Journal of Molecular Structure 1041 (2013) 50–54

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Structural and luminescence properties of Eu^{3+}, Dy^{3+} and Tb^{3+} ions in lead germanate glasses obtained by conventional high-temperature melt-quenching technique

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HIGHLIGHTS

- ▶ Fully amorphous and transparent Ln-doped lead germanate glasses were obtained.
- ▶ Local structure of rare-earth doped lead germanate glasses was examined.
- ▶ Optical properties of Eu^{3+}, Dy^{3+} and Tb^{3+} ions in lead germanate glasses were tested.
- ▶ Spectroscopic parameters for rare earths in lead germanate glass were determined.
- ▶ Luminescence decays curves of the investigated glasses had been studied.

ARTICLE INFO

Article history:
Received 24 January 2013
Received in revised form 21 February 2013
Accepted 26 February 2013
Available online 5 March 2013

Keywords:
Rare earth ions
Lead germanate glasses
Luminescence properties
Local structure

ABSTRACT

The subject of this paper is the structural and luminescence properties of selected rare earth ions in lead germanate glasses. Glasses were obtained by conventional high-temperature melt-quenching technique. Europium, dysprosium and terbium ions were chosen as active dopants. The spectroscopic parameters for Eu^{3+}, Dy^{3+} and Tb^{3+} ions were determined based on excitation and emission measurements as well as luminescence decay analysis. Especially, the luminescence intensity ratios R/O (Eu^{3+}), Y/B (Dy^{3+}) and G/B (Tb^{3+}) were calculated. Luminescence lifetimes for $^5D_0$ state of Eu^{3+} ions, $^4F_{9/2}$ state of Dy^{3+} ions and $^5D_4$ state of Tb^{3+} ions were also determined. The amorphous nature and local structure of the studied lead germanate glass systems was confirmed by X-ray diffraction (XRD) and infrared (FT-IR) spectroscopy.

1. Introduction

Trivalent lanthanides and transition metal ions are incorporated into different oxide [1–4], oxyfluoride [5–9] and fluoride [10–13] optical systems for practical applications as inorganic sources emitting visible light or near-infrared radiation. Some of them, Eu^{3+} or Dy^{3+} as well as Cr^{3+} ions are widely used as spectroscopic probes indicating deviation from the site symmetries of the lanthanide or transition metal ions and the strength of covalent/ionic bonding between the optically active ions and the surrounding ligands in numerous amorphous and crystalline materials [14–23].

Lead germanates belong to a wide family of heavy metal glasses (HMGs) which due to their properties, such as high refractive index, density and low phonon energies find applications in optoelectronics [24,25]. It is clear from the previous studies that lead germanate glasses demonstrate high mechanical strength, high chemical durability and temperature stability with good IR transmission extended up to 4.5 μm, which make these glasses suitable new lasing solid-state materials and promising systems converting infrared radiation into visible light [24–27]. Secondly, it was determined that those systems are less influenced by vibrational frequencies compared to silicate, phosphate and borate glasses [28]. Because of their properties the structure of glasses based on $PbO—GeO_2$ has been investigated using Raman technique [29], X-ray scattering [30] or EXAFS and vibrational spectroscopy [31]. However, such systems are of critical interest in the context of germanium anomaly, which has been observed as altered characteristic, such as the Ge—O distance and the number of nearest O neighbors of Ge atoms [32]. The structural investigations of lead germanate glasses are quite well documented in literature. The local structure of lead germanate glass was modified by lanthanides [32–35], alkaline [36] and heavy metals [37], and the structural changes in the glass network were evidenced mainly by FT-IR spectroscopy. It was expected that the introduction of these modifier oxide components into the binary lead germanate glasses may affect the structural features of the host matrices.

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http://dx.doi.org/10.1016/j.molstruc.2013.02.036

Investigated systems of lead germanate glasses are able to incorporate large concentrations of rare earth ions in the host matrices. Thus, spectroscopic properties of oxide lead germanate glasses doped with praseodymium [38], neodymium [39,40], erbium [41–43] and thulium [44,45] were earlier reported. Studies are also available, where the spectroscopic properties of oxyfluoride lead germanate systems doped with rare earth ions were examined [46–48]. Detailed studies suggest that lead germanates are promising glass materials for near-infrared radiation and up-conversion luminescence. Visible luminescence of rare earth doped lead germanate glasses is less documented in literature. Some previously published works concentrate on phonon sidebands [49], energy transfer processes [50], laser-induced fluorescence line narrowing (FLN) technique [51] and reddish-orange luminescence of Eu^{3+} [24,25], whereas little information is available on luminescence spectroscopy of trivalent dysprosium or terbium ions in lead germanate glasses.

In the present work luminescence properties of lead germanate glasses singly doped with rare earth ions emitting in the visible range (Eu^{3+}, Dy^{3+} and Tb^{3+} ions) are reported. Based on emission spectra and their decays some spectroscopic parameters for rare earth ions such as luminescence intensity ratios R/O (Eu^{3+}), Y/B (Dy^{3+}) and G/B (Tb^{3+}) and luminescence lifetimes from $^5D_0$ (Eu^{3+}), $^4F_{9/2}$ (Dy^{3+}) and $^5D_4$ (Tb^{3+}) excited states were determined. The local structure of the obtained glasses was examined using X-ray diffraction and FT-IR spectroscopy.

