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Analysis of thermal and structural properties of germanate glasses co-doped with Yb^{3+}/Tb^{3+} ions ☆

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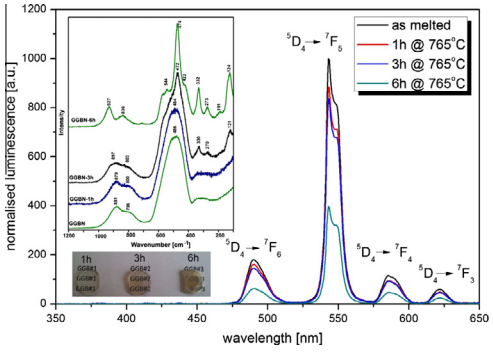
HIGHLIGHTS

- The up-conversion luminescence in germanate glasses co-doped with Yb^{3+}/Tb^{3+} was measured.
- Energy activation of about 330 kJ/mol was determined by Freedman and OFW methods.
- FTIR and Raman spectra analysis were prepared for annealed glass samples.
- As a result of XRD measurements GeO_2 and $Ba_2Ge_4O_4$ crystal phases were localized.

GRAPHICAL ABSTRACT



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ABSTRACT

In the work the new glass compositions in the GeO_2–GaO–BaO system have been prepared and thermal, structural properties of in germanate glasses co-doped with Yb^{3+}/Tb^{3+}ions were studied. Glasses were obtained by conventional high-temperature melt-quenching technique. The study of the crystallization kinetics processes of glasses co-doped with $0.7Yb_2O_3$:$0.7Tb_2O_3$ was performed with DSC measurements. The activation energies have been calculated using Freedman analysis and verified with the Flynn–Wall–Ozawa method. In this order, the DSC curves have been registered with different heating rates, between 5 and 15 degrees/min. The structure of fabricated glasses has been studied by infrared and Raman spectroscopes. The effect of heat treatment on the structural properties was determined. In all glass samples the dominated infrared absorbance band at 800 cm^{-1} corresponds to asymmetric stretching motions of GeO_4 tetrahedra containing bridging (Ge–O(Ge)) and non-bridging (Ge–O^-) oxygens. Additionally, the influence of heat treatment on the luminescent properties was evaluated. Strong luminescence at 489, 543, 586 and 621 nm corresponding to $^5D_4 \rightarrow {}^7F_J$ (J = 6, 5, 4, 3) transitions was measured. The highest upconversion emission intensity was obtained in the germanate glass co-doped with $0.7Yb_2O_3/0.7Tb_2O_3$.

Introduction

Germanate glasses are technological interest because of their various promising properties, such as relatively low-phonon energy (850 cm^{-1}), high refractive index, good RE ions solubility and corrosion resistance, thermal and chemical stability and low

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crystallization ability. Recently, germanate glasses have been used as host materials for infrared and infrared to visible up-conversion applications in optical data storage, integrated lasers, sensors and optoelectronic devices [1–5]. When Yb^{3+}/Tb^{3+} ions co-doped glasses are excited by 980 nm laser radiation, the cooperative energy transfer occurs because there are no intermediate levels in Tb^{3+} ions that can receive single transfers in sequence from Yb^{3+} ions. Therefore, the two excited Yb^{3+} ions can simultaneously transfer their energy to the Tb^{3+} ion, which ascent to the higher excited level [6–8]. As a result of cooperative energy transfer between Yb^{3+} and Tb^{3+} ions, the strong green emission at 543 nm ($^5D_4 \rightarrow {}^7F_5$) is observed in germanate glasses [9]. The selection of a suitable host system is key factor in obtaining efficient co-operative upconversion emission. Researches into the process of controlled crystallization allow to obtain a glass–ceramic material, which combines characteristics of amorphous and crystalline system, leading to a larger arrangement of vitreous atoms in proximity of an optically active ion. An increasing interest in glass–ceramic materials doped with lanthanide ions is related with the possibility of obtaining an effective radiation emission of smaller half-width of a band at the same concentration of the RE ions. As a result, such materials may be used as active elements in devices of integrated optics. Currently, attempts of using glass–ceramic materials doped with rare earth ions to build micro-lasers or optical amplifiers in planar technology are undertaken [10,11]. Controlled crystallization of germanium oxide based glasses has been previously studied for application in the infrared range and in germanium fluoride glasses in the visible range [12,13].

The article presents analysis of the structural, thermal and luminescent parameters of Yb^{3+}/Tb^{3+} co-doped glass from $70GeO_2$–$30[Ga_2O_3$–BaO–$Na_2O]$ system. Based on the differential scanning calorimetry (DSC) measurements the iso-conversional methods are used for the study of crystallization kinetics of fabricated glass. According to Freedman and Flynn–Ozawa–Wall methods the activation energy of crystallization was calculated. The aim of present research was to investigate the influence of heat treatment on the structural and luminescent properties of glass. Furthermore, the impact of annealing time on upconversion emission was determined.

