering of blood components was observed. The research allowed us to estimate the depth to which the excitation radiation penetrates the sample and how thick a layer of blood allows to observe the emission. The presented results are important for developing UCNPs' applications in biomedicine.

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# Surface waveguides with modal shaping in Nd:YAG crystal for sensing applications: design and fabrication with femtosecond laser pulses

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The use of femtosecond lasers for the fabrication of photonic devices integrated in transparent dielectric materials has proven to be a very useful and effective technique as it provides some important advantages over other methods commonly used. Among these advantages, we can name two, the fact that it is a one-step process, and the ability to realize three-dimensional structures inside the material with arbitrary geometry [1]. The fabrication process consists in focusing the ultrashort laser pulses inside the material in such a way as to induce a controlled modification of the refractive index in the irradiated zone, following a desired geometry. The development of this technique has allowed the fabrication of complex photonic circuits, which can be used in different scientific fields, such as biomedicine or optical sensing.

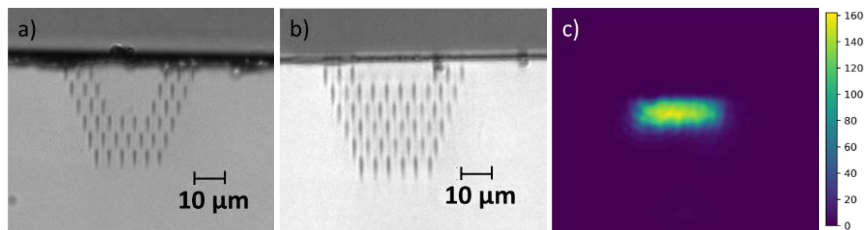


Figure 1: In a) and b), optical microscopy images of the entrance and exit sections, respectively, of a straight waveguide integrated in crystalline Nd:YAG. In panel c) image of the mode of a He-Ne laser (633 nm) coupled in the waveguide.

In this work, we present the design, fabrication and characterization of surface waveguides in Nd:YAG by femtosecond laser pulses. The waveguides, based on “depressed-index cladding” type structures [2], present an optimized design that allows “modal shaping”, which permits to progressively increase the contact area of the guided mode with the top surface of the sample. Nd:YAG has been chosen as the paradigmatic crystal, for being one of the active medium in the fabrication of solid-state lasers and active devices, which in turn presents high stability, isotropy and high transparency in the near-infrared optical range.

These types of structures present a great potential for its integration into high efficiency active optical sensors [3] as we expect a considerable increase in the sensing area, while maintaining a controlled single-mode profile. Although the technique has been demonstrated in Nd:YAG, it could be extended to any other transparent crystal.

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# Toward white light emission from Bi and V codoped borosilicate glasses upon UV excitation

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Developing low-cost phosphors for application in white light emitted diodes (LEDs) is one of the main challenges of current research activity [1]. The use of rare-earth ions (RE) in combination with a suitable host is one of the most used strategies to produce white light emission. However, the weak absorption cross section of RE ions together with their sharp emission bands make quite difficult obtaining intense white emission. In this study we explore a different approach based on Bi and V codoped borosilicate glasses. Borosilicate glasses are cheap materials with excellent mechanical and chemical properties and they possess a good transparency in the visible spectrum [2]. The blue emission of  $\text{Bi}^{3+}$  combines with the intense yellow-orange emission from  $\text{V}^{5+}$  ions to produce broad and intense white light emission upon near UV excitation. A detailed analysis by means of Raman, FTIR, XPS and PL spectroscopy will be shown to correlate the structure and composition of these glasses with their emission properties.

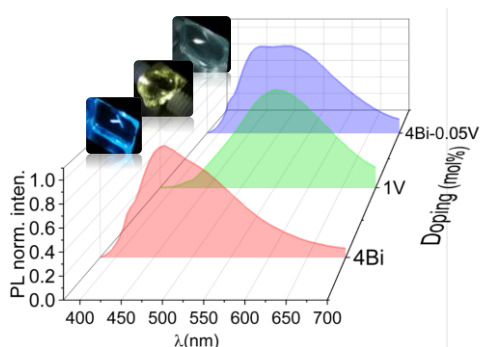


Figure 1: Photoluminescence emission of borosilicate glasses doped with Bi and V. The insets show images of the glasses under 355 nm excitation.

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# Local structures of Tm ions in $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Eu},\text{Tm}$ long persistent phosphorescence phosphor studied by X-ray fluorescence holography and positron annihilation lifetime spectroscopy

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$\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Eu},\text{Tm}$  is newly found long persistent phosphorescence (LPP) phosphor [1]. It has been believed that Eu and Tm ions occupy the Ca site in  $\text{Ca}_2\text{Al}_2\text{SiO}_7$ , because the ionic radii of them are larger than those of Al and Si ions. However, the Tm ion has a trivalent state, different from a divalent state of the Ca ion. This situation makes it difficult for Tm ions to occupy Ca sites simply. The existence of Tm ions at Ca sites will require an additional charge compensation to resolve the charge inconsistency between Tm and Ca ions. Since Tm ions play an important role as an electron trap to cause LPP, it is significant to clarify the local structure and charge compensation mechanism around Tm ions. In the present study, we have investigated local structures of Tm ions in  $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Eu},\text{Tm}$  crystals by X-ray fluorescence holography (XFH) and positron annihilation lifetime spectroscopy (PALS). The former and latter have been successfully applied to the local structure analyses of impurities [2] and vacancy-type defects [3]. Figure 1 shows an atomic image around Tm ions on the (001) plane at  $z=0$  Å, reconstructed from Tm  $L\alpha$ -XFH holograms. The reconstructed atomic image was drawn with grey. Open circles indicate the atomic arrangement around the Ca site, determined by the XRD analysis. The reconstructed atomic image could be seen within open circles, indicating that Tm ions occupy the Ca site. The intensity of the atomic image was weakened remarkably, and comparable to that of artifacts outside open circles. This fact implies that positional fluctuation and lattice deformation are introduced around Tm ions.

This work was partially supported by JSPS Grants-in-Aid for Transformative Research Areas (A) "Hyper-Ordered Structures Sciences" via Grant Nos. 20H05878, 20H05881, 21H05546.

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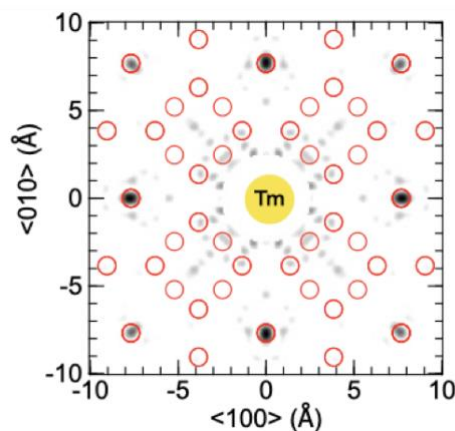


Fig. 1. Atomic image around Tm ions on the (001) plane at  $z=0$  Å, reconstructed from Tm  $L\alpha$ -XFH holograms.

# Luminescence and scintillation properties of Tb,Ce co-doped (Gd,La)<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> for radiation imaging

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Radiation imaging is an important application for scintillators, including medical imaging and alpha particle detection. Brighter scintillators is required to have higher sensitivity.. Ce:(La,Gd)<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> (Ce:La-GPS) has a relatively high effective atomic number ( $Z_{\text{eff}} = 54$ ) and is known as one of the highest light-yielding materials among silicate scintillators. Ce:La-GPS shows the light output and energy resolution of 42,000 photons/MeV and 5 % (662 keV, FWHM), respectively [1]. However, the emission wavelength of Ce:La-GPS is around 390 nm, resulting in low wavelength sensitivity for CCD or CMOS sensors.

Previously, higher optical output and quantum yields can be obtained by co-doping with energy transfer, such as Gd<sup>3+</sup> to Ce<sup>3+</sup> and Ce<sup>3+</sup> to Tb<sup>3+</sup> [2]. To enhance the wavelength sensitivity in photodetectors, optical properties of Tb<sup>3+</sup> was co-doped with Ce:La-GPS was investigated, because green emission derived from the 4f-4f transition of Tb<sup>3+</sup>. We have previously reported Tb:La-GPS with an emission wavelength of 550 nm, which is suitable for X-ray imaging and fluorescent materials[3]. In addition, we have previously reported that the quantum yield of La-GPS is enhanced by the co-doping of Ce and Tb. However, the imaging performance of the co-doped crystals has not been reported. In this study, we report the luminescence and scintillation properties as well as the radiation imaging properties of Tb,Ce:La-GPS.

Compositional screening for Tb and Ce concentration was performed with sintered compacts, and a single crystal of the composition with a high photoluminescence quantum yield was grown by the micro-pulling-down ( $\mu$ -PD) method. Photoluminescence properties were measured with an integrating sphere. Transmittance spectra, excitation and emission spectra were obtained for grown crystals at room temperature. In addition, scintillation properties for gamma and alpha radiation were measured using <sup>137</sup>Cs and <sup>241</sup>Am sources, respectively. Radiation imaging using an <sup>241</sup>Am source was also taken using the high-resolution alpha-ray imaging system with an optical microscope [4]. The grown (Tb<sub>0.015</sub>,Gd<sub>0.735</sub>,Ce<sub>0.015</sub>,La<sub>0.235</sub>)<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> single crystal showed a transmittance of over 80%, and position resolution was about 3 times higher than that of conventional Ce:La-GPS. Details of the luminescence and scintillation properties are discussed in the poster presentation.

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# Tailoring the optical and photometric properties of light sources based on dual-layer ceramics

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Light sources based on ceramics activated with electroluminescent or laser diodes gained considerable interest during last years. Research presented in this work is focused on dual-layer ceramics with various combinations of rare-earth doping of yttrium aluminium garnet ( $Y_3Al_5O_{12}:RE^{3+}$ ,  $YAG:RE^{3+}$ ). Freeze granulation process and granulate pressing was used to obtain two-layer green-bodies sintered into transparent ceramics in the solid-state process. Desired layer thickness was obtained by precise grinding and polishing of the structures.

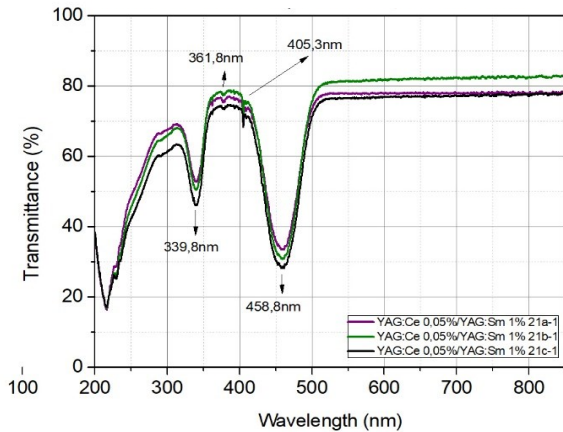


Fig. 1 Transmittance of exemplary dual-layer ceramic samples

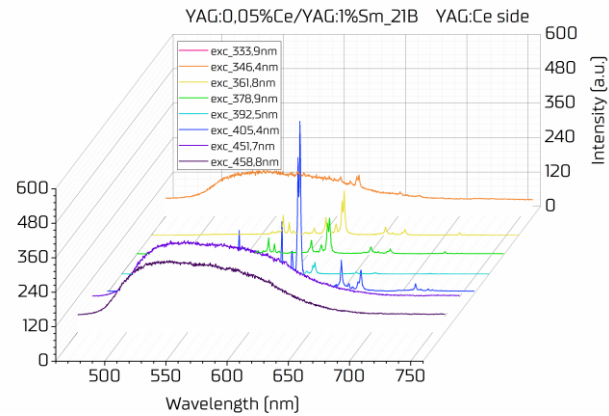


Fig. 2. Emission spectra for YAG:Ce 0,05%/YAG:Sm 1% ceramics for different excitation wavelengths.

Results of transmittance of exemplary dual-layer samples YAG:Ce0,05%/ YAG:Sm1%, with different layer thicknesses, are shown in Fig. 1. High transmittance in the range 500-850 nm indicates a good quality of ceramics. Evolution of emission spectra for different excitation wavelengths is shown in Fig. 2. Proper adjustment of dopant concentration, layer thickness and microstructure of each layer allows to tailor optical properties (absorption, emission, scattering) and photometric (e.g. chromatic coordinates, luminous efficiency) of resulting light source.

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## Ce<sup>3+</sup> centers in scintillating lithium fluorophosphate glasses

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Lithium fluorophosphate glasses in the form of 20Al(PO<sub>3</sub>)<sub>3</sub>-80LiF have been considered as potential scintillator host materials for laser fusion experiments [1]. These glasses have a lithium (Li) content of 31.6 mmol cm<sup>-3</sup> [2] which is essential in enhancing the detector sensitivity to 270 keV, down-scattered neutrons. The detection of these low-energy neutrons is necessary in analyzing the imploded plasma areal density and in understanding the fusion plasma dynamics. As a comprehensive follow-up of our earlier report [3], we then present the spectroscopic characterization, luminescence properties, and scintillation mechanisms of the Ce<sup>3+</sup>-doped lithium fluorophosphate glasses. The fluorophosphate glasses are prepared by melt-quenching method with a chemical composition of 20Al(PO<sub>3</sub>)<sub>3</sub>-80LiF-*x*CeF<sub>3</sub> where *x* ranges from 0.5 to 3.0 mol%. The existence of stable Ce<sup>3+</sup> centers in these glasses is confirmed by x-ray absorption spectroscopy along the higher Ce K-edge energy (40443.0 eV) which allows a more direct measurement of the oxidation states than the commonly accessed Ce L-edge energies (5723.4 to 6548.8 eV). Through the characterization of thinner (~ 2.0 mm) samples, the Ce<sup>3+</sup>-doped APLF glasses have been shown to exhibit absorption and excitation edges as well as intense emission peaks which correspond to the interconfigurational Ce<sup>3+</sup> 5d → 4f transitions. When the doping concentration increases, the self-absorption also increases, and the emission band appears shifted. Moreover, the strong UV emission have fast average lifetimes of less than 30 ns, a quantum yield of ~ 80 % measured under UV excitation, and a scintillation light yield of up to 620 photons/n of a 1.0 MeV neutron (<sup>252</sup>Cf) source. The understanding of the properties and mechanisms of the Ce<sup>3+</sup> centers in these lithium fluorophosphate glasses will likewise pave the way for their development as neutron scintillator materials for laser fusion experiments.