2. Experimental

Series of samples: $45PbO—45GeO_2—9.5Ga_2O_3—0.5Ln_2O_3$ (Ln=Eu, Dy, Tb) in mol% were prepared by mixing and melting appropriate amounts of metal oxides of high purity 99.99% (Aldrich Chemical Co.) as starting materials. Reagents were mixed homogeneously in an agate ball mill for 2 h. Afterwards, they were melted at 1100 °C for 1 h. Next, they were quenched and annealed below *Tg* in order to eliminate internal mechanical stresses. Fully amorphous and transparent Ln-doped glass samples were obtained. The excitation and emission spectra as well as luminescence decays were performed using a Jobin Yvon Fluoromax4 spectrophotometer. The measurements were carried out with a spectral resolution of 0.2 nm. Luminescence lifetimes were determined with the accuracy of 2 μs. The FT-IR spectra were performed by Bruker spectrometer using standard KBr disc techniques. In order to confirm the amorphous nature of the studied systems, the X-ray diffraction patterns were carried out using INEL diffractometer with Cu Kα radiation.

3. Results and discussion

3.1. Structural properties

X-ray diffraction was used to confirm the amorphous nature of the studied samples. Typical diffraction pattern for the studied glass based on $PbO—GeO_2—Ga_2O_3$ system is presented in Fig. 1. It was found that all studied glasses containing rare earth ions (Eu^{3+}, Dy^{3+}, Tb^{3+}) are fully amorphous. Fig. 2 shows typical FT-IR spectrum for the studied $PbO—GeO_2—Ga_2O_3$ glass system. The FT-IR bands for lead germanate glasses were assigned based on literature data [32]. The FT-IR band in the 400–600 cm^{-1} frequency range is observed, which corresponds to Pb—O stretching vibrations of the $[PbO_4]$ structural units along with the deformation modes of the Ge—O glass network. The observed FT-IR bands in the 690–930 cm^{-1} frequency range are responsible for the vibrations of $[GeO_4]$, $[GeO_6]$ germanate units and interconnected through Ge—O—Ge bridges in $[GeO_4]$ structural units. The main FT-IR band located at about 775 cm^{-1} can be due to $[GeO_4]$ tetrahedral structural units attributable to Ge—O—Ge asymmetric stretching modes [32].

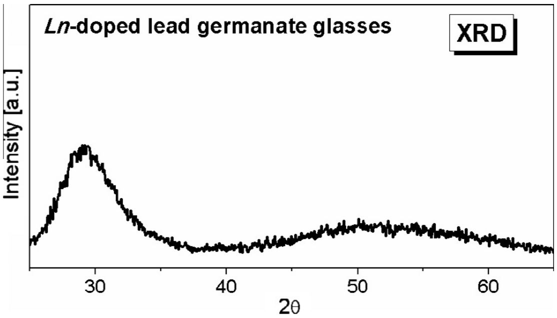

Fig. 1. X-ray diffraction patterns for $PbO—GeO_2—Ga_2O_3$ glasses.

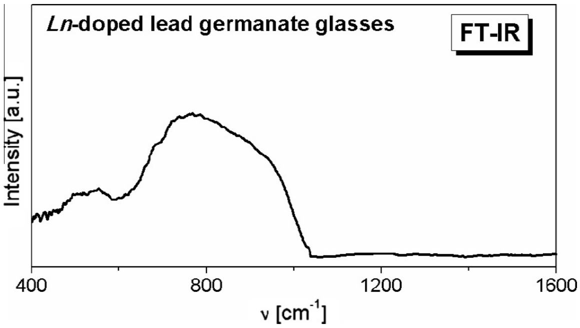

Fig. 2. FT-IR spectra for $PbO—GeO_2—Ga_2O_3$ glasses.

3.2. Excitation and luminescence properties

The excitation spectra for lead germanate glasses doped with rare earth ions (Eu^{3+}, Dy^{3+} and Tb^{3+}) are presented in Fig. 3. For europium ions these spectra were registered at 611 and 590 nm due to $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ transitions, respectively (Fig. 3a). However, excitation spectrum registered at 611 nm has definitely higher intensity. On both spectra two bands connected with $^7F_0 \rightarrow {}^5L_6$ and $^7F_0 \rightarrow {}^5D_2$ transitions were observed. Electron excitation intensity is higher from the ground state to $^5D_2$ level than to the $^5L_6$ excited level. On the excitation spectrum of dysprosium ions six bands were observed (Fig. 3b). These bands can be assigned to transitions originating from the $^6H_{15/2}$ ground state to $^6P_{7/2}$, $^6P_{5/2}$, $^4K_{17/2}$, $^4G_{11/2}$, $^4I_{15/2}$, and $^4F_{9/2}$ excited states of Dy^{3+}. The bands with the highest intensities are due to $^6H_{15/2}$ to $^4K_{17/2}$ and $^4I_{15/2}$ transitions. This spectrum was monitored at 573 nm emission line. Registered spectrum at 480 nm due to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition was characterized by extremely low intensity which makes this useless from the point of view spectroscopic probes. For terbium ions in lead germanate glasses (Fig. 3c) the excitation spectra are characterized by two bands connected with $^7F_6 \rightarrow {}^5D_3$ and $^7F_6 \rightarrow {}^5D_4$ electronic transitions. The excitation spectra were monitored at 543 and 487 nm. The intensity for $^7F_6 \rightarrow {}^5D_3$ transition of trivalent terbium is considerably higher when glass sample is monitored at 543 nm.

Fig. 4a presents luminescence spectrum for europium ions in lead germanate glass registered upon excitation $^5L_6$ state (393 nm). Because of small energy gaps between $^5L_6$, $^5D_3$, $^5D_2$, $^5D_1$ and $^5D_0$ states, the excitation energy was transferred nonradiatively to the $^5D_0$ level, and then visible luminescence was observed due to $^5D_0 \rightarrow {}^7F_J$ ($J = 0–4$) transitions. The ratio of integrate emission intensity of the $^5D_0 \rightarrow {}^7F_2$ transition to the