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Enhanced mid-infrared 2.7 μm luminescence in low hydroxide bismuth-germanate glass and optical fiber co-doped with Er^{3+}/Yb^{3+} ions

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ABSTRACT

In this article, low hydroxide bismuth-germanate glasses doped with Er^{3+} and co-doped with Er^{3+}/Yb^{3+} ions have been synthesized. The fabricated host was characterized by high thermal stability parameter ($\Delta T = 125$ °C), high transmittance in mid-infrared region and low maximum phonon energy (724 cm^{-1}). In order to reduce OH^- ions impact on the transmittance value at the band of 3.1 μm, the modified synthesis process has been conducted in low vacuum conditions (50–70 mbar). The wide transmittance window from 0.515 to 5.5 μm has been determined in terms of optical parameters. Luminescent properties of Er^{3+} ions indicated increase of luminescence intensity at the wavelength of 2.7 μm ($^4I_{11/2} \rightarrow {}^4I_{13/2}$) under 980 nm laser diode excitation resulting from OH^- reduction. Simultaneously, the addition of ytterbium to glass system has increased emission intensity in mid-infrared band due to $Yb^{3+} \rightarrow Er^{3+}$ energy transfer. According to mid-infrared luminescence measurements, molar ratio of co-dopants in developed glass matrix for the maximum emission intensity has been determined. Glass characterized by the highest mid-IR emission intensity has been used as the active core of produced optical fiber.

1. Introduction

Photonic materials operating in the 2.7–3.0 μm range have being currently investigated due to their wide potential applications in both military and civilian field such as remote sensing, eye-safe laser radar, atmosphere pollution monitoring and medical microsurgery [1–4]. In order to obtain luminescence in the mid-infrared region, it is crucial to choose the host material with low maximum phonon energy, high transmittance in required spectral range and high probability of radiative transitions [4–6]. Additionally, an adverse impact of hydroxide groups, which results in characteristic absorption band around 3.1 μm, has to be reduced in order to obtain luminescence in 2.7–3.0 μm region. Therefore, besides appropriate glassy matrix selection, its synthesis process has to be conducted under low vacuum conditions [7].

In technology of mid-infrared matrices the main focus is put on chalcogenide and fluoride glasses, which are characterized by good spectroscopic parameters and lower maximum phonon energy than glasses based on oxides [8–10]. However, these matrices are thermally unstable, have low mechanical and chemical durability, hence their potential applications in optical fiber technology is more expensive and complicated [11,12]. Another kind of amorphous materials are heavy metal oxide (HMO) glasses like germanate (GeO_2-based), tellurite (TeO_2-based) or bismuth-oxide (Bi_2O_3-based) which are also recently developed in mid-IR area [2,13,14]. Considering these materials, special attention has been paid to the last group of glasses due to their advantageous properties like high refractive index ($n > 2$), high thermal stability parameter as well as good chemical and mechanical durability [15–19]. In addition, the bismuth-glasses exhibits a lower maximum phonon energy (707 cm^{-1}) [20] than germanate (805 cm^{-1}) and tellurite (780 cm^{-1}) glasses [21,22].

In order to obtain luminescence in the mid-infrared region, erbium ions have been incorporated into glass matrix. The 2.7 μm emission band in erbium ions results from the radiative transition of Er^{3+}: $^4I_{11/2} \rightarrow {}^4I_{13/2}$ under 980 nm pump radiation [23]. In addition ytterbium, which is an sensitizer in Er^{3+}/Yb^{3+} system due to energy transfer $Yb^{3+} \rightarrow Er^{3+}$ phenomenon, has been introduced to the glass. Ytterbium ions are widely used in up and down-conversion systems like Tb^{3+}/Yb^{3+}, Er^{3+}/Yb^{3+} or Ho^{3+}/Yb^{3+} because of the large absorption cross-section at the wavelength of 980 nm [24–26].

In this study, heavy metal oxide glasses doped with Er^{3+} and co-doped with Er^{3+}/Yb^{3+} ions have been synthesized. Thermal, structural

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and optical properties have been investigated, which define high thermal stability, low phonon energy and high transmittance of obtained glass matrix. Performed investigations allowed to optimize the molar concentration ratio of Er_2O_3/Yb_2O_3 in the glass aiming at maximization intensity of emission at 1.54 μm and 2.7 μm. Based on the luminescence properties, optical fiber with single active core generating radiation from mid-infrared region has been elaborated.

2. Experiment

Set of glass samples with a molar system (60-x-y)[Bi_2O_3–GeO_2] — 40[Ga_2O_3–Na_2O] — xEr_2O_3 — yYb_2O_3, where x and y are molar concentration of active dopants, have been prepared using high purity compounds (99.99%). In Table 1 glass labels, specified concentration and molar ratio of rare earth co-dopants have been presented.

