

Editorial

Rare Earth Doped Glasses/Ceramics: Synthesis, Structure, Properties and Their Optical Applications

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Glasses, glass-ceramics and ceramics belong to three important classes of engineering materials, which are useful in numerous multifunctional and industrial applications [1]. Ceramic materials have attracted a lot of attention due to their advantages. They are ideally suitable to incorporate rare-Earth ions. Thus, ceramic materials with rare-Earth ions are excellent candidates for UV, visible or IR-persistent phosphors [2] and solid-state laser applications [3]. Inorganic glasses belong to the unique amorphous solid-state materials, which are usually thermally stable and formed over a wide region of glass-former concentrations. Since the first demonstration of laser action of Nd^{3+} ions in barium crown glass by Snitzer in 1961 [4], a great number of published works has been carried out on rare-Earth-doped glasses for near-IR lasers [5], broadband optical amplifiers [6], up-conversion luminescence temperature sensors [7] and solid-state-lighting (SSL) applications [8]. Further, several precursor glasses were applied to fabricate optical fibers emitting IR radiation [9]. Transparent glass-ceramics [10], referred to as TGC, are known in the literature data as a new composite material, with their general properties between crystals and glasses. Thermal treatment or laser irradiation introduces structural transformation from precursor glass to transparent glass-ceramics with oxide or fluoride crystals, usually on the nanometric scale. Rare-Earth ions, as optically active ions, are usually incorporated into the crystalline phases. Recently, glass-ceramics have been examined for optical amplifiers, photovoltaic devices, color displays, optical limiters and random lasers [11]. These phenomena are interesting and important from scientific and technological points of view. Systematic studies of radiative and non-radiative relaxation processes and their mechanisms between rare-Earth ions are necessary for knowledge about optical glasses, glass-ceramics and ceramics. These aspects are presented and discussed in this Special Issue, belonging to the section “Advanced and Functional Ceramics and Glasses”.

The aim of this Special Issue is to present novel results for luminescent glasses, glass-ceramics and ceramic materials, which offer important contributions to the development of scientific research in the field of glass/ceramic science and technology, modern photonics and applied spectroscopy. The themed collection includes 11 articles published in the last two years, concerning rare-Earth-doped glasses/ceramics: from synthesis, structure and properties to their potential optical applications.

Synthesis and characterization of germanate ceramics $\text{Li}_2\text{MgGeO}_4\text{:Ho}^{3+}$ are reported by Bednarska-Adam et al. [12]. The studied ceramic system belongs to the monoclinic $\text{Li}_2\text{MgGeO}_4$, which was verified using X-ray diffraction measurements. Spectroscopic analysis revealed the presence of broad blue luminescence, assigned to ceramic matrix and narrow emission bands characteristic for the 4f-4f transitions of holmium ions. The broad blue emission band is associated with the presence of magnesium in ceramic matrix and the occurrence of defects and oxygen vacancies assigned to F-type centers [13].

The effects of the crystalline size of nanophosphors $\text{Y}_3\text{Al}_{1.99}\text{Cr}_{0.01}\text{Ga}_3\text{O}_{12}$ (YAGG: Cr^{3+}) on their optical properties were studied by Boiko et al. [14]. Ceramic phosphors were synthesized on the nanometric scale by the Pechini method and then annealed at various temperatures (900, 1100 and 1300 °C). Formation of a garnet-type structure was well



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observed for the synthesis of nanophosphors YAGG:Cr³⁺ at T = 900 °C [15]. The authors concluded that the higher annealing temperature (>1100 °C) did not improve the optical properties of the studied ceramic phosphors. The nanophosphors YAGG:Cr³⁺ annealed at T = 1100 °C show an acceptable degree of particle agglomeration and may be suitable for practical applications as starting materials for the production of high-quality optical ceramics and luminescent markers for imaging in the first biological window.

The performances of antimony–germanate–silicate glass-ceramics containing Eu³⁺ were elaborated by Żmojda et al. [16]. In particular, the mechanisms of crystallization of EuPO₄ nanocrystals located in antimony–germanate–silicate glasses and their optical properties were investigated in detail. Based on measurements of emission spectra and their decays, the optimal molar concentrations of P₂O₅ and optical dopants (Eu³⁺) in TGC systems were determined. The optimal way to fabricate the antimony–germanate–silicate glass-ceramics in the form of optical fibers is still the appropriate compromise between their luminescent properties and fiber-drawing ability.

Kowalska et al. [17] report near-IR luminescence properties of selected rare-Earth ions (Er³⁺, Pr³⁺, Ho³⁺, Tm³⁺) in titanate–germanate glasses under excitation of Yb³⁺. The resonant Yb³⁺ → Pr³⁺ and Yb³⁺ → Er³⁺ and non-resonant Yb³⁺ → Tm³⁺ and Yb³⁺ → Ho³⁺ energy transfer in co-doped titanate–germanate glass is quite well observed. The introduction of TiO₂ to germanate glass enhances the near-IR emission bands located at 1.3 µm (Pr³⁺: ¹G₄ → ³H₅), 1.5 µm (Er³⁺: ⁴I_{13/2} → ⁴I_{15/2}), 1.8 µm (Tm³⁺: ³F₄ → ³H₆) and 2 µm (Ho³⁺: ⁵I₇ → ⁷I₈). Systematic studies revealed that the lifetimes of Yb³⁺ ions are reduced with increasing TiO₂ content, whereas the energy transfer efficiencies are changed completely different, depending on a pair of Yb³⁺/Ln³⁺ (Ln = Pr, Er, Tm, Ho) in titanate–germanate glass.