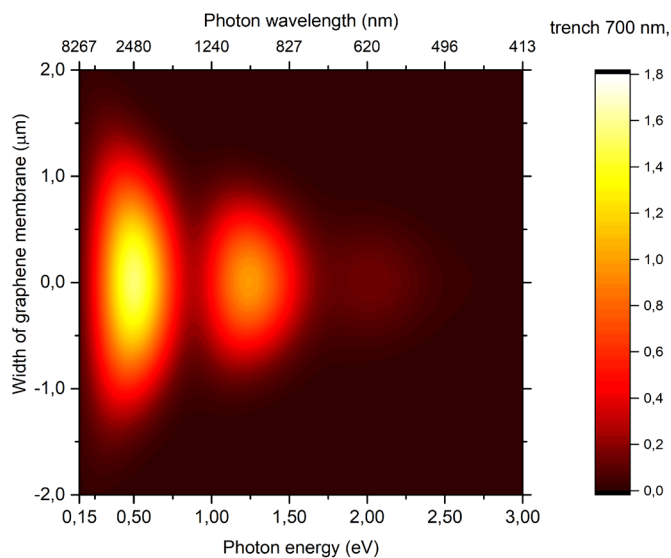
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# Modelling of spectral response of electrically biased suspended graphene over variable trench depth

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**Fig. 1.** Simulated intensity of thermal radiation from suspended graphene for 700 nm trench depth.

The light emission from graphene-based light-emitting devices has attracted considerable interest due to its promising applications in optical modulation and optical sensing [1], [2].

In this work, we present the simulation of the multiple thermal light emission peaks and significant spectral modulation based on the interference effects between the light emitted directly from the graphene and the light reflected from the substrate [3].

We consider the influence of temperature (i.e. applied voltage) and variable trench depth below suspended graphene on thermal emission.

In Fig. 1. we present simulated intensity of suspended graphene thermal radiation over the trench 700 nm depth taking into account temperature gradient of the membrane surface.

## Acknowledgments

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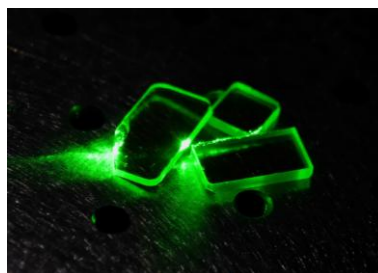
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## Pr<sup>3+</sup> ion energy levels and decay times of scintillating fluoride glasses

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Praseodymium (Pr<sup>3+</sup>)-doped fluoride glasses have been considered as potential scintillator materials due their fast decay times as well as higher band gaps, i.e., shorter absorption edges compared to typical oxide materials. In this work, we report our investigations on novel Pr<sup>3+</sup>-doped scintillating fluoride glasses: namely, 20Al(PO<sub>3</sub>)<sub>3</sub>-80LiF-PrF<sub>3</sub> (1.0 mol% Pr<sup>3+</sup>-doped APLF), 19BaF<sub>2</sub>-33.25CaF<sub>2</sub>-42.75AlF<sub>3</sub>-5YF<sub>3</sub>-PrF<sub>3</sub> (1.0 mol% Pr<sup>3+</sup>-doped BCAYF), and 19BaF<sub>2</sub>-33.25CaF<sub>2</sub>-42.75AlF<sub>3</sub>-15P<sub>2</sub>O<sub>5</sub>-20LiF-PrF<sub>3</sub> (1.0 mol% Pr<sup>3+</sup>-doped BCAPLF) prepared by conventional melt-quenching method. Through x-ray absorption near-edge structure (XANES) spectroscopy along the Pr LIII edge, it was confirmed that the Pr ions in these complex host glasses exist with 3+ oxidation state. Moreover, the Pr<sup>3+</sup>-doped glasses exhibit absorption and emission peaks which correspond to the different interconfigurational 4f5d and intraconfigurational 4f<sup>2</sup> transitions of Pr<sup>3+</sup> ions. The spectroscopy results also indicate that the Pr<sup>3+</sup> ions in these fluorides have a 4f5d excited state configuration that overlaps with the <sup>1</sup>S<sub>0</sub> level of the 4f<sup>2</sup> ground state configuration but with varying gaps between the lowest 4f5d level and the <sup>1</sup>S<sub>0</sub> level. Under x-ray excitation, the UV emissions of the Pr<sup>3+</sup>-doped glasses are primarily dominated by different transitions from the lowest 4f5d level or the <sup>1</sup>S<sub>0</sub> level resulting in different decay times ranging from 23.83 to 190.81 ns. Our findings show that the gap between the <sup>1</sup>S<sub>0</sub> level of the 4f configuration and the lowest level of the 4f5d configuration plays a role in achieving faster decay times due to fewer intraconfigurational 4f<sup>2</sup> transitions in the UV region. Some strategies to obtain fast fluoride glass scintillators (e.g., Pr<sup>3+</sup>-doped APLF) will likewise be put forward especially for future laser fusion experiments.



**Figure 1.** Photograph of the 1.0 mol% Pr<sup>3+</sup>-doped APLF, BCAYF, and BCAPLF glasses.

# Excitonic luminescence in $(\text{Lu},\text{Y})_2\text{SiO}_5:\text{Ce}^{3+}$ single crystals

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Although  $(\text{Lu},\text{Y})_2\text{SiO}_5$  (or  $\text{LYSO}:\text{Ce}$ ) has been identified as a possible scintillator material for medical and nuclear applications, there is still a lack of fundamental knowledge about the final stage of energy relaxation processes, which is crucial for the evaluation of scintillator performance in relevant modern applications, such as the new CMS detector in CERN. One of the most crucial factors influencing scintillator performance is the efficiency of energy transfer from the crystal lattice to the luminescence center ( $\text{Ce}^{3+}$ ), which correlates with the intrinsic luminescence of the matrix. One of the possible mechanisms in  $\text{LYSO}$  is the excitation of  $\text{Ce}^{3+}$  ions via the relaxation of the self-trapped exciton (STE). The purpose of this study is a detailed study of luminescence properties as well as their temperature dependencies of STE in cerium-doped  $\text{LYSO}$  single crystals.

The intrinsic luminescence in Ce-doped  $(\text{Lu},\text{Y})_2\text{SiO}_5$  (or  $\text{LYSO}:\text{Ce}$ ) single crystals has been studied by means of excitation luminescence spectroscopy in the vacuum ultraviolet range under synchrotron radiation. Two experimental stations have been applied for the research. The first one is the photoluminescence endstation (Finestlumi) of FinEstBeAMS of MAX IV synchrotron facility (Lund, Sweden) [1-3], while another one is the Superlumi endstation of P66 beamline at PETRA III of DESY (Hamburg, Germany) [4].

A new, previously not reported luminescence band has been discovered at 250 nm. The excitation spectra of this emission, its temperature behavior as well as time-resolved properties (fast decay) allow us to assign this emission to self-trapped exciton in  $\text{LYSO}$ . Two possible models have been proposed. The first model explains the 250 nm as  $\sigma$  components of the self-trapped exciton, while the second model suggests that it arises from the radiative recombination of the self-trapped exciton in the lutetium sublattice.

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# **Influence of swift heavy ions on structural and luminescent properties of several important optical and scintillator materials**

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Research and development of scintillating materials and novel ionizing radiation detecting devices for particle physics, neutron research, and medical imaging - are on the priority list of many European research centers including CERN.

In the current research radiation damages in the following single crystals relevant for nuclear and high-energy applications have been studied:  $\text{Gd}_3\text{Ga}_2\text{Al}_3\text{O}_{12}:\text{Ce},\text{Mg}$  (GGAG:Ce,Mg),  $\text{Y}_3\text{Al}_5\text{O}_{12}$  (YAG),  $(\text{Lu},\text{Y})_2\text{SiO}_5:\text{Ce}$  (LYSO:Ce),  $\text{PbWO}_4$  and  $\text{PbF}_2$ . These crystals were irradiated by 156 MeV Xe ions with several different fluences in the range  $6.6 \times 10^{10}$ - $2 \times 10^{12} \text{ cm}^{-2}$ .

The induced radiation damages in all samples studied have been characterized by means of optical spectroscopy and VUV luminescence spectroscopy. The dependence of the radiation damage of irradiated crystals on the fluence of incident ions is established. The origin of radiation damage, which has its own characteristics in each specific material, will be discussed.



# Photoluminescence and Raman spectroscopy of Ce<sup>3+</sup> doped Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> single crystalline films LPE grown onto Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> and Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> substrates

**Anton Markovskyi,<sup>a,b)</sup> Vitalii Gorbenko,<sup>b)</sup> Alexander Fedorov,<sup>c)</sup> Piotr Radomski,<sup>d)</sup> Tomasz Runka,<sup>d)</sup> Yuriy Zorenko<sup>b)</sup>**

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The Ce<sup>3+</sup> doped Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> (YAG) and Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> (LuAG:Ce) garnets, prepared in different forms: powders, transparent optical ceramics (OC), bulk single crystals (SC) and single crystalline films (SCF), are widely applied nowadays as luminescent converters in white light-emitting diodes, scintillators, cathodoluminescent screens and screens for the visualization of X-ray images, and other optoelectronic devices. The luminescence and scintillation properties of YAG:Ce and LuAG:Ce garnets in different forms depending on the synthesis process, which largely determines the types of intrinsic defects that predominate (vacancies, antisite defects, and their aggregates with impurities), their concentrations and distributions over the main volume and surface of phosphors [1].

Comparative analysis of YAG SCFs doped with Ce<sup>3+</sup> ions grown onto YAG and LuAG substrates using liquid phase epitaxy (LPE) technique has been studied for the first time in this work by Raman and luminescence spectroscopy using Renishaw InVia Raman microscope. Due to Ce<sup>3+</sup> doping and intense Ce<sup>3+</sup> luminescence the Raman spectra had to be measured using the excitation wavelength of 785 nm. The Raman modes recorded for of YAG:Ce/YAG and YAG:Ce/LuAG are overlapped with electronic transitions attributed to rare earth (RE) trace impurities of the samples. Spectroscopic measurements obtained allow a distinction between SCF and the substrate for homoepitaxy-grown YAG:Ce /YAG and quasi-homoepitaxy-grown YAG:Ce /LuAG structures. Such two modes of film growth can result in the different mechano-optical properties of YAG:Ce SCFs related to the presence of mechanical stress on the SCF/substrate interface in the case of quasi-homo-LPE growth due to different YAG and LuAG lattice constants, and the absence of this phenomenon in the case on homo-LPE growth. Furthermore, the identification of a transition layer between YAG:Ce SCF and LuAG substrate, the width of which was about 2 micrometers was performed. The region, where the transformation from the structure of a YAG:Ce film to LuAG single crystal occurs, can be considered as a Y<sub>3-x</sub>Lu<sub>x</sub>Al<sub>5</sub>O<sub>12</sub> solid solution, where x varies from 0 to 1. The measurements of the Ce<sup>3+</sup> luminescence along the cross-section of epitaxial structures also make it possible to evaluate the transition from the Ce-doped film to the undoped substrate. Such a transition layer in which the luminescence intensity dropped to the minimum level was estimated to be equal to 5 and 9 micrometers for YAG:Ce /YAG and YAG:Ce /LuAG epitaxial structures, respectively.

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# Luminescent Properties of Ce-doped Garnet Transparent Ceramics Prepared by the Spark Plasma Sintering Process

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Transparency is required for the material search of optical materials such as laser or scintillator, and we have investigated their optical properties for transparent single-crystals as scintillators or other optical materials grown by the Czochralski growth, micro-pulling down method [1]. Since around 2010, transparent ceramic scintillators have been studied [2] using the Vacuum sintering process or/and Hot Isostatic Pressing (HIP). Spark Plasma Sintering (SPS) Process is a much simpler and shorter sintering time than other methods, and we have investigated the scintillation properties for the transparent ceramics (i.e. Ce:SrHfO<sub>3</sub>, Nd:Lu<sub>2</sub>O<sub>3</sub>) prepared by SPS process [3,4]. However, such materials had high-melting temperatures, and the preparation of single crystals (good transparent materials) is hard.

In this study, we prepared Gd<sub>3</sub>(Ga,Al)<sub>5</sub>O<sub>12</sub>-based materials with a diameter of 20 mm by SPS process as shown in Fig. 1, and compared the optical and scintillation properties for the same material by Czochralski growth and other techniques. Photoluminescence (PL) and radio-luminescence peaks were located at around 550 nm excited by 420-nm photons, X-ray and 5.5-MeV alpha-rays, and this is the same result as the single crystal and ceramics by HIP. Up to now, the SPS sample had a transparency of around 10-20% which is smaller than the HIP sample (~50%) and single crystal (~80%). The light output was around 13,000 photons/MeV, while HIP and single crystals had that of ~55,000 photons/MeV. The small light output for the SPS sample might be due to low transparency. Although the SPS sample had light output and transparency, as a material search technique, this process is also effective, especially for high melting temperature samples.

