Spectroscopic properties of heavy metal oxide glasses doped with Er^{3+} ions

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Abstract—In this paper, bismuth-germanate glasses doped with erbium ions have been synthesized. The composition of glass has been selected in terms of good thermal stability, high transparency in the near infrared region and high refractive index. The luminescence at a wavelength of 1534nm has been obtained as a result of radiative transition $^4I_{13/2} \rightarrow {}^4I_{15/2}$ in erbium ions due to 98 nm laser diode excitation. Different emission intensity in produced glasses has been observed as a result of various molar concentration of erbium in the glass matrix. The highest luminescence value has been obtained in glass doped with 1.0 mol% Er_2O_3.

The emission at 1.55μm has been continuously in the area of interest of engineers and scientists due to the use in optical amplifiers systems working in the third transmission window [1]. With the addition of erbium in the glass matrix, the luminescence band at the 1534nm wavelength under the excitation with a 980nm commercial high power laser diode can be observed as a result of radiative transition from the excited level $^4I_{13/2}$ to the ground level $^4I_{15/2}$ [2]. The optimization of molar concentration of the rare earth element is key to efficient infrared emission as well as the choice of glass matrix. Among oxide glasses, the heavy metal oxide (HMO) family seems to be the most appropriate structure for the erbium dopant. Bismuth-germanate glasses due to their advantageous properties, such as high refractive index (2.26), low phonon energy (700 cm^{-1}) and high thermal stability parameter (ΔT>100 °C), are an attractive material for near infrared applications [1, 3-4]. Not without significance is the fact that the main glass-forming ingredient (Bi_2O_3) is several times cheaper than its equivalents in phosphate or tellurite glasses.

In the following work, bismuth-germanate glasses doped with various molar concentration of erbium oxide have been produced. Physical and thermal properties have been determined for the perspective of photonic structures applications. Luminescence analysis determines the optimal concentration of erbium at which the emission in the band of 1.55μm has the highest value.

A set of four glass samples with a molar system: $30Bi_2O_3$–$30GeO_2 - 40(Na_2O$-$Ga_2O_3)$ doped with 0.25, 0.5, 0.75 and 1.0 mol% Er_2O_3 has been synthesized by using high purity compounds (99.99%). The well-mixed powder was put into a platinum crucible and melted at 1100°C for 15 minutes under air atmospheric pressure. Next, the molted glass was poured onto a polished brass plate. In order to avoid thermal stresses, the samples were annealed at 400°C for 12 hours. The glasses have been subjected to mechanical processing to obtain high optical quality which is necessary during spectroscopic measurements. A series of samples with dimensions of 10×10×2.5mm^3 has been prepared to determine optical properties. The refractive index at a wavelength of 632.8nm was determined by an m-line apparatus based on the prism coupling technique (Metricon 2010). Absorption spectra were obtained using an Acton Spectra Pro 2300i monochromator in a spectral range of 450÷1800nm as well as the luminescence spectra in a range of 1400÷1700nm using high power laser diode (λ_{exc}=980nm) as a pump source. Characteristic temperatures were determined based on DSC measurements at a heating rate of 10°C/min performed using a SETARAM Labsys thermal analyzer.

Figure 1 shows the DSC curve of fabricated bismuth-germanate glass. Glass transition temperature T_g and onset of crystallization temperature T_x have been determined. Parameter ΔT, which specifies the stability of the glass against the crystallization, is defined as a temperature gap between T_g and T_x ($\Delta T = T_x - T_g$). The obtained thermal stability parameter equals 127 C, which is higher than in other bismuth-germanate glasses [3].

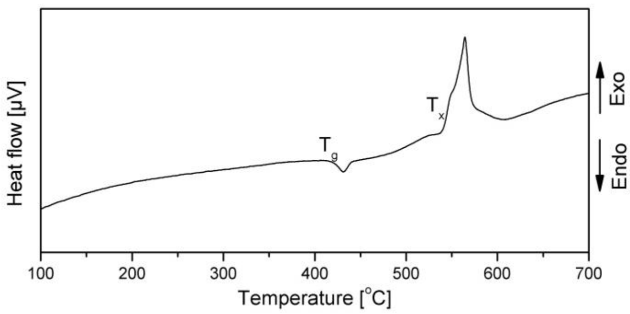

Fig. 1. DSC curve of produced glass doped with 0.5 mol% Er_2O_3

Produced glasses doped with Er_2O_3 have been examined in the context of their physical properties. The value of the refractive index at 632.8 nm is at a level of 2.195,

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which is higher than in the tellurite (2.074) [5] or germanium-borate glasses (1.73) [6]. Thermal, physical and optical properties are summarized in Table 1.

