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Editorial

Special issue: Photoluminescence in rare earths: Photonic materials and devices (PRE'24)



Rare earth elements (REEs) include the lanthanide series elements (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) plus Sc and Y, all highlighted in green in the periodic table of the elements shown in Fig. 1. REEs are a strategic material in this century, due to their unique magnetic, electrical and optical properties, which make them essential for modern technologies, security and defense, and green energy transition [1]. Some of them, e.g., samarium, neodymium, praseodymium, and dysprosium are essential for high-strength and permanent magnets, widely used in several fields, from radar systems to wind turbines, to consumer electronics and aerospace. Even if, despite their name, REEs are not so rare in the Earth's crust, their supply is limited, also because they are primarily extracted from mineral ores, and their production process into useable forms involves multiple stages. Another issue is related to the fact that the production is concentrated in a few countries (especially China), making them geopolitically sensitive.

Rare earth materials possess exceptional optical properties thanks to their distinctive electronic configuration of [Xe]4fⁿ (where n = 0–14) and a wide range of energy levels, which span across a broad spectrum from ultraviolet (UV) to near-infrared (NIR). These properties include adjustable excitation and emission spectra resembling atomic transitions, significant Stokes and anti-Stokes shifts, extended luminescence lifetimes, and outstanding photostability. As a result, they are regarded as a very valuable resource in the field of optical materials. Luminescence properties, and photoluminescence in particular, are very important and are largely exploited in the photonics field [2–4]. It may be recalled that one of the very first lasers (historically, the third one, after the ruby and the U³:CaF lasers) was made using neodymium ion Nd³ in a crystalline matrix of calcium tungstate CaWO₄ [5].

Since the 60s, rare earths materials have experienced rapid growth in optics and photonics, expanding beyond traditional applications like lighting, TV or cell phone displays, lasers, and waveguides to new and emerging areas such as information technology, energy efficiency, sensing and detection, and biomedical applications. In recent decades, a large variety of luminescent materials have been developed by incorporating rare earth ions into different host matrices, including crystalline, amorphous, and glass-ceramic structures, as well as oxides, fluorides, chalcogenides, and organic compounds, or by integrating them into molecular complexes. These materials are being widely employed in light sources and amplifiers, optical displays, fluorescent probes, luminescent labels, frequency converters, detectors, and so on, allowing applications that range from telecommunication to sensing, from medical diagnosis to energy. Despite of it, there is still an increasing demand for novel functions to further extend practical

applications.

To exploit the full potential of rare-earth luminescence, significant research has been devoted to material synthesis and fabrication techniques. Some of the key materials and methods include: hosts such as silica, tellurite, and fluoride glasses that are commonly used for fiber amplifiers and lasers, while ceramics and glass-ceramics offer higher thermal stability and durability to optical waveguides and frequency converters; materials with embedded nanoparticles and quantum dots that enable tunable luminescence for biomedical and sensing applications; thin-film materials, produced by techniques like RF sputtering, sol-gel deposition, chemical vapor deposition and epitaxy which allow precise fabrication of components for solar cells and active integrated photonics.

Despite their success and extensive applications, rare-earth-based photonic materials still face several challenges, related in particular to cost and device efficiency. REEs are relatively scarce, their extraction processes can be costly and environmentally challenging, and the very high demand in consumer electronics and energy fields keeps their price very high. On the devices' side, non-radiative losses and concentration quenching can limit the emission efficiency; the integration with other materials and technologies is not trivial, and ensuring compatibility with silicon photonics and novel quantum platforms is an ongoing research focus. Looking ahead, research is increasingly focused on developing hybrid materials, nanostructured rare-earth composites, and advanced fabrication techniques to enhance the efficiency, scalability, and integration of rare-earth photonic materials.

