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Materials Science Conference on Advanced Functional Materials

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# New nanomaterials and nonlinear optics: a powerful combination?

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Nanotechnology keeps providing novel materials with unique properties. There have been numerous advances in the controlled synthesis and investigations of electrical and optical effects in OD, 1D and 2D materials, the latter ones receiving a lot of attention that has not subsided since the original focus on graphene [1].

It is beyond doubt that at least some of the novel materials can offer a new playground for applications of nonlinear optical phenomena such as nonlinear absorption and nonlinear refraction. Indeed, many reports have indicated the presence of enhanced nonlinear optical effects, but the assessment of suitability of such effects for practical applications remains incomplete [2].

I will review some of the interesting results concerning NLO properties of various materials studied in our group at WUST, including the studies of nonlinear effects in chiral nanomaterials and the use of novel techniques for detecting the NLO phenomena.

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### Specifics of spectroscopic features of Yb<sup>3+</sup>-doped LuPO<sub>4</sub> nano/micro-crystalline orthophosphates

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Orthophosphates doped with  $RE^{3+}$  (rare earth) ions have been the subject of investigations due to high thermal and chemical stability, high values of refractive index, low solubility in water, and even relatively small phonon energy of the matrix *i.e.* about 1100 cm<sup>-1</sup>, that make them attractive from the promising point of view of phosphor, laser and scintillator materials.

Three series of Yb<sup>3+</sup>-doped LuPO<sub>4</sub> (0.5-5 mol % Yb<sup>3+</sup>) in the form of nano/microcrystalline powders crystallizing in a zircon-type tetragonal system were obtained. Nano-materials were prepared by ionic liquid-assisted hydrothermal method (IL HT) [1]. Choline dihydrogen phosphate (IL) - a donor of the phosphate group and an in-situ nanoparticle templating agent, was dissolved in ethylene glycol (HT GE) or water (HT W) which influenced the morphology and physico-chemical properties of obtained samples. This protocol made it possible to fabricate fine nano-size powders exhibiting desired wellcrystallized single-phase phosphate. For comparative studies, the micro-crystalline samples were synthesized *via* reaction in the solid phase taking place at a relatively high temperature, according to the protocol described in [2].

Absorption at 4.2 K, selective excited luminescence at 77 K, and fluorescence decays were used to attempt the precise assignment of  $Yb^{3+}$  energy levels in one  $D_{2d}$  centre of LuPO<sub>4</sub> structure both in nano and microcrystals. This assignment is based on exceptional features due to the unique emission observed from both two lowest levels of  ${}^{2}F_{5/2}$  excited state, split only by 26 cm<sup>-1</sup>, confirmed by calculation of the crystal field parameters from Zeeman spectra [3].

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### Fluorescence Sensing with Plasmonically Active Metallic Nanostructures

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Metallic nanostructures, which feature plasmon resonances in the visible spectral range, can be used for efficient detection of fluorescent species, provided they arrive in sufficient proximity to facilitate strong plasmonic coupling. In this regard, silver nanowires (AgNWs) and silver island films (SIFs) are particularly attractive, as they feature plasmon resonances that span over the whole visible range down to the near infrared.

Our work focuses on applying silver nanostructures, in the form of AgNWs, SIF, as well as laser-printed Ag paths, as platforms for detecting biological species. Silver nanowires are chemically stable in both water and buffer solutions, can be obtained using wet chemistry synthesis, and their surface can be functionalized appropriately. In contrast, silver island films can be fabricated in a controlled way on various surfaces, such as glass, ITO, plastic, and alike, without compromising the sensing ability. The laser-printed Ag paths, on the other hand, can be precisely deposited on a glass surface in an arbitrary pattern. The approaches developed for each type of silver nanostructures yield specific conjugation, allowing for obtaining sensing activity either in solution or in real-time upon deposition of analyte on the surface.

Specificity, selectivity and sensitivity of the chips based on silver nanostructures have been studied using advanced fluorescence spectroscopy and microscopy techniques, including real-time imaging. The comprehensive experimental evidence indicates that spatial geometry constrain with proper surface functionalization, when combined with strong enhancement of the optical response due to plasmonic interactions, make silver nanowires, silver island films, and laser-printed Ag paths, very attractive nanostructures for fast and specific sensing. Importantly, by exploiting the fluorescence enhancement associated with the plasmon resonance in metallic nanostructures, detection of single proteins was demonstrated.

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### Organic and inorganic nanomaterials for chiral photonics

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Chiral nanomaterials are demanded for emerging photonic technologies that rely on the emission or detection of circularly polarized light. However, enhancing chiroptical activity is required to capitalize on these phenomena fully. We address this challenge by relying on the chirality of nanoparticles (NPs) and liquid crystals (LCs).

We undertook three significant research endeavors within the field of chiral nanomaterials. Firstly, we mastered controlling NP size, shape, composition, and surface chemistry, ensuring their chemical compatibility with organic (LC) materials. With that, we can form a variety of NP-organic composites. Secondly, we developed NP-LC films in which nanoparticles exhibit state-of-the-art circular dichroism and circularly polarized luminescence [1,2]. This method is universal and scalable and enables dynamic tuning of the chiroptical properties using thermal- or light stimuli (Figure 1). Finally, we developed the 'chirality writing' method. Namely, we achieve unrestricted control over the handedness of pixels within a single film, opening the way to, e.g., anti-counterfeiting applications [3].

**Figure 1.** A scheme of chiral nanocomposite formed with liquid crystals (bluish helical nanofilaments) and gold nanoparticles (yellow nano bipyramids). Such structure exhibits chiral optical properties.



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### **Glass photonics: advancements and perspectives**

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Glass Photonics is pervasive in a huge number of human activities and drives the research in the field of enabling technologies [1]. Glass materials are the cornerstone of photonic structures crucial for information engineering, biological and medical sciences, sensing, lightning, energy and quantum technologies. The technologic and scientific results obtained in the last 50 years have proved that photonics and glass science smartly cooperate to develop new physics, new devices, and new applications. This cross-disciplinary approach leads to "smart structures", which can perform sensing, and functionalized ones to successfully address socio-economic challenges, such as security, energy saving, efficient and clean industrial production, environmental protection, and fast and efficient communications.

This lecture presents some results obtained in rare earth doped photonic glasses and confined structures, in order to give some highlights regarding the state of art in glass photonics. Starting from planar waveguides and optical fibers, we will move to spherical microresonators, a very interesting class of photonic confined structures. Then we will present 1D-photonic crystals and opals allowing management of optical and spectroscopic properties. Some examples of photonic glass-ceramics [2] as effective hosts for up and down converters and recent developments in flexible photonics [3], will be presented. We will conclude with some remarks about the perspective for glass photonics.

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### Integrated Photonics Platforms developed at Warsaw University of Technology

L-5

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Photonic integrated circuits (PICs) are planar optoelectronic systems integrating multiple photonic components on a common substrate. Compared to their discrete component counterparts, PICs offer significant advantages, including compact size, high reliability, robust mechanical resistance, stable operating parameters, low power consumption, and reduced unit costs in mass production. PICs are utilized across various markets, including optical communication (telecom/datacom), high-performance computing, agrifood and natural resources, critical infrastructure monitoring, industrial sensing and automation, health and wellbeing, consumer electronics, mobility, and space applications [1]. A notable trend in PIC applications is sensing, which often requires extending the spectral range of operation to short (UV-VIS) or long (MIR) wavelengths. In this direction, passive integrated photonics platforms based on silicon materials are being developed at Warsaw University of Technology (WUT). WUT has the competencies to complete the entire technological cycle, from designing elements and layouts through manufacturing to measuring PIC optical parameters. The developed PICs can operate in the VIS, NIR, and mid-IR spectral ranges. This is achieved through the use of silicon nitride (SiN), germanium on silicon (Ge-on-Si), and silicon on insulator (SOI) material platforms. The developed library of basic building blocks includes waveguides, ring resonators, grating couplers, Bragg gratings, multi-mode interferometers, arrayed waveguide gratings multiplexers, and microfluidics interfaces.

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Joint Focus Group of the European Association on Smart Systems Integration (EPoSS)
 And Photonics21, White Paper on Integrated Photonics, 2023





### **Optical fibers doped with YPO**<sub>4</sub>:Ln<sup>3+</sup> nanocrystals

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Optical fibers with lanthanide-doped nanocrystals (LNCs) belong to new nanocomposite materials in which active ions are localized in the crystalline phase. This structure combines the lasing properties of crystals and advantageous features of optical fibers, leading to potentially new active components for lasers, broadband sources, and sensors. Among the most promising techniques for producing fibers with nanocrystals (NCs) are controlled crystallization, introducing NCs into glass prior to fiber fabrication, and nanocrystallization during the fiber drawing process [1].

In this work, the glass powder doping method is discussed as a technique where particles of both glass and nanocrystals are initially mixed. Next, optical fibers are drawn using fiber preforms developed after pre-sintering glass powder with YPO4:Ln<sup>3+</sup> (Ln<sup>3+</sup>=Pr<sup>3+</sup>, Yb<sup>+</sup>) NCs. Analysis of luminescent properties of synthesised YPO4: Ln<sup>3+</sup> NCs and nano-composite optical fibers showed an agreement of their lifetimes reaching the same values for Pr<sup>3+</sup> and Yb<sup>3+</sup> ions equal to  $\tau = 156 \ \mu s$  (~600 nm,  $^1D_2-^3H_4$ ,  $\lambda_{exc}=488 \ nm$ ) and  $\tau = 730 \ \mu s$  (~980 nm,  $^2F_{5/2}-^2F_{7/2}$ ,

 $\lambda_{exc}$ =940nm) respectively. The distribution of the NCs in optical fibers are analysed by TEM-EDS in the core region (FIB-SEM-prepared).

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# Luminescent properties of photonic materials and optical fibers doped with active centers

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New luminescent photonic materials enable new applications in modern light sources, optical radiation conversion systems, telecommunications and information storage, holography, and sensor systems. Examples are the optical fibers currently used in telecommunication, optical amplifier designs, lasers, and measurement systems. They are based mainly on inorganic glasses (silica, silica-free, or fluoride). Another group of photonic materials is polymers, which have found wide application possibilities due to the possibility of their functionalization with organic dyes and lanthanide dopants. The combination of luminescent properties of organic and inorganic compounds may constitute the achievement of new functional optical properties of polymer optical fibers. This work will present the optical properties of silica-free (germanium-based) glasses doped with  $Er^{3+}/Tm^{3+}/Ho^{3+}$ . Optimization of the concentration of active dopants to achieve a broadband emission in the 1.4-2.1 µm range will be shown.

Further, different constructions of double-clad optical fibers and their emission properties under semiconductor laser excitation will be shown. These results will be compared with silica  $Tm^{3+}$ -doped construction of the fiber (fabricated by MCVD-CDT technology), where all fiber laser construction based on the Fabry-Perot resonator for single-mode laser beam generation at a wavelength of 1940 nm with an  $M^2 \approx 1.11$ . Moreover, organic dye and rare-earth (RE) co-doped polymers (and optical fibers) will be presented. The analysis of the RE/dye energy transfer will also be presented.

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### Fabrication and properties of GaAs Tamm plasmon lasers and light emitting diodes

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We will describe the exploitation of Tamm plasmons for lasers and diodes. Tamm plasmon modes are surface modes that appear at the interface between a metallic film and a Bragg mirror and exhibit properties in between cavity modes and plasmons [1]. Their main interest lies in the surface nature of the mode, which makes it possible to integrate them into sources with geometries ranging from simple discs [2] to complex metal metasurfaces [3]. As the field maximum is close to the surface, the metal micro/nano-structuration controls the properties of the source such as its directivity or polarization [4]. The demonstrations of Tamm sources were made with an optical excitation. To move on to applications, electrical excitation of the optical sources is necessary. As the maximum electric field of the Tamm mode is close to the surface, the fabrication of the devices requires special procedure to maintain their emissive properties. dedicated а А process of Ag/GaAs Tamm emitting fabrication devices will be described. For Tamm structures of 5 µm diameter, mode confinement appears in the diode emission with energy discretization [5]. The observation of the electrically excited emission of a Tamm structure is an important step towards exploitating Tamm structures for new optical devices.

