



Structural and optical investigations of rare earth doped lead-free germanate glasses modified by MO and MF₂ (M = Ca, Sr, Ba)



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ABSTRACT

Rare earth doped lead-free oxide and oxyfluoride germanate glasses were synthesized. The rare earths as an optically active ions were limited to trivalent Eu³⁺. One of the glass modifier components is MO (M = Ca, Sr or Ba), which was partially or totally substituted by MF₂ in chemical composition. The influence of glass modifiers on structure of lead-free-germanate glasses was examined using X-ray diffraction analysis. In contrast to samples containing modifier MO (M = Ca or Sr), samples with BaO and/or BaF₂ are fully amorphous. For the amorphous samples, the emission properties of Eu³⁺ ions were studied. The emission spectra of Eu³⁺ ions and their decays in glass samples with different BaF₂ contents were analyzed. Several spectroscopic parameters, such as fluorescence intensity ratio R/O (Eu³⁺) and measured luminescence lifetime for ⁵D₀ state of Eu³⁺ are presented and discussed in details.

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1. Introduction

Inorganic glasses are well known as promising materials in modern photonics. These materials are widely used for visible and near-infrared solid-state lasers [1,2], luminescent lamps [3], flat displays [4] and optical communication systems [5,6]. Due to their unique thermal and spectroscopic properties, they are found in the field of optical fiber technologies [7]. Moreover, germanate glasses doped with various rare earth (RE³⁺) ions have been extensively investigated in the past, and many technological and commercial applications have been realized. Germanate glasses are commonly used due to its promising properties including effective atomic number, low energy phonon of the host, high transparency, low melting point, high temperature stability and good solubility of RE³⁺ ions [8,9]. With substitution of PbO/CdO by PbF₂/CdF₂ in germanate glasses the thermal stability is improved, whereas near-infrared emission and up-conversion processes of RE³⁺ ions are significantly enhanced [10,11]. In spite of advantages both PbF₂/CdF₂ and PbO/CdO are considered to be toxic and they are incompatible with the principles of green chemistry. Consequently, they are being eliminated from various practical applications due to their harmful effects on health and environment. Similar to bismuthate glass system [1], rare earth doped low-phonon germanate glasses without lead or cadmium are recommended for optical applications [2]. In literature the research about synthesis [12] optical properties [13–16], luminescence properties [17–20], structure [21,22], energy transfer [23,24],

phosphorescence decay [25] and white light generation [26] of germanate glasses doped with RE³⁺ are well documented. However, structural and optical aspects for germanate glass systems containing various divalent alkaline glass modifiers were not studied in details. Addition of some alkaline modifiers to the glass host results in glass crystallization. This phenomenon can be due to differences in originated in alkaline character of used modifiers. Only a few works is devoted to inorganic glasses modified by alkaline earth oxides. The influence of alkaline earth oxides (R = Ca, Sr, Ba) on the RO–Na₂O–B₂O₃–Fe₂O₃ glass properties was determined. The dielectric and spectroscopic properties have been analyzed in the light of different oxidation states of iron ions in order to understand the influence of alkaline earth oxides as modifier oxide on the structure and insulating strength/conductivity of glass matrix [27]. Also, silicate glasses containing different alkaline earth fluorides (CaF₂, SrF₂, and BaF₂) were prepared and their crystallization behavior was analyzed using non-isothermal kinetics based on DSC methods. According to Yun-Mo Sung [28], the glass containing CaF₂ showed the fastest kinetics for CaF₂ crystallization, while that containing BaF₂ showed the slowest kinetics for BaF₂ crystallization. In contrast to silicate or borate based glasses, germanate systems with alkaline glass modifiers MO or MF₂ (M = Ca, Sr, Ba) are less examined to the best of our knowledge.

From this point of view, rare earth doped lead-free germanate glasses were synthesized. The rare earths as an optically active ions were limited to trivalent Eu³⁺. It has been well known that trivalent Eu³⁺ ions play an important role in practical application as spectroscopic probe [29–31]. Numerous reported results were focused on studies done for the optical properties of Eu³⁺-doped lead glasses

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[32,33], whereas lead-free glass systems with Eu^{3+} ions are practically unknown.

