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Intense and wide mid-infrared luminescence in bismuth-germanate glass co-doped with $Ho^{3+}/Er^{3+}/Yb^{3+}$ ions

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ABSTRACT

In this work, we focused on the possibility of obtaining intense and wide emission in the mid-infrared spectral range. The bismuth-germanate oxide glasses have been co-doped with erbium, holmium and ytterbium ions. Glasses have been synthesized in terms of high mid-infrared transmittance and low hydroxides content using low vacuum atmosphere (50–70 mBar). In order to maximize the mid-infrared luminescence, optimization of the rare earth ions content has been conducted. The highest emission intensity in the mid-IR has been observed in sample co-doped with molar concentration 0.1 Ho_2O_3/0.7 Er_2O_3/0.25 Yb_2O_3 under 980 nm laser diode excitation. Moreover, rare earth ions system enables to observe broadband mid-infrared luminescence in the range of 2.7–2.9 µm due to the energy transfer and emission band overlap phenomena. Furthermore, wide emission band (FWHM = 193 nm) and high energy transfer efficiency (η = 66.84%) from Yb^{3+} to Er^{3+} and Ho^{3+} ions are favorable from the perspective of further applications in mid-infrared fiber amplifiers and lasers.

1. Introduction

Nowadays, studies focused on new materials for mid-infrared radiation generation are being conducted in scientific centers around the world. The particularly interesting range is located near 3 µm, where exists strong absorption band originating from hydroxide ions, due to the potential and practical applications in civilian or military fields, including eye-safe laser radar, medical microsurgery, remote sensing or atmosphere pollution monitoring [1,2]. Among amorphous materials, non-oxide glasses are mostly used for mid-infrared emission because of the low maximum phonon energy (e.g. 590 cm^{-1} and 350 cm^{-1} in fluoride and chalcogenide glasses [3], respectively). Low lattice vibrations are beneficial in terms of reduced non-radiative relaxation phenomenon, which is competitive processes to quantum radiative transition [4,5]. Despite good structural and spectroscopic properties for mid-infrared emission, non-oxide glasses are characterized by poor chemical durability and mechanical strength as well as low thermal stability, which make it difficult to draw them into optical fibers and limits further application in high power fiber laser systems [6–8]. On the other hand, glasses based on heavy metal oxides are characterized with relatively low phonon energy among oxide materials, which is favorable in terms of generating radiation in the mid-IR region, and possess advantageous properties like high thermal stability parameter, high refractive index, good chemical and mechanical durability [9,10].

Suitable host glass should be doped with proper rare earth ions in order to obtain luminescence in the mid-infrared region. Quantum transition $^4I_{11/2} \rightarrow {}^4I_{13/2}$ between higher energy levels in erbium ions might generate emission in the range of 2.7 µm, while luminescence in the range of 2.85 µm could be observed as a result of radiative transition $^5I_6 \rightarrow {}^5I_7$ in holmium ions [11,12]. In order to increase the population of higher energy $^4I_{11/2}$ level in erbium, which can result in stronger mid-IR luminescence intensity, ytterbium co-dopant is used [13]. Also, Ho^{3+}/Yb^{3+} co-dopants system excited with 980 nm radiation is known, where ytterbium ions are used as a sensitizer effectively transferring energy to holmium ions [14,15].

In this paper, set of glasses triply-doped with $Ho^{3+}/Er^{3+}/Yb^{3+}$ ions with different molar concentration have been synthesized in terms of high thermal stability and high transmittance in the mid-infrared region. The broadband mid-infrared luminescence in the wavelength range of 2.7–2.9 µm (λ_{exc} = 980 nm) have been observed, which was the result of the erbium and holmium emission bands superposition.

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Table 1
The molar percentage of lanthanides incorporated into the developed bismuth-germanate glass.

Glass sample	Co-dopants		
	$(59.75\text{-}x\text{-}y)(Bi_2O_3–GeO_2)$ – $40(Na_2O–Ga_2O_3)$ [mol%]		
	$(x)Ho_2O_3$ [mol%]	$(y)Er_2O_3$ [mol%]	Yb_2O_3 [mol%]
Y1	0	0	0.25
HEY1	0.1	0.25	
HEY2		0.4	
HEY3		0.55	
HEY4		0.7	

2. Experiment

Glasses with molar composition of $(59.75\text{-}x\text{-}y)(Bi_2O_3–GeO_2)$ – $40(Na_2O–Ga_2O_3)$ – xHo_2O_3 – yEr_2O3 – $0.25Yb_2O_3$ were synthesized with the standard melt-quenching method using high purity compounds (99.99%, Sigma-Aldrich). Glass labels and specified composition of rare earth co-dopants have been included in Table 1.

The homogenized powder was placed into a platinum crucible and melted at 1050 °C for 30 min. Hydroxide groups concentration within the glass matrix has been minimalized due to the modified synthesis method, which was conducted in a furnace maintaining low vacuum conditions (50–70 mBar) throughout the entire process. The molten glass was poured on a polished brass plate and forthwith placed in the annealing furnace at 400 °C for 12 h in order to remove thermal stresses. Next, glass samples were subjected to the mechanical processing to obtain high optical quality indispensable for spectroscopic measurements. The density was measured using the hydrostatic weighing method, refractive index at the wavelength of 632.8 nm was determined by m-line spectrometer Metricon 2010. Absorption and luminescence spectra (using high power semiconductor laser diode $\lambda_{exc} = 980$ nm as a pump source) were measured using Stellarnet Green-Wave Spectrometer (0.44–1.1) µm, Acton Spectra Pro 2300i monochromator with PbS and PbSe detectors (1.1–2.5 and 2.5–3.0, respectively) µm. A system PTI QuantaMaster QM40 coupled with a tunable pulsed optical parametric oscillator (OPO), pumped by the third harmonic of an Nd:YAG laser (OpotekOpolette 355 LD) has been used for luminescence decay measurements. The laser system was equipped with a double 200 mm monochromator, a multi− mode UV−VIS PMT (R928) and Hamamatsu H10330B−75 detectors controlled by a computer. Luminescence decay curves were recorded and stored by a PTI ASOC−10 (USB−2500) oscilloscope with an accuracy of ± 1 µs.