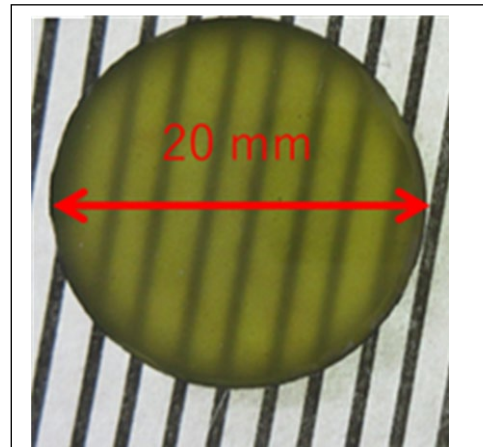


Fig. 1 Photograph of Gd<sub>3</sub>(Ga,Al)<sub>5</sub>O<sub>12</sub>-based scintillator prepared by SPS.

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# Highly luminescent borogermanate glass with mixed perovskite CsPb(Br,I)<sub>3</sub> and (Cs,Rb)Pb(Br,I)<sub>3</sub> nanocrystals: properties and applications

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Materials containing perovskite nanocrystals have unique luminescent properties: such as high emission coefficients, narrow bands, and the possibility to obtain radiation in the entire visible range by changing the size of nanocrystals and the ratio of halogens and alkalis [1]. Despite the large number of proposals for the use of perovskite nanocrystals, for example, in solar batteries, LEDs, various detectors, scintillators, etc. [2], many of their properties are unstable while nanocrystals are contacting with air oxygen. To stabilize the properties of perovskite nanocrystals, they are usually placed in a polymer or glass matrix [3].

A series of borogermanate glasses of the system 23.59 B<sub>2</sub>O<sub>3</sub> – 38.09 GeO<sub>2</sub> – 6.41 Na<sub>2</sub>O – 5.03 ZnO – 1.38 P<sub>2</sub>O<sub>5</sub> – 2.85 TiO<sub>2</sub> – 4.99 K<sub>2</sub>O – 5.41(1-y) Cs<sub>2</sub>O – 5.41y Rb<sub>2</sub>O – 2, 26 PbO - 9.98(1-x) Br - 9.98x I mol.%, where x = 0; 0.4; 0.5; 0.6; 0.75; 1; y = 0; 0.25; 0.5; 0.75. Glass was synthesized in an air atmosphere at a temperature of 950°C for 30 min. Perovskite nanocrystals precipitated in the glass matrix upon annealing from 470°C.

In glasses, for which x and y are equal to zero (rubidium and iodine are absent in the composition), mostly CsPbBr<sub>3</sub> with admixture of Cs<sub>4</sub>PbBr<sub>6</sub> perovskite crystals were nucleated. They have intense luminescence in the region of 500-530 nm, depending on the mean size of the crystals. When iodine ions were added, the luminescence maximum can be tuned in the range 500÷680 nm, depending on the bromine/iodine ratio. The maximum quantum yield was 40% for the composition with x=0.75. With the advent of rubidium, (Cs,Rb)<sub>4</sub>PbBr<sub>6</sub> (or (Cs,Rb)PbI<sub>3</sub>) nanocrystals were precipitated. With an increase in the rubidium content, the nanocrystals luminescence maximum shifted to the blue region, the luminescence quantum yield increased up to 51%, and the decay time increased up to 10 ns. Such luminescent properties make it possible to use the materials as scintillators.

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# Dual green-red emission of Mn-doped Li<sub>2</sub>O-ZnO-GeO<sub>2</sub> glass-ceramics

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Manganese ions as a transition ion are attracted by the fact that under the influence of redox conditions of material synthesis, different coordination, and crystal field strength, they can tune the wavelength of their luminescence maximum from the blue to the red region of the spectrum [1]. On the one hand, commercial red phosphors doped with Mn<sup>4+</sup> are known [2], which in many respects are not inferior to similar materials with Eu<sup>2+</sup>. On the other hand, green crystalline phosphors doped with Mn<sup>2+</sup> with a long lifetime are known [3]. At the same time, in amorphous materials, Mn<sup>2+</sup> exhibits both yellow-orange and green luminescence with a large half-width and lower intensity [4].

Mn-doped lithium-zinc-germanate glass had the composition of (30-x)Li<sub>2</sub>O-xZnO-70GeO<sub>2</sub>, where x=5; 7.5; 10; 15; 20; 22.5 mol.%. Glass-ceramics synthesis was carried out via homogeneous crystallization followed by interfacial-controlled growth. Glass-ceramics synthesis at 530–580°C led to nucleation of Li<sub>2</sub>Ge<sub>4</sub>O<sub>9</sub> и Li<sub>2</sub>ZnGeO<sub>4</sub> nanocrystals with narrow luminescence of a doublet structure at 667 nm, corresponding to Mn<sup>4+</sup> ions. In the composition containing 20 mol. % ZnO, the spectrum was dominated by a broad band with a maximum in the region of 540 nm, which was characteristic of Mn<sup>2+</sup> ions in a tetragonal environment.

Glass-ceramics synthesized at 640°C and more possessed nucleation of Li<sub>2</sub>Ge<sub>4</sub>O<sub>9</sub> и Li<sub>2</sub>Ge<sub>7</sub>O<sub>15</sub> and two luminescence bands at 540 and 667 nm simultaneously. At low concentrations of ZnO, the spectrum is dominated by the band at 667 nm, which was characteristic of Mn<sup>4+</sup> ions. With an increase in the concentration of zinc oxide, the intensity of this band decreased with a simultaneous increase in the intensity of the band at 540 nm, corresponding to Mn<sup>2+</sup> ions. So, the final intensity ratio of different Mn luminescence bands depended on the Li/Zn ratio in the glass composition.

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# Structure and luminescence properties of Dy<sup>3+</sup> doped Li<sub>3</sub>Ba<sub>2</sub>Gd<sub>3</sub>(WO<sub>4</sub>)<sub>8</sub> tungstate for applications in wLEDs

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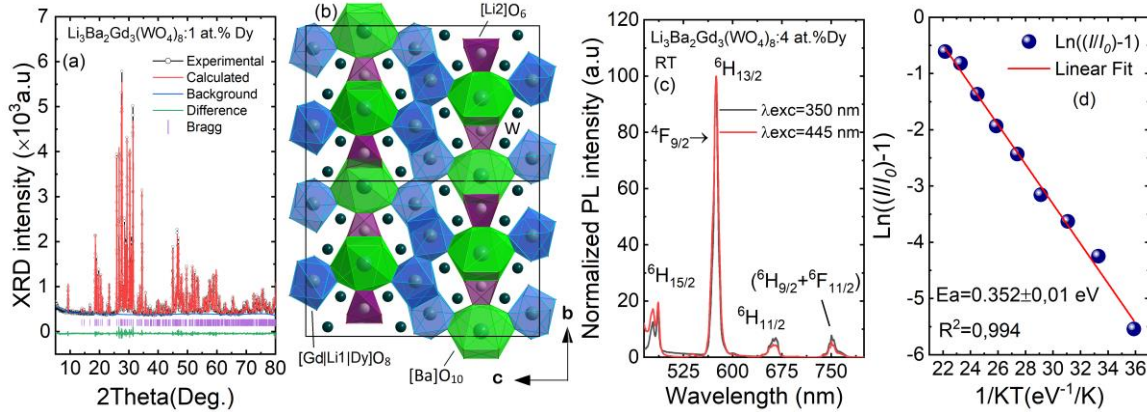
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Recently, efforts have continually been made to realize solid-state lighting devices based on white light-emitting diodes (wLEDs). The approach of combining yellow phosphors and blue InGaN diodes is widely used to achieve white light. Among the activator RE<sup>3+</sup> ions, dysprosium ions (Dy<sup>3+</sup>) are attractive for achieving yellow emission. The <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>13/2</sub> and <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>15/2</sub> transitions of Dy<sup>3+</sup> fall in the yellow and blue spectral ranges, respectively, of which the <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>13/2</sub> one is known to be hypersensitive to the crystal field [1]. In this work, yellow emitting tungstate phosphors with composition Li<sub>3</sub>Ba<sub>2</sub>Gd<sub>3</sub>(WO<sub>4</sub>)<sub>8</sub> doped with different concentrations of Dy<sup>3+</sup> (from 1 to 10 at.%) were prepared by the solid-state reaction method at 900°C. Their structural (fig.1(a) and (b)), spectroscopic and optical properties were studied systematically in this work.. The identified broad, and strong excitation peak at 450 nm indicates that Li<sub>3</sub>Ba<sub>2</sub>Gd<sub>3</sub>(WO<sub>4</sub>)<sub>8</sub>:Dy phosphors are suitable to be pumped by a blue laser diode (LD). Under excitation at 445 nm, the phosphor showed a stronger yellow emission peak at 575 nm which corresponds to the Dy<sup>3+</sup>: <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>13/2</sub> transition, fig.1(c).



**Fig. 1** (a) Rietveld refinement of Li<sub>3</sub>Ba<sub>2</sub>Gd<sub>3</sub>(WO<sub>4</sub>)<sub>8</sub>: 1 at. % Dy; (b) crystal structure of Li<sub>3</sub>Ba<sub>2</sub>Gd<sub>3</sub>(WO<sub>4</sub>)<sub>8</sub>: Dy along b-c crystallographic axis; (c) luminescence spectra of Li<sub>3</sub>Ba<sub>2</sub>Gd<sub>3</sub>(WO<sub>4</sub>)<sub>8</sub>: 4at. % Dy under 350 and 450 nm excitations; (d) activation energy graph for thermal quenching of 4 at.% Dy<sup>3+</sup> doped quaternary tungstate.

The activation energy of thermal suppression was calculated to be  $0.352 \pm 0.01$  eV, fig.1(d). The measured absolute photoluminescence quantum yield was around 10.5%. The results presented in this work show that Li<sub>3</sub>Ba<sub>2</sub>Gd<sub>3</sub>(WO<sub>4</sub>)<sub>8</sub>: Dy<sup>3+</sup> phosphors with strong yellow emission can be promising candidates for white-light emitting LED (wLED) applications.

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# Optical thermometry properties of a novel quaternary tungstate $\text{Li}_3\text{Ba}_2\text{Gd}_3(\text{WO}_4)_8$ : Ho, Tm

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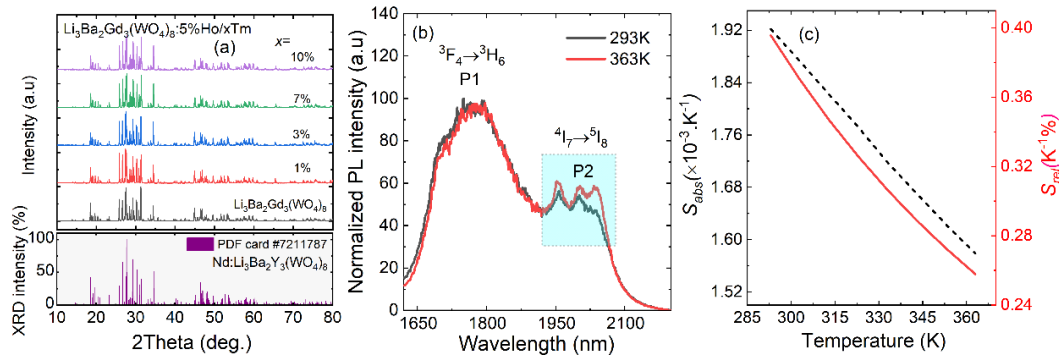
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In luminescence thermometry, the temperature is determined from the changes in the fluorescence measurement. Indeed, there are several temperature-dependent parameters that can be taken into account, such as the fluorescence intensity ratio (FIR), changes in the emission peak and the fluorescence lifetime. In recent years, temperature detection using upconversion luminescence (UC) of trivalent lanthanide ions ( $\text{Ln}^{3+}$ ), such as thulium ions ( $\text{Tm}^{3+}$ ) and holmium ions ( $\text{Ho}^{3+}$ ), has received much attention. This method is founded on the temperature dependence of the FIR of two thermally coupled energy levels, and thus it allows non-contact temperature sensing [1].

In this work, we succeeded in synthesizing new monoclinic microcrystals of quaternary tungstates  $\text{Li}_3\text{Ba}_2\text{Gd}_3(\text{WO}_4)_8$ :  $\text{Ho}^{3+}$ ,  $\text{Tm}^{3+}$  using the modified sol-gel method of Pechini. The purity of obtained phase was confirmed by XRD, fig.1(a). The obtained microparticles show an irregular shape with a size of about 0.6  $\mu\text{m}$ . The photoluminescence spectrum in the short-wavelength infrared (SWIR) region of the obtained microcrystals, excited at 808 nm, shows two main bands attributed to electronic transitions:  $^3\text{F}_4 \rightarrow ^3\text{H}_6$  (1774 nm, P1) of  $\text{Tm}^{3+}$  and  $^5\text{I}_7 \rightarrow ^5\text{I}_8$  (2037 nm, P2) of  $\text{Ho}^{3+}$ , fig.1(b).



**Fig. 1** (a) X-ray diffraction (XRD) patterns of  $\text{Li}_3\text{Ba}_2\text{Gd}_3(\text{WO}_4)_8$ :5 at.%Ho, x at.%Tm with different doping concentration of  $\text{Tm}^{3+}$  ions (1, 3, 7 and 10); (b) Emission spectra of  $\text{Li}_3\text{Ba}_2\text{Gd}_3(\text{WO}_4)_8$ : 5 at.%Ho, x at.%Tm under excitation at 808 nm at temperatures of 293 and 363 K; (c) Absolute ( $S_{\text{abs}}$ ) and relative ( $S_{\text{rel}}$ ) sensitivities as a function of temperature from 285 to 370 K for  $\text{Li}_3\text{Ba}_2\text{Gd}_3(\text{WO}_4)_8$ : 5 at.%Ho, 10 at.%Tm

The FIR P2/P1 increase with temperature due to thermally coupled levels. The relative  $S_{\text{rel}}$  and absolute  $S_{\text{abs}}$  sensitivities were evaluated, fig.(c).  $S_{\text{rel}}$  was at a maximum of 0.39  $\% \cdot \text{K}^{-1}$  at Room temperature of 293K. The repeatability of the measurement was examined by the relative standard deviation and cycle test. The temperature resolution  $\delta T$  parameter is 2.27 at 298K and it's increased to 3.49K at 363K. All these results reveal the potential application of  $\text{Li}_3\text{Ba}_2\text{Gd}_3(\text{WO}_4)_8$ :  $\text{Ho}^{3+}$ ,  $\text{Tm}^{3+}$  microparticles for optical thermometry.