The next paper published in this Special Issue is concentrated on inorganic glasses singly doped with Pr³⁺ ions [18]. Spectroscopic properties of Pr³⁺ ions in borate-based glass with Ga₂O₃ and BaO, lead–phosphate glass with Ga₂O₃, gallo–germanate glass modified by BaO/BaF₂ and multicomponent fluoride glass based on InF₃ were compared. Visible emission of Pr³⁺ is modulated from red/orange for borate glass and lead–phosphate glass with Ga₂O₃ via yellowish orange for gallo–germanate glass with BaO/BaF₂ to nearly white light for fluoride glass based on InF₃. The positions and spectral linewidths for near-IR emission bands at the optical telecommunication window corresponding to the ¹G₄ → ³H₅, ¹D₂ → ¹G₄ and ³H₄ → ³F₃, ³F₄ transitions of Pr³⁺ ions depend strongly on glass matrices and excitation wavelengths. The authors concluded that low-phonon InF₃-based fluoride glass and gallo–germanate glass with BaO/BaF₂ are excellent candidates for broadband near-IR optical amplifiers operating at E-, S-, C- and L-bands [19].

The influence of TeO₂/GeO₂ molar ratios on spectroscopic properties of Eu³⁺-doped oxide glasses is reported by Leśniak et al. [20]. Glasses were investigated to explore their potential application as an efficient host material for rare-Earth doping and optical fiber drawing and characterized using different experimental techniques, i.e., DSC, Raman, MIR, refractive index, PLE, PL spectra and time-resolved spectral measurements. Several spectroscopic parameters, among others, the fluorescence intensity ratio R/O and the measured lifetime of Eu³⁺, were determined. Based on luminescence measurements, glass with the highest content of GeO₂ was selected for optical preform and fiber fabrication.

Another article from this Issue deals with rare-Earth (Eu³⁺) and transition metal (Cr³⁺) in glasses containing extremely different glass-formers B₂O₃ and GeO₂ [21]. The Cr³⁺ ions are located at octahedral sites, which was evidenced by EPR spectroscopy. Independently of the molar ratio of glass-formers GeO₂:B₂O₃, red emission of Cr³⁺ was successfully observed. Intensities of emission bands originating to transitions of Eu³⁺ and fluorescence intensity ratio R/O are reduced with increasing B₂O₃ content. On the other hand, the increase in B₂O₃ concentration results in an enhancement in the ⁵D₀ lifetime of Eu³⁺. The results clearly indicate that spectroscopic properties of transition metals and rare-Earth ions should also be controlled by the choice of glass-network-formers.

Structural and photoluminescence investigations of silicate glass-ceramics with CaF_2 nanocrystals co-doped with $\text{Tb}^{3+}/\text{Eu}^{3+}$ ions are described by Pawlik et al. [22]. The series of glass-ceramics with CaF_2 nanocrystals were fabricated using the sol-gel method, which is a suitable alternative for photonic materials [23]. The presence of an energy transfer process between Tb^{3+} and Eu^{3+} was evidenced by the excitation/emission spectra measurements. In particular, the emission decay curve analysis confirmed partial segregation of Tb^{3+} and Eu^{3+} ions inside CaF_2 nanocrystals formed during a controlled heat treatment process.

Spectroscopic properties of rare-Earth ions have also been examined for glasses with the general formula $\text{PbO-Ga}_2\text{O}_3\text{-Me}_x\text{O}_y\text{-Ln}_2\text{O}_3$ ($\text{Me} = \text{Ge, Si, P, B}$ and $\text{Ln} = \text{Eu, Er}$), belonging to a wide family of heavy metal glasses [24–26]. This topic was addressed by Pisarska et al. [27]. The experimental results are presented and discussed in two parts of the published paper. The first part consists of phonon sideband analysis from the excitation spectra of Eu^{3+} . The second part is concerned with the near-IR emission of Er^{3+} ions in heavy-metal-oxide glasses. Correlation between the measured lifetimes of rare-Earth ions, the energy gaps between interacting levels and the phonon energies of these glass systems are well evidenced.

The next paper, published by Górný et al. [28], summarizes comparative analysis for lead borate glasses and glass-ceramics singly doped with Dy^{3+} ions. In particular, the Commission Internationale de l’Eclairage (CIE) chromaticity coordinates (x, y) were calculated for glasses and glass-ceramics in relation to potential applications for white light-emitting diodes (W-LEDs). It was well demonstrated that spectroscopic properties and chromaticity coordinates of lead borate systems can be effectively controlled by modification of the chemical composition of glass hosts and changing the excitation wavelengths.

Kuwik et al. [29] describe the influence of oxide glass-modifiers on the structural and spectroscopic properties of phosphate glasses doped with rare-Earth ions. The authors used the modifier MO ($\text{M} = \text{Ca, Sr, Ba}$) to improve spectroscopic properties of Eu^{3+} and Er^{3+} ions in phosphate glass. Independently of the kind of glass modifier, the intense red (611 nm) and near-IR (1500 nm) emissions were observed for Eu^{3+} and Er^{3+} . Fluorescence intensity ratio R/O due to $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (red) and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (orange) transition of Eu^{3+} depends significantly on the modifier MO ($\text{M} = \text{Ca, Sr, Ba}$). The lifetimes $^5\text{D}_0$ (Eu^{3+}) and $^4\text{I}_{13/2}$ (Er^{3+}) increase with increasing ionic radius of alkaline earth ion $\text{CaO} < \text{SrO} < \text{BaO}$. The results suggest the applicability of phosphate glasses with oxide modifiers (CaO, SrO, BaO) as potential red (Eu^{3+}) and near-IR (Er^{3+}) luminescent materials in photonic devices.

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