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Effect of Temperature on Upconversion Luminescence in Yb^{3+}/Tb^{3+} Co-Doped Germanate Glass

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In the article effect of temperature on the cooperative energy transfer in germanate glass co-doped with Yb^{3+}/Tb^{3+} under 976 nm laser diode pumping was investigated. The optimization of Tb^{3+} concentration on the upconversion luminescence was determined. Strong luminescence at 489, 543, 586, 621 nm corresponding to ${}^5D_4 \to {}^7F_J$ ($J = 6$, 4, 3) transitions and luminescence at 381, 415, 435 nm resulting from ${}^5D_3$, ${}^5G_6 \to {}^7F_J$ ($J = 6$, 5, 4) transitions were presented. The highest upconversion emission intensity was obtained in glass co-doped with 0.7 Yb_2O_3/0.7 Tb_2O_3 (mol%). The effect of temperature on the luminescent properties of germanate glass in the range of 5–250 °C indicates the presence of competing phenomena: an increase in the effective absorption cross--section of Yb^{3+} ions donor as a function of temperature and migration of energy between pairs of ions Yb^{3+}–Yb^{3+} and of multiphonon excitation levels ${}^7F_J$.

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1. Introduction

Glasses and optical fibers doped with rare earths emitting in the visible range have numerous applications: 3D displays, medical diagnostics, optical sensors [1–6]. Such demand for compact, optical sources and amplifiers of radiation forces seeking new glassy materials doped with rare earths. Moreover, the changes in luminescent properties of glasses doped with rare earths under the influence of temperature makes them an attractive material for construction of optical temperature sensors used for monitoring the temperature in the highly corrosive materials, power stations, oil refineries, coal miners and the building fire detection [7].

Germanium-based glasses, due to high solubility of rare earths and low energy of phonon (900 cm^{-1}) which allow efficient conversion of radiation excitation in the field of IR to VIS, are a great alternative for tellurium glasses [8–12]. In addition, good mechanical properties and high stability allow to form them into fiber structures. In glass co-doped with Yb^{3+}/Tb^{3+} during radiation pumping at the wavelength of 976 nm a cooperative energy transfer from a pair of Yb^{3+} ions to the Tb^{3+} ion may occur and as a result of ${}^5D_3/{}^5D_4 \to {}^7F_J$ ($J = 6$, 5, 4, 3) transitions an emission in the range of VIS occurs [13–18].

2. Experimental

The glasses with molar composition $(60\text{–}x\text{–}y)GeO_2$–$25Ga_2O_3$–11BaO–$4La_2O_3$–$xYb_2O_3/yTb_2O_3$ ($x = 0.7$, $y = 0.07$, 0.15, 0.35, 0.7) were melted from spectrally 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 600 °C 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 $6\times6\times2$ mm^3 were prepared. The luminescence spectrum within the range from 300 to 650 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. The Peltier device in the range of 5–25 °C and electric furnace in the range of 25–250 °C were used to control the temperature during the study of the influence of the temperature on luminescence properties of the produced germanium glass co-doped with $0.7Yb_2O_3$/$0.7Tb_2O_3$. The temperature of glasses was measured using a platinum-lineage thermocouple.

3. Results and discussion

3.1. Upconversion luminescence

Terbium ions do not absorb pumping radiation (976 nm) directly. Instead, they become excited in the course of cooperative energy transfer from Yb^{3+} ions. Figure 1 presents emission spectra of germanate glasses co-doped with $0.7Yb_2O_3/(0.07\text{–}0.7)Tb_2O_3$ mol.% under excitation of Yb^{3+} by laser diode with $\lambda_p = 976$ nm, $P_{pump} = 2$ W.

The upconversion emission spectra consist of seven emission bands related to ${}^5D_4 \to {}^7F_J$ ($J = 6$, 5, 4, 3) and ${}^5D_3$ (${}^5G_6$) $\to {}^7F_J$ ($J = 6$, 5, 4) transitions of Tb^{3+}. As for the excited state ${}^5D_4$, it is populated in the course of cooperative energy transfer between a pair of excited Yb^{3+} and a neighboring Tb^{3+} by 2-photon process

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

Furthermore, three emission bands with several times lower emission intensity were measured at 381, 415, and

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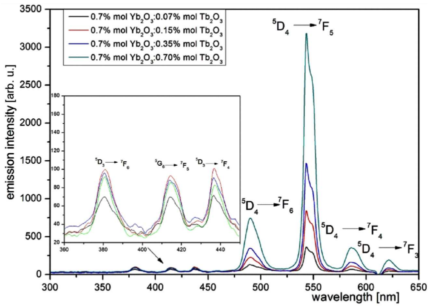

Fig. 1. Emission spectra of the Yb^{3+}/Tb^{3+} co-doped germanate glasses, $\lambda_p = 976$ nm.

