Optical and Acoustical Methods in Science and Technology

Spectroscopic Properties of Yb^{3+}/Tb^{3+} Doped Germanate Glasses

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In the article the cooperative energy transfer in GeO_2–GaO–BaO glass system doped with Yb^{3+}/Tb^{3+} under 980 nm laser diode excitation was investigated. The influence of Tb^{3+} concentration on the luminescent properties was determined. Measured strong luminescence at 489, 543, 586, 621 corresponds to $^5D_4 \rightarrow {}^7F_J$ ($J = 6$, 4, 3) transitions and luminescence at 381, 415, 435 nm results from $^5D_3$, $^5G_6 \rightarrow {}^7F_J$ ($J = 6$, 5, 4) transitions. Mechanism and energy diagram involved in observed emission were discussed. The highest upconversion emission intensity was obtained in the germanate glass doped with 0.7 Yb_2O_3/0.7 Tb_2O_3.

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1. Introduction

The glasses and optical fibres doped with lanthanides, as a result of infrared frequency conversion to the visible range, may be applied in numerous applications: data recording/data storage systems in HD quality, 3D displays, medical diagnostics, optical sensors [1–10]. Demand of optical fibre sources and amplifiers compactness, forces researching for new glassy materials doped with rare earth elements. Germanium-based glasses, thanks to a high solubility of rare-earth elements (5 mol.%) as well as a low phonon energy (900 cm^{-1}) enable an effective conversion of IR radiation to VIS radiation and make an alternative to tellurite as well as to heavy metal oxide (HMO) glasses [11–17]. Furthermore, excellent mechanical properties and high thermal stability makes it possible to form them into optical fibres.

The glass doped with Yb^{3+}/Tb^{3+} ions excited with the laser radiation at 976 nm may result in a cooperative energy transfer from Yb^{3+} ions to Tb^{3+} ion — and thanks to $^5D_3/^5D_4 \rightarrow {}^7F_J$ ($J = 6$, 5, 4, 3) transitions an emission occurs in the VIS range [18–24].

The article presents results of the optimization of optical parameters of Yb^{3+}/Tb^{3+} doped glass from GeO_2–Ga_2O_3–BaO system. The aim was to obtain the highest intensity of upconversion emission. Furthermore, the spectrum of upconversion was characterized by determining the impact of pumping radiation on the process of energy transfer. Mechanisms responsible for the process of IR to VIS frequency conversion were analyzed.

2. Experimental

The glasses from the GeO_2–Ga_2O_3–BaO — $x Yb_2O_3$/$y Tb_2O_3$ ($x = 1$, $y = 0.07$, 0.15, 0.35, 0.7) system were melted from pure (99.99%) raw materials. The homogenized set was placed in a platinum crucible and melted in an electric furnace in temperature of 1500 °C for 30 min. The molten glass was poured out onto a brass plate and then exposed to the process of annealing at 610° for 12 h. Homogeneous and transparent glasses were obtained without visible effect of crystallization. In order to determine spectral properties a series of samples with the dimensions of $6 \times 6 \times 2$ mm^3 were prepared. The spectral transmission measurement within the range from 0.18 to 0.5 μm was taken using Hamamatsu TM-C10082CAH spectrometer and within range 0.5 to 1.7 μm an Acton Spectra Pro 2300i monochromator with an InGaAs detector. The glass density, ρ, was calculated using the method of hydrostatic weighing. The refractive index (633 nm) was determined with Metricon 2010 refractometer. The characteristic temperatures of the obtained glasses were calculated based on the measurement taken with a SETARAM Labsys thermal analyzer using the differential scanning calorimetry (DSC) method. The luminescence spectrum within the range 300–750 nm was measured at a station equipped with a Stellarnet GreenWave spectrometer and a pumping laser diode ($\lambda_p = 976$ nm) with an optical fibre output having the maximum optical power $P = 30$ W.

3. Results and discussion

3.1. Physicochemical properties

The basic parameters of the fabricated germanate glass doped with Yb^{3+}/Tb^{3+} are listed in Table.

TABLE

Optical and physical properties of germanate glass.

Density ρ [g/cm^3]	Transition temperature T_g [°C]	Crystallization temperature T_x [°C]	Refractive index n (633 nm)
4.4	618	815	1.688

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A relative significant difference $T_g - T_x = 197\,^{\circ}\mathrm{C}$ indicates that glassy matrix is thermally stable and therefore it is possible for it to be transformed into optical fibre (Fig. 1).