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# **Spectral Imaging of cultural assets using newly developed fluoride ultraviolet optics**

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Spectroscopic techniques are attracting attention as a non-destructive method of analyzing cultural assets. Here, we introduce a new approach to survey cultural assets using imaging spectroscopy. Our study is expected to bring a new perspective on the background of these cultural assets.

# Optical and luminescence investigation of barium borate doped with Ce<sup>3+</sup> under ultraviolet (UV) excitation for scintillating glasses

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**Abstract.** The melt quenching approach has been used to create Ce<sup>3+</sup>-doped barium borate glasses with varying CeF<sub>3</sub> and B<sub>2</sub>O<sub>3</sub> concentrations. The CeF<sub>3</sub>-doped 10La<sub>2</sub>O<sub>3</sub>-20BaO-(70-x) B<sub>2</sub>O<sub>3</sub>: xCeF<sub>3</sub> scintillating glasses are characterized by their physical, structural, optical, and luminescence characteristics, and the best CeF<sub>3</sub> concentration is determined to be 0.0-3.0 %mol. Systematically, the effect of CeF<sub>3</sub> on the performance of glass, including its density, absorption, and luminescence properties under ultraviolet (UV) excitation, was investigated. The findings indicated that an increase in CeF<sub>3</sub> concentrations led to an increase in the density of the glasses while simultaneously leading to a decrease in the molar volume. In the photoluminescence (PL) spectra, a broad emission band was seen to have a maximum peaking of about 385 nm. This band was ascribed to 5d-4f transitions of Ce<sup>3+</sup> ions, and it was observed that these transitions occurred. The optimal doping concentration of CeF<sub>3</sub> contents is 0.5 mol%. The Ce<sub>LIII</sub>-edge X-ray absorption near-edge structure analysis shows that the Ce<sup>3+</sup> increases with increasing CeF<sub>3</sub> concentration, which indicates that the starting material.

**Keyword:** Borate glass, Ce<sup>3+</sup>, Optical properties, Photoluminescence.



# Terahertz time domain ellipsometry and its application in wide-bandgap semiconductors characterization

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Terahertz ellipsometry is an emerging characterization technique to study the dielectric and conductivity properties of various materials. The terahertz region refers to the frequency band between the millimeter and infrared waves of the electromagnetic spectrum, and in this region many low-energy excitations are present such as phonons, plasmons, magnon and rotational transitions [1-5]. The carrier dynamics that occur at terahertz frequencies also elucidate the optical properties of materials. Hence, terahertz investigations are employed in studying next-generation materials such as wide-bandgap semiconductors and other functional materials [1-3].

In terahertz ellipsometry the material properties are probed by irradiating polarized terahertz pulses and then measuring the change in the polarization state of the reflected waves. Figure 1a shows the schematic diagram of the Tera Evaluator terahertz time-domain ellipsometer (Nippo Precision Co., Ltd.) that is capable of highly precise measurements [1]. Figures 1b and 1c show the real and imaginary parts of the refractive index spectra of wide-bandgap GaN single crystals with different conductivities obtained by terahertz ellipsometry. From the refractive index, the free-carrier properties such as the carrier concentration and mobility are extracted by fitting to the Drude optical conductivity model. We demonstrate that terahertz ellipsometry is a practical tool for materials characterization owing to its non-contact and non-destructive approach. At the presentation, we will show the experimental results for GaN,  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, ZnO, and SiC.

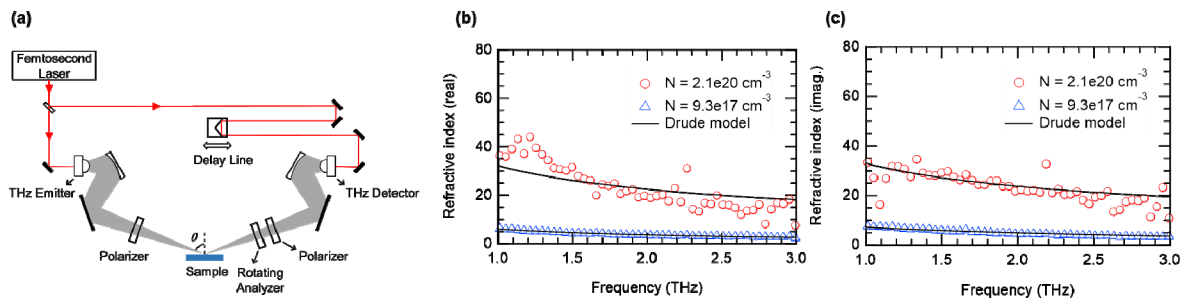


Figure 1. (a) Experimental setup and (b,c) real and imaginary parts of the refractive index spectra of GaN single crystals with different carrier concentrations  $N$ .

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# Rare earth-diamond hybrid structures for optical quantum technologies

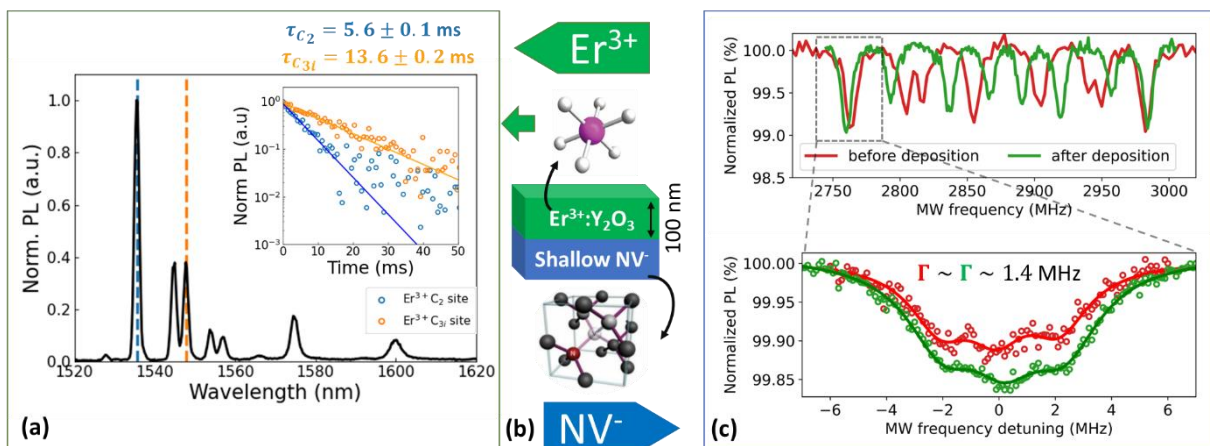
**I. G. Balasa<sup>1</sup>, M.A. Arranz-Martinez<sup>1</sup>, P. Perrin<sup>1</sup>, M. Ngandeu Ngambou<sup>2</sup>, D. Serrano<sup>1</sup>, J. Achard<sup>2</sup>, A. Tallaire<sup>1</sup>, P. Goldner<sup>1</sup>**

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The challenge of developing hybrid quantum materials aims to associate distinct optically active centers to achieve new functionalities while preserving the underlying properties of each component. In this work, we combine two optically active materials that have been broadly used for quantum applications and are compatible with scalable fabrication techniques: shallow NV<sup>-</sup> color centers in diamond [1] and rare earth (RE) ions in thin films [2]. Here, we present a hybrid structure sketched in Fig. (b) that consists of an Er<sup>3+</sup> doped Y<sub>2</sub>O<sub>3</sub> thin film deposited by direct liquid injection chemical vapor deposition (CVD) on a diamond substrate in which shallow NV<sup>-</sup> were implanted. We investigate the crystallinity of the thin film and the optical properties of the embedded Er<sup>3+</sup> ions, and how the spin and optical properties of the NV<sup>-</sup> are affected by the thin film. The photoluminescence spectrum of the <sup>4</sup>I<sub>13/2</sub>-<sup>4</sup>I<sub>15/2</sub> Er<sup>3+</sup> transition measured at 10 K is reported in Fig. (a) and confirms that Er is in the trivalent configuration in the cubic phase of Y<sub>2</sub>O<sub>3</sub>. The inset of Fig. (a) also presents the decays of the two Er occupational sites in Y<sub>2</sub>O<sub>3</sub>: C<sub>2</sub> and C<sub>3i</sub>, measured at 10 K. The obtained decay times are 5.6 ± 0.1 ms and 13.5 ± 0.2 ms respectively and are comparable to bulk crystal references (8.5 ms and 14.6 ms [3]) thus proving that no major non-radiative or quenching effects arise in the nanostructured thin film. Optical and spin properties of the NV<sup>-</sup> before and after the thin film deposition are reported in Fig. (c). The top of Fig. (c) presents a wide optically detected magnetic resonance (ODMR) spectrum where the 8 peaks correspond to the degeneracy lift due to 4 distinct projections of the applied magnetic field on the NV axis for two different spin projections (m<sub>s</sub>=±1). The bottom part of Fig. (c) is a zoom into one of the spin transitions indicating a constant linewidth around 1.4 MHz, before or after deposition. The spin properties of the NV<sup>-</sup> at the diamond/film interface have thus not been altered. In conclusion, this is a first proof of the possibility of integrating the rare-earth ions with NV<sup>-</sup> centers at the nanoscale level for developing hybrid solid state quantum systems.



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# Inorganic nanoparticles based on rare earth elements for advanced applications

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The exceptional luminescence properties and specific electronic structure make lanthanide ions ( $\text{Ln}^{3+}$ ) excellent candidates for different applications, e.g., in radiotherapy as sensitizers. Sharp, intense, and well-defined emission bands related to the f-f transitions, the tunable color of the luminescence, and different excitation wavelengths enable the creation and produce materials that can prevent falsifying important documents or identify cancer cell bioimaging [1–3]. Inorganic matrices based on fluorides are ideal for lanthanide ions' doping due to their relatively low phonon energy, which enables them to avoid luminescence quenching. For this reason, nanomaterials based on fluorides doped with  $\text{Yb}^{3+}/\text{Er}^{3+}$ ,  $\text{Tm}^{3+}$ , and  $\text{Ho}^{3+}$  were used to modify the Lyocell cellulose fibers and paper [4]. It resulted in a different luminescence color, including green, red, or blue emission activated by NIR and UV excitation. Furthermore, this type of modification enables to produce the luminescent markers for documents and goods protection against counterfeiting. Moreover, the core@shell type nanoparticles based on  $\text{NaYF}_4$  fluoride matrix doped with suitable pairs of  $\text{Ln}^{3+}$  ions can show bright emission, around 800 nm, under 975 nm excitation, but also under 1532 nm. This type of luminescence highlights the unique and universal properties of  $\text{Ln}^{3+}$  for designing luminescent nanoparticles for various potential applications, such as confocal microscopy [2].

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# Optical modulation and humidity sensing performance of Tb:Ce complex inhibited polymeric nanofibres

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In the present work we carried out systematic study on optical alteration in Tb:Ce(Sal)<sub>3</sub>Phen, Eu(DBM)<sub>3</sub>Phen complexes inhibited in polyvinyl alcohol (PVA) polymeric nanofibres, while assembled in stacked formation. We report the feasibility of Tb:Ce(Sal)<sub>3</sub>Phen and Eu(DBM)<sub>3</sub>Phen complex dispersed electrospun nanofibres for humidity sensor. Structural, morphological and spectroscopic properties of the synthesized nanofibres were systematically compared using Fourier transform infrared spectroscopy, scanning electron microscopy and Photoluminescence analysis. Synthesized Tb:Ce(Sal)<sub>3</sub>Phen and Eu(DBM)<sub>3</sub>Phen complexes inhibited in nanofibres yields characteristic vivid green emission of Tb<sup>3+</sup> and red emission from Eu<sup>3+</sup> under UV excitations. The presence of Ce<sup>3+</sup> ions alongwith the salicylate ligand and Tb<sup>3+</sup> ion a help to expand the absorption range (290 nm-400 nm) subsequently the emission in blue and green regions. Our analysis revealed the linear enhancement of emission intensity with addition of Ce<sup>3+</sup> ions. The stacking of different layers of complexes reveal the precise control over the color alteration simply by adding layers, without compromising emission intensity due to interaction between the active ions. Upon exposing the flexible Tb:Ce(Sal)<sub>3</sub>Phen and Eu(DBM)<sub>3</sub>Phen complexes dispersed nanofibres mat in different humidity environments, photoluminescence emission intensity shows a linear variation. The prepared nanofibres film shows a good reversibility, small hysteresis, cyclic stability and acceptable response and recovery times i.e. 35 and 45 seconds. The humidity sensing mechanism was proposed on the basis of infrared absorption analysis of dry and humid nanofibres. The detailed colour analysis and photophysics of the observed results will discuss in detail.