Table 1. Properties of bismuth-germanate glasses doped with Er_2O_3

PARAMETER	VALUE
Refractive index *n* (at 632.8 nm)	2.19±0.05
Glass density ρ [g/cm^3]	7.25±0.05
Transformation temperature T_g [ºC] (DSC)	419±1
Crystallization temperature T_x [ºC] (DSC)	546±1
Stability parameter of glass ΔT [ºC]	127±2
Concentration of all active ions N [10^{20} ions/cm^3]	1.49 – 2.90*
Average interionic radius [Å]	14.88 – 9.37*

*Data for glasses doped from 0.25 to 1.0 mol% of Er_2O_3

Taking into account the determined refractive index, density, characteristic temperatures and stability parameter, the values were slightly different as a function of erbium concentration. On the other hand, the concentration of all active ions and average interionic radius values varied considerably from each other, the direction of change was in line with expectations.

The absorption coefficient spectrum in the range from 450 to 1650 nm for glass doped with 0.5 mol% Er_2O_3 has been shown in Fig. 2.

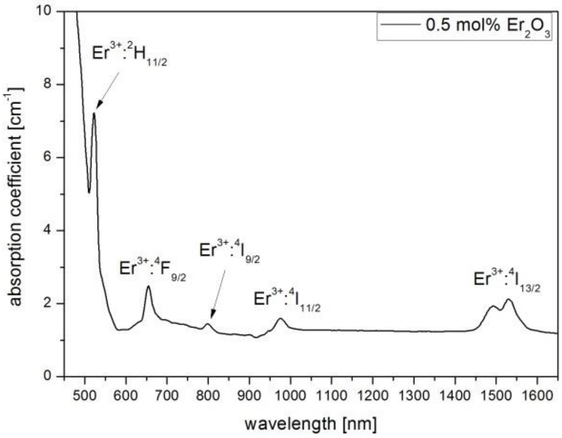

Fig. 2. The absorption coefficient spectra of bismuth-germanate glass doped with 0.5 mol% Er_2O_3

The spectra have revealed five absorption bands centered at wavelengths 523, 654, 798, 976 and 1534nm. Characteristic absorption bands correspond to the transition from the Er^{3+} ground state $^4I_{15/2}$ to the higher excited levels $^2H_{11/2}$, $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$, respectively. The level of absorption bands increases with the extinction of rare earth ions. In comparison with phosphate and germanate glasses, the presence of a large molar amount of Bi_2O_3 in the glass matrix results in red-shifting of an UV absorption edge (at about 550nm). This phenomenon is typical for heavy metal ions due to weaker metal-oxygen bond strength [3]. Taking into account the band at a wavelength of 976 nm, which is associated with the $^4I_{15/2} \rightarrow {}^4I_{11/2}$ transition, it is used to efficiently pump the glass with the radiation of a commercial high power laser diode (λ=980nm).

Figure 3 shows the luminescence spectra of fabricated glasses under 980 nm optical excitation. In a range of 1400–1700 nm, strong emission at 1534nm corresponding to the transition $^4I_{13/2} \rightarrow {}^4I_{15/2}$ has been obtained.

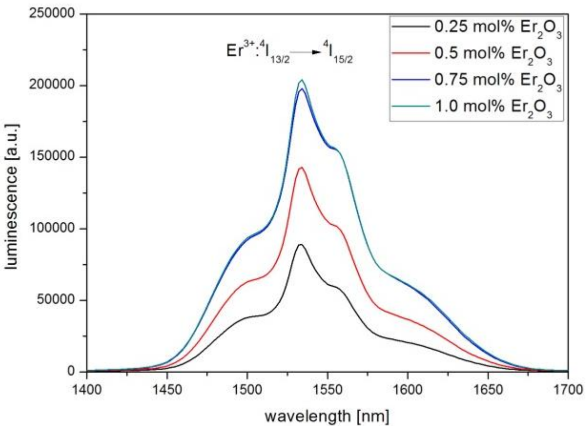

Fig. 3. The luminescence spectra of fabricated glasses doped with Er_2O_3

As a result, the lowest emission value has been obtained in the sample doped with 0.25 mol% Er_2O_3. On the other hand, the highest luminescence has been observed in the sample doped with 1.0 mol% Er_2O_3.