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# Novel virus-like particle arrays exhibiting surface lattice resonance for ultrasensitive biodetection

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Severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) that causes COVID-19 has stimulated the scientific world to intensify studies aimed at developing quick and safe ways of detecting viruses in human body. Currently, there are two widely used diagnostic methods: molecular diagnostics and serologic test. The first one is considered to be a very sensitive, but time-consuming, whereas the second is fast and simple but cannot be applied for early COVID-19 diagnosis. Thus, there is a need for developing new methods that would provide fast and reliable detection of viruses. Surface-enhanced Raman scattering (SERS) is a powerful analytical technique used in chemistry, pharmacology and biomedicine for studying biological systems, e.g. proteins, tissue, bacteria and viruses. This method, based on the appearance of the so-called localized surface plasmon resonance (LSPR) in noble metal nanostructures that amplifies vibrational signals from the analyte deposited onto them, deserves consideration in biodetection due sensitivity towards even nanomolar concentrations of biomolecules, with the measurements being performed in a label-free way [1]. By utilizing the capillary-assisted particle assembly (CAPA) [2], we have prepared an innovative matrix composed of SARS-CoV-2 virus-like particles (VLPs) characterized by the presence of the LSPR in the gold cores and the surface lattice resonance (SLR) related to the periodic arrangements of particles. The SLR further amplifies the SERS signals originating from molecules specifically binding to VLPs [3], making the fabricated system suitable for applications in ultrasensitive biodetection [4].

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# Thin-film perovskite solar cells fabricated by the PVco-D process

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Hybrid organic-inorganic halide perovskites have become the most promising materials in photovoltaics. In just a few years, the energy conversion efficiency of hybrid perovskite solar cells has increased dramatically from an initial bright value of 9% to over 24%. Their remarkable properties, including high carrier mobility, low carrier recombination rate, and tunable spectral absorption range, are attributed to the unique electronic properties of these materials.

Despite the undoubted progress in the conversion efficiency of perovskite solar cells, understanding hybrid perovskites' basic structural, optical, and electrical properties is limited. The presentation will include the research results on the relationship between low-temperature structural, electrical, and optical properties of hybrid perovskite thin films produced by the unique physical vapor co-deposition (PVco-D) The technique. experimental study will be compared with theoretical simulations performed using SCAPS 1D software.



Fig.1. The idea of the PVco-D process.



### PL-2

### **Toward Precision Manufacturing with Electron Microscopes**

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This presentation will delve into my studies within the realm of nanomaterials synthesis and the sophisticated examination of materials via electron beam methodologies. Central to my research is the pioneering employment of a transmission electron microscope (TEM) as a tool for precision synthesis. This approach facilitates the exact construction, modification, and comprehensive analysis of materials on a near-atomic or an atomic scale, offering unparalleled spatial and temporal precision. My talk will highlight the electron beamdriven techniques and engineering practices that enable meticulous control in the assembly and refinement of nanomaterials. By showcasing the breakthroughs in precision synthesis, my work marks a significant stride towards the refined fabrication of materials using electron microscopes, thereby setting the stage for innovative advancements in the fields of nanotechnology and materials science.

#### ACKNOWLEDGMENTS

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### More than just color: Inverse opals as sensors

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Nanostructured materials are widespread in nature and are an invaluable source of inspiration for scientists. Among them, periodic porous materials are often responsible for structural coloration, as observed in butterfly wings and beetle shells. An approach to mimic such structures is to exploit colloidal templating to generate ordered, interconnected porous materials, named inverse opals (IOs). Here, we demonstrate that IO have applications much beyond pigments and can be used to create simplistic sensing devices that exploit both coloration and the interconnected periodicity.

IOs display structural color due to the periodic variation of refractive index (RI) resulting from the porous structure. The coloration can be selectively suppressed by infiltrating the pores with a liquid with a RI close to the one of the matrix, and this principle can be used to fabricate sensors. So far, mostly sensors based on surface functionalization sensible to changes in the physical proprieties of the infiltrating liquid were developed. In contrast, we developed sensors exploiting selective surface functionalization, which are able to change the wettability of the surface itself upon the adsorption of an analyte, e.g. volatile organic compounds or water pollutants.

IOs are also ideal to improve the performance of established electrochemical sensors thanks to their high surface area. However, overcoming the insulating nature of typical IO matrix materials is a key challenge for their application as electrode materials. I will show how we combine colloidal assembly, atomic layer deposition and surface functionalization to design conductive IOs as glucose sensing platforms. An insulating IO scaffold is coated with uniform layers of conducting aluminium zinc oxide and platinum, and subsequently functionalized with glucose oxidase embedded in a polypyrrole layer. The final device can sense glucose down to 1 nM and is not affected by the presence of common interferents, providing a promising platform for miniaturized sensors.





### Integrated Fluorescence Messenger Polymers for Spatially Resolving Micro-to-Nano Processes

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Spatially resolving processes, such as stimuli, contact forces, stresses, and/or damage, is highly desirable towards developing next generation smart materials[1-2]. Materials that can "tell" us when something is happening. Towards this goal, we develop ways of integrating fluorescence into functional polymer architectures such that polymer conformation is readily spatially revealed by confocal microscopy. Our methods include integrating fluorescence self-quenching[3] and Förster resonance energy transfer (FRET)[4] capabilities into functional polymer brush layers on planer surfaces, taking the concept of "touch" sensitive surfaces to the nanoscale. Towards the more general, we show how the free FRET-integrated polymer chains can be integrated into a secondary matrix (electrospun fibers)[5] to report on nanostructure, irregularities, and damage. Our systems provide a non-invasive optical measure of changing material properties, which holds great promise for identifying material properties and stimuli in real-time, and spatially resolved. In this seminar, I will discuss these systems and their exciting applications going forward.

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MASCA

### Metal-modified TiO<sub>2</sub> photocatalysts for hydrogen production from water decomposition under UV/Vis and simultaneous CO<sub>2</sub> and N<sub>2</sub> reduction to valuable chemicals

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Titanium dioxide  $(TiO_2)$  stands out as a premier photocatalyst for reducing carbon dioxide with hydrogen from water into valuable chemicals. Modifying known  $TiO_2$ photocatalysts with metals and metal oxides, such as Ru, Pt, Cr, Co, Ni, and Cu, seems to be the right method for enhancing selectivity in chemical production. Ruthenium (Ru) emerges as a promising candidate for  $TiO_2$  modification, owing to its capability for hydrogen evolution from water decomposition and carbon dioxide reduction to produce valuable chemicals [1].

The various ruthenium precursors are typically utilized for ruthenium-containing catalysts, among which,  $RuCl_3$  is the most commonly used. In this work, we used the ruthenium oxychloride ammoniated Ru-red ( $H_{24}Cl_6N_{14}O_2Ru_{30}$ ) as a precursor for sol-gel method preparation which has not been extensively documented in existing literature. Prepared samples contained up to 1 wt. % of Ru.

All ruthenium-TiO<sub>2</sub> photocatalysts showed significantly higher photoactivity compared to the commercial TO<sub>2</sub> P25 from Evonik Industries AG(Germany). It can be observed that the Ru-TiO<sub>2</sub> material containing 0.5 % Ru stands out from the others, and the amount of hydrogen was 639  $\mu$ mol/g<sub>material</sub>/dm<sup>3</sup> with high selectivity. Depending on the composition of the input gas mixture, carbon monoxide, methane and ammonia were also present in the products. The dependencies of photoactivity on the composition and properties of the photocatalysts used will be presented.



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### Rational design of carbonaceous materials for (electro)catalysis

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The use of electrical current to direct organic reactions offers a sustainable alternative to traditional methods that frequently rely on harmful chemicals and generate considerable waste. This approach, leveraging voltage instead of high temperature or pressure, enables complex reactions to occur under ambient conditions, representing a notable advancement in green chemistry. The good example is electrochemical hydrogenation in water, which negates the need for the high temperatures and pressurized hydrogen by utilizing water as the proton source, thus bypassing the use of gaseous hydrogen. However, the reported studies predominantly employ noble metals as cathode materials falling in the same utility trap as common electrocatalytic reactions for small molecule activation like water splitting [1].

Heteroatom-doped carbons have demonstrated their high activity in electrocatalytic activation of small molecules (e.g., ORR, HER), yet their potential in electrosynthesis remains unexplored. In my talk, I will show a few examples of the synthesis and applications of N-, O-, and P-doped porous carbons for electrochemical hydrogenation reactions [2].

This research marks a significant step forward in the development of specialized electrodes for organic electrosynthesis, sidestepping the need for expensive, scarce, or toxic elements typical of conventional catalytic processes. Through specific interactions that emulate enzymatic binding, these electrodes facilitate targeted chemical reactions [3].

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### Novel perovskite-type oxides for selected electrochemical applications

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Perovskite-type oxides are known for their very broad compositional flexibility, which enables designing materials with unique structural, transport, magnetic, catalytic, electrochemical, and other functional properties. Additionally, the oxygen sublattice in such compounds may exhibit large deviation from the stoichiometry, with either disordered or ordered oxygen vacancies. Tuning the mentioned properties is feasible in perovskites, which enables obtaining advanced materials, suitable for usage in various electrochemical applications. This work summarizes results concerning development of perovskite-type oxygen electrode materials for Solid Oxide Cells, as well as oxygen storage materials for pressure/temperature swing absorption processes. Starting with the more common A-site layered RE(Ba,Sr)Co<sub>2-y</sub>Mn<sub>y</sub>O<sub>5+ $\delta$ </sub> (RE: selected rare-earth cations;  $0 \le y \le 2$ ) oxides, a possibility of replacing cobalt with environmentally benign copper is discussed, yielding RE(Ba,Sr)Co<sub>2-y</sub>Cu<sub>y</sub>O<sub>5+ $\delta$ </sub> series, as well as purely Cu-based La<sub>1-x</sub>(Ba,Sr)<sub>x</sub>CuO<sub>3-δ</sub>. Issues related to maintaining high electrocatalytic activity toward the oxygen reduction/evolution reactions, and sufficient mixed ionic-electronic conductivity are presented in more details. Also, an emerging field of the high entropy (multicomponent) approach is discussed regarding designing of functional perovskites for the electrochemical applications [1-6].

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### **Optical properties of cerium ions in GaInN matrices**

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Rare earth (RE) ions doped semiconductors are the subject of research due to the unique combination of their optical and electrical properties providing the high potential of these materials in new optoelectronic devices [1]. Among the RE ions family,  $Ce^{3+}$  has the simplest  $4f^{1}$  configuration. Upon excitation, electrons of cerium ions are promoted from the 4f to the 5d state, and then strong broadband emission occurs, originating from parity allowed  $4f^{0}5d^{1} \rightarrow 4f^{1}5d^{0}$  transition. The 5d electrons are weekly shielded from the lattice, so the transition energies are significantly affected by the crystal field strength, and in various host crystals cerium ions show emission from the near UV up to red spectral range [2].

In this work, we studied the possibility of controlling the optical properties of  $Ce^{3+}$  ions implanted into  $Ga_{1-x}In_xN$  matrices (x = 0, 0.04, 0.08) by the changes of host bandgap and crystal field strength induced by replacing some amount of Ga<sup>3+</sup> by In<sup>3+</sup> cations with larger revealed bright radius. The samples and thermally stable broadband ionic photoluminescence (PL) with the PL peak wavelengths decreasing from 680 nm in GaN:Ce to 570 nm in Ga<sub>0.92</sub>In<sub>0.08</sub>N:Ce. The room-temperature decay kinetics consisted of two main short-time component in nanosecond components: time scale, compatible with  $4f^05d^1 \rightarrow 4f^15d^0$  transition, and long-time component with the decay times decreasing from 34 µs for GaN:Ce to 23 µs for  $In_{0.08}Ga_{0.92}N$ :Ce. The possible causes of the observed effects will be discussed.