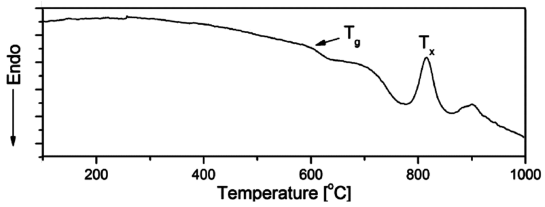

Fig. 1. DSC curve of the germanate glass.

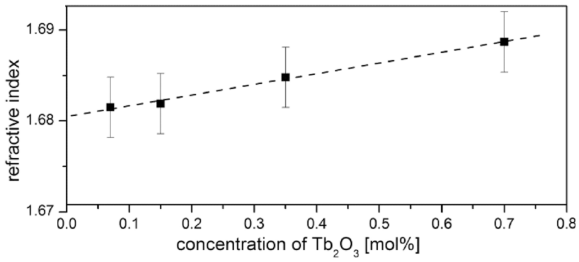

Fig. 2. Refraction index of germanate vs. concentration of Tb_2O_3, $Yb_2O_3 = 1$ mol.%.

Figure 2 presents the effect of doping of glass with $x\mathrm{Yb_2O_3}/y\mathrm{Tb_2O_3}$ ($x = 1$, $y = 0.07$, 0.15, 0.35, 0.7) ions. The increase of terbium ions concentration causes higher value of the refraction index. This phenomenon is significant within the field of active optical fibre technology, because the same glass matrix may be applied onto both core and cladding of the fibre. The difference in the refraction index within the core as well as the cladding, required in the single-mode optical fibres can only be controlled even by means of doping the glass with terbium and ytterbium ions.

3.2. Absorption coefficient

Absorption coefficient spectra of the glass doped with $0.7\mathrm{Yb_2O_3}/0.7\mathrm{Tb_2O_3}$ is presented in Fig. 3.The glass is characterized by a high transmission level both in the visible range and near infrared. Wide absorption band with a maximum absorption at 976 nm is typical for ytterbium and corresponds to the quantum transition $^2F_{7/2} \rightarrow {}^2F_{5/2}$.

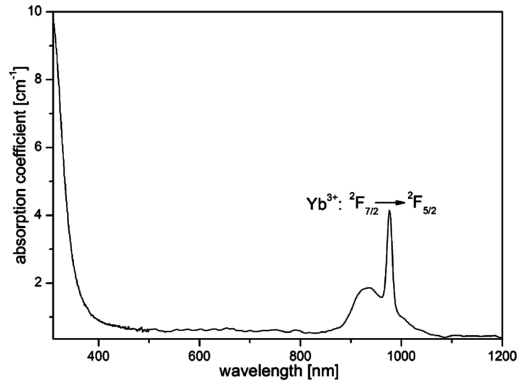

Fig. 3. Absorption coefficient of the germanate glass doped with $0.7\mathrm{Yb_2O_3}/0.7\mathrm{Tb_2O_3}$.

Absorption bands resulting from the presence of terbium ions were not measured in the investigated spectral range. Typical for terbium, absorption in the range of 350–550 nm are too low to be measured for dopant concentration $Tb_2O_3 = (0.07\text{–}0.7)$ mol.%. Moreover, absorption bands below 400 nm are covered by absorption edge of UV radiation of germanate glass.

3.3. Upconversion emission

Figure 4 presents emission spectra of germanate glasses doped with $1\mathrm{Yb_2O_3}/(0.07\text{–}0.7)\mathrm{Tb_2O_3}$ mol.%, excited by 2 W power pump ($\lambda_p = 976$ nm).

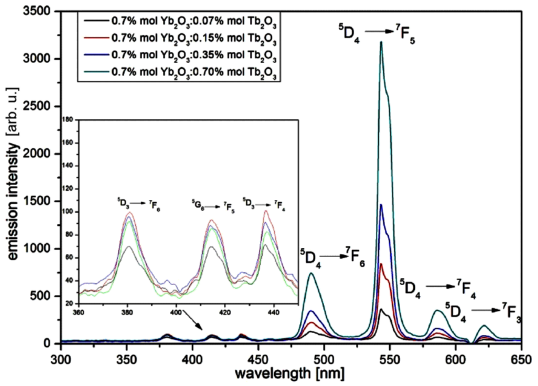

Fig. 4. Emission spectra of the Yb^{3+}/Tb^{3+} germanate glasses, $\lambda_p = 976$ nm.