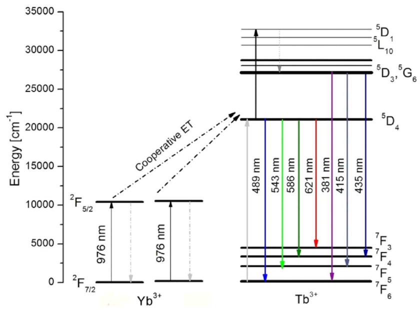

Fig. 2. Simplified energy level diagram of Tb^{3+}/Yb^{3+} ion with upconversion luminescence mechanisms.

435 nm, which correspond to $^5D_3$ ($^5G_6$) $\to$ ^7F_J ($J = 6$, 5, 4) transitions, respectively. The $^5D_3$, $^5G_6$ level is populated by 3-photon process. This phenomenon can be described by the following mechanism:

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

The highest intensity of emission was obtained with the concentration $0.7Yb_2O_3/0.7Tb_2O_3$ (mol.%). The efficiency of a cooperative energy transfer $Yb^3 \to Tb^{3+}$ increases as the distance between the interacting rare earth ions gets smaller and the concentration of Tb^{3+} increases. However, there are observed phenomena which limit the concentration of active dopant. They are clusterings of lanthanides ions and energy migration between the pairs of Yb^{3+}–Yb^{3+} [19].

3.2. Influence of temperature on upconversion luminescence in Yb^{3+}/Tb^{3+} co-doped germanate glass

Figure 3 presents emission spectra of germanate glasses co-doped with $0.7Yb_2O_3/0.7Tb_2O_3$ mol.% in temperatures 10, 50, 100, 250 °C. Analysis of the luminescence intensity of each emission band showed its increases with the temperature range from 5 to 25 °C (Figs. 4, 5).

The increase of the effective absorption cross-section of a donor-Yb^{3+} ions under the influence of temperature is caused by a phenomenon of the increase in the number of phonons which are involved in filling the upper Stark sublevels of the $^2F_{5/2}$ multiplet and is described as follows [20]:

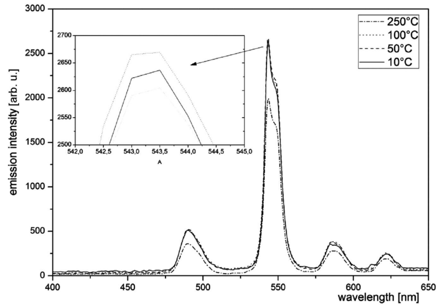

Fig. 3. Upconversion emission spectra of germanate glass co-doped with $0.7Yb_2O_3/0.7Tb_2O_3$ as a function of temperature.

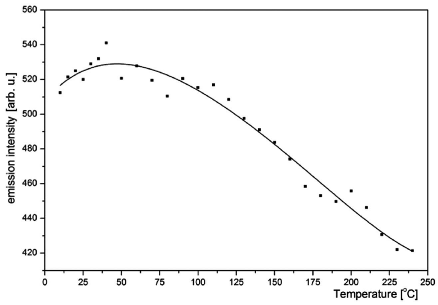

Fig. 4. Upconversion emission intensity at 543 nm of germanate glass co-doped with $0.7Yb_2O_3/0.7Tb_2O_3$ as a function of temperature.

$$\sigma_{abs} = \sigma_{abs}^0 \left[\exp\left(\frac{E_{phonon}}{k_B T} \right) - 1 \right]^{-p}, \quad (3)$$

where σ_{abs}^0 is the absorption cross-section at resonance, E_{phonon} is the phonon energy, k_B is the Boltzmann constant, T is the temperature, p is the number of phonons involved in the Yb^{3+} ions excitation process. It was noticed that at temperatures above 25 °C luminescence intensity of all emission bands connected with quantum transitions in terbium ions decreases linearly. Quenching of luminescence in the temperature range of 25–250 °C is connected with the depopulation of the basic level as a result of multiphonon excitation of ^7F_J levels and with the phenomenon of energy migration between pairs of Yb^{3+}–Yb^{3+} ions [19, 20]. The rate of the Yb^{3+}–Yb^{3+}