In this context, the "Photoluminescence in Rare Earths: Photonic Materials and Devices" (PRE) workshops have served, since 2005, as a distinguished platform for researchers, scientists, and industry experts to discuss the latest developments in rare-earth-doped photonic materials and their applications. These biennial workshops (PRE'05 and PRE'07 in Trento, Italy; PRE'10 in Firenze, Italy; PRE'12 in Kyoto, Japan; PRE'14 in San Sebastian, Spain; PRE'16 in Greenville, USA; PRE'17 in Rome, Italy; PRE'19 in Nice, France; PRE'22 with a double event, in Mexico and in Poland; and, the most recent, PRE'24 again in Trento, Italy) have gained significant recognition over the years as a crucial gathering point for knowledge exchange in the realm of rare-earth photoluminescence and its implications for photonics and optoelectronics. By bringing together experts from academia and industry, these workshops have been fostering collaboration, knowledge sharing, and innovation in rare-earth photonics.

Overall, more than 1100 scientists and students from over 30 countries have attended the PRE Workshops in their ten years' history.

This article is part of a special issue entitled: PRE'24 published in Ceramics International.

Periodic Table of the Elements He В С N Li Be O Ne Na Mg ΑI Si Р s CI Ar Τi ٧ Cr Fe Zn κ Ca Sc Mn Co Ni Cu Ga Ge As Se Br Kr Rb Sr Zr Nb Rh Pd Ag In Sb Mo Tc Ru Cd Sn Te Xe 57-71 w Pt ΤI Pb Cs Ra Hf Ta Os Ir Ri Pο Δt Re Hg Rn Διι 87 88 104 106 113 118 Rf Fr Ra Db Sg Bh Hs Mt Ds Rg Cn Uut FI Uup Lv Uus Uuo Ce Tb Dу Yb Lanthanides La Pi Nd Pm Sm Eu Gd Ho Er Tm Lu 103 Th Pa U Cf Actinides Ac Np Pu Am Cm Bk Es Md Fm No Lr

Fig. 1. Periodic table of the elements, in which the rare earth elements are highlighted in green. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

The average size of each event, around 100 people, makes for a collegial environment where students and world experts can mingle and talk in an informal and effective way. After each Workshop, a Special Issue of a prestigious journal (Optical Materials or Ceramics International) was arranged to publish some of the works presented in the event.

The present Special Issue (SI), too, was born with the aim of publishing selected papers presented at PRE'24, but then has enlarged its scope, collecting other works dealing with PRE topics. The Call for Papers has been very successful, and we received more than 80 submissions, testifying the interest of the scientific community towards these topics. Here we try to introduce the papers collected in this SI grouping them according to the primary application; the task is not trivial, as in many cases the material's properties can be exploited in different fields.

A substantial group of papers addresses fundamental issues, concerning materials' synthesis and processing, as well their characterization through the theoretical and experimental analysis of their structural and optical properties. Overall, Europium is one of the most studied rare earth elements, characterized by strong main emissions in the 580-720 nm wavelength band, due to the transitions ${}^5D_0 \longrightarrow {}^7F_1$, ${}^5D_0 \longrightarrow {}^7F_2$, $^5D_0 \longrightarrow ^7F_4$. Therefore, it is not surprising that here, too, there are a few articles dealing with the structural and luminescent properties of Europium-doped materials, such as hydroxyapatite [6], phosphosilicate glass-ceramics (co-doped with Dysprosium) [7], zeolites [8], Terbium-aluminoborate [9], Yttrium oxide nanoparticles [10], and composite films obtained by incorporating the inorganic phosphor SrAl₂O₄:Eu², Dy³ and the lanthanide complex Sm (DBM)₃phen (DBM = Dibenzoylmethane; Phen = 1, 10-phenanthroline) in a poly (vinyl alcohol) (PVA) matrix [11]. Other materials that have been investigated in depth are: Pr,Ce:Gd₂O₂S scintillation ceramics [12], Sm-doped Gd₂Zr₂O₇ transparent ceramics [13], Dy-doped multi-component borate glasses [14], Cu²:Li₂Al₂SiO₆ glasses [15], Pr³:LaYbO₃ and Pr³, Tb³: LaLuO3: perovskites [16], and Nd,Y:CaF₂ crystals irradiated by high-energy He ions [17]. A method for large-scale synthesis of heavy REE-based β -NaY_{0.5}F₄:Gd_{0.5}@ β -NaYbF₄:Tm@ β -NaLuF₄ nanoparticles with optimized cationic composition is discussed in Ref. [18]. Finally, Raman and photoluminescence spectroscopies have been employed to analyze the properties of Er3 -implanted nano tetragonal BaTiSnO3

