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Spectroscopic analysis of trivalent Nd^{3+}/Yb^{3+} ions codoped in PZS host glasses as a new laser material at 1.06 μm

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Abstract: This paper reports on the spectral results of Nd^{3+}/Yb^{3+} ions codoped $50P_2O_5$-30ZnO-20SrO (PZS, in mol.%) glasses which were prepared by a melting technique. The glass transition temperature and spectroscopic properties of these glasses were estimated. From the absorption spectra, Judd-Ofelt (J-O) intensity parameters (Ω_k), were calculated. Using J-O intensity parameters, several radiative properties such as spontaneous transition probabilities (A_R), radiative branching ratios (β_R) and radiative lifetimes (τ_R) were determined for the exciting levels of the Nd^{3+} ions. The large value of the stimulated integrated cross-section and the lifetimes of Nd^{3+} level revealed the potential of the present glasses as a candidate for generating laser emission at 1.06 μm as continuous wave laser action and exploited for optical device fabrication. A broad emission band from 950 to 1100 nm was detected when the Nd^{3+}/Yb^{3+} was co-doped in PZS glasses excited by 805 nm lighting diode (LD). The energy transfer process from $Nd^{3+}\rightarrow Yb^{3+}$ in co-doped phosphate glasses was described in this paper.

Keywords: phosphate glasses; Nd^{3+},Yb^{3+} ions; optical spectroscopy; Judd-Ofelt analysis; luminescence; rare earths

Glasses have been known since long time as a convenient host for RE ions, especially Nd^{3+}, to be used for the fabrication of solid-state lasers, optical telecommunication, sensor and other flat panel technologies like plasma display panels (PDP) and recently for white light emitting diodes (W-LEDs)[1,2]. However, because the radiative/nonradiative energy transfer of RE^{3+} ions is highly dependent on the environment surrounding them, the host materials, where RE^{3+} ions reside, should be appropriately selected[3].

The local structure effect and the high RE ion solubility of the phosphate glasses make them be attractive materials for a wide photonic applications such as lasers, optical amplifiers, photosensitivity, optical storage and faraday rotators, but the short length of these devices generally imposes a higher RE concentration on deleterious non-radiative processes which worsen the device performances. Co-doping with second rare earth elements such as ytterbium ions (Yb^{3+}) is generally used to improve the pump absorption and to partially reduce these parasitic effects[4]. In fact, the two-level energy diagram, only the ground state $^2F_{7/2}$ and excited state $^2F_{5/2}$, avoids problems associated with excited state absorption, cross-relaxation and upconversion[5,6].

The optimization of the laser efficiency of RE ions in glasses becomes possible only when their spectroscopic and related properties are well understood[7]. In this frame, we reported the fabrication of phosphate glasses ($50P_2O_5$-30ZnO-20SrO in mol.%) codoped with 3000 ppm Nd_2O_3/3000 ppm Yb_2O_3 and 30000 ppm Nd_2O_3/30000 ppm Yb_2O_3. The Judd-Ofelt theory was used to study the spectroscopic properties of Nd^{3+} from absorption spectrum and refractive index of the sample. The three parameters Ω_2, Ω_4, Ω_6 and a series of other optical properties such as absorption line strength, radiative transition probabilities fluorescence, brunching ratios and theoretical radiative lifetime were evaluated. A broad emission band from 950 to 1100 nm was detected when glasses were excited by 805 nm LD. The energy transfer process from $Nd^{3+}\rightarrow Yb^{3+}$ co-doped in phosphate glasses was described in this paper.

1 Experimental

Glasses with the composition of $50P_2O_5$-30ZnO-20SrO (PZS, in mol.%) codoped by rare earth ions (3000 ppm Nd^{3+}/3000 ppmYb^{3+} , 30000 ppm Nd^{3+}/30000 ppm Yb^{3+}) were prepared by the conventional quenching melt technique. They were melted in alumina crucibles, the temperature was controlled by the special program under argon atmosphere. Composites were cast in a steel mold at room temperature followed by annealing at 420 ºC for

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2 h. The density of these bulk glasses was determined by using a gas pycnometer (Model: UltraPyc 1200e). The prepared glasses were examined by X-ray diffraction (XRD) (Siemens D 6000) using Cu Kα radiation at 40 kV in the 2θ range from 5º to 90º.

The calorimetric measurements of prepared glasses were carried out in Setaram (DSC 131 Evo). The prepared sample (15 mg) was sealed in an aluminum pan and it was tempered at 15 K/min. An empty aluminum pan was used as reference and in all cases flow of nitrogen was maintained at 40 mL/min in order to extract the gases emitted by the reaction, which are highly corrosive to the sensory equipment installed in the DSC 131 Evo furnace. The absorption spectra were measured by using a UV-VIS-NIR double beam spectrophotometer (JASCO V-570 spectrophotometer) in the wavelength range of 190–1100 nm. The emission spectra were measured with an FLS980 type spectrometer pumped by laser diode (LD). All the measurements were performed at room temperature.