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### Growth of Bulk Oxide Crystals using the "Oxide Crystal Growth from Cold Crucible (OCCC)" method

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So far, the growth of bulk high-temperature oxide crystals is usually carried out using precious metal crucibles. In recent years, the sharp increase in the price of such metals (especially Ir, Pt and Rh) has become a major issue in the production of these oxide crystals. This circumstance forces both researchers and company engineers to look for other methods for obtaining crystals. One of the most promising candidates is the cold container method[1]. This method has been used for many years to produce ultra-high melting point crystals such as cubic zirconia. In this method, the material is kept in a molten state inside a water-cooled copper basket. In this case, heating is carried out using an RF coil due to the penetration of the field into the gaps between the tubes of the basket. Further, in the traditional cold

container technique, the crystal can be grown in the melt volume by slowly raising the inductor. In the presented work, growth is carried out by contacting the seed with the melt and slowly pulling upward similar to the classical Czochralski (CZ) method. We have labeled the proposed method, the "oxide crystal growth from cold crucible (OCCC)" method, which is a fusion of the cold container method and CZ methods (Fig.1). Using such technique makes it possible to solve several problems at once, namely: avoid using a metal crucible, avoid contact of the melt with the container, use any growth atmosphere, including pure oxygen. Using the proposed method, we successfully grew a range of different crystals: Ce: GAGG[2], Ce: La-GPS, LiTaO<sub>3</sub>,  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>[2] (Fig.2). The first two crystals showed scintillation properties comparable to crystals grown from Ir crucibles using the CZ method. Recent results on crystal growth using the OCCC method will be reported together with its characterization result.







Fig.2. Photo of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystal

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### Surface Phosphor Thermometry Imaging Applied to Near-Wall Combustion

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Near-wall combustion is a critical process occurring in various energy systems, such as air-breathing propulsion devices [1]. Increasing the operating gas temperature or designing smaller systems with enhanced power densities are two solutions to obtain highly-efficient systems but it raises additional issues regarding the thermal management of walls, i.e. challenges for material durability or pollutant emissions [2].

Spatial distribution of wall temperature is a key component of near-wall combustion. Thermographic phosphor thermometry is a semi-invasive laser diagnostic routinely used in a large variety of applications to measure surface temperature [3]. Coated on the surface of interest, the phosphorescence signal is detected after an energy excitation (e.g. laser source). Two principal measurement strategies are retrieved in the literature [4]: the time-resolved approach consists in measuring a phosphorescence decay, whereas the time-integrated (or spectral intensity-ratio) strategy relies on measuring the modification of the phosphorescence spectrum with temperature. Though the former is usually implemented, the latter is well-suited for two-dimensional measurements at a moderate cost-in-use, but presents important temperature uncertainty levels [5].

This talk aims at improving the temperature uncertainty with the spectral intensity ratio method. First, a numerical multi-objective optimization routine is implemented to select the best optical filters that enhance the temperature uncertainty on a large range of temperature. Second, different spatial filtering strategies in terms of spatial resolution and spatial temperature uncertainty are benchmarked. Eventually, this technique is used to obtain spatial correlations of wall temperature during the interaction between a flame and an air-film cooled wall. This framework is demonstrated with the Mg<sub>4</sub>FGeO<sub>6</sub>:Mn<sup>4+</sup> thermographic phosphor.

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### Significant increase in critical currents using nano-sized defects in REBaCuO-type high temperature superconductors

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High-temperature superconductors of the REBaCuO type (where RE are selected rare earth metals) constitute a group of materials important for applications using high values of currents and critical fields, including the so-called irreversibility field below which the superconductor shows zero resistance to direct current. After a brief introduction to the physics of magnetic vortices, the properties of which are crucial for determining the values of the mentioned parameters, we will discuss the potential of the superconductor YBa2Cu3O7-d as a material capable of transmitting currents without losses with densities of the order of  $10^{6}$  A/cm<sup>2</sup> and maintaining the superconducting state in fields above 100 T. The key issue in the discussed topic is to increase the critical current density without significantly deteriorating other important parameters of the superconductor, such as the critical temperature or the upper critical field. This translates into lower costs of manufactured devices and an expansion of the area of high-energy applications. In the presentation, we will report how to increase the critical current density in REBaCuO superconductors by introducing nanosized structural defects into the CuO chains. Moreover, by identifying the mechanisms that determine the anchoring force of vortex threads, we will determine what general properties effective anchoring centers should have in strong magnetic fields. It is worth noting that REBaCuO compounds are the only ones that can be used in fields above 1 T (up to approx. 12 T) at an easily achievable temperature of liquid nitrogen (77 K). The presentation is a summary of research conducted by the authors over many years and presents both previously published results obtained for powder materials [1] and completely new ones regarding single crystals, partially published in [2, 3]. Due to the significant anisotropy of REBaCuO, mainly studies conducted on single crystals provide reliable results regarding the anisotropic properties of critical currents in this type of compounds, which remain the most important in the field of high-energy applications of high-temperature superconductors.

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### Sensing 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 embedded in polymers or 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 (Figure(a)); (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 much stronger linear optical properties, applied to soft mechanochemistry (Figure(b)).



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





### Current Generation of OLED Emitters and how to go beyond

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Organic light-emitting diodes (OLEDs) have revolutionized displays, offering superior viewing angles, contrast, and colour compared to traditional LCDs. However, the quest for even better performance continues. This text explores the current state of OLED emitters and exciting possibilities for the future, focusing on third and fourth-generation technologies like TADF, RTP, and hyperfluorescence.

**First Generation (Fluorescent)** OLEDs utilized fluorescent emitters, limited by a theoretical internal quantum efficiency (IQE) of 25%. **The Second Generation** (**Phosphorescent**) emitters offered a significant leap, with a potential IQE of 100% due to their ability to harvest both singlet and triplet excitons (excited states). However, stability issues, particularly for blue emitters, plagued this generation.

Thermally Activated Delayed Fluorescence (TADF) emerged as a game-changer, addressing the limitations of phosphorescence. TADF emitters can theoretically achieve 100% IQE by converting triplet excitons into emissive singlet states through a process called reverse intersystem crossing (rISC). This generation offered **Higher efficiency** because TADF materials can harvest both singlet and triplet excitons, leading to brighter and more energy-efficient displays. **Improved stability** compared to phosphorescent emitters, some TADF materials exhibit better stability, particularly for blue emitters. However, designing efficient and stable TADF emitters remains a challenge. Researchers are actively developing new materials with optimized properties.

The quest for even better OLEDs continues with the exploration of fourth-generation emitters like **RTP (Room-Temperature Phosphorescence)**, where materials can achieve long phosphorescence lifetimes at room temperature, potentially leading to displays with lower power consumption and improved colour purity. **Hyperfluorescence** is when we utilize multiple singlet exciton generation mechanisms within a single molecule, potentially exceeding the 100% IQE limit of traditional emitters. These technologies are still under development, but they hold immense promise for pushing the boundaries of OLED performance.

Here, we would like to present our path in developing efficient, stable, and colour-tuneable TADF, RTP, and hyperfluorescent materials crucial for next-generation OLED displays and lighting.





# Tuning the molecular interactions of organic molecules in thin films for novel temperature optical indicators

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Excited state intramolecular proton transfer (ESIPT) molecules have demonstrated unique fluorescent properties including large values of Stokes shift [1]. However, their application in thin films and related technologies is limited and mainly focused on the realization of efficient white light organic light-emitting diodes (WOLEDs) [2]. In frame of exploring new applications for ESIPT compounds, we have designed and synthesized two benzothiazole isomers with tailored optical properties in thin films. First, we have demonstrated that tuning of fluorescence emission wavelength and fluorescence quantum yield for those compounds resulted from modified (inter)molecular interactions in thin films. The latter were achieved by optimization of several parameters, including selection of solvent used for deposition and by studying the effect of the annealing temperature [3]. Basing on this approach, we have also elaborated more advanced materials in form of thin films incorporating ESIPT molecules. It was achieved by doping the ESIPT analogues with a novel far-red fluorescent dye, thus realizing organic Förster resonance energy transfer (FRET) systems. We have explored the role of their molecular interactions by studying their morphology and fluorescent properties. Such analysis enabled us to develop unique FRET temperature indicators, which are air-stable, capable of detecting multiple temperature ranges, and compatible with naked eye inspection under UV illumination.

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### Semiconductor nanomaterials from synthesis to applications

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Colloidal semiconductor nanocrystals offer significant advantages such as large-scale solution processing and adjustable optoelectronic properties through precise synthesis and surface chemistry modification. These features make them highly attractive for a wide range of applications, including photovoltaics [1], catalysis, and even biology and medical applications. One of the most commonly used groups of inorganic materials in optoelectronics is A(II)B(VI) semiconductors (e.g., ZnTe, ZnS, CdSe), which are chalcogenides of group 16 elements of the periodic table, such as sulfides, selenides, or tellurides. A key factor determining the further application of these materials is the development of methods for producing and modifying new materials with controlled optical and surface properties. This work focuses on the general strategies and recent developments in the controlled synthesis of colloidal semiconductor nanocrystals in terms of crystalline structure, particle size, and their surface passivation, as well as their applications.

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### Halides as Electrolytes for All-Solid-State Batteries

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Ternary halides of the rare-earth elements (R = Sc, Y, La-Lu), of alkali- and pseudoalkali-metals (A = Li-Cs, Ag, NH<sub>4</sub>, In, Tl, ...) and the triad (X = Cl, Br, I) have been synthesized at great length decades ago [1,2]. Their crystal structures determined as well as some of their properties (luminescence, magnetism, ionic conductivity). The formula type  $A_3RX_6$ appears most frequently, and all crystal structures contain isolated  $[RX_6]^{3-}$  octahedra with the A<sup>+</sup> cations in appropriate coordination polyhedra, the smaller ones, (A = Li, Na, Ag) predominantly also in an octahedral environment.

The crystal structures may be derived mostly from closest packings of halide and, for the larger A's, spheres and/or as derivatives of simple binary trihalides, such as AlCl<sub>3</sub> or FeCl<sub>3</sub>. In these, for the formula  $A_3RX_6$ , there are six octahedral and 12 tetrahedral holes of which one is occupied by  $R^{3+}$  and three by A<sup>+</sup> where under-occupancy of some interstices is possible. This leads to high A<sup>+</sup>-cation conductivity, especially for A = Li, Na, Ag, well known since the 1990's [2].

Recently, the engineering of all solid-state batteries, ASSB's, led to a resurrection of  $A_3[RX_6]$  type compounds. Although somewhat difficult to prepare, for thermodynamic reasons and for their moisture sensitivity, the iodides,  $Li_3[RI_6]$ , should be the most interesting as the interstices in the hexagonal or cubic closest packed iodide structures are the biggest and the packing the "softest" (most polarizable), thus Li<sup>+</sup>-ion conductivity should be the "fastest" at the lowest temperatures. This is indeed the case.

 $Li_3[YI_6]$  crystallizes with a cubic closest-packed iodide lattice (C2/m, Z = 2) with the  $Li^+$  ions disordered over three crystallographically distinct positions [3]. There are two other phases frequently observed of which one is richer and the other poorer in  $Li^+$  content. They may even be better ionic conductors.

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### Composite Thermoelectric Materials with Attuned Electronic Structure and Mismatched Phonon Structure (AES-MPS)

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The energy conversion efficiency of thermoelectric elements depends directly on the so-called averaged thermoelectric figure of merit ZT<sub>aver</sub>. Achieving a high ZT<sub>aver</sub> in practice means producing a material that exhibits high ZT values over a wide temperature range. To this end, we have proposed a new strategy for the development of TE composites, which we call the Attuned Electronic Structure-Mismatched Phonon Structure (AES-MPS) concept. The AES-MPS concept was developed based on the classical approach to heat and charge transport in inhomogeneous systems, in the framework of the Effective Medium Theory (EMT).

The experimental verification of AES-MPS concept has been carried out on various inorganic composites eg.  $CoSb_3$  – PbTe [1], GeTe-WC [2], La<sub>0.95</sub>Sr<sub>0.05</sub>Co<sub>0.95</sub>Mn<sub>0.05</sub>O<sub>3</sub>-WC [3] SrBi<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub>-La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>. In-In<sub>4</sub>Se<sub>3</sub> porous systems as well as inorganic-polymer systems based on Cu<sub>14</sub>Sb<sub>4</sub>S<sub>x</sub> tetrahedrites [4]. We have shown that in a composite consisting of Mn and Sb co-doped GeTe as a matrix and WC as a dispersed phase, the simultaneous effect of enhanced thermoelectric power factor and reduced phonon thermal conductivity results in an exceptionally high figure of merit ZT<sub>max</sub> of 1.93 at 773 K and great energy efficiency of 14%.