Approximately 5 g well mixed powder was put into a platinum crucible and melted at 1050 °C for 30 min under low vacuum atmosphere. This procedure reduces the content of OH^- ions in the glass matrix, which is exposed to the hydroxide groups from atmosphere during the synthesis process. The molten glass was casted at a polished brass plate and annealed at 400 °C for 12 h in order to avoid thermal stresses. Glass has been subjected to the mechanical processing to obtain high optical quality, which is necessary during spectroscopic measurements. Series of samples with dimensions of $10 \times 10 \times 2$ mm^3 have been prepared to determine optical properties. Characteristic temperatures were designated based on differential scanning calorimetry measurements at the heating rate of 10 °C/min performed using the SETARAM Labsys thermal analyzer. 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 5° to 90°. The 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, the amount of the samples and KBr was precisely weighed. The absorption spectra was obtained using an Acton Spectra Pro 2300i monochromator in the spectral range of 450–1650 nm as well as the infrared emission spectra in the range of 990–1060 nm, 1400–1750 nm and 2550–2900 nm using high power laser diode ($\lambda_{exc} = 980$ nm) as a pump source. For glasses synthesized in air and low vacuum atmosphere infrared transmittance spectra in the range of 2500–7500 nm were determined using the Carl-Zeiss M80 spectrophotometer.

3. Results and discussion

3.1. Thermal and structural analysis

In Fig. 1 the DSC curve for the fabricated glass BGG has been presented. The characteristic temperature of T_g, T_x and T_m are 416 °C, 541 °C and 765 °C, respectively. The thermal stability parameter ΔT, defined as the temperature gap between T_g and T_x, amounts 125 °C which is relatively high in comparison to non-oxide structures, like fluoride (73 °C) or chalcogenide (55 °C) [1,12], as well as tellurite (66 °C) [27] and other bismuth-germanate glasses (51 °C) [20]. Parameter ΔT is used as a rough criterion to characterize glass thermal stability. Moreover, the large value of ΔT and low melting point temperature T_m indicate that glassy matrix is thermally stable and the process of optical fiber manufacturing is less complicated in comparison to antimony (T_m = 950 °C) [28], phosphate (T_m = 1270 °C) [29] and germanate glasses (T_m = 1350 °C) [30], respectively.

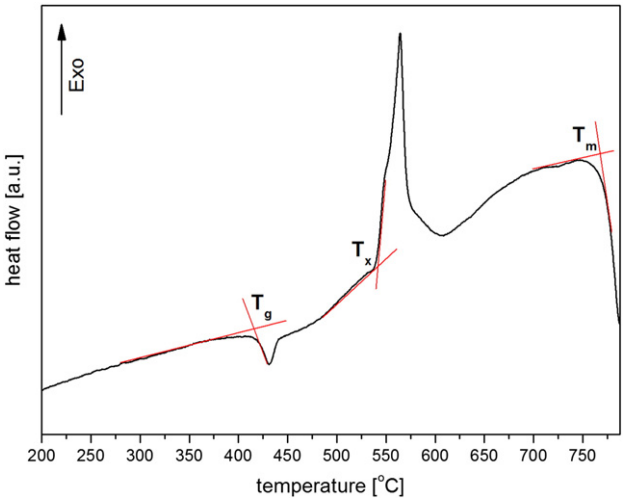

Fig. 1. The DSC curve of synthesized bismuth-germanate host glass.

Another common thermal stability indicator characterizing amorphous structures is the Hrüby parameter, defined as follow:

$$K_H\,[a.u.] = \frac{T_x - T_g}{T_m - T_x} \quad (1)$$

If photonics materials are characterized by thermal stability parameters ΔT and K_H higher that 100 °C and 0.5, respectively, than the possibility of forming the material into photonic structures is high due to lower probability of crystallization [31–33]. In fabricated glass Hrüby parameter K_H equals to 0.558, which is a higher value than in the fluoride (0.246), chalcohalide (0.163), tellurite (0.302) or other bismuth-germanate (0.316) matrices [2].

X-ray crystallography (XRD) measurement technique verifies glass amorphous nature or identifies crystalline phases in the structure of glass-ceramic. Diffraction pattern of fabricated glasses is characterized by a broad and continuous halo effect in the range of 20–35°, which confirmed the completely amorphous structure (Fig. 2).

The MIR spectrum of investigated glass has been presented in Fig. 2 – inset. In the range from 400 to 1400 cm^{-1} three absorption bands have been characterized. Two of them, located at wavenumbers 449 cm^{-1} and 634 cm^{-1}, are associated with bending and stretching vibrations of Bi—O and Bi—O$^-$ bonds in BiO_6 units, respectively. Third absorption band located at 724 cm^{-1} is associated with the bending vibrations of Ge—O bonds in GeO_4 molecules and determines the maximum phonon energy of synthesized glass [34–36]. Its value is significantly lower than in the known boron (1400 cm^{-1}), phosphate (1200 cm^{-1}), silicate (1100 cm^{-1}) or germanate (900 cm^{-1}) glasses [37].

Low phonon energy of host glass is beneficial from the standpoint of mid-infrared luminescence, which is a result of radiative transition $^4I_{11/2} \rightarrow {}^4I_{13/2}$ in erbium ions. Competing process is the fast non-radiative relaxation, which converts the energy to matrix nuclear vibrations and reduces the emission intensity. The obtained low value of maximum phonon energy in developed HMO glass reduces the probability of non-radiative transitions and improves the mid-IR luminescence parameters.

Table 1
Molar percentage of erbium and ytterbium oxides incorporated into bismuth-germanate glass.

Sample	Er_2O_3 (%mol)	Yb_2O_3 (%mol)	Er_2O_3:Yb_2O_3 ratio
BGG	0	0	–
Y1	0	0.75	–
E1	0.25	0	–
E2	0.5	0	–
E3	0.75	0	–
EY13	0.25	0.75	1:3
EY12	0.25	0.5	1:2
EY11	0.25	0.25	1:1
EY21	0.5	0.25	2:1
EY31	0.75	0.25	3:1