Experimental

The germanate glasses were prepared according to following of molar compositions: $68.6GeO_2$–$30[Ga_2O_3$–BaO–$Na_2O]$–$0.7Yb_2O_3$–$0.7Tb_2O_3$. A homogenized set was placed in a platinum crucible and melted in an electric furnace at 1550 °C for 60 min in oxide atmosphere. In order to obtain dimension repeatability, the glass melt was poured into a brass mold and then subjected to annealing process at 590 °C for 12 h. A uniform and transparent glass with no visible effect of crystallization was obtained. Characteristic temperatures were determined based on DSC measurements at the different heating rates of 5, 10 and 15 K/min performed using the SETARAM Labsys thermal analyzer. Analytical "free-models" of Freedman and Flynn–Wall–Ozawa were used to analyze the DSC data and to determine the activation energy of crystallization. Glass–ceramic material was carried out as a result of parent glass heat treatment at 765 °C for three different time duration, 1 h, 3 h and 6 h, respectively. FTIR spectra were recorded with a Bruker Company Vertex 70v spectrometer. Spectra were collected in the middle infrared regions (MIR) 1400–400 cm^{-1} after 128 scans at 4 cm^{-1} resolution. Samples were prepared by the standard KBr pellets methods. Raman studies were carried out using Horriba Yvon Jobin LabRAM HR micro-Raman spectrometer equipped with a CCD detector. Excitation wavelength of 532 nm was used and beam intensity was about 10 mW. Acquisition time was set to 30 s. The X-ray diffraction investigations were carried out in a Panalytical Empyrean powder diffractometer using Cu Kα($\lambda_{K\alpha}$ = 1.54186 Å) radiation in the 2θ range from 10° to 60°. The luminescence spectrum of the glasses in a range of 350–750 nm was measured using the Stelarnet GreenWave monochromator and laser diode (λ_{exc} = 976 nm) with an optical fiber output.

Results and discussion

Thermal analysis and crystallization kinetics of germanate glass

DSC curves of glass samples at a heating rate of 5, 10 and 15 K/min are shown in Fig. 1. The ΔT, defined as the temperature gap between T_g and T_x, in all cases is larger than 205 °C, which is relatively high compare to tellurite and HMO glasses [14,15]. Parameter ΔT is common used as a rough criterion to measure glass thermal stability. Moreover, the large value of ΔT indicates that glassy matrix is thermally stable and can be used as an active material in optical fiber manufacturing. From presented DSC curves, it is noted that upon increasing the heating rate the glass transition and crystallization peak shift towards higher temperatures.

This shifting of the peak to higher temperatures can be explained by considering that the crystallization rate increases with increasing heating rate, so that crystalline volume fraction α increases to a greater extent in a short time and consequently the peak height also increases.

Friedman analysis

The kinetics of crystallization can be described by the following rate equation assuming Arrhenius temperature dependence of the rate constant [16,17]:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_A}{RT}\right) f(\alpha) \tag{1}$$

where t is the time, T is the temperature, α is the conversion fraction that represents the volume of the crystallized fraction, A (s^{-1}) is the pre-exponential (frequency) factor, E_A (kJ mol^{-1}) is the activation energy, R is the universal gas constant and $f(\alpha)$ is the reaction model.

For various heating rates β the most common differential iso-conversional method is that of Friedman method [18]. This method can be obtained directly from (1) at a specific crystallization fraction, as:

$$\ln\left(\frac{d\alpha}{dt}\right) = C_F(\alpha) - \frac{E_A}{RT_{\alpha i}} \tag{2}$$

where the subscript i denotes different heating rates and the parameter $C_F(\alpha) = \ln(Af(\alpha))$. For a specific α value and several heating rates β, pairs of $(d\alpha/dt)_{\alpha i}$ and $T_{\alpha i}$ are determined experimentally from the DSC diagram. The parameters E_A and $C_F(\alpha)$, at this specific value of α, are then estimated from a plot of $\ln(d\alpha/dt)_{\alpha i}$ versus $1/T_{\alpha i}$ across at least three different heating rates (Fig. 2).

This method can be used to calculate the local activation energy of crystallization E_A at specific α, using different heating rates. In fabricated glasses the average activation energy E_A is 265 ± 10 kJ mol^{-1}.

Flynn–Wall–Ozawa analysis

Another method of kinetic crystallization studies which is useful in obtaining kinetic parameters related to the glass crystallization process is Flynn–Wall–Ozawa (FWO) technique [19,20]. According to the Doyle approximation [21] this method is given as follows:

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