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### From Dual Frequency Nematics to Ferroelectric Twist-Bend Nematics - the short story

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The concept of the nematic phase dates back almost to the beginning of the history of liquid crystals. In 1916 Max Born, based on his attempts to apply mathematical methods to describe liquid crystal theories, speculated that a polar liquid could exist if the dipoles of the components are large enough so that the dipole-dipole interactions between them could overcome the thermal fluctuations. For over a century, Born's theory remained in the sphere of historical curiosities, until 2017, when two research groups demonstrated the existence of a new phase of N<sub>F</sub>, for the compounds DIO and RM734. This phase shows a symmetry breaking resulting in director **n** being different from **-n**. Another important discovery among new nematic phases is the chiral heliconical N<sub>TB</sub> phase, which is most often exhibited by bimesogenic compounds, and whose model compound is CB7CB and odd CBnCB homologues. This work will present the development from early compounds exhibiting a nematic monotropic ferroelectric phase, through compounds with the enantiotropic N<sub>F</sub> phase, to the latest discovery of compounds exhibiting a twist bend ferroelectric phase N<sub>TBF</sub>, which is a chiral polar phase, from the point of view of the organization of matter, it is a blend of heliconical and polar phases.

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### Liquid crystalline structures for unconventional microlasers

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Photonic band structures, which are commonly formed by liquid crystals (LC) incorporating chiral molecules are promising photonic materials owing to their ability to control light propagation at different frequencies. Albeit, the first observations of lasing from liquid-crystal media were recorded forty years ago, nowadays, when nano- and microphotonics rapidly develop, the engineering of microstructures providing laser light on-demand generated in-situ seems to be one of the most important fields photonic materials engineering. There are a variety of liquid-crystal phases, primarily those containing chiral components, that exhibit a periodic structure and consequently give rise to a photonic bandgap. Here we give a snapshot of the research done on laser emission from different liquid-crystal media and structures, indicating random lasing, band-edge lasing, and defect-mode lasing. We shortly comment on available mechanisms of emitted wavelength tuning.

Current challenges that lie in the search for smart materials and structures for micro-photonics as well as the plethora of potential applications of tunable microlasers inspired us to study the lasing induced in various periodic self-assembled LC structures. Here we present observations of lasing obtained in dual-frequency-based, near defectless, cholesteric structures, exhibiting a relatively big *Q*-factor. Such structures have been tested also after their polymerization, which suppresses the temperature-induced shift of lasing wavelength. The other example of a unique bandgap material are so-called blue phases. Here we report and discuss a newly observed and mastered at our group, the topologically protected, spatially distributed lasing form 3D, dye-doped, highly ordered blue phase structures. The high-intensity, topologically protected multidirectional emission was obtained from macroscopic (of the diameter of several millimeters) monodomain samples of BFI and BFII. We show an example of the unique lasing, sourcing from the custom-made microcavity, formed between two, distributed Bragg reflectors. The cavity was LC-filled with custom-tailored, high birefringent, dye-doped nematic liquid crystal. The unique emission of a two coherent beams with an opposite circular polarization sourcing from the resonant X- and Y-polarization modes of opposite parities in LC-tunable microcavity is presented and discussed. A similar emission from a cavity with a perovskite emitter is shown.




### Magnetic materials for 3D printing

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Modern society demands innovative techniques to manufacture advanced devices that make our daily lives more efficient. Additive manufacturing (AM) is a technology that is growing rapidly and enables quick production of prototypes and small batches of objects at a lower cost. The ability to build devices using AM from magnetic materials introduces new possibilities and solutions in areas where magnetic materials are used, such as electric motors, generators, transformers, sensors, and magnetic coolers.

This study focuses on the physical properties of magnetic composites made from acrylonitrile butadiene styrene (ABS) and iron (Fe) powder for 3D printing. The materials were produced by mixing ABS with Fe and thermally compounding them through a single-screw extruder. They were characterized through structural, magnetic, thermodynamic, and mechanical aspects. Structural measurements showed that the Fe particles remained stable and did not undergo agglomeration or oxidation throughout the composite synthesis process. Further, magnetic investigations confirmed the presence of soft ferromagnetic characteristics in each of the samples. These findings demonstrate the efficacy of the composite formation method employed and the successful preservation of the iron particles' structural integrity and magnetic properties during the synthesis process.

The performance of the obtained materials was compared with a commercially available polylactide-based (PLA) and Fe-based composite, and it was found that they were equally good. From these composites, a filament with a diameter of 1.75 mm was created and components of electrical devices were printed. The devices created using this method were fully functional and can be an alternative in specific applications.





# Anisotropic magnetocaloric effect in single crystals of Zintl phases: EuIn<sub>2</sub>P<sub>2</sub>, EuIn<sub>2</sub>As<sub>2</sub>, and Eu<sub>5</sub>In<sub>2</sub>Sb<sub>6</sub>

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EuIn<sub>2</sub>P<sub>2</sub> and EuIn<sub>2</sub>As<sub>2</sub> crystalize in a hexagonal structure (space group P6<sub>3</sub>/mmc), which facilitates the appearance of uniaxial anisotropy. Both compounds exhibit ferromagnetic order of the Eu magnetic moments within the ab plane, however, interlayer coupling favors non-collinear parallel arrangement of the adjacent planes in the phosphide, and antiparallel arrangement in the arsenide. The Curie and Néel temperatures are 24 K and 16.1 K, respectively. The crystal structure of Eu<sub>5</sub>In<sub>2</sub>Sb<sub>6</sub> is orthorhombic (space group Pbam) and the compound undergoes two subsequent antiferromagnetic phase transitions at 14 K and 7.1 K.

Recently, similar Eu-based compounds have been in the spotlight not only for their interesting magnetic properties, but also for the possible presence of non-trivial topological states. In addition, such materials are known to exhibit a significant magnetocaloric effect (MCE). Our own research was aimed at studying a special type of MCE, called rotational (RMCE). In RMCE, the entropy change stems from varying magnetic field direction, while keeping its magnitude, which simplifies the design of practical devices. The three selected compounds allowed us to test different types of long-range magnetic ordering in the presence of magnetocrystalline anisotropy of different strength.

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# L-30

# Temperature invariant luminescence manometry for pressure sensing and imaging

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Although ruby is considered as the gold standard in optical pressure measurement techniques (luminescence manometry)[1], it has several limitations, including low sensitivity to pressure changes, sensitivity to temperature changes, and the inability to facilitate two-dimensional imaging of pressure changes. These limitations necessitate the exploration of new solutions.

In response to these challenges, we have developed a novel measurement technique for imaging pressure changes, utilizing phosphors that exhibit broadband  $Cr^{3+}$  ion emission associated with the  ${}^{4}T_{2} \rightarrow {}^{4}A_{2}$  electronic transition [2,3]. In this case the metrological figure of merit is the ratio of emission intensities integrated into two spectral gates (luminescence intensity ratio, LIR) overlapping this emission band. The energy of the  ${}^{4}T_{2}$  level of  $Cr^{3+}$  ions is highly sensitive to variations in the crystal field strength induced by pressure changes, leading to a shift in the spectral position of the band and, consequently, a monotonic change in the LIR. On the other hand change in temperature does not affect the spectral position of emission bands providing thermally invariant pressure readout. This approach has resulted in materials with world-record manometric sensitivity (>120%/GPa).

Importantly, this proposed ratiometric technique allows for rapid two-dimensional mapping of pressure changes by analysing luminescence maps recorded in two spectral bands. During this lecture the potential of the proposed solution will be demonstrated through several case studies involving phosphors doped with  $Cr^{3+}$  ions.

**Acknowledgement:** This work was supported by the National Science Center (NCN) Poland under project no. DEC-UMO- 2020/37/B/ST5/00164.

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# Exciton kinetics in coupled quantum dot dimers

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In analogy to atoms and molecules, a quantum dot (QD), as a zero-dimensional object, can be considered at a certain level of abstraction as a building block of collective, intentionally organized systems. Due to the atomic analogy and "by design" approach to the symmetry, such structures are frequently called as artificial molecules or QD-molecules (QDMs). From the experimental point of view, results obtained by detection of single photons emitted by a single QD and a single QD-molecule are qualitatively different. These differences are not only related to the increased number of emitted photons but go deeper into the probabilities of kinetic processes.



In the case of an isolated QD, the expected photon statistics should fall into one of the known models describing the dark state formation (e.g. Efros-Rosen, HC, MRC or D-type blinking model), or a mixed blinking type. However, due to the QD-QD coupling, the balance probabilities of regarding the kinetics of excited states relaxation in an inter-system QD will also depend on the temporal

Fig. 1 (a) Representative HR-TEM image of a QD-QD dimer along with the STM like projection of the bonding state. (b) Representative spectrally resolved temporal evolution of photons emission from a QD-QD dimer.

state of the QDs located in immediate vicinity. In a consequence, the mutual impact will depend on the coupling strength i.e., distance between the QDs, being barely perceptible or even dominate the processes of radiative relaxation. More strictly, changes to the balance of radiative relaxation kinetics are implicated by mutual charge exchange by the inter-system QDs.

Hence, out interest in this matter is to identify the excitonic kinetics that is responsible for the cardinal change in the photon statistics observed for coupled QDs comparing to an isolated QD. We'd like also to put some light on the self-limitation of the charge transfers and the conditions needed for the dark state formation in the mutually interacting QDs.





# Microstructure to biocompatibility and mechanical properties relationship for Zr-based bulk amorphous/crystalline composites

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The discovery of metallic glasses and the development of bulk metallic glasses (BMGs) with critical dimensions in the tens of millimeters have broadened the scope of their applications. Zr-based BMGs are particularly attractive for biomedical applications due to their desirable biocompatibility, superior hardness, strength, low elastic modulus, wide range of elastic deformation, exceptional wear resistance, and fatigue resistance. The absence of grain boundaries, the presence of abundant passivating elements, and the high degree of chemical homogeneity contribute to their exceptional corrosion resistance. Recent research has shown that the brittleness and low macroscopic ductility of BMGs can be greatly improved by creating bulk metallic glass matrix composites (BMG-MCs) [1]. The composite structure has also been reported to improve mechanical properties of Zr-based BMGs. In this paper we present the relationship between microstructure and mechanical properties in relation to biocompatibility for selected Zr-based alloys.



Fig. 1 Nanoindentation mapping of instrumented hardness ( $HV_{IT}$ ) with distributions and loaddisplacement F-h curves for the  $Zr_{50}Ti_5Cu_{10}Ni_{10}Be_{25}$  BMG-MC.

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# Adsorption of carbon dioxide on raw and modified vermiculite

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Reduction of air pollution is one of the major priorities in today's society. Carbon dioxide is classified as one of the most harmful gas. Its emissions are generated during fossil fuel burning, waste management, combustion and are responsible for global warming [1]. The interest on developing of new adsorbents with the ability to abate various air pollutants has been growing. Clay materials, especially vermiculite - trioctahedral mica-type mineral with 2:1 layered structure are increasingly used as adsorbents from gas phase [2].

The aim of presented work was carbon dioxide adsorption on vermiculite. Acid activated samples (W\_Cl\_x) were prepared by acid treatment with different concentrations of hydrochloric acid (1, 2, 3, 4 mol L<sup>-1</sup>). Vermiculite was subjected to modification in order to increase its porosity and adsorption properties. The prepared adsorbents were characterized using the BET specific surface area analysis, thermogravimetry (TG), X-ray diffraction (XRD) and scanning electron microscopy (SEM). Applied modifications significantly increase specific surface area from 78,21 m<sup>2</sup> g<sup>-1</sup> for unmodified sample (W\_REF) to 490.28 m<sup>2</sup> g<sup>-1</sup> for W\_Cl\_4. Obtained results showed that acid treatment tunes the material's functional properties by increasing the contact surface and generating more active sites in its structure. The adsorption performance in terms carbon dioxide adsorption capacities follows the order of W\_REF (25.91 mg g<sup>-1</sup>) < W\_Cl\_1 (25.99 mg g<sup>-1</sup>) < W\_Cl\_2 (42.15 mg g<sup>-1</sup>) W\_Cl\_4 (57.02 mg g<sup>-1</sup>) < W\_Cl\_3 (68.79 mg g<sup>-1</sup>). Acid activation significantly improved carbon dioxide adsorption properties of modified samples compared to raw material. These results demonstrate that vermiculite-based samples have potential for being used as effective CO<sub>2</sub> adsorbents and acid treatment is promising technique for improving adsorption properties of clay minerals.