One of the glass components is MO ($M = \text{Ca}, \text{Sr}$ or Ba), which was partially or totally substituted by MF_2 in chemical composition. Firstly, structural properties of lead-free germanate samples modified by MO and/or MF_2 ($M = \text{Ca}, \text{Sr}, \text{Ba}$) were examined using X-ray diffraction (XRD). The fully amorphous samples were selected for further optical investigations.

2. Experimental

Series of lead-free oxide and oxyfluoride germanate glasses with different glass modifiers were prepared by mixing and melting appropriate amounts of metal anhydrous oxides and fluorides of high purity (99.99%, Aldrich Chemical Co.) as starting materials. The chemical compositions of obtained samples are presented in Table 1. The appropriate amounts of all components were mixed homogeneously together. After that mixtures were melted at 1200 °C and kept for 45 min in argon at protective atmosphere. Next, they were quenched and annealed below glass transition temperature T_g [34] in order to eliminate internal mechanical stresses. The X-ray diffraction patterns were measured using an X'Pert Pro diffractometer. The Cu X-ray tube (with $\text{K}\alpha_1$ and 2 radiation) operating at 40 kW/30 mA was used. Diffraction patterns were measured in step-scan mode with a step size of 0.05° and time per step of 10 s.

Optical measurements were performed on a PTI QuantaMaster QM40 coupled with tunable pulsed optical parametric oscillator (OPO), pumped by a third harmonic of a Nd:YAG laser (Opotek Opolette 355 LD). The luminescence was dispersed by double 200 mm monochromators. The luminescence spectra were registered using a multimode UV-VIS PMT (R928) detector controlled by a computer. Luminescence decay curves were recorded and stored by a PTI ASOC-10 [USB-2500] oscilloscope with an accuracy of $\pm 1 \mu\text{s}$. All measurements were carried out at room temperature.

3. Results

Lead-free germanate systems containing Eu^{3+} ions have been analyzed as a function of type glass modifier and/or its concentration. The oxide modifiers MO (where $M = \text{Ba}, \text{Ca}, \text{Sr}$) was partially or totally replaced by fluoride modifiers. The chemical compositions of the studied Eu^{3+} doped samples are given in Table 1. Structural properties of prepared samples modified by different alkaline oxides were characterized using X-ray diffraction analysis and are presented in Fig. 1. For non-transparent samples with modifier MO ($M = \text{Sr}$ and Ca), crystalline phases $\text{Sr}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ and $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ were identified. Then, fully amorphous and transparent samples with BaO and/or BaF_2 were selected for further optical characterization. Fig. 2 presents excitation spectra of as prepared lead-free germanate glasses doped with Eu^{3+} ions. The spectra were monitored at $\lambda_{\text{em}} = 611 \text{ nm}$. The main intense bands located at 393 nm and 464 nm correspond to ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ and ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ transitions of Eu^{3+} , respectively. Next, the influence of fluoride modifier's content on luminescence spectra of Eu^{3+} ions was examined.

Table 1
Chemical compositions of the studied Eu^{3+} doped samples.

Samples	Chemical composition [mol%]
Oxide	
(1)	$60\text{GeO}_2\text{--}30\text{BaO--}9.5\text{Ga}_2\text{O}_3\text{--}0.5\text{Eu}_2\text{O}_3$
(2)	$60\text{GeO}_2\text{--}30\text{CaO--}9.5\text{Ga}_2\text{O}_3\text{--}0.5\text{Eu}_2\text{O}_3$
(3)	$60\text{GeO}_2\text{--}30\text{SrO--}9.5\text{Ga}_2\text{O}_3\text{--}0.5\text{Eu}_2\text{O}_3$
Oxyfluoride	
(4)	$60\text{GeO}_2\text{--}25\text{BaO--}5\text{BaF}_2\text{--}9.5\text{Ga}_2\text{O}_3\text{--}0.5\text{Eu}_2\text{O}_3$
(5)	$60\text{GeO}_2\text{--}20\text{BaO--}10\text{BaF}_2\text{--}9.5\text{Ga}_2\text{O}_3\text{--}0.5\text{Eu}_2\text{O}_3$
(6)	$60\text{GeO}_2\text{--}30\text{BaF}_2\text{--}9.5\text{Ga}_2\text{O}_3\text{--}0.5\text{Eu}_2\text{O}_3$