powders [19]. Another research group has studied the structural, morphological and optical characteristics of ${\rm Eu}^3$, ${\rm Bi}^3$ co-doped ${\rm Gd}_3{\rm PO}_7$ phosphors fabricated via solid-state reaction [20].

Photoluminescence of RE-doped materials has long been successfully exploited for the development of active optical waveguides and devices, such as light sources, optical amplifiers and lasers. Optical fibers obviously play an important role in this scenario, in particular for sources in the eye-safe 1.4–2.4 µm band. A review on recent advances in high-gain Ho,Tm germanate glass fibers, with broadband emission around the 2 μm wavelength is presented in Ref. [21], whereas references [22,23] describe eye-safe broadband emission in Tm³ /Ho³ co-doped multi-ring-profile silica optical fibers fabricated by Modified Chemical Vapor Deposition Chelate Doping Technology (MCVD-CDT), and enhanced 2 μm emission behavior in Ho³ /Yb³ /Ce³ co-doped bismuth-tellurite fibers, respectively. Mode-locked pulsed fiber lasers, doped with Er and Tm and emitting at 1.5- and 2-µm, respectively, were developed by using single-walled carbon nanotubes (CNTs) as saturable absorbers [24]. A promising material for eye-safe laser applications is also presented in Ref. [25], constituted by Er, Ce co-doped BGe1-xSixO (BGSO) single crystals grown by the Bridgman method. A broadband near-infrared emission in barium gallo-germanate (BGG) glasses has been investigated in Ref. [26]: multicore fibers doped with Cr3 /RE (emission in $0.9-2.1 \ \mu m$ range) and Bi^3 /RE (emission in 1.2–2.1 μm range) have been drawn and tested. A glass-powder-nanocrystals doping method of a glass matrix, used to develop new Yb-doped optical fibers for sensing and laser applications, is reported in Ref. [27]. A special class of lasers is the one realized in microspherical whispering gallery mode (WGM) cavities: here, lasers emitting above 1600 nm in Erbium-doped tellurite glass microspheres with diameters around 40 µm are presented, which are pumped in the 1550-1560 nm band, with the advantage of strongly reduced thermal effects [28].

Five more papers investigate the structural and photoluminescence properties of different materials. An experimental investigation of the crystallization process of Tb³ /Yb³ -co-doped sol-gel silica-hafnia glass-ceramic films deposited by spin coating is reported in Ref. [29]: the achievable high transparency makes these films suited to the use as luminescent light concentrators for photovoltaic applications. SiAlON ceramics are well known for their exceptional mechanical, thermal, and

chemical stability, which recently have been exploited in optical applications, too, also due to their excellent transparency in the mid-IR range: here, excellent results in ultraviolet photon upconversion in Er-doped [30] and up- and down-conversion in Nd-doped [31] SiAlON are presented. Co-doping of Nd:CaF $_2$ and Nd:SrF $_2$ crystals with La and Gd proved to be effective in increasing the upper level lifetimes of Nd, thus making these materials suitable for developing laser diode-pumped high repetition rate ultrashort lasers [32].