# Growth, scintillation properties, pulse shape discrimination capability of (Ca,Sr)I<sub>2</sub>:Eu scintillator

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Inorganic scintillators are widely used in underground astroparticle physics experiments, such as dark matter searches and neutrino-less double beta decay. In the searches for neutrino-less double beta decay ( $0\nu\beta\beta$ ), scintillators are required to have a high energy resolution in order to distinguish between the mono-energetic electron pairs produced by  $0\nu\beta\beta$  and the continuous-energy electron pairs produced by  $2\nu\beta\beta$ . The main advantage of scintillators containing  $^{48}\text{Ca}$  is that  $^{48}\text{Ca}$  has the highest Q value (4.3 MeV) of the  $0\nu\beta\beta$  candidate isotopes. Good particle identification performance of the scintillator is also very important to discriminate the electron pairs produced by  $0\nu\beta\beta$  from the environmental background. We have successfully grown single crystal  $\text{CaI}_2$  scintillators and have reported high light yield of 107,000 ph/MeV and excellent pulse shape discrimination (PSD) capability [1, 2]. However,  $\text{CaI}_2$  is known to exhibit strong cleavage along the c-plane, which has made it difficult to enlarge the size of the crystal and caused the degradation of energy resolution. In this study, undoped / Eu-doped (Ca,Sr)I<sub>2</sub> with Sr substitution at the Ca site of  $\text{CaI}_2$  was grown and evaluated with the aim of reducing the cleavage feature of  $\text{CaI}_2$ .

Crystal growth was performed using vertical Bridgman-Stockbarger method in quartz ampoules (inner diameter: 6 and 8 mm). Some of the results obtained in this study are shown in Figure 1. The Sr substitution shifted the powder X-ray diffraction (XRD) peaks of the  $\text{CaI}_2$  phase to the low-angle side. Scintillation light yield remained above 95,000 ph/MeV even with 20% Sr substitution. PSD performance will also be reported in this presentation.

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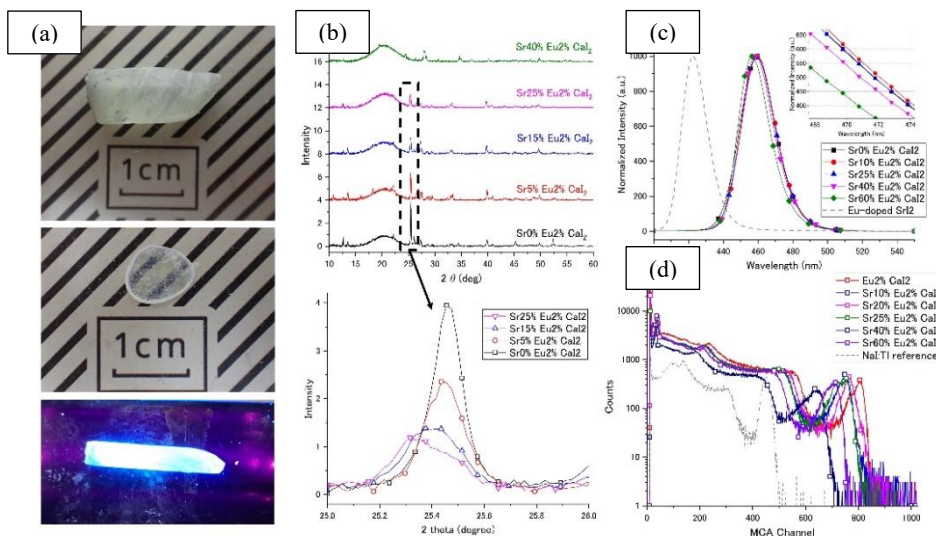


Fig.1 (a) Photographs, (b) powder XRD results, (c) X-ray radioluminescence, and pulse height spectra of  $^{137}\text{Cs}$  for the grown (Ca,Sr)I<sub>2</sub>:Eu single crystals

# Optical and Scintillation Properties of Pr<sup>3+</sup>-Doped (La, Y)<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> Single Crystals

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**1. Introduction** Pr<sup>3+</sup>-doped materials are promising candidates for scintillator applications because of their fast 5d<sub>1</sub>-4f emission in wide bandgap host materials with medium- or high-crystal field strength. As for the study of Pr<sup>3+</sup>-doped scintillators, single crystal growth and optical characterization of scintillators with garnet-structure, e.g. Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> and Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>, and pyrochlore-structure, e.g. Lu<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>, have been performed [1-3]. These studies have shown that Pr<sup>3+</sup> 5d<sub>1</sub>-4f emission has faster decay time compared to Ce<sup>3+</sup> 5d<sub>1</sub>-4f emission, which would be suitable for applications requiring high timing resolution, for example time-of-flight positron emission tomography (TOF-PET). In this study, we focused on Pr<sup>3+</sup>-doped (La,Y)<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> to develop novel Pr<sup>3+</sup>-doped scintillators, and carried out single crystal growth and characterization.

**2. Materials and Methods** The crystal growth was performed using micro-pulling-down ( $\mu$ -PD) method [4]. As starting materials, we used Y<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, Pr<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> powders with a purity of more than 99.99%. The crystal structure of the grown crystals was estimated by the powder X-ray diffraction analysis. In addition, the photoluminescence (PL) excitation and emission spectra and scintillation properties such as the light outputs and decay times were evaluated.

**3. Results** The crystals grown by  $\mu$ -PD method are illustrated in Figure 1. We were succeeded in growing transparent (Pr<sub>x</sub>La<sub>0.600</sub>Y<sub>0.400-x</sub>)<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> (x = 0.001-0.020) crystals. After cutting and mirror polishing to 1 mm thickness, the PL excitation and emission spectra were measured. From the PL emission spectra, the typical broad emission due to the Pr<sup>3+</sup> 5d<sub>1</sub>-4f transitions was observed in the wavelength range of 250-340 nm (Figure 2). These emission peaks were identified as 5d<sub>1</sub>-<sup>3</sup>H<sub>4</sub>, -<sup>3</sup>H<sub>5</sub>, -<sup>3</sup>H<sub>6</sub>, -<sup>3</sup>F<sub>3,4</sub> transitions, respectively, from the short wavelength side. Details of the optical and scintillation properties of Pr<sup>3+</sup>-doped (La,Y)<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> crystals will be presented.

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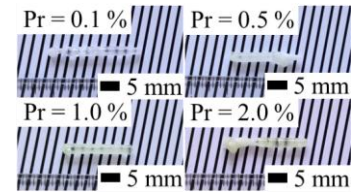


Fig. 1 Photograph of the grown Pr:(La, Y)<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> crystals.

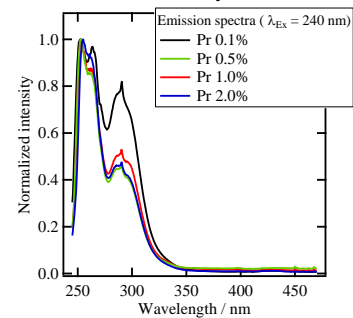


Fig. 2 PL emission spectra of Pr:(La, Y)<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>.

# Crystal Growth and Optical Properties of Ce-doped (Gd, Y, Tb)<sub>3</sub>Ga<sub>3</sub>Al<sub>2</sub>O<sub>12</sub> Scintillators for X-ray Imaging

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Akihiro YAMAJI<sup>b), c)</sup>, Takashi HANADA<sup>b)</sup>, Yuui YOKOTA<sup>b)</sup>,  
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**Introduction** Scintillators are widely used in X-ray imaging, which are applied for medical diagnostics and airport security controls. To obtain images with excellent contrast in short exposure times, scintillators are required to have high density and light yield. Recently, it has reported that substituting ternary by quaternary garnet in the matrix material dramatically improves the light yield of Ce- and Tb-doped scintillators. Korzhik et al. estimated a very high light yield of 200,000 ph/MeV for Tb-doped (Gd, Y)<sub>3</sub>Ga<sub>3</sub>Al<sub>2</sub>O<sub>12</sub> (GYAGG:Tb) ceramics [1]. However, single crystals of GYAGG:Tb has not been reported. In this study, we report on the growth of GYAGG:Ce, Tb single crystals using the micro-pulling-down method and the evaluation of their scintillation properties and imaging performances.

**Materials and Methods** As starting materials, CeO<sub>2</sub>, Tb<sub>4</sub>O<sub>7</sub>, Gd<sub>2</sub>O<sub>3</sub>, 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 with a purity of 99.99% were used and weighed in stoichiometric composition. Ce 0.5% doped GYAGG:Tb crystals were grown by the micro-pulling-down ( $\mu$ -PD) method [2]. The Tb concentrations were varied at 0.5, 5.0, 10.0, and 15.0 mol%.

**Results** The crystals grown by  $\mu$ -PD method are shown in Fig. 1. We were succeeded in growing transparent GYAGG:Ce, Tb crystals. In the photoluminescence (PL) emission spectra (Fig. 2), the typical emission spectra associated with the Ce<sup>3+</sup> 5d<sub>1</sub>-4f transition and Tb<sup>3+</sup> 4f-4f transition were simultaneously observed in GYAGG:Ce, Tb crystals. The results of scintillation properties and X-ray imaging tests will be presented.

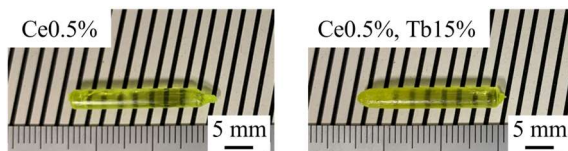


Fig. 1 Photograph of the grown GYAGG:Ce, Tb crystals

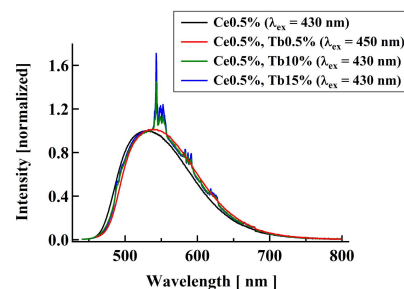


Fig. 2 PL Emission spectra of GYAGG:Ce, Tb crystals

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# Er<sup>3+</sup>-doped CaF<sub>2</sub> nanocubes: Synthesis and optical characterization

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Fluoride nanoparticles activated with trivalent lanthanide ions (Ln<sup>3+</sup>) are arousing great interest in applications that demand efficient luminescent transitions and, therefore, high quantum efficiency values. Additionally, it is also common that the application needs of high emission intensities, only achievable if a large number of optical centers is available [1]. However, it is not easy to simultaneously satisfy both requirements and, in general, a compromise between quantum efficiency and high values of active ion densities must be sought.

The population dynamics in Ln<sup>3+</sup>-doped nanoparticles (NPs) is in general complex, being strongly dependent on the active ion concentration. In diluted NPs the population dynamics is governed by radiative and non-radiative transitions, while in high concentrated NPs the situation is clearly different: As the active ion concentration increases, the spontaneous transitions start to compete with ion-ion interactions (energy migration and cross relaxation processes). These loss mechanisms, usually known as concentration quenching processes, are usually appreciable under CW and pulsed excitation conditions. Additionally, when lifetime measurements are performed, there is another important aspect that should be under consideration: the possibility of radiation trapping; that is, the reabsorption of the emitted radiation.

In this work, CaF<sub>2</sub>:Er<sup>3+</sup> NPs with variable dopant concentration were synthesized by a direct precipitation method [2]. X-Ray Powder Diffraction, SEM and TEM have been used to analyze the particle crystalline structure and morphology. The basic spectroscopy of Er<sup>3+</sup> ions has been studied under CW and pulsed excitation as function of the dopant level. The dependence of the emission intensity of the main emission bands reveals the presence of luminescence quenching processes. The dynamics of the emitting manifolds, recorded under pulsed excitation, has confirmed the presence of these processes together with the existence of radiation trapping. A treatment, commonly used in bulk doped materials, has been applied to determine the intrinsic total transition probabilities of the main erbium emitting levels in absence of quenching and radiation trapping. The intrinsic total transition probability of <sup>4</sup>I<sub>13/2</sub> level has been used to perform a modified Judd-Ofelt analysis. Finally, the non-radiative transition probabilities of <sup>4</sup>I<sub>11/2</sub>, <sup>4</sup>F<sub>9/2</sub> and <sup>2</sup>H<sub>11/2</sub>:<sup>4</sup>S<sub>3/2</sub> levels, calculated from the intrinsic transition probabilities and the radiative ones, has allowed to determine the gap law in the CaF<sub>2</sub>:Er<sup>3+</sup> NPs.

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# Tracer-based sorting with lanthanide-activated phosphors for plastics recycling

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In 2018, the EU agreed on ambitious targets: to increase the reuse and recycling of plastic waste to 50% by 2025 and 55% by 2030, compared to 35% in 2020. A new tracer-based sorting (TBS) of plastics is complementary to existing near-infrared sorting and can significantly improve the sorting of bulk end-of-life plastics from industrial and municipal waste. A key element of the TBS technology is different sorting codes based on luminescent tracers with specific excitation/emission spectral lines and high photoluminescence quantum yield. Unique properties of lanthanide ( $\text{Ln}^{3+}$ ) luminescence, such as large Stokes and anti-Stokes shifts, high signal-to-noise ratio, high resistance to photo- and photochemical degradation, availability of cheap NIR laser diodes for excitation, sharp emission lines make them promising as photonic tracers for plastics recycling [1,2].

In our work, we present examples of the  $\text{Ln}^{3+}$  luminescent tracers used in the TBS process and explain a new way to distinguish between different types of packaging materials (e.g., food grade and non-food grade polyolefin packaging).

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# Growth and scintillation properties of $\text{LaCl}_3/{}^6\text{LiCl}/\text{SrCl}_2$ ternary eutectic for thermal neutron detection

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<sup>d)</sup> C&A corporation, Japan.

