Spectroscopic study of $Yb^{3+}/Er^{3+}$-doped antimony-phosphate glasses for fiber amplifiers

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Abstract—In this paper the optical spectroscopic properties of $Yb^{3+}/Er^{3+}$ co-doped antimony-phosphate glasses were investigated. The absorption and luminescence spectra were measured and the emission cross-section for $I_{15/2} \rightarrow I_{13/2}$ transition of $Er^{3+}$ was calculated on the basis of the McCreery theory. The resonant energy transfer (ET) between $Yb^{3+} \rightarrow Er^{3+}$ ions was investigated pumping at 976nm. As a result of optimization of rare earth concentration the best efficiency of energy transfer in fabricated glasses was obtained for molar composition $1\%Y_2O_3 : 0.5\%Er_2O_3$.

INTRODUCTION

In fiber optic technology, erbium-doped optical glasses are a widely developed group of materials that are characterised by radiation emission of approx. 1.5μm wavelength, considered to be “eye-safe”. The properties of the $Er^{3+}$ ion related to the possibility of radiation amplification have been applied in order to construct the erbium-doped fiber amplifier (EDFA) operating in the third transmission window [1]. Because of the three-level quantum system of energy levels in the erbium ion, obtaining population inversion requires applying a high-power pumping diode [2]. In order to improve the population rate at the metastable level of the $Er^{3+}$ ion ($I_{13/2}$), the $Yb^{3+}$ ions are introduced to the matrix, which are characterised by a large absorption cross-section of the $I_{7/2} \rightarrow I_{5/2}$ transition. Moreover, excellent spectral matching between emission of $Yb^{3+}$ ions ($I_{5/2} \rightarrow I_{7/2}$), and absorption of $Er^{3+}$ ions ($I_{13/2} \rightarrow I_{9/2}$) leads to efficient resonant energy transfer between the excited levels of rare earth ions [3].

Phosphate glasses characterised by a high stimulated emission cross-section, high amplification factor besides low probability of the reverse energy transfer from $Er^{3+} \rightarrow Yb^{3+}$, are an excellent material for the construction of highly efficient fiber amplifiers. Nevertheless, because of their relatively low chemical resistance and spectral transmission range limited by $OH^-$ ions to approx. 3000cm$^{-1}$, technologists are required to carry out a chemical analysis in order to improve the physicochemical properties of these glasses [4]. Properly modifying the composition of a glass matrix by introducing oxide ions participating in the energy exchange with $OH^-$ groups, it is possible to improve their physicochemical and optical parameters. In addition, the combination of two glass-forming elements with radically different levels of oscillatory vibrations of covalent bonds brings about the rise in the efficiency of energy transfer between activator ions, minimizing non-linear effects at the same time [5].

The article presents the findings of research on optical properties of $Er^{3+}$ and $Yb^{3+}/Er^{3+}$-doped antimony phosphate glasses. The mechanism of energy transfer between $Yb^{3+} \rightarrow Er^{3+}$ has been described. For that purpose the obtained matrices have been excited with the 976nm-wavelength radiation.

EXPERIMENT

A series of glasses doped with $Yb^{3+}$, $Er^{3+}$ and co-doped with $Yb^{3+}/Er^{3+}$ ions were prepared from special high purity agents (99.99%). A homogenous set of antimony-phosphate glass samples with molar composition: 65$P_2O_5 + 25(Sb_2O_3 + Al_2O_3 + Yb_2O_3 + Er_2O_3) + 10$MgF$_2$ was melted at 1350°C for 60 min. in a platinum crucible, using an electrically heated furnace. After that the fused glass was poured into a brass plate and annealed near glass transition temperature ($T_g$) for 12h to remove thermal stress. Homogenous and transparent glasses were obtained without any visible effect of crystallization. Light transmission measurements of fabricated samples were performed in a range of 0.5–1.1μm by using an Acton Spectra Pro 2300i monochromator with an InGaAs detector. The luminescence spectrum within the range from 900 to 1700 nm was measured at a station equipped with a Acton Spectra Pro 2300i spectrometer and a laser diode ($\lambda$$_{P}$$=976$nm and 940nm) with an optical fiber output having the maximum optical power P=31W.

RESULTS AND DISCUSSION

Absorption coefficient

Based on spectral transmission, the absorption coefficient spectrum of the obtained glass doped with $Er^{3+}$ and $Er^{3+}/Yb^{3+}$ ions (Fig. 1) has been calculated. Introducing two different activators to the matrix at the same time leads to a complication of energy structure and division of a pumping radiation quantum by means of energy transfer between the donor and the acceptor. It has been observed

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that antimony-phosphate glass due to a high molar concentration of Yb$_2$O$_3$, is characterised by strong absorption of the $^{2}F_{7/2} ightarrow ^{2}F_{5/2}$ transition at the wavelength of 978 nm. Absorption bands resulting from the complex structure of erbium corresponding to the following transitions: $^{4}I_{15/2} ightarrow ^{2}I_{13/2}$, $^{4}F_{9/2}$, $^{4}I_{11/2}$, $^{4}I_{13/2}$, are similar for both glasses.

![Fig. 1. Absorption coefficient spectra for Er$^{3+}$ and Yb$^{3+}$/Er$^{3+}$ co-doped antimony-phosphate glasses.](image)

The strong and wide absorption band around 980 nm for Yb$^{3+}$/Er$^{3+}$ co-doped samples has a strong optical density owing to a large spectral overlap between Yb$^{3+}$ emission ($^{2}F_{5/2} ightarrow ^{2}F_{7/2}$) and Er$^{3+}$ absorption ($^{4}I_{15/2} ightarrow ^{4}I_{13/2}$). Furthermore, ytterbium ions have a larger absorption coefficient than erbium ions (at this band) which leads to efficient pumping at 976 nm.