Upconversion spectrum consists of seven emission bands, resulting from the quantum transition in the terbium structure (Fig. 5). Terbium ions do not directly absorb pump radiation 976 nm. The process of their excitation occurs as a result of cooperative energy transfer from ytterbium ions. Luminescence band with the highest intensity of 543 nm corresponds to the $^5D_4 \rightarrow {}^7F_5$ transition, whereas emission bands of 489, 586, 621 nm result from $^5D_4 \rightarrow {}^7F_J$ ($J = 6$, 4, 3) transitions. Population of $^5D_4$ level is achieved by cooperative energy transfer from the pair of excited Yb^{3+} ions to a neighbouring Tb^{3+} ($^5D_1$) ion

$$2\times\mathrm{Yb}^{3+}(^2F_{5/2})+\mathrm{Tb}^{3+}(^7F_6) \rightarrow 2\times\mathrm{Yb}^{3+}(^2F_{7/2})+\mathrm{Tb}^{3+}(^5D_4). \quad (1)$$

Furthermore, emission bands measured at 381, 415 and 435 nm (Fig. 4, inset) corresponding to $^5D_3$, $^5G_6 \rightarrow {}^7F_J$ ($J = 6$, 5, 4) transitions and they intensity are several times lower. The level of $^5D_3$, $^5G_6$ is populated according to the following diagram. Terbium ions, excited as a result of cooperative energy transfer to the level of $^5D_4$ absorb the pump radiation of 976 nm excited state absorption (ESA) and are excited to the $^5D_1$ level. The

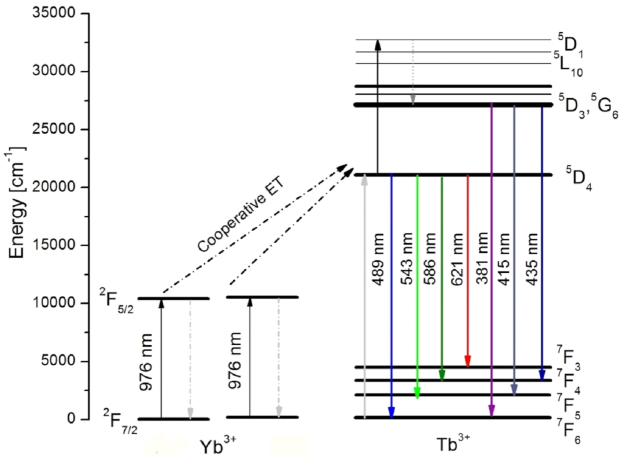

Fig. 5. Simplified energy diagram of Tb^{3+}/Yb^{3+} ions with upconversion luminescence mechanisms.

second excitation channel is energy transfer from yet another excited $Yb^{3+}(^2F_{5/2})$ ion. In the next phase, a rapid non-radiative relaxation $^5D_1 \rightarrow {}^5D_3$ occurs. This process is described by the following equation:

$$Tb^{3+}(^5D_4)+Yb^{3+}(^2F_{5/2}) + h\nu \rightarrow \text{relaxation, } Tb^{3+}(^5D_3). \quad (2)$$

The influence of Tb^{3+} concentration on luminescence spectra with constant concentration of 0.7 mol.% Yb^{3+} is presented in Fig. 6. As the Tb^{3+} concentration increases, so does the intensity of all the bands of luminescence spectra. In the investigated range (0.07–0.7)Tb_2O_3 the relationship is linear. The maximum of emission was obtained with the concentration ratio $0.7Yb_2O_3/0.7Tb_2O_3$.

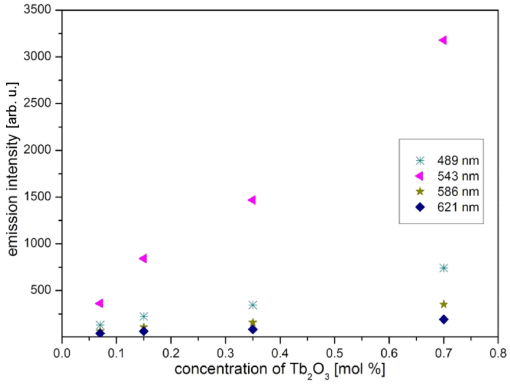

Fig. 6. Effect of concentration of Tb^{3+} on the upconversion luminescence.