[Background] Thermal neutron detectors are widely used in a variety of fields, including homeland security, boron neutron capture therapy, and astrophysics. The basic principle of thermal neutron detection is to convert thermal neutrons to low-energy radiation using  ${}^3\text{He}$ ,  ${}^6\text{Li}$ ,  ${}^{10}\text{B}$ , and  ${}^{113}\text{Cd}$  [1]. Recently, increasing demand and supply disruptions have limited the use of  ${}^3\text{He}$  gas, pointing to the need for the development of inorganic solid scintillators for thermal neutron detection. Indeed, several new single-crystal scintillators for neutron detection have been reported in the past decade. Among them,  $\text{LiCaAlF}_6$  (LiCAF) is the most promising candidate for  $\text{LiCaAlF}_6$ -based single-crystal scintillators because it contains  ${}^6\text{Li}$  in its host lattice and has the ability to discriminate between neutron and gamma-ray pulse shapes [2]. However, being chemical compound, the  ${}^6\text{Li}$  content is limited by the chemical formula and cannot be increased. Therefore,  ${}^6\text{Li}$ -containing eutectic materials such as  $\text{LiF}/\text{CaF}_2$ ,  $\text{LiF}/\text{LaF}_3$ ,  $\text{LiCl}/\text{CeCl}_3$ ,  $\text{LiCl}/\text{Li}_2\text{SrCl}_4$ ,  $\text{LiCl}/\text{BaCl}_2$ ,  $\text{LiBr}/\text{CeBr}_3$ ,  $\text{LiBr}/\text{LaBr}_3$ ,  $\text{CeCl}_3/\text{LiCl}/\text{CaCl}_2$ [3] etc. have been investigated to achieve higher neutron capture cross sections. In this study,  $\text{LaCl}_3/{}^6\text{LiCl}/\text{SrCl}_2$  ternary eutectic was investigated as a novel thermal neutron scintillator.

[Results] Ce and Eu doped  $\text{LaCl}_3/{}^6\text{LiCl}/\text{SrCl}_2$  ternary eutectic were grown by the VB method in a quartz ampoule with 4 mm inner diameter. Figure 1 shows a example photograph of the prepared Ce: $\text{LaCl}_3/{}^6\text{LiCl}/\text{SrCl}_2$  ternary eutectic plate cut from the grown eutectic rod. The eutectic plate showed slight transparency. Expected  $\text{LaCl}_3$ ,  ${}^6\text{LiCl}$  and  $\text{SrCl}_2$  phases were observed by powder XRD and BEI analysis. The Ce doped eutectic showed 360 nm emission ascribed to  $\text{Ce}^{3+}$  4f5d transition. Figure 2 shows the scintillation decay curve of the Ce: $\text{LaCl}_3/{}^6\text{LiCl}/\text{SrCl}_2$  ternary eutectic under  ${}^{252}\text{Cf}$  thermal neutron excitation. The decay time was 16.0 ns (87.3%) ,162.7 ns (12.7%). The light yield was 32,000 photons / neutron. The detailed growth method, eutectic structure, scintillator properties and pulse shape discrimination capability will be reported on the presentation.

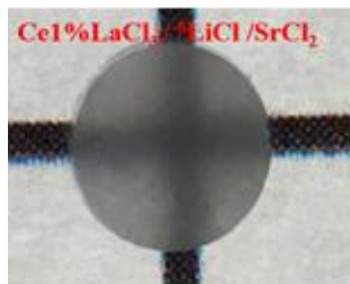


Fig. 1 A photograph of the eutectic plate.

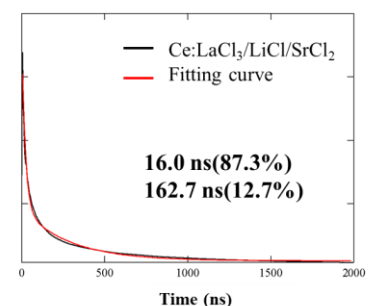


Fig. 2 Scintillation decay curve of the Ce doped eutectic.

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# A novel CeCl<sub>3</sub>/NaCl/SrCl<sub>2</sub> ternary eutectic scintillator for fast and high resolution radiation imaging applications

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**[Introduction]** Scintillators are used in a wide range of fields such as medicine as medical equipment including X-ray computed tomography and non-destructive testing. In these applications, sintered Tb:Gd<sub>2</sub>O<sub>2</sub>S powder and Tl:CsI whisker fabricated by vapor deposition are the most common scintillators, and the fineness of the arranged structure determines the position resolution. To realize high-resolution imaging, we have focused on phase-separated scintillator fibers (PSSFs), such as GAP/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> [1] and BaCl<sub>2</sub>/NaCl/KCl, CsI/CsCl/NaCl [2], have been proposed as new scintillator materials. Such scintillators can be obtained through the unidirectional solidification of the eutectic composition. For PSSFs, the scintillator phase with a high refractive index can be grown as a fiber-like structure in the growth direction. Higher sensitivity can be achieved with PSSFs compared to powdered or needle scintillators by increasing the thickness of the PSSFs. In this research, a novel ternary eutectic scintillator of CeCl<sub>3</sub>/NaCl/SrCl<sub>2</sub> was investigated.

**[Results]** In the CeCl<sub>3</sub>/NaCl/SrCl<sub>2</sub> eutectic, CeCl<sub>3</sub> with the highest refractive index was selected as the scintillator phase (CeCl<sub>3</sub>:2.2@380nm, NaCl:1.54@nD and SrCl<sub>2</sub>:1.65@nD). CeCl<sub>3</sub> was reported with its excellent scintillation such as high light yield (30,000 photons/MeV); and fast decay time with four components of 4.4 ns (6.6%), 23.2 ns (69.6%), 70 ns (7.5%) and >10  $\mu$ s (16.3%). The volume ratio of CeCl<sub>3</sub> : NaCl : SrCl<sub>2</sub> is 34.3 : 22.0 : 43.7 and calculated density of the eutectic is 3.17 g/cm<sup>3</sup>. Crystal growth was performed by the vertical Bridgman–Stockbarger method in a quartz ampoule with an inner diameter of 4 mm. Expected CeCl<sub>3</sub>, NaCl and SrCl<sub>2</sub> phases were observed by powder XRD analysis. The ampoule was pulled down at a rate of 0.2 mm/min. The grown eutectic was cut and polished to give optically transparent 1 mm thick samples (Fig. 1). The BEI image of the growth direction is shown in Fig. 2. Each phase appears to be uniformly dispersed and align along the growth direction. 360 nm emission was observed under X-ray irradiation and was ascribed as Ce<sup>3+</sup> 4f5d emission of CeCl<sub>3</sub>. Scintillation decay time was as fast as 6 ns (17.5%), 12 ns (29%) and 28ns (53.5%). Eutectic structure, luminescence properties and imaging test results will be shown in my presentation.

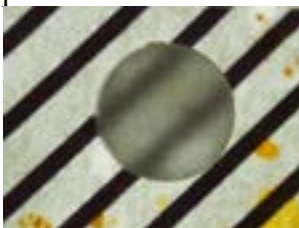


Fig. 1 A photograph of the eutectic plate.

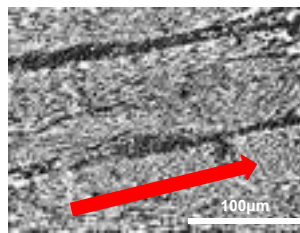


Fig. 2 BEI of the growth direction. (Red arrow indicate growth direction)

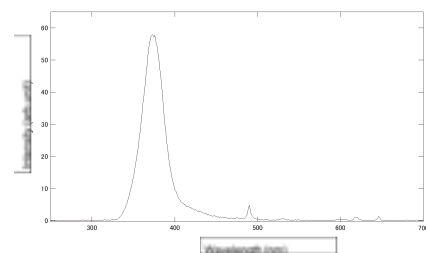


Fig. 3 Radioluminescence spectra of the eutectic under X-ray excitation

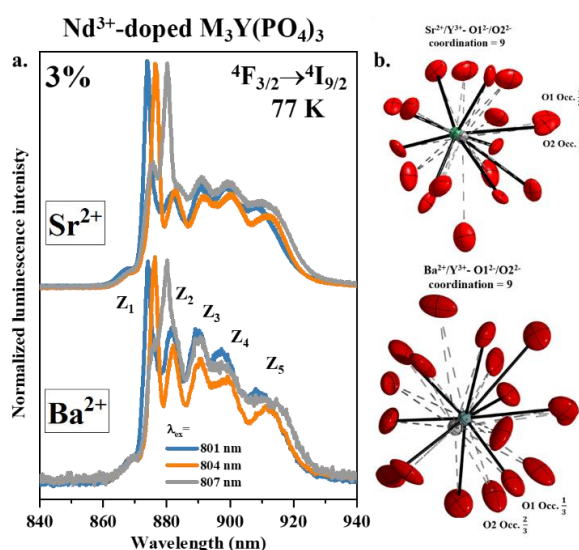
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# Structural and spectroscopic properties studies of perovskite-type cubic Nd<sup>3+</sup>-doped M<sub>3</sub>Y(PO<sub>4</sub>)<sub>3</sub> (M = Sr<sup>2+</sup> or Ba<sup>2+</sup>) solid-solution

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Considering perovskite-type cubic phosphates of chemical formula M<sub>3</sub>Y(PO<sub>4</sub>)<sub>3</sub> (M = Sr<sup>2+</sup> or Ba<sup>2+</sup>) as potential candidates to obtain new optical polycrystalline ceramics with high transparency, two series of eulytite-type Nd<sup>3+</sup>-doped Ba<sub>3</sub>Y(PO<sub>4</sub>)<sub>3</sub> and Sr<sub>3</sub>Y(PO<sub>4</sub>)<sub>3</sub> solid-solution were obtained. First, the relationship between their structure and spectroscopic properties as well as the effect of the size of divalent Sr<sup>2+</sup>/Ba<sup>2+</sup> cation creating a network was investigated in detail. The samples were synthesized *via* the conventional high-temperature solid-state reaction method. All the obtained materials are mono-phase and crystallize in the cubic system (s.g.  $I\bar{4}3d$ , No. 220).



Site selective luminescence spectra of 3% Nd<sup>3+</sup>-doped M<sub>3</sub>Y(PO<sub>4</sub>)<sub>3</sub> (M=Sr<sup>2+</sup>, Ba<sup>2+</sup>) at 77 K (a) and coordination of Y<sup>3+</sup>/Ba<sup>2+</sup> and Y<sup>3+</sup>/Sr<sup>2+</sup> cations by possible O<sup>2-</sup> anions (b).

Furthermore, the crystal structure of Ba<sub>3</sub>Y(PO<sub>4</sub>)<sub>3</sub> and Sr<sub>3</sub>Y(PO<sub>4</sub>)<sub>3</sub> was solved based on the small single crystals selected from micro-crystalline powders. In such a cubic structure, the M<sup>2+</sup>/Y<sup>3+</sup> cations are randomly disordered on a single crystallographic site with C<sub>3</sub> point symmetry. The Nd<sup>3+</sup> ions reside at the Y<sup>3+</sup> symmetry site but partial substitution of Ba<sup>2+</sup> or Sr<sup>2+</sup> sites cannot be excluded. Studied phosphates show not only cation disorder but also disorder in the oxygen sublattice, which is reflected in their spectroscopic properties. The multisite character and the inhomogeneous distribution of Nd<sup>3+</sup> in both types of materials, determined using absorption at 4.2K and laser-excited site-selective spectroscopy at 77K, are also clearly seen in the excited state dynamics of

<sup>4</sup>F<sub>3/2</sub> doublet analysis. The samples activated up to 20 mol% demonstrated a weak concentration quenching process and a greater order for the barium host lattice.

## Acknowledgments:

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# Fabrication of Mach-Zehnder interferometer structures based on low-cost SiO<sub>2</sub>:TiO<sub>2</sub> optical platform for integrated photonics applications

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A new construction of Mach-Zehnder interferometer based on a sol-gel SiO<sub>2</sub>-TiO<sub>2</sub> (silica-titania) material platform is proposed. According to the current experience on this topic [1,2], the silica-titania waveguide platform proves its advantage due to low cost, low loss, and easy-to-develop integrated optics systems. The integrated photonic circuits studied here were obtained for very attractive optical platforms: Si/SiO<sub>2</sub> and Si/SiO<sub>2</sub>/SiO<sub>2</sub>:TiO<sub>2</sub>. The SiO<sub>2</sub>:TiO<sub>2</sub> thin films were deposited *via* a sol-gel dip-coating method. Such systems, modelled in detail are capable of operating from visible to near-IR wavelength ranges. The Mach-Zehnder configurations investigated in this work are attractive for on-chip sensing devices. Fabricating highly effective and economical photonic devices of such is the final purpose of discussed research.

The study is organized into two parts. In the first part, a detailed investigation of photolithography parameters' is presented. The determination of best factors such as UV exposure dose, development time or hard-baking temperature was very important. The search for the best parameters was aimed at obtaining continuous, defect-free, well-separated waveguides (WG) of Mach-Zehnder structures with specific separation between WGs. In the second part, the results of etching silica-titania waveguiding structures, based on optimized lithographic patterns, are presented. The fabrication of Mach-Zehnder WG structures on SiO<sub>2</sub>-TiO<sub>2</sub> films was well-controlled by etch rate of the samples by utilizing dry etching technique - inductively coupled plasma reactive-ion etching (ICP-RIE). The first results showed faster and more efficient etching for silica-titania films supported on Si/SiO<sub>2</sub> substrates in comparison to already studied glass substrates.

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## Acknowledgments

The research was co-financed by the Foundation for Polish Science from the European Regional Development Fund within the project POIR.04.04.00-00-14D6/18 "Hybrid sensor platforms for integrated photonic systems based on ceramic and polymer materials (HYPHa)" (TEAM-NET program).