Precise and stable tailoring of emission color(s) is a major issue for LED light sources, not yet completely solved. Thus, a few papers in this SI deal with this topic, starting with a review that aims to provide a comprehensive understanding of the current challenges in the field of RE-based perovskite LEDs [33]. Blue and neutral/cold white light-emissions may be achieved using Tm³ doped Dy³ /Tm³ co-doped, respectively, lithium-aluminum-zinc phosphate glasses [34]. White light emission with cold (with correlated color temperature (CCT) in the range 5000 to 7000 K) or warm (CCT below 5000 K) appearance has been obtained by exploiting up-conversion in yttrium ytterbium gallium garnet (Yb-YGG) single crystals, grown by an innovative method, doped with various concentrations of Er³ Tm³ ions [35]. Currently, many phosphor-converted white-light LEDs are lacking cyan (480–520 nm) and near-infrared (700–950 nm) spectral components, which negatively affects the biothermal effects of the illuminant. According to Ref. [36], a full-spectrum warm white light may be produced by combining a Ce³, Cr³: Ca₂LuAl₃Si₂O₁₂ garnet, showing cyan-green emission band upon excitation by violet light, with a commercial yellow-red phosphor. An interesting result is reported in Ref. [37], where it was shown that La³ /Dy³ /Eu³ tri-doped (K_{0.5}Na_{0.5})NbO₃ transparent-ferroelectric ceramics, prepared via conventional solid-state reactions, permits to regulate the characteristics of emitted white light by adjusting the excitation wavelength.

Modulation of the red-to-green emission ratio in Yb3 ,Er3 :NaYF4 upconverting nanoparticles has been obtained by adjusting the pH of the reaction medium during the synthesis by the solvothermal method [38]. Multicolor emission is reported from Eu-doped mixed metal orthoborate Ba₂ZnTb₂(BO₃)₄: the color can be continuously tuned from green to orange and eventually to red upon excitation at 377 nm by changing the Eu³ /Tb³ ratio [39]. Another candidate for multicolor light-emitting devices is represented by lead-free Cs2KInCl6 double perovskite, doped with Dy, Sm and Tb [40]; this paper analyzes in detail the energy transfer and the self-trapped excitons emissions in this material. Cool orange emission by nanophosphor composites of Sm:MgO-La_{1-x}AlO₃, synthesized in-situ using the Pechini sol-gel method, is described in Ref. [41]. Promising upconversion phosphors based on Er³ /Yb³ codoped SrTiO3 ceramics, showing green emission and with tailored optical properties depending on the sol-gel synthesis conditions, are proposed in Ref. [42]. A completely different approach is described in another paper, where 2.6 mm thick and mm-to-cm long light guides made in Dy³ single- and Dy³ /Tb³ double-doped borate glass are proposed as blue-to-green light converters [43]. A different color impression at the output face of the glass bar is obtained depending on the output structure, either rough or with pyramidal shape.

Besides up-conversion, down-conversion is also widely exploited in photovoltaic applications to increase the absorption of solar light by silicon solar cells. Here, as an example, two materials are proposed: ${\rm Tb}^3\ /{\rm Yb}^3$ - doped silica-hafnia glass-ceramic films produced via sol-gel technique [44] and Nd 3 single and Nd 3 /Yb 3 co-doped CaTiO $_3$ ceramic powder synthesized using the polymerized-complex method [45].

Counterfeiting is a growing global concern that affects many industries; among the advanced security features needed to mitigate counterfeit threats, one promising approach is based on the use of RE-doped luminescent materials. Here we have some examples [46–49]: a proof-of-concept of security inks is demonstrated by integrating a SiO₂-Al₂O₃-CaF₂ ceramic matrix co-doped with various REEs into printable commercial inks used in the offset printing industry [46];

luminescent cellulose fibers containing Yb^3 , Ho^3 : $Ba_2V_2O_7$ nanoparticles have been tested, which may be introduced in high quality textiles and paper products to protect them against counterfeit [47]; core-shell-shell microspherical particles doped with Er^3 and Eu^3 , exploiting up- and down-conversion emissions, have been tested in anticounterfeiting inks [48]; core-shell Er^3 -Yb 3 -doped nanoparticles produce intense up-conversion emissions which render them suitable for applications in latent fingerprint detection and security ink, but also for thermometric sensors [49].

