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Structural and luminescence studies of europium ions in lithium aluminium borophosphate glasses

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Abstract: Eu^{3+} doped borophosphate glasses with the chemical composition $20Li_2O$-$30Al_2O_3$-$10B_2O_3$-$40P_2O_5$-xEu_2O_3 (where x=0.05 mol.%, 0.1 mol.%, 1.0 mol.%, 1.5 mol.% and 2.0 mol.%) were prepared by conventional melt quenching technique. The structural and luminescence properties of the prepared Eu^{3+} doped borophosphate glasses were studied and compared with reported results. The XRD pattern showed the amorphous nature of the prepared glasses. Whereas, the FTIR spectra revealed the vibrational modes in the prepared glasses. The bonding parameters ($\bar{\beta}$ and δ) were calculated through the excitation spectra. Judd–Ofelt (J–O) intensity parameters were calculated from the emission spectra and were used to determine transition probability (A), stimulated emission cross-section (σ_P^E), radiative lifetime (τ_R) and branching ratios (β_{exp}) for the transition $^5D_0 \rightarrow {}^7F_j$ (j=1, 2, 3 and 4) of Eu^{3+} ions. Furthermore, the luminescence intensity ratio (R) of $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ transition was also calculated. Transition $^5D_0 \rightarrow {}^7F_2$ had the highest value of stimulated emission cross-section and branching ratios and the results were comparable with the reported values. This indicated that the present glass is promising host material for Eu^{3+} doped fiber amplifiers.

Keywords: europium ions; luminescence properties; borophosphate glasses; Judd–Ofelt analysis; decay time; rare earths

In this day and age, the huge gap between the supply and demand has led to energy crisis and environmental pollution. In order to solve the present problems, the renewable energy, the new environmental friendly energy and low energy consumption devices are needed. In this case, the light emitting diodes (LEDs) are a good example of ideal energy saving and environmentally friendly devices as mentioned by Dillip et al.[1]. Much research work has been carried out for developing optical devices based on fluorescent material doped with rare earth ions[2]; this is due to their potential technological and commercial applications[3].

Among the rare earth ions, europium is a special element as usual dopant ion because it shows properties of valence fluctuation, that is, the valence state is divalent or trivalent[4]. Rare earth ions doped glasses are of great interest because of their applications in bulk lasers, solid state lasers, infrared-to-visible up-converters, temperature sensors, electroluminescent devices, planar waveguides, memory devices, flat panel displays, optical fiber amplifiers, field emission displays, high density memory devices, glass laser, high density frequency domain optical data storage, waveguide lasers and colour display devices[5,6]. Among the rare earth ions family, Eu^{3+} ion shows narrow red light emission due to its transition from $^5D_0 \rightarrow {}^7F_2$ state with high luminescence efficiency which is very sensitive to small changes in the chemical surrounding of the Eu^{3+} ion and is used in photonic applications. Europium ion shows very narrow and intense orange/red emission bands, so its compounds are promising for various optical applications. The emission from non-degenerate $^5D_0$ to $7F_j$ (j=0–6) levels gives site symmetry around active ions and number of sites available for active ions[7].

Host matrix plays an important role in determining the performance of the luminescence material. Glasses as laser hosts have advantages such as mass production at low cost and form fibers more easily than single crystals. The emission properties in the glasses are characterized by broader emission spectra, a radiation lifetime with a non-exponential decay law, and a peculiar temperature dependence of the quantum efficiency[8]. Significant changes in the luminescence behavior have been achieved with the addition of heavy metal ions, transition metal ions and alkaline/alkaline metal ions into the host matrix[9–13]. The excitation and emission transitions are due to the transition among the 4f electronic states in the trivalent rare earth (RE) ions, which are highly sensitive

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to the symmetry, structure of the local environment and phonon energy of the host matrix[14,15].

In the present work, lithium aluminium borophosphate was chosen as host material to study the luminescence properties of the Eu^{3+} ions. Kumar et al.[4] have reported on the fluorescence lifetime and Judd-Ofelt parameters of Eu^{3+} doped $SrBPO_5$, they have suggested that the alkaline earth borophosphate should be a good candidate for luminescence for rare earth ions. Besides that, Arunkumar and Marimuthu[14] also have investigated Eu^{3+} doped lithium fluoroborate glasses, they showed that the samples have longer lifetime of the $^5D_0$ metastable state which indicates that the prepared glasses are suitable for laser application. As mentioned before, the transitions level that occurs in the Eu^{3+} ion are to be very dependent to environment in which it is surrounded. Therefore, it will be interest to investigate the luminescence properties of Eu^{3+} ions in borophosphate crystal by varying its concentration. Hence, in this work we presented the local structure and luminescence properties of lithium aluminium borophosphate glasses doped with different concentrations of Eu^{3+} ion.