# Application of hard metal (Al, Cu, Cr) masks for dry etching of sol-gel-derived silica-titania photonic structures

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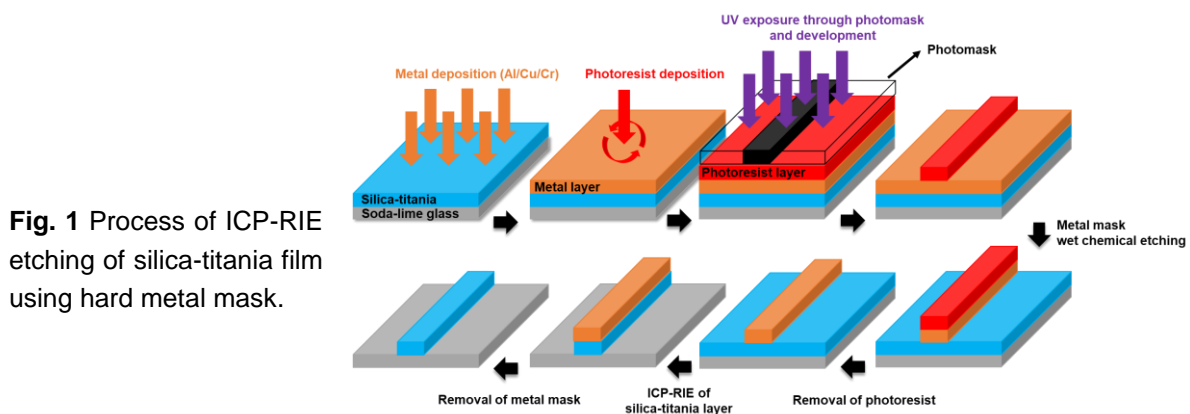
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Inductively coupled plasma reactive ion etching (ICP-RIE), despite being known for a long time, is still used for etching a variety of different materials to obtain photonic devices. Films based on silica-titania, fabricated using both sol-gel and dip-coating methods are promising materials for this application due to their relatively low optical losses, stability over time and low fabrication costs [1]. However, the main challenge in this field is obtaining high dimensional control and high overall quality (e.g. roughness of waveguides' sidewalls) of photonic structures in nanoscale.

In this work we present utilization of ICP-RIE method for fabrication of the optical waveguide structures in the SiO<sub>2</sub>-TiO<sub>2</sub> films formed using sol-gel synthesis and dip-coating method on soda-lime glass substrates. Instead of implementation of an organic photoresist mask for ICP-RIE, three different types of metal mask – aluminium (Al), copper (Cu) and chromium (Cr) were used. The technological process is schematically presented in the Figure 1. Quality of the obtained waveguides was compared to structures obtained in similar process but with the photoresist masking layer instead of metal. It was found that application of the hard metal mask could improve the quality of the etching, especially the roughness of waveguides' sidewalls.



**Fig. 1** Process of ICP-RIE etching of silica-titania film using hard metal mask.

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The research was co-financed by the Foundation for Polish Science from the European Regional Development Fund within the project POIR.04.0400-00-14D6/18 "Hybrid sensor platforms for integrated photonic systems based on ceramic and polymer materials (HYPha)" (TEAM-NET program).

# Fabrication of surface relief gratings (SRGs) in hydrogen bonded polymer-dye complexes and their replication for security features

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Surface relief grating (SRG) structures may be fabricated in hydrogen bond complexes of a polymer with an azo-dye in a holographic setup – utilizing two interfering laser beams (Fig. 1) [1]. Fabricated surface patterns can be transferred into a target film through preparation of a soft elastomeric stamp (PDMS). Replication of the pattern may be performed in e.g. thermoplastic polymer films by means of thermal nanoimprint lithography (TNIL) [2].

Tuning of geometry in the holographic setup allows for fabrication of the structures with various spatial periodicity. Differential visual effect of the fabricated patterns is specific and can be used in originality protection features. Finding reliable materials for both fabrication and reproduction of the grating structures seems to be important technological aspect.

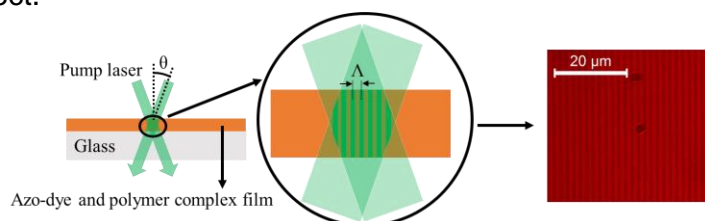


Fig. 1 Schematic representation of SRG fabrication using holographic method and optical microscopy image of a grating fabricated in thin film of azo-dye and polymer complex.

In this work, we present the results of the grating structures fabrication in different polymer films using different methods. Poly(4-vinyl pyridine) (P4VP) films doped with various azo dyes, as well as other azo materials were employed for the laser inscription. In such films, the grating structures were fabricated using two interfering laser beams. Then, using thermal nanoimprint lithography (TNIL), the grating structures were reproduced in thin submicrometric poly(methyl methacrylate) (PMMA) and poly(vinyl alcohol) (PVA) films with various thickness. Diffraction efficiency of the reproduced gratings strongly depends on parameters of the transfer process e.g. temperature. It was found, that thickness of the films does not influence the diffraction efficiency of the replicated gratings. Further work is being carried out to accelerate and enhance the process of the inscription of the periodic structures and their transfer to various type of the substrates.

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# Organic dye-doped systems based on different matrices: properties and potential applications in fluorochromic temperature indicators and photonics

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Embedding of organic luminescent dye into some matrices may induce specific interaction between them. This in turn may influence the luminescent properties of the dye due to presence of its different forms e.g. separated or aggregated. A variety of organic luminescent dyes and matrices (liquid crystals, polymers) enables for fabrication of different systems with designed properties such as spectral range of emission but also with additional functionalities such as temperature sensitivity [1].

Here, we describe the systems based on organic luminescent dyes and different matrices (Fig. 1). They may be used for fabrication of thermofluorochromic materials (liquid crystal matrices) or thin films serving as waveguides (polymer matrices). In the selected liquid crystalline matrix a visible change of the luminescent properties upon heating from crystalline (Cr) to nematic (N) or isotropic (Iso) phase was found for selected dyes. This finding served as base for preparation of thermofluorochromic indicators. The studies were performed for the known commercially available dyes but also for the novel dye from diketofurofuran family (DFF). For the latter, detailed studies (e.g. determination of solubility and quantum yield of emission) in several crystal and liquid crystal matrices were additionally performed. On the other hand, the properties of the dye-doped polymer films fabricated using the dip-coating method were investigated using profilometry and spectroscopic ellipsometry. Depending on the material, films with different thickness (in the submicrometric range) and refractive index (up to 1.62) were fabricated. The selection of dyes from different families allowed obtaining films emitting in the visible spectral range. Moreover, it was found that the high photoluminescence quantum yield of the dyes could be maintained or drastically decreased in a polymer matrix (compared to the values reported for liquid solutions). The results were dependent on the type of the investigated dye.

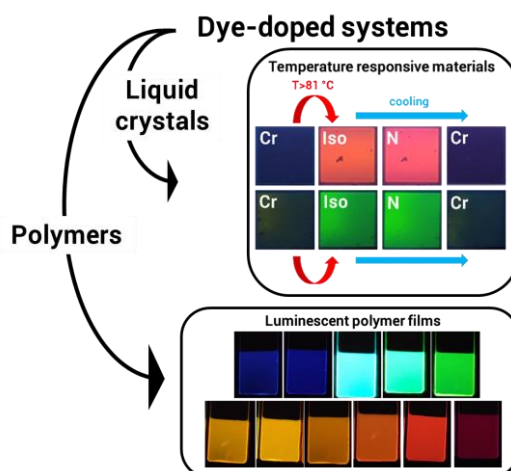


Fig. 1 Photographs of the fabricated dye-doped liquid crystalline and polymer systems for different application.

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# Structural and spectroscopic properties of nano-crystalline Nd<sup>3+</sup>-doped GdPO<sub>4</sub> obtained by ionic liquid and oleic acid-assisted methods

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We report the detailed analysis of both structural and spectroscopic investigation of monazite-type Nd<sup>3+</sup>-doped GdPO<sub>4</sub> nano-powders obtained *via* three wet synthesis methods *i.e.* ionic liquid assisted hydrothermal (IL HT) and microwave method (IL MW) as well as oleic acid assisted hydrothermal method (OA HT). Powder X-ray diffraction confirmed that the obtained GdPO<sub>4</sub> nano-powders crystallize in a monoclinic system ( $P2_{1/n}$ ) with the average grain size ranging from 40 to 100 nm, the smallest grains are obtained *via* IL MW method, and no other phase has been detected for any of the materials obtained. SEM and TEM were used to demonstrate the differences in the morphology and grain size, which results in the spectroscopic properties of nano-materials. Nine-fold coordinated Gd<sup>3+</sup> ion in GdPO<sub>4</sub> is easily substituted by the Nd<sup>3+</sup> one with the C<sub>1</sub> symmetry due to their similar ionic radii, so that high-resolution low-temperature absorption and emission spectra do not show any structural distortion. The <sup>4</sup>F<sub>3/2</sub> excited state dynamics studied at 77 K have shown abnormal behavior, similar to that already observed for Nd<sup>3+</sup> ion embedded in the YPO<sub>4</sub> and LuPO<sub>4</sub> tetragonal orthophosphates crystallizing in xenotime-type crystal system [1,2].

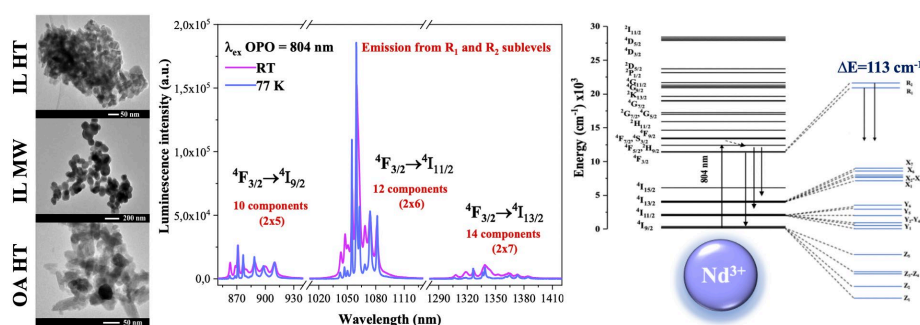


Fig. 1 TEM micrographs, emission spectra and energy level diagram of Nd<sup>3+</sup>-doped GdPO<sub>4</sub> nanoparticles.

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## Acknowledgments:

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# Optimization of photolithography process using negative tone resist towards obtaining high-quality photonic structures

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In recent years in the integrated optics field of science scientists were focused on optimizing processes for the mass manufacture of photonic devices [1]. One of the most common methods used to obtain waveguide structures in photonic integrated circuits (PICs) is the photolithography process, which is a remarkably efficient technique for microtechnology. It includes several sub-processes such as applying photoresist, exposing to ultraviolet (UV) light and developing the pattern. Conventional photomasks used in photolithography are rigid, fused quartz plates covered with patterned microstructures of an opaque material such as chrome.

In this work, we have investigated the effects of modifying parameters of the photolithography process carried out on soda-lime glass with a SiO<sub>2</sub>-TiO<sub>2</sub> layer using fast, negative tone cross-linking photoresists based on polymers. One of the main goals of our research is to create a silica-titania optical waveguide platform and incorporate optical components using etching methods. Photolithography parameters like UV exposure dose, the development time of the resist, as well as dilution of the developer and post-processing hard-bake, were optimized in order to achieve high-quality structures on the analyzed substrates. We believe that this work will be highly beneficial for the researchers working on the photolithography process.

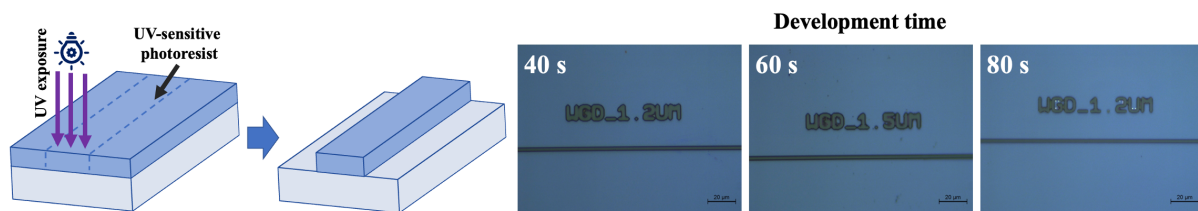


Fig. 1 Scheme of photolithography process and microscope images of obtained structures depending on the development time.

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# Structural and optical properties of dysprosium-doped calcium-oxyapatites $\text{Ca}_{10-2x}\text{Dy}_x\text{Li}_x(\text{PO}_4)_6\text{O}_2$ ( $0 \leq x \leq 1$ )

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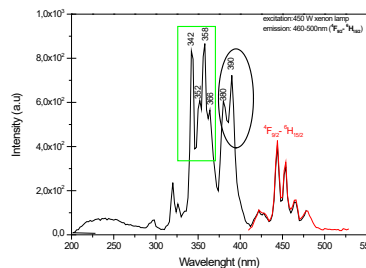
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A series of  $\text{Ca}_{10-2x}\text{Dy}_x\text{Li}_x(\text{PO}_4)_6\text{O}_2$  (CDLPO) ( $x = 0.1, 0.2, 0.3, 0.4$  and  $1$ ) phosphors was synthesized successfully via a solid-state method at high temperature. The effects of synthesis parameters,  $\text{Dy}^{3+}$  concentration and charge compensator  $\text{Li}^+$  co-doping on the structural and vibrational properties of CDLPO samples were investigated.

The structural and morphological studies of the CDLPO phosphors were carried out by X-ray diffraction (XRD), Infrared spectroscopy, Raman scattering spectroscopy and Scanning Electron Microscopy (SEM). Calcium-oxyapatite system shows a common apatite structure and occurs as a continuous solid solution.

According to the  $\text{Dy}^{3+}$  emission spectra, two different cation sites have been identified in this apatite structure. Two emission bands of the  $\text{Dy}^{3+}$  ion are observed, the blue band (460–500 nm) corresponding to the  $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$  transition and the yellow band (550–600 nm) due to the  $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$  transition. The overlap between the emission band of one site and the excitation band of the other site corresponds to an energy transfer phenomenon (Fig. 1). Correlations between the luminescence results and the structural data are discussed.



**Figure 1.** Excitation (black line) and emission (red line) spectra of  $\text{Ca}_{9.2}\text{Dy}_{0.4}\text{Li}_{0.4}(\text{PO}_4)_6\text{O}_2$  sample at room temperature.

