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Effect of BaF_2 addition on luminescence properties of Er^{3+}/Yb^{3+} co-doped phosphate glasses☆

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ABSTRACT

Er^{3+}/Yb^{3+} co-doped phosphate glasses (P_2O_5-Al_2O_3-BaO-BaF_2-K_2O-Er_2O_3-Yb_2O_3) with varying BaF_2 content, were prepared by a conventional melt quenching technique and their spectroscopic properties were examined through the Raman, absorption, emission and decay measurements. Raman spectra (350–1400 cm^{-1}) of the Er^{3+}/Yb^{3+} co-doped phosphate glasses with varying BaF_2 content, were recorded upon laser excitation at 785 nm. Near infrared luminescence spectra were measured in the 1400–1600 nm region under 970 nm diode laser excitation and characteristic band was observed at 1533 nm corresponding to $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ion. The decay curves for the $^4I_{13/2}$ level of Er^{3+} ion, were measured and the lifetime is found to decrease from 7.94 to 7.70 ms when BaF_2 content increases from 0 to 8 mol% and then increases up to 7.83 ms with further increase in BaF_2 content (12 mol %). The emission cross-section, lifetime and figure of merit for the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ion were evaluated and compared to the other host matrices. The upconversion luminescence was measured and intense red emission was observed for all the studied samples.

1. Introduction

Trivalent erbium (Er^{3+}) ions have been recognized as one of the most popular and efficient ions for near infrared (NIR) emission at around 1.53 μm corresponding to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition, for optical amplification at the third telecommunication window.[1,2] This emission has been essential to increase the transmission capacity in Er^{3+}-doped fiber optical amplifiers (EDFAs) used in wavelength-division-multiplexing (WDM) network systems.[3] It is well known that the commercial EDFAs used nowadays based on silica glass exhibit a relatively narrow bandwidth that limits the transmission capacity of the WDM systems.[4] High pumping rates are required to obtain population inversion in three level system of Er^{3+} for optical amplification at 1.5 μm. In this direction, ytterbium (Yb^{3+}) sensitized Er^{3+} emission starts to play an important role to obtain high gain bandwidth because of the large spectral overlap between $^2F_{5/2} \rightarrow {}^2F_{7/2}$ emission of Yb^{3+} and $^4I_{15/2} \rightarrow {}^4I_{11/2}$ absorption band of Er^{3+} which results in an efficient energy transfer. It can also significantly improve the up-conversion emission properties of the materials.

A lot of work has been done on spectroscopic properties of Er^{3+} singly doped and Er^{3+}/Yb^{3+} co-doped glasses such as tellurites,[5,6] borates,[7] germanates,[8,9] and phosphates,[10–15] for the development of efficient optical amplifiers with broad and flat gain profiles. Particularly, heavy metal fluoride (PbF_2 and CdF_2) based rare earth doped glasses/glass-ceramics exhibited efficient luminescence when compared to the other modifiers.[16–18] In recent years, the demand for alternative materials of Pb and Cd is growing, since they have been designated as toxic substances. Therefore, rare earth doped glasses/glass-ceramics with different fluoride modifiers (LaF_3/GdF_3) have been studied and reported elsewhere.[19,20] It

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is worth to note that among fluoride modifiers, MF_2 (where M = Ba, Ca, and Sr) modifiers are mainly used successfully to obtain nano-structured glass-ceramics. Zur et al.[21] studied the effect of BaF_2 addition on spectroscopic properties of Pr^{3+} and Er^{3+}-doped lead free germanate and borate glasses. Kumar et al.[22] also reported that addition of BaF_2 could enhance the luminescence properties of Nd^{3+} ion in fluorophosphate glasses. So the development of BaF_2 containing glasses doped with rare earth ions are of immense scientific and technological interest for optical device applications. To the best of our knowledge, the spectroscopic properties of Er^{3+}/Yb^{3+} co-doped phosphate glasses modified with BaF_2 content are not explored. Since long phosphate glasses have been receiving great attention because of their attractive and promising properties that include good chemical durability, high rare earth solubility, and high laser damage threshold.[10–15] Another important feature of phosphate glasses is their thermal and mechanical strength that allows for the realization of optical fibers that can be fusion spliced with commercial optical fiber components based on silicate glasses.[23]

Hence, the present study elucidates the spectroscopic properties of Er^{3+}/Yb^{3+} co-doped phosphate glasses modified with BaF_2 content. The structural properties were studied from Raman analysis. The absorption, luminescence and upconversion studies were carried out through spectroscopic techniques.

2. Experimental procedure

All the samples were prepared from the high purity (>99.9%) starting chemical constituents $NaH_2PO_4 \cdot H_2O$, Al_2O_3, BaO, BaF_2, K_2O, Er_2O_3 and Yb_2O_3. The samples were prepared according to the molar composition (mol%): $62.85P_2O_5 - 8Al_2O_3 - (12\text{-}x)BaO - xBaF_2 - 13K_2O - 0.15Er_2O_3 - 4.0Yb_2O_3$, where $x = 0$, 4, 8 and 12. Calculated quantities of the chemicals (total weight of about 25 g) were mixed in an agate mortar and heated up to 1200 °C for 3 h in a platinum crucible so that a homogeneously mixed melt was obtained. Then, the melt was poured onto a preheated brass mould kept at 250 °C and subsequently annealed at 300 °C for 12 h in order to remove stress and strain inside the glass samples. The samples were then ground to a thickness of about 2.36 mm with silicon carbide adhesive paper and finally polished with cerium oxide powder. The thickness of the samples was determined with a micrometer at different parts of the sample surface.