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# Advancements in Bio-Nanoparticles for Sustainable Wastewater Treatment: Applications, Challenges, and Future Perspectives

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This study presents recent advancements in utilizing bio-nanoparticles for sustainable wastewater treatment, focusing on their applications, advantages, challenges, and future perspectives. Bio-nano particles derived from biological sources offer promising solutions for addressing water pollution challenges. They demonstrate remarkable efficacy in adsorption, biodegradation, coagulation, electrochemical treatment, and advanced oxidation processes. Notably, these particles exhibit higher surface area and reactivity compared to traditional materials, leading to improved contaminant removal. Their ability to be customized for specific applications minimizes the impact on non-target species, while their renewable nature presents cost-effective and environmentally friendly alternatives to traditional methods. However, challenges such as recovery and scale-up hinder their widespread implementation. To overcome these challenges, innovative recovery methods and scalable production techniques are proposed. Additionally, interdisciplinary research initiatives and global collaborations are emphasized to unlock the full potential of bio-nano particles in addressing the global water crisis.





# Oxygen-reach amorphous TiO<sub>2</sub> as a raw material for the preparation of self-cleaning and antibacterial coatings active in visible light and in the dark

P-4

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Heterogeneous photocatalysis is one of the most effective methods of purifying the aquatic environment from even pharmaceuticals that are difficult to remove by other methods, such as antibiotics or hormones. One of the most frequently studied photocatalysts is titanium dioxide which requires light in the UV range to operate. Many scientific studies focus however at sensitizing this oxide to the visible light range. In this work, we present amorphous  $TiO_2$  obtained using peroxide-assisted sol-gel method. We demonstrate the activity of this material in the decomposition of a standard pollutant - methylene blue dye in a process catalyzed by visible light and taking place in the dark. Additionally, we also show that  $H_2O_2$ -sensitized TiO<sub>2</sub> is able to kill bacteria (*Escherichia* coli and Enterococcus faecalis) both in the light and in the dark. When explaining the activity of our material, we point to the role of the so-called adoxygen groups formed as a result of H<sub>2</sub>O<sub>2</sub> modification. By eliminating all thermal processes during the preparation of the material, it retains its amorphous form, constituting a sponge maximally saturated with adoxygen groups with oxidizing potential (superoxo and peroxo groups). In this work, we also show the prospects for using sensitized  $H_2O_2$  -TiO<sub>2</sub> as raw material for the preparation of self-cleaning or antibacterial coatings.





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# Electronic structure of hexagonal ScN, YN, and LuN

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Experimental reports on flattened hexagonal atomic layers in ScGaN alloys started interest in crystal and electronic structures of rare earth nitrides in the phase of boron nitride. Theoretical investigations indicate the transition between the cubic ground state and hexagonal metastable structure in these systems under tensile strain.

In this presentation, the structural and electronic properties of hexagonal bulk and monolayer rare earth nitrides are discussed based on the results of the density functional theory calculations. Band gaps of hexagonal bulk and monolayer rare earth nitrides, i.e., the indirect ( $\Gamma$ -K) E<sub>g</sub> from 1.34 to 1.69 eV found for the bulk systems, are predicted to be wider than those of the corresponding cubic phases. Furthermore, the strong spin–orbit coupling in monolayer YN and LuN leads to characteristic splitting of valence bands in the K point in the Brillouin zone, which is similar to that present in transition metal dichalcogenides.

Novel hexagonal 3D and 2D phases of rare earth nitrides are promising materials for applications in optoelectronics.

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# Machine Learning for half-Heusler Phases:

#### From Lattice Parameter to Thermoelectric Performance

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The fusion of ab initio methods with Machine Learning (ML) continues to garner unabated interest. Thanks to the application of increasingly sophisticated ML methods, it becomes feasible to explore and predict diverse targets.

A Support Vector Regression (SVR) method tailored for solving regression problems in multi-dimensional spaces exhibits robust predictive validation compared to results obtained from first principles. By utilizing a large group of semi-Heusler compounds (*XYZ* form) analyzed for six targets (lattice parameter; band gap for GGA and modified Becke-Johnson GGA exchange-correlation parametrizations; bulk modulus; lattice thermal conductivity; thermoelectric Power Factor), it became possible to conduct a comprehensive analysis of the relationships between features of the elements constituent (eleven elemental features were included, e.g., atomic radii and electronegativity, whereas all possible over 2000 combinations of the predictors were considered for each target) and the parameters of the ternary phase *XYZ*.

Such an approach facilitates a significant reduction in the required computational resources while simultaneously maintaining high throughput and the ability to test a numerous of half-Heusler phases for potential applications in thermoelectricity based solely on the properties of the elemental features.

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# Magnetocaloric effect in Zintl phase Eu<sub>3</sub>In<sub>2</sub>As<sub>4</sub>

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Eu<sub>3</sub>In<sub>2</sub>As<sub>4</sub> is an antiferromagnetic axion insulator demonstrating hybridorder topological states [1]. It crystallizes in an orthorhombic structure with space group *Pnnm* [1, 2]. Recent advancements show the existence of a field-induced single pair of Weyl points that may result in unique magnetotransport features [3]. In this study, we explored the magnetic properties and magnetocaloric effect (MCE) in the Eu<sub>3</sub>In<sub>2</sub>As<sub>4</sub> single crystals. At  $T_N = 4.2$  K, Eu<sub>3</sub>In<sub>2</sub>As<sub>4</sub> undergoes a second-order type phase transition from antiferromagnetic (AFM) to paramagnetic (PM) state. At T = 2 K, a metamagnetic transition appears at a field of ~ 0.3 T. Magnetization isotherms do not show any hysteresis, revealing perfect magnetic reversibility along the field applied perpendicular to the *c* axis, leading to a large reversible MCE. The maximum entropy change (- $\Delta S_m$ ) of ~ 22.3 J/kg K is obtained at 7.3 K for the field change ( $\mu_0 \Delta H$ ) of 5 T. The considerable MCE value without magnetic hysteresis makes it a competitive candidate for magnetic refrigeration in low-temperature regions.

This study was supported by the National Science Centre (Poland) under grant 2021/41/B/ST3/01141.

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# Composite magnetic refrigerants consisting of intermetallic Laves phase compounds for use as an active magnetic regenerator for hydrogen liquefaction

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Hydrogen is rapidly becoming a preferred type of fuel, however, its liquefaction using today's vapor-compression technology is energy consuming and expensive [1]. Magnetic cooling based on the magnetocaloric effect is an energy-efficient and environmentally friendly alternative, but improvements in refrigerants are crucial for its success. This method can be implemented across a broad temperature range, from ultra-low to a few hundred Kelvin temperatures. The ideal magnetic refrigerant exhibits consistent magnetocaloric properties across system's operating temperature range. This work presents an innovative method of creating composite magnetic refrigerants that provide a uniform magnetocaloric response over a wide temperature range. Laves phase compounds are promising magnetic refrigerants for low-temperature applications [2]. The novel composites are manufactured using high-isostatic-pressure (HIP) synthesis and are composed of three different magnetic intermetallic compounds, HoNi<sub>2</sub>, DyNi<sub>2</sub>, and TbNi<sub>2</sub>, with a Laves phase structure that exhibit large magnetocaloric properties in the temperature range of 13 to 37 K. The isothermal entropy change derived from magnetization data for composite materials confirmed a nearly uniform material response. For a 1 and 2 T magnetic field change, the magnetic entropy changes were 2.2 and 4.4 J/kgK, with a deviation of ~ 0.45 and 1.0 J/kgK, respectively, in the temperature range of  $\sim$  13-42 K. By utilizing the innovative high-pressure synthesis technique, we have paved the way to high-performing magnetic composite materials that can be used in cryogenic magnetic coolers operating over a broad temperature span, expanding the possibilities of what can be achieved and laying the foundation for cost-effective, clean hydrogen energy.

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### Utilizing guartz crystal microbalance for physical vapor deposition processes

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The guartz crystal microbalance (QCM) is a canonical device to monitor film thickness rate in vacuum deposition processes that measure frequency changes corresponding to mass changes on the nanogram scale. The project defined the QCM setup to enhance its precision for measurements in vacuum sputtering processes [1], facilitating better control and optimization. It provides a better workflow for preparation samples for further microscope experiments independently of PVD machinery and other equipment used for research. The way of fitting QCM into each particular deposition process included re-engineering the sensor head to enhance sensitivity and accommodate a broader range of materials, adjustments to the electronic feedback system, creating a fast, reliable connection that maintains vacuum integrity between sputtering device and thickness gauge. Newly developed concurrent processing software allows real-time data acquisition and visualization independently. These modifications showed in a series of sputtering experiments that optimization works as expected.

Initial tests showed a significant reduction in resulted variability and improved repeatability of measurements. The new setup was compared against traditional methods using SEM-FIB (FEI Helios Nanolab 600i with Ga source device) microscope, confirming the enhanced accuracy and reliability of the modified QCM in capturing detailed film deposition dynamics. All identified uncertainty sources resulted in possible unexpended uncertainty of just 1 nm.

The enhanced capabilities of the QCM pave the way for novel applications. The modifications are a step forward that offers enhanced precision and adaptability for future challenges in nanotechnology. My work encourage scientists to develop or adapt measurement devices to save time, reduce costs, and alleviate tedious tasks common in our field.

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# Effect of temperature on electrical properties of single-layer Mo(S<sub>x</sub>Se<sub>1-x</sub>)<sub>2</sub> FET

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2D materials such as transition metal dichalcogenides (TMDs) and their alloys are being intensively investigated for future applications in electronics and sensors. 2D TMDs exhibit new properties that differ from their bulk counterparts. In the present study, the electrical properties of monolayer FET based on Mo(SxSe<sub>1</sub>-x)<sub>2</sub> crystals were investigated. The samples were prepared using mechanical exfoliation and the dry transfer method [1]. To characterize the number of layers, Raman spectroscopy measurements were performed, which prove that single crystal layers were obtained. Specially prepared SiO<sub>2</sub>/Si substrates with 5 µm separated gold planar electrical contacts were used to fabricate the structures. The example results of the effect of temperature (T) on the electrical properties of the FET for the MoS<sub>0.82</sub>Se<sub>1.18</sub> alloy are shown in Fig. 1. The temperature significantly influences the threshold voltage (V<sub>T</sub>), which varies nonlinearly from -5.5 V for T = 400 K to 5.0 V for T = 300 K. The FET has the best performance at T = 350 K, for which the highest drain current (I<sub>D</sub>) and on/off current ratio (1.3×10<sup>5</sup>) were obtained. The lowest on/off current ratio is  $1.4 \times 10^3$  at T = 450 K. For comparison, this parameter for MoS<sub>2</sub> at room temperature is  $1 \times 10^6$  [2].



Fig. 1: Effect of temperature on the properties of single-layer MoS<sub>0.82</sub>Se<sub>1.18</sub> FET:
 (a) threshold voltage (V<sub>T</sub>), on/off current ratio and (b) output characteristics at constant gate-source voltage.

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# KPFM investigation of monolayer membranes based on Mo(S<sub>x</sub>Se<sub>1-x</sub>)<sub>2</sub> alloys

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Atomically thin two-dimensional (2D) alloys have received much attention recently because of their potential in flexible electronic and optoelectronic applications. They can be alloyed by substitution in place of a metal or chalcogenide atom, with negligible effects on lattice deformation, but with significant effects on optical, mechanical and electrical properties. In particular, monolayer transition metal dichalcogenide (TMD) alloys are unique 2D semiconductors in which the energy gap can be tuned by alloying [1,2]. Investigating and understanding the dependence of electrical properties, including surface electric potential, on strain is crucial to the development of advanced flexible electronics based on 2D TMDs [3,4]. We performed Kelvin force microscopy (KPFM) of a series of monolayers based on  $Mo(S_xSe_{1-x})_2$  alloys on Au-coated SiO<sub>2</sub> substrates. Raman spectroscopy measurements were also performed to confirm the thickness of the fabricated membranes. The purpose of our work was to understand the influence of the substrate, chemical composition and material structure on the electrical properties of the membranes studied. We demonstrated the existence of differences in surface potential between membranes made from different TMD materials and their alloys, indicating differences in the conductivity of the materials.