3. Results and discussion

3.1. Glass characterization

Table 2 presents physical and thermal properties of previous fabricated BGG base glass and HEY(1–4) glasses co-doped with $Ho^{3+}/Er^{3+}/Yb^{3+}$ ions. Developed glasses are characterized by a high refractive index from the range of 2.187–2.1916. Value of the refractive index increases along with the glass density (7.353–7.496 g/cm^3) with a decrease of total molar concentration of lanthanides relative to bismuth oxide, which results from the higher molar mass of the bismuth in relation to the molar masses of rare earth ions.

Table 2
Physical and thermal properties of manufactured bismuth-germanate glasses.

PARAMETER	BGG [16]	HEY(1–4)
Refractive index n (632.8 nm)		2.187–2.1916
Density ρ [g/cm^3]		7.353–7.496
Transformation temperature T_g [°C]	416	
Crystallization temperature T_x [°C]	541	
Maximum phonon energy ħω [cm^{-1}]	724	

Development bismuth-germanate glass is characterized with thermal stability parameter $\Delta T = 125$ °C, which is a higher value in comparison to non-oxide (fluoride: $\Delta T = 73$ °C) and another oxide (tellurite: $\Delta T = 66$ °C) materials [6,17]. A large value of ΔT parameter indicates that glass matrix is thermally stable and could be formed into photonic structures without crystallization effects [18]. The low value of maximum phonon energy is desirable in terms of good emission parameters in the mid-infrared and reduced probability of non-radiative relaxation. Based on our previous investigation on FTIR spectroscopy [16], maximum phonon energy of fabricated glass is 724 cm^{-1}, which is lower in comparison to tellurite (790 cm^{-1}) or germanate (900 cm^{-1}) glasses [19,20].

3.2. Absorbance and transmittance properties

Absorption coefficient spectra of bismuth-germanate glasses co-doped with rare earth ions in the range of 440–2500 nm have been presented in Fig. 1. The position of UV absorption edge, which results from intrinsic energy bandgap, has been localized at 515 nm. In comparison to the germanate (440 nm) or tellurite (425 nm) glasses [19,21], large molar amount of bismuth oxide in the glass matrix decrease energy gap, which shifts the ultraviolet absorption edge to the longer wavelengths. This phenomenon is typical for glasses based on heavy metal oxides as a result of reduced bond strength between the metal and oxygen atoms [22].

In the investigated range, characteristic absorption bands connected with the complex structure of lanthanides ions have been identified in four co-doped glasses. Presence of absorption bands is associated with the ground-state absorption phenomenon under the broadband light source. In synthesized co-doped glasses absorption bands at the wavelength of 1532, 978, 796, 654, 523 and 467 nm corresponds to the GSA transitions in erbium ions from $^4I_{15/2}$ ground level to higher energy levels $^4I_{13/2}$, $^4I_{11/2}$, $^4I_{9/2}$, $^4F_{9/2}$, $^2H_{11/2}$ and $^4F_{7/2}$, respectively. Similarly, absorption bands at the wavelength of 1958, 1122, 890 nm corresponds to the GSA transitions in holmium (Ho^{3+}: $^5I_8 \rightarrow {}^5I_5$, $^5I_6$ and $^5I_7$, respectively) ions and absorption band at 980 nm corresponds to the transition in ytterbium (Yb^{3+}: $^2F_{7/2} \rightarrow {}^2F_{5/2}$) ions. Taking into account absorption bands positions, radiation of 980 nm wavelength from high power semiconductor diode could excite simultaneously both ytterbium and erbium ions due to the two ground state absorption processes: Yb^{3+}: $^2F_{7/2} \rightarrow {}^2F_{5/2}$ and Er^{3+}: $^4I_{15/2} \rightarrow {}^4I_{11/2}$. This increases population density of lanthanides excited quantum states and luminescence intensity [16].

3.3. Mid-infrared emission properties

Fig. 2a presents mid-infrared emission in the wavelength range of 2.55–2.95 µm in synthesized glasses co-doped with a different molar concentration of lanthanides under optical excitation by the $\lambda = 980$ nm laser diode. The wide luminescence spectrum is a result of the superposition of two emission bands at the wavelengths of 2.7 µm and 2.85 µm originating from Er^{3+}: $^4I_{11/2} \rightarrow {}^4I_{13/2}$ and Ho^{3+}: $^5I_6 \rightarrow {}^5I_7$ radiative transitions, respectively. Mid-IR emission intensity increases as a function of erbium oxide concentration growth, which indicates incensement of the population at higher energy levels of erbium ($^4I_{11/2}$) and holmium ($^5I_6$) ions. The highest luminescence intensity has been observed in bismuth-germanate glass co-doped with the molar concentration of 0.1 Ho_2O_3/0.7 Er_2O_3/0.25 Yb_2O_3.

To explain this phenomenon of increasing emission intensity in the function of erbium oxide growth, possible energy transfer mechanisms have been presented in Fig. 2b. Ytterbium ions are excited to higher quantum level $^2F_{5/2}$ under 980 nm optical pump radiation. Next, erbium ions could be excited to $^4I_{11/2}$ multiplet both through ground state absorption (GSA) and due to the $Yb^{3+} \rightarrow Er^{3+}$ energy transfer (ET1)