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 $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} was calculated on the basis of the McCumber 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 ($^4I_{13/2}$), the Yb^{3+} ions are introduced to the matrix, which are characterised by a large absorption cross-section of the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition. Moreover, excellent spectral matching between emission of Yb^{3+} ions ($^2F_{5/2} \rightarrow {}^2F_{7/2}$), and absorption of Er^{3+} ions ($^4I_{15/2} \rightarrow {}^4I_{9/2}$) 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: $65P_2O_5 + 25(Sb_2O_3 + Al_2O_3 + Yb_2O_3 + Er_2O_3) + 10MgF_2$ 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 (λ_p=976nm and 940nm) with an optical fiber output having the maximum optical power P=31W.

RESULTS AND DISCUSION

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_2O_3, is characterised by strong absorption of the ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition at the wavelength of 978 nm. Absorption bands resulting from the complex structure of erbium corresponding to the following transitions: ${}^4I_{15/2} \rightarrow {}^2H_{11/2}$, ${}^4F_{9/2}$, ${}^4I_{9/2}$, ${}^4I_{11/2}$, ${}^4I_{13/2}$, are similar for both glasses.

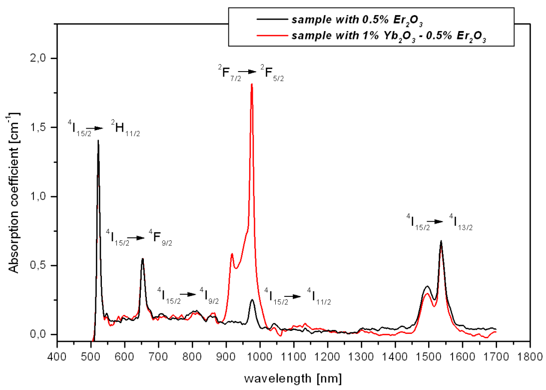

Fig. 1. Absorption coefficient spectra for Er^{3+} and Yb^{3+}/Er^{3+} co-doped antimony-phosphate glasses.

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 (${}^2F_{5/2} \rightarrow {}^2F_{7/2}$) and Er^{3+} absorption (${}^4I_{15/2} \rightarrow {}^4I_{11/2}$). 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+} $\sigma_{abs}(\lambda)$ has been calculated by means of the following relation [5]:

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

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 $\sigma_{em}(\lambda)$ at the wavelength of 1536nm has been determined

$$\sigma_{em}(\lambda) = \sigma_{abs}(\lambda)\exp\left[\frac{\varepsilon - hc\lambda^{-1}}{kT}\right], \quad (2)$$

where ε can be calculated by the expression:

$$\exp(\varepsilon / kT) = 1.1\exp(E_0 / kT), \quad (3)$$

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

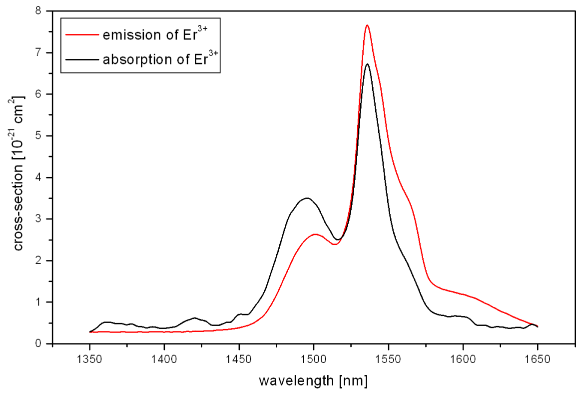

Fig. 2. The absorption and emission cross-section of Yb^{3+}/Er^{3+} co-doped antimony-phosphate glass.

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 $6.8 \cdot 10^{-21}cm^2$ and $7.74 \cdot 10^{-21}$ 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 ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ 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.

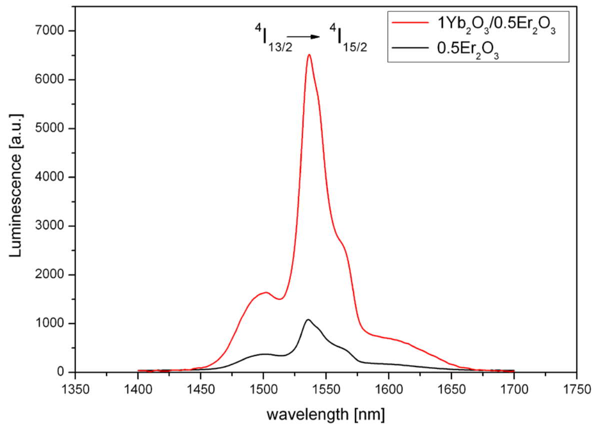

Fig. 3. The luminescence spectra of antimony-phosphate glasses doped with Er^{3+} and Yb^{3+}/Er^{3+} ions under 976nm LD excitation.

As a result of optimizations of rare earth concentration, the best efficiency of energy transfer was obtained for molar composition $1\%Y_2O_3$: $0.5\%Er_2O_3$. A strong and wide absorption band of ytterbium ions increases pump rate of Yb^{3+}/Er^{3+} system. For this reason, the contribution to $^4I_{13/2}$ level population from ET by $^2F_{5/2}(Yb^{3+})$ + $^4I_{15/2}$ (Er^{3+}) → $^2F_{7/2}(Yb^{3+})$ + $^4I_{11/2}$ (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 $^4I_{11/2}$ 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 $^4I_{11/2}$ (Er^{3+}) and efficient resonant energy transfer (ET) from Yb^{3+} → Er^{3+} can be attained.

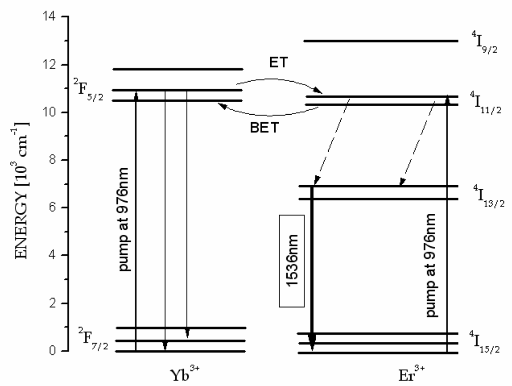

Fig. 4. Simplified energy level scheme with mechanism of energy transfer.

The high phonon energy of antimony-phosphate glass (~1200cm^{-1}) increases the probability of non-radiative relaxation of Er^{3+} ($^4I_{11/2}$ → $^4I_{13/2}$). The weak pump absorption of $^4I_{15/2}$ → $^4I_{11/2}$ transitions exhibit that energy transfer by $^2F_{5/2}(Yb^{3+})$ + $^4I_{15/2}$ (Er^{3+}) → $^2F_{7/2}(Yb^{3+})$ + $^4I_{11/2}$ (Er^{3+}) is the main process in $^4I_{13/2}$ state population and the back energy transfer (BET) from Er^{3+} to Yb^{3+} can be neglected.

These phenomena lead to high population density of $^4I_{13/2}$ state and increase the intensity of emission of $^4I_{13/2}$ → $^4I_{15/2}$ 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 1.5μm. Introduction of Yb^{3+} ions to lattice increase the pumping efficiency at 976nm and leading to increase intensity of luminescence of $^4I_{13/2}$ → $^4I_{15/2}$ 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+} → 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_2O_3: 0.5%Er_2O_3. The fabricated new antimony-phosphate glasses are very promising materials for fiber amplifier and laser applications.

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