1 Experimental

Glasses with the chemical compositions $20Li_2O$-$30Al_2O_3$-$10B_2O_3$-$40P_2O_5$-xEu_2O_3 (x=0.05 mol.%, 0.1 mol.%, 0.5 mol.%, 1.0 mol.%, 1.5 mol.% and 2.0 mol %) were prepared using a conventional melt-quenching method. These glass matrices are represented as 0.05Eu, 0.1Eu, 0.5Eu, 1.0Eu, 1.5Eu and 2.0Eu for 0.05 mol.%, 0.1 mol.%, 0.5 mol.%, 1.0 mol.%, 1.5 mol.% and 2.0 mol.% of Eu^{3+}, respectively. The corresponding masses of the starting material were weighed by the analytical balance and mixed thoroughly in porcelain crucible. This was followed by placing the samples in an electric furnace at 400 ºC for 20 min to facilitate evaporation of water and CO_2. The samples were then melted in an electric furnace at 1100 °C for 5 to 10 min depending on the amount of dopant used. Finally, the melts were then poured onto a stainless steel plate and annealed at 400 °C for 8 h in order to remove strain.

In order to study the photoluminescence properties of the glass, the samples were ground into fine powder and placed in the holder. The photoluminescence properties of the glass samples were then measured using a Jasco FP-8500 spectroscope at room temperature. For FT-IR, measurements were carried out using KBr pellets method. The structures of the prepared samples were analyzed using analytical tools such as X-ray diffraction (XRD), Fourier transform infrared (FT-IR) and photoluminescence spectroscopy (PL). The XRD measurements were carried out with Cu Kα radiation (wavelength=0.15406 nm) operating at 40 kV, 30 mA with Bragg-Brentano geometry at room temperature using Siemens Diffractometer D5000. The diffraction patterns were collected at constant (2θ) steps of 0.04º, where 2θ from 10º to 70º for 4 s. For FT-IR, measurements were carried out using KBr pellets method. The infrared spectra of the glasses were recorded by a Perkin-Elmer Spectrum One FT-IR spectrometer over the range of wavenumber 400 to 4000 cm^{-1} at room temperature using 100 scans at 4 cm^{-1} resolution. The wavelength accuracy was at 0.1 cm^{-1} at 1600 cm^{-1} and the available OPD (optical path difference) velocities were 2 cm/s. The excitation and emission spectra of all the samples with different molar ratios of manganese ion were recorded at room temperature by a JASCO FP-8500 Series fluorescence spectrometer equipped with a 150 W xenon lamp as excitation source. The sensitivity of the spectrometer was 5000:1(RMS) while the resolution for the spectra obtained was ±1.0 nm at 546.1 nm, excitation and emission bandwidth at 5 nm and the wavelength accuracy was ±1.0 nm. The measurements were carried out at room temperature in the wavelength range of 200 to 800 nm.

2 Results and discussion

2.1 X-ray diffraction analysis

Fig. 1 shows the XRD pattern of Eu^{3+} doped lithium aluminium borophosphate glasses. It is observed that the

Table 1 Composition of Eu^{3+} doped lithium aluminium borophosphate glasses (mol.%)

No.	Sample code	Li_2O	Al_2O_3	B_2O_3	P_2O_5	Eu_2O_3
1	0.05Eu	20	30	10	40	0.05
2	0.1Eu	20	30	10	40	0.1
3	0.5Eu	20	30	10	40	0.5
4	1.0Eu	20	30	10	40	1.0
5	1.5Eu	20	30	10	40	1.5
6	2.0Eu	20	30	10	40	2.0

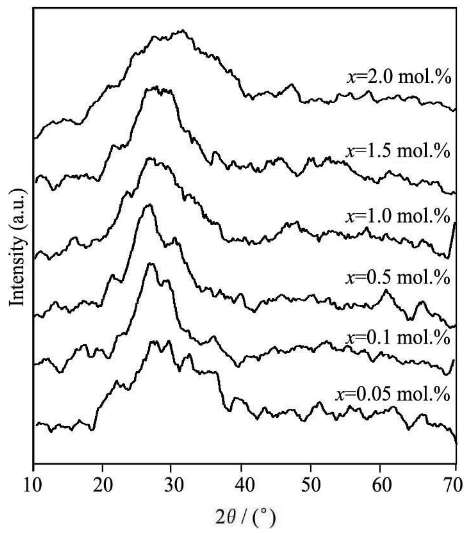

Fig. 1 XRD patterns of $20Li_2O$-$30Al_2O_3$-$10B_2O_3$-$40P_2O_5$-xEu_2O_3 (where x=0.05 mol.%, 0.1 mol.%, 0.5 mol.%, 1.0 mol.%, 1.5 mol.% and 2.0 mol.%)