**Analysis of absorption and stimulated emission cross-sections**

Based on the absorption spectrum, the absorption cross-section of Yb$^{3+}$ and Er$^{3+}$ $\sigma_{\text{abs}}(\lambda)$ has been calculated by means of the following relation [5]:

$$\sigma_{\text{abs}}(\lambda) = \frac{2.303 \log(1/T(\lambda))}{Nl},$$  \hspace{1cm} (1)

where $T(\lambda)$ is transmission spectra, $N$ is the ion concentrations of Yb$^{3+}$ or Er$^{3+}$, $l$ is the sample thickness. Using the McCumber method [6], the stimulated emission cross-section of erbium $\sigma_{\text{em}}(\lambda)$ at the wavelength of 1536nm has been determined

$$\sigma_{\text{em}}(\lambda) = \sigma_{\text{abs}}(\lambda) \exp\left[\frac{\epsilon - \frac{hc\lambda}{kT}}{kT}\right],$$  \hspace{1cm} (2)

where $\epsilon$ can be calculated by the expression:

$$\exp(\epsilon / kT) = 1.1\exp(E_0 / kT),$$  \hspace{1cm} (3)

where: $E_0$ – energy interval between the lowest multiplets of $^{4}I_{13/2}$ and $^{4}I_{15/2}$ levels at the temperature $T$, $h$ is the Planck constant and $k$ is the Boltzmann constant.

![Fig. 2. The absorption and emission cross-section of Yb$^{3+}$/Er$^{3+}$ co-doped antimony-phosphate glass.](image)

Figure 2 shows the absorption and stimulated emission cross-sections of erbium as the function of a wavelength. The peak values of absorption and emission cross-section are $6.8 \cdot 10^{-21} \text{cm}^2$ and $7.4 \cdot 10^{-21} \text{cm}^2$, respectively. They are larger than the values in the phosphate and silicate glasses [7]. The strong peak of luminescence was observed at 1536nm, which corresponds to $^{4}I_{13/2} \rightarrow ^{4}I_{15/2}$ radiative transition in antimony-phosphate glasses doped with Er$^{3+}$ and Yb$^{3+}$/Er$^{3+}$ ions under 976nm laser diode excitation. As shown in Fig. 3, the intensity of emission of Yb$^{3+}$/Er$^{3+}$ co-doped glass is much stronger than an Er$^{3+}$ singly doped glass.

![Fig. 3. The luminescence spectra of antimony-phosphate glasses doped with Er$^{3+}$ and Yb$^{3+}$/Er$^{3+}$ ions under 976nm LD excitation.](image)

As a result of optimizations of rare earth concentration, the best efficiency of energy transfer was obtained for molar composition 1%Y$_2$O$_3$: 0.5%Er$_2$O$_3$. A strong and wide absorption band of ytterbium ions increases pump...
rate of Yb\(^{3+}/Er\(^{3+}\) system. For this reason, the contribution to \( ^4I_{15/2} \) level population from ET by \( ^2F_{5/2}(Yb^{3+}) + ^4I_{15/2}(Er^{3+}) \rightarrow ^2F_{7/2}(Yb^{3+}) + ^4I_{11/2}(Er^{3+}) \), will be much greater than that from the ground state absorption process of Er\(^{3+}\) ions.

**Mechanism of energy transfer in Yb\(^{3+}/Er\(^{3+}\)) system**

The simplified energy level diagram of Yb\(^{3+}\)/Er\(^{3+}\) co-doped antimony-phosphate glass shown in Fig. 4 is helpful in understanding the mechanism of ytterbium sensitisation of erbium ions in a lattice under 976nm excitation. When the glass sample is excited by a laser diode (976nm), Yb\(^{3+}\) and Er\(^{3+}\) ions are excited simultaneously to \(^2F_{5/2}\) and \(^1I_{11/2}\) energy levels, respectively. As a result of high absorption cross-section of ytterbium ions, the population density of \(^2F_{5/2} (Yb^{3+})\) state is larger than \(^1I_{11/2} (Er^{3+})\) and efficient resonant energy transfer (ET) from Yb\(^{3+}\) \(\rightarrow\) Er\(^{3+}\) can be attained.

These phenomena lead to high population density of \(^4I_{13/2}\) state and increase the intensity of emission of \(^4I_{13/2} \rightarrow ^4I_{15/2}\) transition for Yb\(^{3+}/Er\(^{3+}\) co-doped glass.

**CONCLUSIONS**

In the present paper, the spectroscopic properties of Er\(^{3+}\) doped and Yb\(^{3+}/Er\(^{3+}\) co-doped antimony-phosphate glasses were investigated. The fabricated glasses exhibit good thermal stability, significantly wide near the infrared emission and the great stimulated emission cross-section at 1.5\(\mu\)m. Introduction of Yb\(^{3+}\) ions to lattice increase the pumping efficiency at 976nm and leading to increase intensity of luminescence of \(^4I_{13/2} \rightarrow ^4I_{15/2}\) transition. In order to optimize the composition of ytterbium sensitized erbium doped antimony-phosphate glasses, the absorption cross-section of Yb\(^{3+}\) ions at a pump wavelength, energy transfer efficiency of Yb\(^{3+}\) \(\rightarrow\) Er\(^{3+}\), as well as absorption cross-section of erbium must be determined. As a result of optimizations of rare earth concentration, the best efficiency of energy transfer in fabricated glasses was obtained for molar composition 1\%Y\(_2\)O\(_3\): 0.5\%Er\(_2\)O\(_3\). The fabricated new antimony-phosphate glasses are very promising materials for fiber amplifier and laser applications.

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**References**