Linear refractive index measurements of the glass samples were carried out using a prism coupler system at 632.8 nm. The density was measured according to Archimedes' principle, where the weight of a volume of distilled water equivalent to that of the glass sample was obtained to a precision of 0.0001 g. Raman spectra were recorded by an inVia Raman microscope (Renishaw) at 785 nm laser excitation. The UV–VIS–NIR absorbance spectra (300–1700 nm) of glass samples were recorded using a spectrophotometer (Agilent Technologies) with wavelength resolution of 1.0 nm. The emission spectra were recorded by exciting the samples at 970 nm from a continuous wave laser diode (CWLD). The CWLD was focused onto a sample with a 5 cm focal length lens. The signal emitted was focused onto a SP-2357 monochromator (Acton Research) and detected by InGaAs detector (Thorlabs DET10C). The system was controlled with a PC where emission spectra were obtained. Special care was taken to maintain the alignment of the set up in order to compare the intensity of the emission signal between different characterized samples. The decay time measurements were conducted using a standard setup comprising a pulsed laser diode with frequency of 9 Hz and an InGaAs detector to register the 1533 nm emission.

3. Results and discussion

Physical properties of the Er^{3+}/Yb^{3+} phosphate glasses ($62.85P_2O_5-8Al_2O_3-(12 - x)BaO-xBaF_2-13K_2O-0.15Er_2O_3-4.0Yb_2O_3$, where $x = 0$, 4 mol%, 8 mol% and 12 mol%) with varying BaF_2 content, were determined and are tabulated in Table 1.

3.1. Raman spectra

Fig. 1 depicts the Raman spectra of the Er^{3+}/Yb^{3+} phosphate glasses modified with BaF_2 content. The band at around 350 cm^{-1} is assigned to the bending vibration of phosphate structural units. A shoulder near 421 cm^{-1} appeared with the addition of BaF_2, which is related to the symmetric stretching vibrations of fluorine species bonded by the modifying cations.[24] The bands at around 527 and 739 cm^{-1} are assigned to the stretching vibrations of P–O–P bonds in phosphate chains.[25] The band at around 1047 cm^{-1} and a shoulder near 1113 cm^{-1} are due to the PO_4 and PO_3 stretching vibrations within Q^0 and Q^1 type phosphate tetrahedral, respectively.[26–28] In addition, a shoulder at higher wavenumbers near 1212 cm^{-1} is related to the PO_2 stretching vibrations typical of metaphosphate units.[29] The band at around 1364 cm^{-1} is assigned to the symmetric stretching vibration of P–O bonds. From this Raman analysis, we observed two things: a shoulder near 421 cm^{-1} appeared with the addition of BaF_2 (4%–12%) and its intensity also increased with increasing BaF_2 content; the band at around 1113 cm^{-1} is more pronounced without BaF_2. Thus, Raman data clearly indicate that the formation of P–F bonds appeared in the present glasses with the addition of BaF_2 content. As a result, we may expect low multiphonon relaxation rates which in turn enhance the radiative emission properties of the Er^{3+}/Yb^{3+} co-doped phosphate glasses modified with BaF_2 content.

3.2. Absorption and near infrared spectra

Fig. 2 shows the absorption spectra of Er^{3+}/Yb^{3+} co-doped phosphate glasses modified with BaF_2 content. As can be seen from Fig. 2, the absorption spectra that exhibited bands at 356, 365, 377, 407, 442, 451, 488, 520, 545, 652, 975, and 1533 nm, were due to the transition from the $^4I_{15/2}$ ground state to the excited $^2K_{15/2}$, $^4G_{9/2}$, $^4G_{11/2}$, $^2G_{9/2}$, $^4F_{3/2}$, $^4F_{5/2}$, $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$ states of Er^{3+} ions, respectively. It is worth to note that much stronger absorption peak at around 975 nm in Er^{3+}/Yb^{3+} co-doped samples was due to the absorption from the ground $^2F_{7/2}$ state to the excited $^2F_{5/2}$ state of Yb^{3+} ions, whose absorption cross-section at 975 nm is much larger than that of Er^{3+}. This indicates that co-doping with Yb^{3+} ions can greatly enhance the absorption at the 970 nm pump band.

Table 1
Physical properties of Er^{3+}/Yb^{3+} co-doped phosphate glasses.

BaF_2 (%)	Thickness (cm)	Density (g/cm^3)	Concentration ($\times10^{19}$ ions/cm^3)	Refractive index@632.8 nm
0	0.236	2.9589	3.7023	1.5170
4	0.233	2.9615	3.6807	1.5177
8	0.235	2.9331	3.6269	1.5179
12	0.237	2.9664	3.6439	1.5195