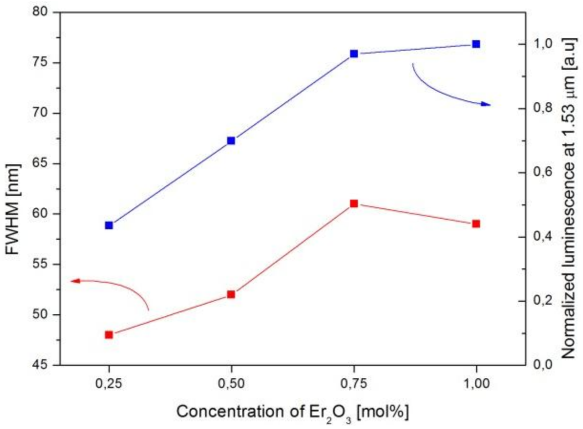

Fig. 4. Changes of FWHM and luminescence intensity in samples doped with erbium

It was indicated that the emission value increases linearly as a function of dopant growth to 0.75 mol% Er_2O_3. Above this concentration the luminescence signal is only slightly higher, which may indicate that a concentration of 1 mol% Er_2O_3 is the limit of effective emission. A higher amount of RE dopant may result in luminescence quenching phenomenon due to energy migration between Er^{3+} ions [7]. Additionally, in fabricated bismuth-germanate glasses the full width at half maximum changes from 48 to 61 nm in a sample doped with 0.25 and 0.75 mol% Er_2O_3, respectively (Fig. 4). Broadening luminescence spectra at 1.53µm in erbium ions, which is connected with $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition, can be explained by the dipolar coupling theory [8]. The random effect of electric or magnetic dipole coupling between adjacent atoms in the same host resulted in a frequency shift of atomic resonances.

Table 2. Obtained values of cross-section coefficients in produced glasses

Glass sample dopant	Absorption cross-section at 1534nm [10^{-20}cm^2]	Emission cross-section at 1534nm [10^{-20}cm^2]
0.25 mol% Er_2O_3	1.113	1.204
0.5 mol% Er_2O_3	1.177	1.230
0.75 mol% Er_2O_3	1.206	1.280
1.0 mol% Er_2O_3	1.235	1.321

Figure 5 presents absorption and emission cross-sections of erbium ions in produced glass doped with 1.0 mol% Er_2O_3. The calculated absorption cross-section coefficients have been based on the transmission spectrum according to the following formula [6]:

$$\sigma_{abs}(\lambda) = \frac{2.303\log(T(\lambda)^{-1})}{Nl}, \qquad (1)$$

where: $T(\lambda)$ – spectral transmission, N – concentration of dopant ions [ions/cm^3], l – thickness of the glass sample [cm].

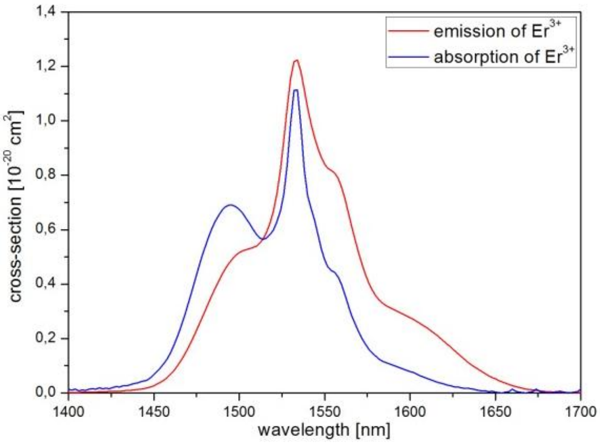

Fig. 5. Absorption and emission cross-section coefficients obtained in the glass doped with 1.0 mol% Er_2O_3

Emission cross-section coefficients, which values indicate the possibility of obtaining strong luminescence band, have been calculated by the following relation [6]:

$$\sigma_{em}(\lambda) = 1.1\sigma_{abs}(\lambda)\exp\left(\frac{E_0 - \frac{hc}{\lambda}}{kT}\right), \qquad (2)$$

where: E_0 – energy difference between the lowest levels of splitted ground-state and excited multiplets [cm^{-1}], h – the Planck constant, c – speed of light, k – the Boltzmann constant, T – ambient temperature.

The values of the cross-sections at 1534nm obtained in glass samples doped with different molar concentrations of Er_2O_3 have been presented in Table 2.

It has been observed that the values of emission cross-section are higher than those in phosphate, tellurite and germanate glasses [9-11]. This phenomenon indicates the possibility of obtaining high efficiency of photonic structures based on fabricated bismuth-germanate glasses.

In this work a series of heavy metal oxide bismuth-germanate glasses doped with erbium ions has been synthesized. The DSC analysis and physical measurements confirmed their high thermal stability ΔT=127°C, UV absorption edge at 550nm and high refractive index (2.19). As a result of luminescence measurements (λ_{exc}=980nm), an emission at a wavelength of 1534nm has been observed. A linear increase in emission intensity has been observed as a function of molar dopant growth in samples up to 0.75 mol% Er_2O_3. However, in the sample doped with 1.0 mol% Er_2O_3 only a small emission increase has been observed. Considering the obtained results, the fabricated glass is a promising material for near infrared applications.

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