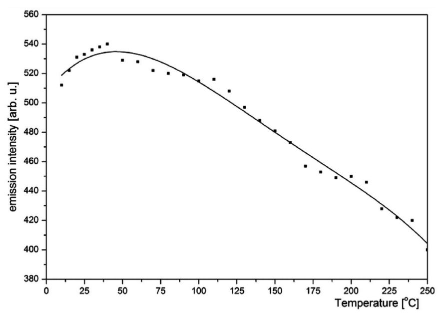

Fig. 5. Upconversion emission intensity at 489 nm of germanate glass co-doped with $0.7Yb_2O_3/0.7Tb_2O_3$ as a function of temperature.

energy migration processes describes the following relation (4):

$$P_{\mathrm{Yb-Yb}} = \frac{3h^4c^4}{4\pi^4\tau_{\mathrm{R}}}\left(\frac{1}{R_{\mathrm{YbYb}}}\right)^6 \times Q_{\mathrm{Yb}}\int\frac{F_{\mathrm{e}}(E)F_{\mathrm{a}}(E)\,\mathrm{d}E}{E^4}. \quad (4)$$

R_{YbYb} is the distance between ytterbium ions, Q_{Yb} is the integrated absorption cross-section of ytterbium, $F_{\mathrm{a}}(E)$ is the normalized absorption spectra, $F_{\mathrm{e}}(E)$ is the normalized emission spectra.

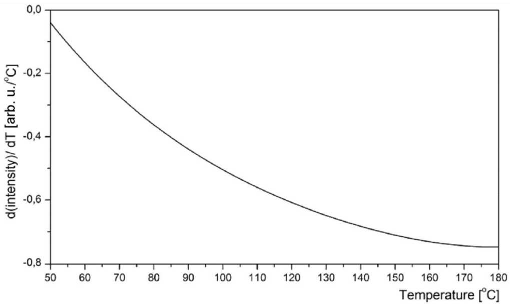

Fig. 6. Sensitivity defined as d(intensity)/dT as a function of temperature.

Produced germanium glass co-doped with $0.7\mathrm{Yb_2O_3}/0.7\mathrm{Tb_2O_3}$ can be used to construct luminescent temperature sensors operating in the range of 50–180 °C. The maximum rate of change of the luminescence signal that has been obtained under the temperature d(intensity)/dT is 0.75 a.u./°C (Fig. 6).

4. Conclusions

As a part of the research, spectroscopic properties of the glass from system $\mathrm{GeO_2}$–$\mathrm{Ga_2O_3}$–BaO co-doped with $\mathrm{Yb^{3+}}/\mathrm{Tb^{3+}}$ ions which is characterized by high thermal stability and low energy of phonons were manufactured and examined. Emission bands at the wavelengths of 489, 543, 586, 621 nm which correspond to ${}^5D_4 \rightarrow {}^7F_J$ (J = 6, 5, 4, 3) transitions, respectively, and are related to 2-photon process of the excitation of the conversion were observed as a result of $\mathrm{Yb^3} \rightarrow \mathrm{Tb^{3+}}$ cooperative energy transfers (λ_{p} = 976 nm). Furthermore, three emission bands of repeatedly smaller intensity has been measured: 381, 415, 435 nm corresponding to ${}^5D_3$, ${}^5G_6 \rightarrow {}^7F_J$ (J = 6, 5, 4) transitions which result from the 3-photon process.

The efficiency of the $\mathrm{Yb^3} \rightarrow \mathrm{Tb^{3+}}$ cooperative energy transfer increases due to the decrease in the distance between interacting rare earth ions, thus the increase in the $\mathrm{Tb^{3+}}$ concentration. Glass co-doped with $0.7\mathrm{Yb_2O_3}/0.7\mathrm{Tb_2O}$ (mol.%), in which the effect of the temperature on luminescence properties has been examined, is characterized by the highest upconversion emission intensity. The increase in the intensity of luminescence in every emission band due to the increase of the temperature in the range of 5–25 °C is caused by the increase of effective crosssection for the absorption of the $\mathrm{Yb^{3+}}$ donor ions under the influence of the temperature. Quenching of luminescence in the temperature range of 25–250 °C is connected with competing processes: energy migration between pairs of $\mathrm{Yb^{3+}}$–$\mathrm{Yb^{3+}}$ ions and depopulation of the basic level as a result of multiphonon excitation of the ${}^7F_J$ levels. The maximum rate of change of the luminescent signal is caused by mentioned processes in the range of 50–180 °C is 0.75 a.u./°C. Obtained results allow to conclude that produced germanium based glass co-doped with $0.7\mathrm{Yb_2O_3}/0.7\mathrm{Tb_2O_3}$ is a promising material for the construction of optical sources of radiation operating in the range of 0.54 μm.

Acknowledgments

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