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# Multi-Scale Characterization of Martensite Modulation in Ni-Mn-Ga-Co-Fe Heusler Alloys Using Atomic Force Microscopy

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This study presents a comprehensive atomic force microscopy (AFM) investigation of the topography of martensite phases in a series of Ni-Mn-Ga-(Co-Fe) magnetic shape memory Heusler alloys. The complex martensitic structure of these alloys, which enables their multifunctional behaviour [1], was quantitatively analysed at various length scales using AFM and a proposed geometrical model of the martensite relief. The hierarchical twins-within-twins microstructure was identified, with at least two levels of twins observed: meso-scale twins with  $\sim 20~\mu$ m periodicity and micro-scale twins with  $\sim 250~\mu$ m periodicity (Fig. 1). Despite variations in twin periodicity, all levels shared consistent relief angles (2a) close to theoretical values for 5M modulated and NM martensite. These findings, confirmed by XRD studies, provide insights into the type of martensite modulation in the produced alloys. The AFM technique, combined with the proposed model, enables detailed characterization of the martensitic relief crucial for understanding the functional properties of these alloys.



Fig. 1 AFM 2D and 3D topographic images of the  $Ni_{48}Mn_{31}Ga_{20}Co_1$  Heusler alloy showing hierarchical twins-within-twins martensite structure with characteristic relief angle (2a).

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#### Emerging possibilities of transmission electron microscopy imaging at WUST

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Transmission electron microscopy (TEM) is a powerful imaging technique that has been known for about 100 years. With the use of specific techniques, it can provide information about materials' morphology, crystallographic structure, and processes occurring at the nanoscale. Not all materials can be imaged using this technique, as it is restricted to only very thin, around 100 nm thick electron transparent samples, but with increasing interest, new preparation methods are being developed [1]. TEM is used in a variety of sciences, such as materials engineering and nanotechnology, for structure analysis and observing crystal structures, and life science, to image the interior of cells and the structure of molecules. In my presentation, I will discuss the physical principles of electron microscopy, show the resolution capabilities of TEM on distinct materials, and correlated techniques, namely energy dispersive spectroscopy (EDS), differential phase contrast imaging (DPC), and a more advanced method of liquid cell TEM.



Fig. 1 Representation of different imaging techniques: (a) TEM image of gold nanorod with visible atomic planes; (b) DPC image of a magnet – the colours indicate the magnetic field directions; (c) image of liquid-cell sample containing gold nanoclusters in water; (d) STEM image of quantum dots with elemental mapping of sulphur (e) and cadmium (f).

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#### A route to highly transparent non-cubic calcium phosphate ceramics: impact of starting powder, LiF doping, and SPS sintering conditions

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Our objective is to achieve a new good-quality and mechanically durable high-transparency material that, when activated by rare earth ions, can be used as laser sources, scintillators, or phosphors. Considering hexagonal hydroxyapatite, which shows anisotropy, the particle size of the initial powder is extremely important and should be of the order of several tens of nanometers. In this work, transparent micro-crystalline ceramics of non-cubic  $Ca_{10}(PO_4)_6(OH)_2$  calcium phosphate were fabricated *via* Spark Plasma Sintering (SPS) from two types of nanopowders i.e., commercially available (COM. HA) and laboratory-made (LAB. HA) via the hydrothermal (HT) protocol. Our study cantered on examining how the quality of sintered bodies is affected by the following parameters: the addition of LiF sintering



*Fig. 1 Graphical representation of HA ceramics fabrication using SPS method.* 

agent, the temperature during the SPS process, and the quality of the starting nanopowders. The best optical ceramics were obtained from LAB. HA nanopowder with the addition of 0.25 wt.% of LiF sintered at 1000°C and 1050°C (Fig. 1) [1].

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# CUBIC EULYTITE-TYPE M<sub>3</sub>Y(PO<sub>4</sub>)<sub>3</sub> (M=Sr<sup>2+</sup>,Ba<sup>2+</sup>) PHOSPHATES AS NEW PROMISING MATERIAL FOR TRANSPARENT CERAMICS

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In this study, eulytite-type cubic phosphates with the chemical formula  $M_3Y(PO_4)_3$  (M=Sr<sup>2+</sup>, Ba<sup>2+</sup>) were investigated as potential candidates for developing new polycrystalline ceramics with high transparency. These phosphates were not previously studied in sintered form. The first polycrystalline sintered ceramics based on eulytite-type phosphates were produced using micro-powders. Dense ceramic bodies were obtained through uniaxial cold pressing followed by annealing. Different parameters such as i) the type of alkaline cation in the chemical formula (Ba<sup>2+</sup>/Sr<sup>2+</sup>), ii) preparation of the starting powder using the use of ball-milling, and iii) the variations between single and cyclic uniaxial pressing were analyzed. The



Fig. 1 The photos of translucent micro-crystalline ceramics of Sr<sub>3</sub>Y(PO<sub>4</sub>)<sub>3</sub> and Ba<sub>3</sub>Y(PO<sub>4</sub>)<sub>3</sub>
(a), total Forward Transmission (TFT)
(b); SEM micrographs ceramics (c) [1].

phase purity of the translucent samples was examined using X-ray diffraction (XRD), and their microstructure was precisely analyzed with Scanning Electron Microscopy (SEM). The research demonstrated that samples containing Ba<sup>2+</sup> exhibited greater transparency, likely due to a more ordered structure. Enhanced light transmission in these samples was also confirmed by transmission spectra, as shown in **Figure 1**.

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# Developing NIR-emitting nano- and micro-crystalline YPO<sub>4</sub> and GdPO<sub>4</sub>: Unraveling energy transfer dynamics in Nd<sup>3+</sup>/Yb<sup>3+</sup> co-doped systems

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Luminescent materials have garnered significant attention due to their extensive applications in fields such as bioimaging, optical sensing, and photonic devices. The unique optical properties of NIR-emitting lanthanide ions, like Nd<sup>3+</sup> and Yb<sup>3+</sup>, particularly their sharp emission lines and long-lived excited states, make them ideal candidates for these applications. For instance, gadolinium orthophosphate (GdPO<sub>4</sub>), exhibits unique magnetic properties suitable for MRI, enhancing contrast due to the paramagnetic nature of  $Gd^{3+}$  ions. Simultaneously, the luminescent properties of Nd3+ and Yb3+ ions facilitate optical imaging. Yttrium orthophosphate (YPO<sub>4</sub>) doped with these ions is also explored for its exceptional luminescence efficiency, making them ideal for solid-state lasers as well as bioimaging.

This comparative study investigates the energy transfer mechanisms between  $Nd^{3+}$  and  $Yb^{3+}$  ions in nano/micro-crystalline GdPO<sub>4</sub> and YPO<sub>4</sub>, which crystallize





in distinct lattice structures - GdPO<sub>4</sub> adopts a monazite structure, while YPO<sub>4</sub> crystallizes in a zircon structure. X-ray diffraction (XRD) analysis confirmed the phase purity and crystallinity of the synthesized nano-crystals while scanning transmission electron microscopies (SEM/TEM) revealed their morphology and size distribution. Using a combination of low-temperature high-resolution spectroscopic techniques, including absorption and photoluminescence spectroscopy, we systematically analyzed the efficiency and dynamics of energy transfer in these materials. The strong emission of Yb<sup>3+</sup> and Nd<sup>3+</sup> ions was successfully achieved simultaneously for both, nano- and micro-materials. An energy transfer mechanism between these ions was proposed for the studied host matrix.

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#### Pressure dependence measurement of band gap for TMASI perovskite

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 $(C_4SH_3CH_2NH_3)_2SnI_4$  (TMASI) is recently developed Pb-free two-dimensional perovskite and as a representative of hybrid organic-inorganic material has promising potential application in solar cells and space technology. For better understanding of optical properties of this new material we perform photoluminescence measurement under hydrostatic pressure at room temperature. See Fig. 1. It allowed us to identify band gap evolution of TMASI and determinate the bandgap pressure coefficient ( $\alpha = -191,5 \pm 1,1 \ meV/GPa$ ).







# Ni<sup>2+</sup>-doped phosphors – novel class of luminescent manometers

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A novel and recently intensively explored avenue in luminescence manometry is the ratiometric approach based on the broad emission band of phosphors. This approach offers the potential to significantly enhance sensitivity to pressure changes, along with improved precision and reading accuracy, compared to the traditional approach reliant on pressure-induced spectral shift of emission band. A key breakthrough is also the achievement of temperature-independent readout, overcoming a major hurdle that has compromised the reliability of pressure measurements. Recently, the emission associated with the  ${}^{4}T_{2g} \rightarrow {}^{4}A_{2g}$  transition of  $Cr^{3+}$  ions has received extensive attention in a case of ratiometric pressure sensing, demonstrating the potential of this approach in the development of remarkably sensitive manometers [1]. Hence, it is advisable to exploit phosphors characterized by broadband emission. Given this perspective, phosphors doped with Ni<sup>2+</sup> ions emerge as prime candidates for pressure sensing, due to the strong sensitivity of the energy of the  ${}^{3}T_{2g}$  level to the strength of the crystal field, which is dependent on the applied pressure [2]. Nevertheless, comprehensive investigations into pressure-dependent spectroscopic studies of Ni<sup>2+</sup> ions have yet to be conducted, leaving their potential for pressure sensing unexplored.

Accordingly, we investigated the pressure-dependent spectroscopic properties of Ni<sup>2+</sup> ions in doped ZnGa<sub>2</sub>O<sub>4</sub> spinel. The studies revealed a significant spectral shift of the broad emission band associated with the  ${}^{3}T_{2g} \rightarrow {}^{3}A_{2g}$  electronic transition of Ni<sup>2+</sup> ions (approximately 10 nm/GPa). Consequently, this enabled the development of a pressure sensor operating in a ratiometric readout mode, based on the ratio of the intensities of a  ${}^{3}T_{2g} \rightarrow {}^{3}A_{2g}$  band integrated into two spectral ranges. Obtained results indicate that Ni<sup>2+</sup> ions present a promising avenue for the development of highly sensitive luminescent pressure sensors.

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# **Tailoring Upconverting Nanoparticle Architecture** for Enhanced Förster Resonant Energy Transfer Sensing

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Upconverting nanoparticles (UCNPs) based on a lanthanide doped NaYF<sub>4</sub> are able to emit photons with higher energy than the energy of excitation photons. As a result of forbidden  $f \rightarrow f$ electronic transition, lanthanide ions exhibit long luminescent lifetimes. Moreover, these nanoparticles offer sharp absorption and emission peaks, no photobleaching, efficient anti-Stokes emission and low toxicity[1]. Due to that, UCNPs can serve as energy donors to organic dyes in a process known as Förster Resonant Energy Transfer (FRET)[2]. Even though there were many achievements in this field, some challenges still remain[2]. One of them is finding perfect composition and chemical architecture of nanoparticles for which FRET would be most efficient. In the present work we investigated the effect of lanthanide-doped nanoparticle architecture on energy transfer to the ATTO dye. Three types of nanoparticles were obtained and next functionalized with the dye: NaYF4:20%Yb, 2%Er core-only and NaYF4@ NaYF4:20%Yb, 2%Er, NaYF<sub>4</sub>:50%Yb@ NaYF<sub>4</sub>:20%Yb, 2%Er core-shell nanoparticles. The nanoparticles were synthesized by thermal decomposition method, which is well described in literature[3]. Structure and morphology of obtained UCNPs were investigated using transmission electron microscopy (TEM) and X-Ray diffraction analysis (XRD). Subsequently, absorption and upconversion emission spectra were measured for nanoparticles, for ATTO dye and for an UCNPs-ATTO complex. Our goal is to study FRET at single nanoparticle level and get quantitative information on number of molecules attached to single UCNP as well as sensitivity of dye detection using spectral and luminescence decay measurements.

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# Fixation of amyloid spherulites stained with gold nanoclusters for multimodal bio-imaging: TEM and fluorescence microscopy

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The self-assembly of misfolded proteins into so-called amyloids are the hallmark of numerous neurodegenerative diseases such as Alzheimer's and Parkinson's disease [1]. It is therefore important to understand the structural properties of amyloids in relation to its function in the development of pathology. As different imaging techniques provide specific and thereby, limited information on samples, the simultaneous or subsequent use of complementary modalities can be beneficial in acquiring more comprehensive data on amyloid structures and functional characteristics. For example, electron and fluorescence microscopy can respectively gather both spatial and functional information about a specific molecule [2]. However, traditional sample preparation method for electron microscopy usually requires fixation and treatment with contrasting agents (e.g. osmium tetroxide) which can alter biological samples and impair fluorescence [3]. Therefore, a fixation protocol that preserves data quality and is compatible across modalities is needed. Moreover, a multi-modal staining agent that allows optimized electron microscopy contrast and in-resin fluorescence must be used.