The vertical (V) polarized spontaneous Raman spectra of the prepared glass were acquired using a Thermo Scientific DXR Raman microscope spectroscopy with 532 nm excitation ((532 nm Laser type Diode-pumped, solid state (DPSS)) and acquisition time was set to 30 s. The incoming signal vertically surface of the bulk sample, and V-polarized Raman scattered signal was collected in the backscattering geometry with a 100x microscope objective.

2 Results and discussion

Highly homogeneous, transparent and not hydroscopic glasses (PZS codoped 3000 ppm Nd^{3+}/3000 ppm Yb^{3+} and 30000 ppm Nd^{3+}/30000 ppm Yb^{3+}) were obtained in the present work. Fig. 1 shows XRD patterns of the quenched bulk glass samples. The patterns of these samples do not show any peaks, which mean that these glasses are in glassy phase. Fig. 2(a) shows that the color of these glasses changed from sky blue to violet depending on the ratio of codoped ions Nd^{3+}/Yb^{3+} in the composition. The value of density, ρ, of the prepared glass samples increases from 3.0348 to 3.1552 in g/cm^3 when the concentration of Nd^{3+}/Yb^{3+} ions increases from 3000 to 30000 ppm in the host glasses due to increasing molecular weight of the constitute of glass matrix leading to more dense glass.

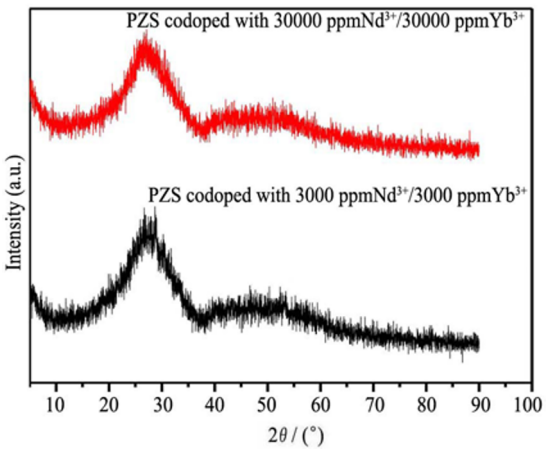

Fig. 1 XRD patterns of the prepared glasses

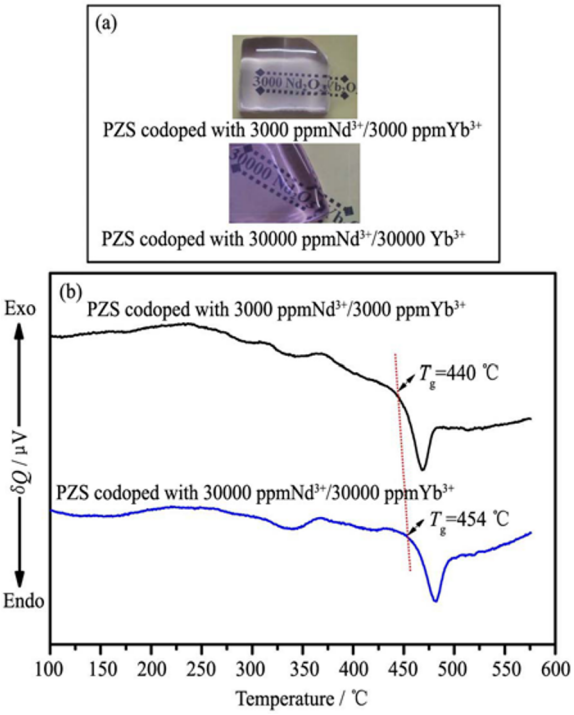

Fig. 2 Photo picture of phosphate glasses codoped with 3000 and 30000 ppm Nd_2O_3/Yb_2O_3 (a) and DSC trace of phosphate glasses codoped with 3000 and 30000 ppm Nd_2O_3/Yb_2O_3 (b)

Fig. 2(b) shows the DSC thermal calorimetric of the prepared glasses at a heating rate of 15 K/min. The glasses transition temperature T_g was obtained, which increases from 444 to 454 ºC when the ions Nd^{3+}/Yb^{3+} increases from 3000 to 30000 ppm in the host glasses. The increase of T_g could be explained by the increase of the rigidity, otherwise, cross link density otherwise decreases the non-bridging oxygen (NBO) of the network host glass matrix when the Nd^{3+}/Yb^{3+} ions concentration rises.

The optical absorption spectrum of Ln^{3+} ions serves generally as a basis to understand their spectroscopic properties. Fig. 3 shows the optical absorption spectrum of phosphate glasses codoped with 3000 ppm Nd_2O_3/3000 ppm Yb_2O_3 and 30000 ppm Nd_2O_3/30000 ppm Yb_2O_3 recorded in the 300–1100 nm spectral range at room temperature along with the band assignments. In this spectral range, nine absorption bands were observed at 352, 430, 470, 524, 580, 682, 744, 802, 872 nm corresponding to transitions from the ground state $^4I_{9/2}$ to various excited states within the *4f* shell of the Nd^{3+} ion and also a strong absorption band at 980 nm which corresponds to $^2F_{7/2}\rightarrow{}^2F_{5/2}$ transition for ytterbium ions. It is