The efficiency of cooperative energy transfer $Yb^3 \rightarrow Tb^{3+}$ increases as the distance between the interacting rare earth ions gets smaller and the concentration of Tb^{3+} increases. However, there are phenomena which limit the concentration of active dopant. They are clustering of as well as energy migration between the pairs of Yb^{3+}–Yb^{3+} [21]. The dependence of luminescence intensity as a function of the pump radiation allows analyzing the mechanisms of upconversion in the obtained germanate glass. The relation between the upconversion emission intensity I_{UP} from the pump intensity I_{IR} is determined by the condition

$$I_{UP} \propto I_{IR}^n, \quad (3)$$

where n is the number of photons absorbed in the infrared to the number of photons emitted in the visual spectrum. The rise in the pump radiation intensity increases the number of absorbed photons to the Yb^{3+} laser level, and according to condition (3), the emission intensity in the visual spectrum increases [3]. In practice, the dependence of upconversion intensity versus pump power is lower than I_{IR}^n. As the power of the pump increases, the effect of saturation as well as the effect of competition between linear processes occur and the upconversion process takes place [25].

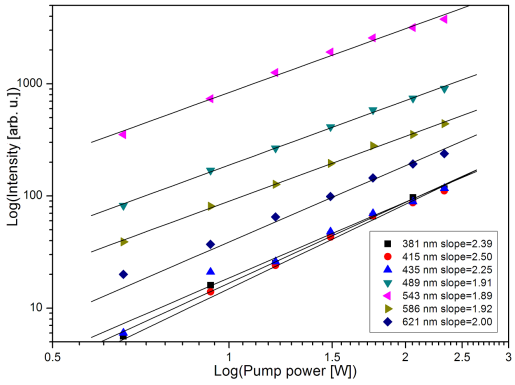

Fig. 7. Dependence of upconversion emission intensity of $0.7Yb^{3+}/0.7Tb^{3+}$ codoped germanate glass on excitation power ($\lambda_P = 980$ nm).

The intensity of emission bands versus pump power is presented in Fig. 7. The slope of the straight lines in the diagram (Fig. 7) for the luminescence band: 381, 415, 435 nm correspond to the values: 2.39, 2.50, 2.25, which proves that according to the energy level diagram presented in Fig. 5 there occurs a three-photon conversion process. The slope of characteristics in the instances of emission bands: 489, 543, 586 and 621 nm are below 2, which indicate two-photon processes. Emission bands resulting from the three-photon process are several times lower than two-photon ones. However, the three-photon processes were observed in each of the investigated glasses doped with $0.7Yb_2O_3/(0.07–0.7)Tb_2O_3$.

4. Conclusions

In the article glasses from the GeO_2–GaO–BaO system doped with Yb^{3+}/Tb^{3+} ions were investigated in order to obtain emission in visible range. The glasses are optimised to characterise by low phonon energy and high thermal stability needed in optical fibre manufacturing. Measured emission bands at 489, 543, 586 and 621 nm

wavelength correspond to the transitions $^5D_4 \rightarrow {}^7F_J$ ($J = 6, 5, 4, 3$). They result from cooperative energy transfer between $Yb^{3+} \rightarrow Tb^{3+}$ ions in two-photon conversion process. The lower intensity emission bands at 381, 415 and 435 nm, correspond to the $^5D_3$, $^5G_6 \rightarrow {}^7F_J$ ($J = 6, 5, 4$) transitions and result from three-photon process. It has been observed that efficiency of cooperative energy transfer ($Yb^{3+} \rightarrow Tb^{3+}$) increases as the distance between the interacting rare earth ions gets smaller and the concentration of Tb^{3+} increases. However the highest upconversion intensity occurs in the glass doped with $0.7Yb_2O_3/0.7Tb_2O_3$. The presented results indicate that elaborated germanate glass doped with $0.7Yb_2O_3/0.7Tb_2O_3$ is a promising material that can be used to produce optical fibre sources.

Acknowledgments

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