# New transparent optical ceramics based on isotropic and anisotropic oxide structures - challenges and perspectives

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**E. TOMASZEWICZ**,<sup>c)</sup> **S. COTTRINO**,<sup>d)</sup> **V. GARNIER**,<sup>d)</sup> **G. FANTOZZI**,<sup>d)</sup>  
**S. Le FLOCH** <sup>e)</sup>, **O. BOISRON**<sup>e)</sup>, **Yannick GUYOT**,<sup>e)</sup> **Georges BOULON**<sup>e)</sup>

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Transparent ceramics with high optical quality are used in various applications, including industrial processing, medicine, aerospace, and high-power laser physics owing to the superior features of ceramics such as enlargement, ease of compositing, uniformity, high concentration of soluble active elements and high mechanical strength. However, so far, only a few compositions of transparent ceramics are well-developed. Transparent polycrystalline ceramics with cubic crystal structures have played important roles in a wide variety of solid-state laser applications, whereas for non-cubic structures, single crystal only has been used. Most transparent ceramics have a cubic crystal structure, and the development of novel ceramics with advanced mid-infrared lasing, magneto-optic properties, scintillation or lighting capability is still being actively pursued.

In general, it is very difficult to achieve high transparency in sintered polycrystalline ceramics due to the various defects that remain after sintering, such as pores, vacancies, secondary phases, impurities, grain boundaries and surface roughness which acts as a light-scattering source.

Here, we present the results of many attempts to obtain sintered polycrystalline ceramics showing transparency from both oxide materials crystallizing in a cubic crystal system as well as in a non-cubic one. For sintering were used nano and micro-powders un-doped and doped with Nd<sup>3+</sup> ion, which is a very important ion from the potential application point of view *i.e.* as a laser dopant and as a structural probe. The tests were carried out using both a very simple vacuum sintering method as well as a much more advanced Spark Plasma Sintering (SPS) technique. This method is efficient to consolidate ceramics at low temperatures in a short time and made it possible to obtain transparent materials.

## **Acknowledgments:**

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# ***Silicon optomechanical crystal cavities for microwave signal processing and biosensing***

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Optomechanical cavities have become an increasingly important area of research in recent years, with the potential to enable new technologies in fields ranging from quantum computing to sensing and telecommunications [1]. Utilizing a blue-detuned laser to operate an optomechanical cavity can produce fascinating physics and phenomena. One such phenomenon is phonon lasing, which causes the input light to be modulated by a collection of high-purity harmonics that originate from the mechanical resonance of the cavity's fundamental tone [2]. This paper explores how this phenomenon can be utilized to process wireless signals in the optical domain. We demonstrate that by using a silicon optomechanical crystal cavity with a mechanical breathing mode around 4 GHz, we can generate a microwave tone with low phase noise ( $< -100$  dBc/Hz at 100 kHz), making it suitable for practical applications such as satellite communications. We also discuss how the system's stability can be improved by locking two different mechanical modes and bringing them into the phonon lasing states. Moreover, we show that the cavity acts as a nonlinear mixer, making it possible to perform frequency up-conversion on realistic data streams that comply with wireless communication standards [3]. Our findings suggest that ultra-compact optomechanical cavities have the potential for use in the next generation of wireless networks and satellite communications. However, applications in biosensing have also been explored in many optomechanical systems. Specifically, the use of those type of optomechanical crystal cavities as optical and mechanical sensors could be integrated in photonic integrated circuits using cost-effective silicon technology, and providing a better sensing performance than separated photonic and mechanical devices.

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# Recent progress on GAGG (Ce,Mg) single crystal growth and their performance for high energy physics.

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## Abstract

Because of the well-developed crystal growth technology under stationary stable regime, (Ce,Mg)-codoped GAGG single crystal, which has garnet structure are promising candidate for scintillator applications. In addition, (Ce,Mg) ions-doped gadolinium aluminum gallium garnet crystal ( $\text{Ce}^{3+}, \text{Mg}^{2+}:\text{Gd}_3\text{Al}_2\text{Ga}_3\text{O}_{12}$ ,  $\text{Ce}^{3+}, \text{Mg}^{2+}:\text{GAGG}$ ) as inorganic oxide material has the advantages of high density, large effective atomic number, high light yield, good energy resolution, fast decay time, and stable physical and chemical properties. With the objective to investigate the feasibility to built a calorimeter based on GAGG assembly single crystal, the effects of the doping concentration (Ce,Mg) and the use of various co-dopant on the light output and the timing properties of GAGG were studied. In the frame of this work, deferent GAGG single crystals were grown (**Figure 1**) as bulk crystal and single crystal fibers by Czochralski and micro-pulling down techniques. They are well characterized to investigate the impact of the composition and the growth parameters on the crystal performance to be used for the next generation of calorimeter for the high energy physics.

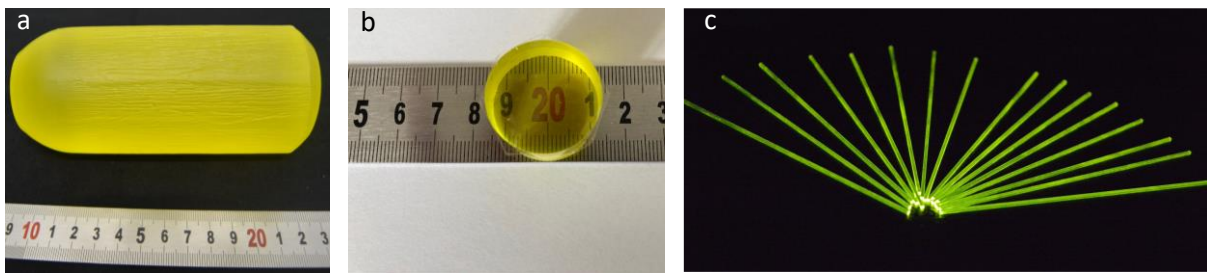


Figure 1 . (a) (Ce,Mg) GAGG crystal grown by Cz, (b) polished (Ce,Mg)GAGG crystals and (c) (Ce,Mg)GAGG single crystal fibers under UV light (263 nm) .

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# “Chirality at the molecular scale: materials and spectroscopy”

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Chirality is a property of symmetry that occurs at all scales. Two objects are chiral if their mirror images do not overlap. In living organisms, chirality has an essential importance, since most of the mechanisms of molecular recognition or biological signal transmission are triggered by this asymmetry. Chirality, at the molecular scale, also plays a fundamental role in the light-matter interaction. We speak of "electromagnetic chirality" for a medium filled with chiral objects, of sub-wavelength size. It is this "electromagnetic chirality" that is at the heart of our research works, through the design, realization and study of chiral materials in the solid state, generally in the form of thin films or powders, but also in solution.

In this context, we develop at ILM within the MNP team, two themes around chirality at the molecular scale: (i) Chiral integrated optics. Here, we want to free planar photonics from the linear polarization diktat, using chiral materials with very high rotational power; (ii) chiral spectroscopies that we have developed in order to study different chiral systems. Our collaboration with colleagues from Strasbourg University provides a nice example of these investigations mixing chiroptical and linear anisotropy properties, applied to soft mechanochemistry.

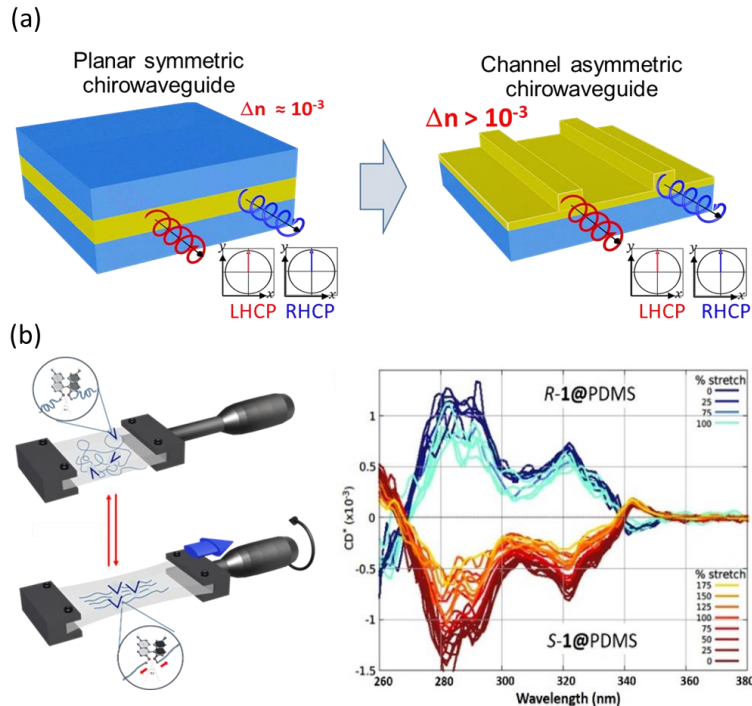


Figure: (a) Planar and Chanal chirowaveguides with circularly polarized eigenmodes, (b) Circular dichroism variation of doubly linked BINOL in PDMS under stretching

# Crucible-free bulk crystal growth of oxide single crystals using OCCC method

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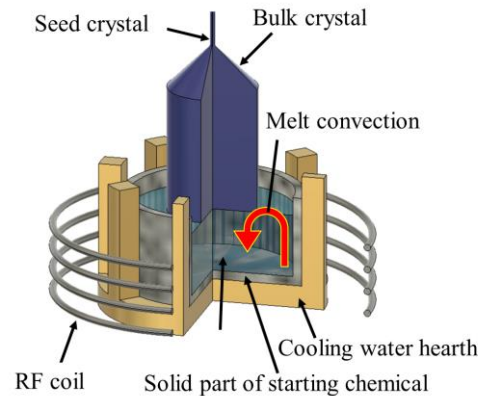
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Recently it has been found that the Mg<sup>2+</sup> codoping in Ce doped Gd<sub>3</sub>(Ga,Al)<sub>5</sub>O<sub>12</sub> (GAGG:Ce) has increased the light yield and accelerated scintillation decay [1-3]. These effects need further systematic study for full understanding. The detailed discussion is being carried out based on the influence of co-doping, induced host defects, and cerium charge state. So far, the GAGG-based crystals are grown under the Ar or N<sub>2</sub> atmosphere. This generates large amount of oxygen vacancies and Ga vacancies in the crystal. Such a growth atmosphere is necessary to protect the iridium crucible from oxidation.

We report the growth of Ce:GAGG single crystals based on crystal pulling from a melt using a cold container without employing a precious-metal crucible [4-8]. This novel method is described in detail. We have labeled the proposed method, which is a fusion of the skull-melting and CZ methods, the “oxide crystal growth from cold crucible (OCCC)” method. The scintillation properties of the OCCC-grown Ce:GAGG crystals were compared with those of crystals grown by the conventional CZ technique. The best samples from the set are fully comparable in all characteristics with the commercial reference crystal, demonstrating the practical potential of this method. Avoidance of an expensive precious-metal crucible in this method makes crystal growth much more economical [9].

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**Fig.1** Schematic image of OCCC method.



# BiBO: An Effective Nonlinear Crystal for Femtosecond Optical Parametric Oscillators

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Tunable sources of ultrashort laser pulses based on efficient nonlinear materials have a lot of applications in different scientific, medical and industrial applications [1]. BiB<sub>3</sub>O<sub>6</sub> (BIBO) is one of the last nonlinear crystals that because of its flexible phase-matching (PM) possibilities, relatively low group velocity mismatches and large effective nonlinear coefficients has proved its strong performance for generating tunable femtosecond pulses in the visible and near-IR spectral ranges [2,3]. Although, the biaxial structure of this crystal makes some complications for using its full capacity in its different optical planes.

As the first demonstration of a synchronously pumped femtosecond optical parametric oscillator (SPOPO) based on BIBO, we demonstrated a visible femtosecond SPOPO, pumped by the femtosecond blue pulses at 400 nm, produced as the second harmonic of the output of a Kerr-lens mode-locked (KLM) Ti:sapphire laser with 76 MHz repetition rate [3]. In this SPOPO which had a signal output, tunable across the visible spectral range of 500-700 nm, with <150 fs pulses, type I ( $e \rightarrow o + o$ ) PM in the  $yz$  optical plane of BIBO was applied. The intracavity frequency doubling of this SPOPO resulted in producing tunable femtosecond pulses across the UV spectral range of 250-350 nm [4]. Later a Near-IR SPOPO directly pumped by Ti:sapphire laser at 800 nm inside the  $xz$  optical plane of BIBO was reported [5].

After the introduction of higher power KLM Yb:KGW laser family, a high power SPOPO using ( $o \rightarrow e + e$ ) PM in the  $yz$  optical plane and pumped by 515 nm green pulses, producing signal and idler pulses in the spectral ranges of 688-1057 nm and 1150-1900 nm respectively, was reported [6]. Taking advantage of the full capabilities of the green-pumped SPOPO based on BIBO requires the application of the PM inside its  $xz$  optical plane also, as an important part of the tunability of signal and idler pulses that can be produced by BIBO.

Recently we have presented the application of ( $e \rightarrow o + o$ ) phase matching scheme in a high power SPOPO inside the  $xz$  optical plane of BIBO. The pump laser was a Yb:KGW that can produce up to 6.8 W of average power with ~100 fs pulses and 76 MHz repetition rate. More than 3.5 W of second harmonic green femtosecond pulses that were generated inside a 1-mm thick BIBO crystal were applied as the pump pulses for our SPOPO. The OPO produces signal and idler pulses in the spectral ranges of 620-695 nm for signal and 1988-3040 nm for idler pulses. The generated signal power range, is from 700 mW at the shortest wavelength of 620 nm (limited by transparency of the corresponding idler pulse) up to 1 W at higher wavelengths. The compressed signal pulses have durations as short as 35 fs.

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