Gold nanoclusters, defined as ultra-small and atomically-precise nanoparticles, capped with supramolecular ligand have shown great promise as probes for multi-modal bioimaging with light and electron microscopy due to their ability to emit near infrared (NIR) luminescence and their high electron density, respectively [4]. Herein, we present the method of fixation of amyloid spherulites which are spherical superstructures of amyloid fibrils radially growing from a central point. Due to the heterogenous character of these structures, we utilized as functional imaging markers the amphiphilic 12-crown-4 ether-capped gold nanoclusters to allow sufficient binding to the molecules. In detail, we compare images of label-free and stained spherulites, both hydrated (in aqueous solution) and fixed, under brightfield, polarized light, and fluorescence microscopy. Finally, we provide structural analysis of the fixed amyloid spherulites with transmission electron microscopy. This research demonstrates an effective sample preparation methodology of staining and fixation for the multi-modal bioimaging of amyloid spherulites.





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# Nanoparticle sizing and counting across many applications and industries

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Particles from approximately 10 nm to over and above 10 micrometers formed the basis of two decades of research in nanotechnology. Spanning over 4 orders of magnitude, such a size range is mostly impossible to investigate in one instrument while allowing for full particle size distribution and number concentration measurements. This has changed in 2016 with new multi laser particle tracking system from HORIBA (ViewSizer 3000)[1]. We describe how multi-spectral NTA/PTA works and why this system is a breakthrough. We also cover applications from Viruses, EVs, to nanoBubbles and nanomaterials.

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### SARS-CoV-2 protein surface modification of Zn<sub>2</sub>GeO<sub>4</sub>:Mn UV-excited luminescence nanomaterials

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 $Zn_2GeO_4:Mn$  (ZGO:Mn) is a representant of nanomaterial showing intense persistent luminescence, that once excited, can exhibit green luminescence properties after the excitation source has ceased. This property enables the potential use of these materials e.g. in bioimaging or bio-tracking [1]. Proper surface functionalization, with e.g. SARS-CoV-2 proteins, can in the next step enhance the effectiveness of using given materials in biosensing or studying virus-cell interactions [2].

This work presents the results we have obtained regarding pH-dependent, microwave-assisted synthesis of six Zn2GeO4:Mn nanomaterials (i.e. each given for different pH value), morphology imaging, and optical properties characterization as well as their surface modification with SARS-CoV-2 proteins.

Our studies confirmed that the usage of different pH values during the nanoparticle synthesis affects the morphology as well as the optical properties of the obtained ZGO:Mn. The nanomaterials surface exhibiting the strongest emission has been successfully modified with SARS-CoV-2 proteins. We are focused on providing further studies upon (i) the characterization of persistent luminescence properties of obtained nanomaterials, (ii) the biocompatibility evaluation of nanomaterials modified via SARS-CoV-2 antibodies, and (iii) the effect of the improved cellular uptake of modified nanoparticles by cancer cells.

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### Two-photon circular dichroism of Au<sub>38</sub> gold nanoclusters enantiomers protected with achiral ligand

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Mirror images of chiral objects are non-superimposable. Chirality itself, as a fundamental symmetry property of molecules, is of great importance for all known living systems on earth. Furthermore, as the enantioselectivity is one of the factors governing biological activities [1], the comprehensive understanding of chiroptical properties of materials at nanoscale might be beneficial. Synthetic protocols for chiral nanomaterials are already well-established and, among variety of available structures [2], atomically-precise noble metal nanoclusters are unique do to the strict control over the number and mutual organization of metal atoms [3]. Atomically-precise clusters are composed of a metal core protected by staple-like motifs ( $Au_x(SR)_y - SR -$  thiolate ligand) and their physicochemical properties are governed by quantum confinement effect. Interestingly, atomically-precise clusters can be made chiral at distinct levels: chiral arrangement of the staples, chiral organisation of kernel, chiral arrangement of protecting ligands or the presence of intrinsically chiral ligands themselves [4].

In this work, we study nonlinear chiro-optical properties of  $Au_{38}(SCH_2CH_2Ph)_{24}$  nanoclusters enantiomers composed of face-fused bi-icosahedral achiral  $Au_{23}$  core and 3 short  $Au(SCH_2CH_2Ph)_2$  and 6 long  $Au_2(SCH_2CH_2Ph)_3$  protecting staples arranged in a clockwise- or anti-clockwise manner [5]. In our work, the protecting ligand –  $SCH_2CH_2Ph$  is achiral. We present that two-photon circular dichroism of  $Au_{38}$  nanoclusters enantiomers can be determined via polarimetric z-scan technique [6], where circularly polarized light is used as an excitation source. The corresponding relative magnitude (comparing to dimensionless dissymmetry factor "g" registered via one-photon CD) is enhanced, 178 times.

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# Chiral properties of atomically-precise DNA-stabilized silver nanoclusters probed by two-photon excitation

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A promising family of chiral materials that can be used in bioimaging or biosensing are atomically precise nanoclusters (NC). Prominent among them are DNA-stabilized silver nanoclusters (Fig. 1(a)), which consist of a few to few tens silver atoms. Depending on the number of silver atoms and the DNA strand used NC exhibit different optical properties. The advantage of Ag-DNA are: narrow-band fluorescence, displaying a wide palette of sequenceselected emission colors that range from visible to near infrared (NIR) wavelengths and high quantum yields in select cases [1].

The poster will present preliminary results of optical and chiral properties in both linear and nonlinear regime, particularly: two-photon absorption cross sections [2], two-photon circularly polarized luminescence (CPL) and fluorescence-detected circular dichroism (FDCD). Due to their near-infrared emission, and chiral properties Ag-DNA are promising fluorophores in the biological tissue transparency windows.



Figure 1. (a) Overall structure of  $(DNA)_2[Ag_{16}Cl_2]^{8+}$  [3] (b) Absorbance, emission and (c) CD spectra of  $(DNA)_2[Ag_{16}Cl_2]^8$  (pink) and  $(DNA)_2[Ag_{15}]^{9+}$  (orange).

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# Hydrophobic epoxy-composite coating modified by acidalkyl chain with anti-icing properties

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This research focuses on developing epoxy composite coatings designed for passive anti-icing applications. The coatings were created by curing an epoxy resin mixed with micro and nano fillers, utilizing a modified hardener. To enhance the surface texture, sandblasting was employed. Previous studies have shown that epoxy resin composite coatings modified with fluoro-oxiranes exhibit strong superhydrophobic and anti-icing properties [1]. This study investigates the potential of replacing these fluorinated modifiers with environmentally and health-friendly alternatives, specifically long-alkyl chain acids. A comparative analysis was conducted between coatings modified with acids and those with fluoro-oxiranes. The use of long-alkyl chain acids resulted in a lower water contact angle (WCA) compared to the fluorinated versions. While initial findings show increased ice adhesion, the results still indicate that these coatings have promising anti-icing properties, demonstrating the potential of longalkyl chain acids as a sustainable alternative for anti-icing applications.

#### Acknowledgments



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# Spatially resolving pH towards the nanoscale using conformationally fluorescent polymer brushes

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Understanding the mechanism of charge transport is important for the development of energy storage devices, however, it is difficult to trace how charge travels in electrolytic solution [1]. Polymer brushes (PBs) are ideal for analysing such transport in aqueous systems, due to pH-responsive transitions in polymer conformation as water undergoes autohydrolysis in an electric field, producing pH changes. Therefore, a simple system constructed with pH-responsive PBs integrated with conformational fluorescence, which transduces changes of polymer conformation into fluorescent output, is being explored for spatial sensing [2,3] and understanding the nature of charge transport in aqueous media under an applied field [4].

Reversible The Surface-Initiated Photoinduced Electron Transfer Addition -Fragmentation Chain Transfer (SI-PET-RAFT) polymerization was used to synthesize PBs, with CDTPA-derived RAFT agent, as homogeneous surfaces. A monomer mixture containing METAC) cationic (([2-(methacryloyloxy)ethyl] trimethylammonium chloride), and (Hydroxyethyl methacrylate, HEMA) were used, where HEMA conjugates to Alexa Fluor 488 via NHS-coupling, and Alexa Fluor 555-maleimide is conjugated to thiol end-groups, creating our Förster resonance energy transfer (FRET) system. We investigate how solution pH causes PB conformational transitions, which translates into FRET signals due to changes in the proximity between fluorophores. These signals are spatially resolved through the "eyes" of confocal laser scanning microscopy towards the nanoscale. Going forward, these pH-responsive brushes will be placed between complex electrodes, where upon applying voltage bias, the pH of the solution changes due to electrolysis, which can be sensed through FRET output from surface immobilized brushes. Together, our work allows for spatially resolving subtle changes in pH, dynamically, and in greater resolution than has been achieved previously.

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# **Fmoc-Assisted Solution-Phase Synthesis of Sequence and Chirality Defined Oligourethanes**

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Nature employ perfectly defined macromolecules to accomplish various chemical process in order to accelerate specific chemical reactions essential for life [1]. For example, enzymes are nature's most sustainable catalysts which possess precise structures with controlled sequences and chirality to perform remarkable functions. To emulate similar properties and functions in abiotic systems, chemists have synthetic sequence-defined macromolecules that has emerged as a new class of sought polymer architecture with an absolute control over monomer sequence and exquisite structures [2]. The defineexploration d macrof omolecsequence-ules in material science remains largely unexplored, primarily due to the formidable challenges associated with their synthesis, which is often low yielding and time-consuming [3].

In order to overcome these challenges, we have design and synthesize Fmoc-assisted stereo-controlled sequence-programmable oligourethanes in solution phase. The work describe step economical synthesis where the deprotection and coupling steps are performed via two-step one pot strategy without intermediate purification leading to rapid and improved synthetic procedure. The protocol is optimized with library of modified chiral monomers. The proposed approach allowed development of scalable and efficient synthetic routes for stereochemically-controlled sequence-defined oligourethanes comprising various structural and functional groups.

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# Designing of selective probes for detection of bioactive impurities of water

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Pollution of the environment and water resources with bioactive chemicals has become an increasingly urgent problem in recent years. The greatest emphasis is placed on species called endocrine-disrupting chemicals (EDC). These substances can negatively affect the endocrine system of humans and animals, which can lead to the development of many diseases. There are many groups of dangerous chemicals classified as EDC, however, this project mainly focused on bisphenol A. Bisphenol A (BPA) is a chemical that is a common additive in plastic manufacturing, mainly polycarbonates and epoxy resins, but it may affect estrogen receptors. Because of the big problem of plastic pollution in the environment, BPA-type substances also easily seep into water supplies. The presence of this chemical confirms the necessity of constant monitoring of water resources because disturbing the sex endocrine system may lead to the development of some diseases, including cancer, or a decline in fertility[1].

The project aims to develop an EDC sensor based on a new class of materials, sequentially defined polymers (SDPs). This new class of compounds combines structural precision, similar to biomolecules such as proteins, DNA, or RNA, and the high stability and chemical resistance that are characteristic of polymers. Macromolecules' properties and functions may be designed by the control of the primary sequence of monomers. Programmable macromolecules will be equipped with fluorescent markers, which will be responsible for signaling the bioactive water pollutant detection[2,3].

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# Anthracene derivatives: Lighting Up Optoelectronics towards All-Optical Synapses

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Within the realm of spectroscopically active materials, anthracene and its derivatives have emerged as particularly captivating and versatile substances. Their unique structure, consisting of a flat and rigid three-phenyl ring system, coupled with an electron-rich  $\pi$ -conjugated network, imparts extraordinary photophysical and photochemical properties. These properties make anthracene derivatives highly appealing for further exploration through chemical functionalization [1].

In this study [2], we examine three meticulously characterized anthracene derivatives, focusing on their chemical structure and product purity. Extensive quantum chemical calculations were performed to elucidate their optical and nonlinear optical properties, revealing the mechanism of photoinduced conformational transformation—a pivotal discovery in this research. Experimental analyses included fundamental optical properties and advanced nonlinear optical phenomena, such as z-scan experiments, second harmonic generation (SHG), and third harmonic generation (THG). Notably, we experimentally validated a groundbreaking all-optical switching phenomenon in these materials, marking a significant advancement and enhancing their potential applications, among other in the all-optical synapses.