The recent decades have seen the growth of new directions exploiting both down- and up-conversion emission of RE ions. Besides the security applications described above, the sensing field has also become more and more important, as testified by a noticeable group of papers in this SI [50–59]. The majority of these works propose various materials for temperature sensing, mostly based on the thermal dependence of the up-conversion emission [50-57]. Luminescence properties combined with gas sensing capability have instead been demonstrated using Eu³: MoO₃ 1D ice-lolly-like nanorods, that proven to be highly efficient for the detection of Triethylamine (TEA) [58]. The search for a simple, portable specific sensor for on-site qualitative detection of Sc³, that is particularly important for environment pollution control in industrial solid waste, has led to the optimization of the bottom-up process for the preparation of carbon dots; color changes (from green to blue) upon simple UV irradiation were effective for achieving visual detection of the specific presence of Sc³ [59].

Finally, another prominent group of papers is dealing with biomedical applications, in particular bioimaging. Recent advances in design strategies, preparation methodologies and functional modifications of RE nanocrystalline scintillators, with their particular application for X-ray-excited bioimaging and deep-tissue antitumor therapy are reviewed in Ref. [60]. A combination of luminescence and confocal Raman spectroscopy to monitor the uptake and internalization of Eu-doped laponite nanoparticles into the J774 macrophage cell line is discussed in Ref. [61]. Here, laponite is the carrier for drug delivery system, while the Eu³ ions act as a luminescent model of the fluorescent drug. Applications in botany and plant grow are also gaining interest: fluorescence bioimaging was tested by using Eu-doped strontium aluminate nanoparticles in plant cell culture [62], and Eu³:SrLa₂(-MoO₄)₄ red phosphors with layered scheelite structure was used to convert a 394 nm LED light into red light, which was beneficial for plant growth [63]. A direct application to medical therapy is proposed in Ref. [64], where upconversion films containing BaLu₂F₈:80 %Yb³ /0.5 %Tm³ microcrystals, excited at 980 nm, provide a high-intensity UV emission for non-contact prevention of bacterial infections in open wounds. Förster resonance energy transfer (FRET)-based biosensors have a wide range of applications, from biochemistry to cell biology and drug discovery; here, the synthesis of core triple shell upconverting nanoparticles is described, that allowed to design and test a biochemical sensing platform with enhanced FRET efficiency [65].

As the field continues to evolve, rare-earth-doped materials will remain at the forefront of breakthroughs in telecommunications, lighting, biomedical imaging, quantum technologies, and beyond. With ongoing advancements in material science and device engineering, rare-earth-based photonics is poised to drive the next generation of optical and optoelectronic technologies. PRE Workshops will continue to provide a valuable platform for discussion and collaboration.

The next workshop, PRE'26, will take place in Hangzhou, the capital of China's Zhejiang province, from March 22 to 25, 2026. Home to nearly 12 million people, Hangzhou hosts the headquarters of major global tech companies and several prestigious universities. Experts, early-career researchers, and PhD students are warmly invited to participate in PRE'26 and contribute to advancing the knowledge and applications of rare-earth materials and their compounds.

We conclude by expressing our gratitude to everyone who contributed to the success of PRE'24, from the co-chairs and the scientific and organizing committees to, last but not least, all the attendees. We deeply appreciate all the authors who submitted their papers to this Special Issue. Furthermore, this publication would not have been possible without the dedication of expert reviewers and the invaluable support of Ceramics International's editorial staff. Special thanks go to General Editor Dr. Pietro Vincenzini and Associate Editor Maurizio Ferrari, as well as Xingyi Peng, Jacqueline Jieyi Zhu, and Kirsten Mottram.

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