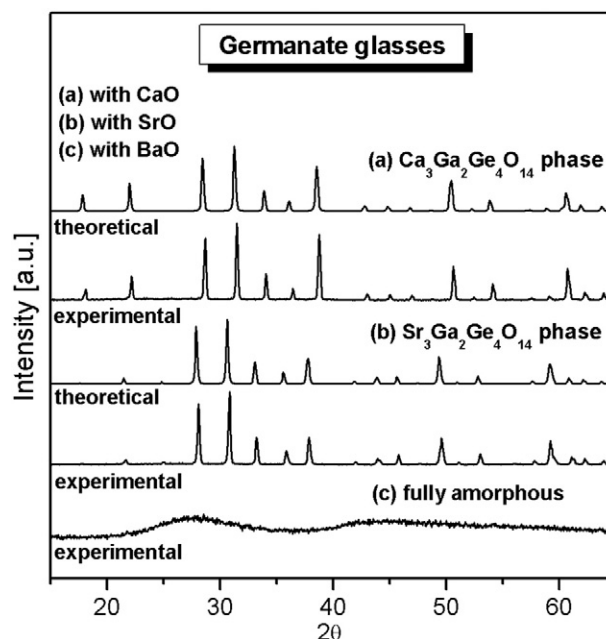


Fig. 1. X-ray diffraction patterns for lead-free germanate glasses with different oxide modifiers MO ($M = \text{Sr}, \text{Ca}, \text{Ba}$).

Concentration of barium fluoride in glass samples changed from 0% up to 30% (in mol%). The luminescence spectra were recorded upon the excitation ${}^5\text{L}_6$ state ($\lambda_{\text{exc}} = 393 \text{ nm}$) of Eu^{3+} and are presented in Fig. 3. Based on emission spectra, the luminescence intensity ratio R/O (also known as R factor) defined as the integrated luminescence intensities of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition of Eu^{3+} was calculated. Luminescence decays from the ${}^5\text{D}_0$ excited state of Eu^{3+} were also measured (Fig. 4). Based on the decays, measured luminescence lifetime for ${}^5\text{D}_0$ state of Eu^{3+} was determined as a function of BaF_2 content. Fig. 5 shows correlation between luminescence lifetimes, R factor and MF_2 concentration ($M = \text{Ba}$) for Eu-doped lead-free germanate glasses.

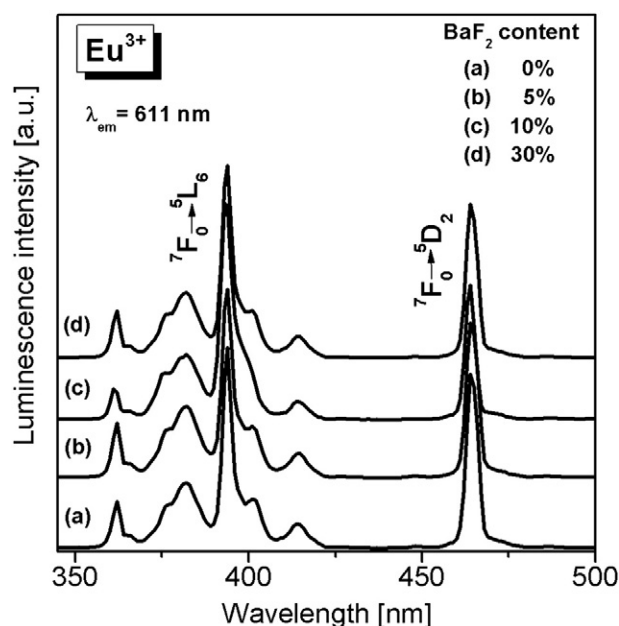


Fig. 2. Excitation spectra of Eu^{3+} ions in lead-free germanate glasses with different contents of fluoride modifier BaF_2 .

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