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# Polydiacetylenes as components of thermochromic paints

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Polydiacetylenes (PDAs) are compounds with unique chromatic properties, which consistently intrigued researchers. The system of conjugated unsaturated bonds of PDA monomers may polymerize as a result of exposure to UV or gamma radiation, leading to a change in color. Additionally, the color of polymerized PDAs can further shift in response to various external stimuli such as pH, temperature or enzymes. This shift is caused by the twisting of the polymer backbone, which alters the level of conjugation within the system. Depending on the specific PDA structure, this color change can be either reversible or irreversible. Due to these unique properties, PDAs can be used as components of thermochromic paint. Such paint can be used in so-called intelligent packaging. These packages not only serve traditional purposes such as protecting against damage and external factors, but also provide monitoring and informative functions. This feature is particularly beneficial for frozen foods stored at -18 °C, as any rise in storage temperature could lead to defrosting and spoilage.

The presented research focuses on utilizing polydiacetylenes as components in thermochromic paints. The obtained active ingredients and the thermochromic paints exhibit an irreversible color change upon exceeding a specific temperature. The temperature at which this color change occurs in both the compounds and the thermochromic paint compositions was determined using an optical microscope and UV-DSC.



Figure 1. The general mechanism of polymerization of polydiacetylene derivatives.

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# Thermochromic polymeric paints for application in intelligent packaging

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Monitoring temperature is crucial for preserving the quality of various products such as frozen food, pharmaceuticals, and biological materials, all of which require specific low temperatures during storage and transportation. Even a single temperature increase can compromise these items, leading to thawing and spoilage of frozen products, or reduced efficacy of pharmaceuticals and biological materials. Traditionally, temperature monitoring has relied on temperature data loggers. However, disposable loggers are costly, and returning reusable ones presents logistical challenges.

This study explores the potential of thermochromic polymeric paints as an innovative solution for temperature monitoring in packaging. These paints, containing diacetylene derivatives, undergo irreversible color changes when temperature thresholds are exceeded, providing clear visual cues of temperature breaches. Typically, applied to obtain indicators by screen-printing onto plastic foils resistant to low temperatures. The effectiveness of these indicators was tested through simulated freezing and thawing processes, with color changes confirmed using UV-Vis spectroscopy. Additionally, optical microscopy was employed to determine the temperatures at which the color changes occur.

This solution offers a cost-effective and easily interpretable alternative to traditional temperature logging methods, thereby enhancing the reliability and efficiency of managing temperature-sensitive products.



**Figure 1.** The principle of operation of an indicator made by screen printing on polypropylene foil using a thermochromic paint based on a biepoxy base, containing a diacetylene derivative at a level of 10%.

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# Organic dyes-doped ionogels as new, potential thermochromic indicators

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Ionic liquids (ILs) are gaining popularity due to their unique physicochemical properties, including thermal and electrochemical stability, near-nonvolatility, secured ionic conductivity, and recyclability. ILs by themselves, have a danger of leaking because of their intrinsic liquid qualities, and their difficulty in utilization limits their practical application. As a result, much research has gone into solidifying or gelling ILs in order to make high-performance IL-based solid-state materials.

Ionogel (IG) is a new category of hybrid materials and one of the most promising ionic conductive materials based on ILs, not only retain almost all of the properties of ILs except for flow, but they are also safer, have better mechanical properties, and are easier to process, resulting in a broader range of applications. They are produced by mixing the ionic liquid with a matrix that forms a solid host network. It can significantly reduce issues of pure ILs by trapping both ionic liquid and organic dye in amorphous silica-like network *via* sol-gel process, by synthesizing ionogels.

The presented materials consist of silica crystal lattice synthesized by sol-gel method, ionic liquid and organic dye. Here, we show that it is possible to synthesize such a hybrid material using the advantages of each of its components to achieve thermochromic indicator. Final properties of material depend on the type of ionic liquid used and its concentration. So far, no attempts have been made to investigate the relationship between the structure of an ionic liquid and properties of silica-based ionogel. We examined ionogels using thermal, structural and spectroscopic methods. Preliminary tests have shown that the phase transition temperatures of the ionogels are independent of the melting points of the ionic liquids used. Additionally, it has been shown that we are able to design a material both by changing the cation and the anion of an ionic liquid.

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# Fabrication of luminescent disc-shaped photonic microstructures *via* wet-chemical etching of hybrid sol-gel layers

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Sol-gel materials based on silica (SiO<sub>2</sub>) and titania (TiO<sub>2</sub>) precursors are good candidates for low-cost photonic material platform alternative to those based on polymers, InP, Si on insulator (SOI), and SiN [1]. However, the fabrication of active luminescent components on this platform is challenging due to the high-temperature heat treatment required to obtain the final material. In contrast, materials based on organically modified silica (ORMOSIL) and TiO<sub>2</sub> precursors are characterized by low optical losses, and can be prepared at lower temperature enabling them to be doped with organic luminescent dyes [2].

Here, we continue our research on the fabrication of thin layers using a combination of ORMOSIL and titanium(IV) ethoxide (TET) precursors with Rhodamine B (RhB) dye. The photolithography and wet-chemical etching of the sol-gel films were employed to obtain well-separated sol-gel waveguides and discs with different diameters [3]. The etching time in buffered hydrofluoric acid (BHF) controlled the depth of the luminescent microstructures. We found that extending the layers' annealing time at 200 °C improved etching selectivity, enabling the fabrication of under-etched sol-gel goblet microstructures (**Fig. 1**). Scanning Electron Microscopy (SEM) was employed to assess the shape and quality of the microstructures. Additionally, UV-Vis photoluminescence measurements were conducted to characterize their luminescent properties, revealing alterations in the emission spectrum shape with prolonged heat treatment at 200 °C. Spectroscopic ellipsometry confirmed the stability of the films over approximately 2 months of storage. With their high refractive index and luminescent properties, these sol-gel microstructures hold promise for integration in photonic devices such as light amplifiers or sensing systems.

#### LUMINESCENT SOL-GEL MICROSTRUCTURES

**Fig. 1** SEM images (tilted view) their FIB cross-section view of the microstructures etched in sol-gel layers.



CONTROL OF ETCHING TIME AND ANNEALING OF THE LAYER

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# Enhanced Optical Performance in Liquids through SPLASH Device: Multicolor Lasing and White Emission

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We demonstrate the Spectrally Programmable Liquid-state Active System for Highperformance (SPLASH) [1], enabling multicolor lasing and white emission. This innovative liquid, three-color emitting device offers exceptional tunability within a single Liquid Crystal Cell (LCC). It consists of a Coumarin 540 (CM540)-doped liquid crystal mesophase, an ionic liquid with Rhodamine 6G (R6G) dye, and a Stilbene 420 (SB420)-infused water-based solution. SPLASH achieves significant multicolor tunability through both lasing and fluorescence, producing White Light Fluorescence (WFluo) and White Light Hybrid-Emission (WHE) with two lasing and one fluorescence band. Its fluid-like nature and compact design allow for easy scalability, making it ideal for high-impact applications such as Li-Fi technology [2] or laser displays [3].



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# P-35

# Organic emitters for luminescent liquid crystalline materials – synthesis and properties

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Liquid crystalline materials doped with luminescent particles (organic emitters, nanoparticles) are widely studied due to their numerous potential applications in optoelectronic devices [1]. The majority of liquid crystals consist of organic, pi-conjugated molecules, which typically exhibit fluorescence, primarily in the UV region. Proper modification of the molecular structure allows for the adjustment of optical parameters while preserving crucial properties such as solubility and miscibility with LC mixtures. The development of molecules maintaining a rod-like structure also enables the preservation of the order parameter in the mixture, thus achieving polarized emission, which can be tuned while in the liquid crystalline phase. The tunability of such materials can manifest in two ways: directionality of absorption/emission polarization or emission intensity, offering potential applications in devices such as switchable optical filters and polarizers [2,3].

In this work, we present a selection of different molecular designs of organic emitters based on the traditional concept of rod-like liquid crystalline molecules. Alterations of optical properties were achieved by extending pi-conjugation in molecules, introducing heterocycles into the molecules, or incorporating electron-donating and -accepting groups. We characterized the mesomorphic properties and solubility in various LC mixtures, as well as spectral properties. Furthermore, we formulated LC mixtures incorporating synthesized emitters and evaluated the polarization state of emitted light, along with emission intensity across varying applied voltage levels. The emitters posses high values of quantum yield and high solubility in LC mixtures. Doping the emitters to LC mixtures allows to obtain materials with high dichroic ratio and switchable emission intensity.

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# Bulk microencapsulation of cholesteric liquid crystal by emulsification

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Liquid Crystals (LC) are omnipresent in today's life and essential for the development of many modern technologies. It is therefore not surprising that an immense interest brought them to a very mature stage. By doping them with proper chiral agents Cholesteric Liquid Crystals (CLC's), having helically-twisted arrangement, may be obtained. Their characteristic optical behaviour make them a prime material for various applications, *e.g.* sensors, anti-counterfeiting or information encryption [1-3]. In spherical shape they have tuneable and highly selective omnidirectional reflections, both visible and invisible to human eye [4]. To preserve such shape various attempts of encapsulations have been conducted recently [1-3]; whilst a very precise control is offered by microfluidic devices a very low output penalises the technique [5]. On the other hand bulk emulsification technique offers good scalability with a less precise control over the capsules size [1,2,6].

This work presents results of application of such bulk emulsification method. Various shell materials were used to encapsulate CLC (exhibiting light reflection in the visible range) by photopolymerization. The emulsification conditions were carefully evaluated, along with the choice of type of the monomer and photoinitiator, influencing size, form as well as chemical and physical stability of the produced capsules. Highly stable and smooth capsules with narrow size distribution were fabricated.

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# Fabrication of colloidal superballs from polystyrene-based spheres

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Creating hierarchical arrangements of materials allows for exploring novel materials with distinct characteristics. This can be achieved via evaporationinduced self-assembly of monodisperse colloidal nanoor microspheres into superballs [1]. A drop template and non-solvent dispersion medium for the clusters are created using microfluidics to improve this technique [2]. Although this method is highly controlled, it is timeconsuming and costly. Alternative approaches besides microfluidic technique non-solvent evaporation are explored.



Figure. SEM image of colloidal superballs made of polystyrene-based spheres.

The current research presents a technique for creating cluster superballs without relying on microfluidics. The approach utilizes polystyrene-based materials and the technique of solvent evaporation. This study presents a creation of superballs by evaporating the solvent of polystyrene beads from an emulsion. The dispersed phase of the emulsion is formed by cross-linked polystyrene spheres in dichloromethane. The cross-linked polystyrene beads showed solvent swelling without dissolving, unlike non-cross-linked polystyrene beads. During the evaporation of the solvent, the spheres underwent self-organization and formed superballs. The presence of the structures (Figure) was confirmed by a scanning electron microscope (SEM) analysis.

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# P-37

# Who are we? In search of answers to the question of determining the nature of the dye occurring in dye-doped opals and its properties

P-38

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Thanks to their optical properties, photonic crystals (PCs) are a very interesting group of modern materials. Photonic crystals are structures with a periodic distribution of the refractive index in one, two or three dimensions. They are called artificial opals or colloidal crystals and their formation is possible through the self-assembly process of uniformly-sized spheres within colloidal systems [1]. The applicability of PCs is further enhanced by the possibility of doping with stimuli-responsive compounds.

This presentation will be about a preparation and characterization of PCs doped with luminescent dye – ethyl eosin (EE). By doping with this dye, a material with sensor properties and unique optical properties such as angle-dependent emission was obtained. The study placed significant emphasis on determining the luminescence properties of opals and dyes, specifically their quantum yield (QY). Moreover, obtained photonic crystals exhibit a rapid change in luminescence properties and color after contact with vapors of inorganic acids commonly used in industry. Furthermore, the three-dimensional opal doped with ethyl eosin exhibits selective change



Dependence of QY on the weight fraction of the dye in the EE-doped PMMA opals.

in the presence of nitric acid(V), unlike the dye solution. The luminescent and sensing properties, coupled with reversibility, render this material fascinating.

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