Influence of europium (Eu^{3+}) ions on the optical properties of lithium zinc phosphate glasses

M Shwetha, B Eraiah[1]
Department of Physics, Bangalore University, Bengaluru-560056, Karnataka, India

E-mail: eraiah@rediffmail.com

Abstract. Europium doped lithium zinc phosphate glasses with composition xEu_2O_3-(15-x) Li_2O-45ZnO-40P_2O_5 (where x=0, 0.1, 0.3 and 0.5 mol %) named as EP0, EP1, EP3 and EP5 respectively, are prepared by melt-quenching method and the influence of Eu^{3+} ions on physical and optical properties of these glasses has been studied. Optical properties were studied using optical absorption spectra which was recorded at room temperature in the UV-Visible region. Optical direct band gap and indirect band gap energies were measured and their values range from 3.167 to 4.23eV and 2.08 to 3.02eV, respectively. Refractive indices have been measured with respect to different concentration of europium ions. Fluorescence spectroscopy measurements have been performed by excitation in the UV-Visible range, which resulted in the significant fluorescence peaks. The luminescence color of the glass system is characterized using Commission International de l'Eclairage de France 1931 standards.

1. Introduction

Rare earth ions doped glasses are of greater interest for a wide range of applications such as development of solid-state laser hosts, optical detectors, optical fibers, LED's, multicolor phosphors and color displays [1-4], due to the fact that Ln^{3+} ions exhibit significant features such as many excited levels, sharp absorption and emission peaks from ultraviolet to infrared region and longer lifetime. The optical properties of these glasses depend on the chemical composition which also defines the structure and nature of the glasses [5]. Superior transparency, variety of compositions and easy production make oxide glasses most favourable and useful as host materials for rare earth ions [6]. Among all the oxide glasses, phosphate glasses can store optical energy at greater densities which can be extracted efficiently, hence they receive much scientific attention. Also, phosphate glasses possess low melting temperature, low glass transition temperature, high ultraviolet and infrared transmissions [7], high transparency, low dispersion, large solubility of rare earth ions and good thermo-optical properties [8-11]. Additionally, these glasses derive great deal of interest due to their extensive applications in optical data transmission, detecting, sensing and lasing technologies [12]. Lithium oxide is a glass modifier and zinc oxide acts as a network former as well as network modifier depending on the chemical composition. ZnO containing phosphate glasses are commonly used in most applications due to the good optical properties, non-toxicity and non-hygroscopic nature of ZnO [13]. The presence of Li_2O and ZnO decreases the hygroscopic nature of the phosphate glasses and also improves the chemical durability and polarization [14,15]. Among the lanthanide ions used to optically stimulate glasses, Eu^{3+} ions are mostly used because Eu^{3+} ions emit narrow fluorescence band and have longer optically active state lifetimes [16-18]. These materials are generally used as red phosphors in field emission technology and high luminescence efficient light emitting diodes [19-22].

In this work, the influence of Eu^{3+} ions on the optical properties of lithium zinc phosphate glasses has been reported by employing various characterization techniques.

2. Experimental

By conventional melt quenching method, Eu^{3+} doped lithium zinc phosphate glasses of different molar compositions were prepared. Analar grade chemicals (Eu_2O_3, $LiOH.H_2O$, ZnO, and $NH_4H_2PO_4$) were weighed appropriately and mixed thoroughly. The powdered mixture was taken in porcelain crucibles and kept in an electric furnace which was set at temperature 1000°C. The molten liquid was quenched using a brass mold and a brass block. Transparent glass samples were obtained and were annealed below their glass transition temperature to obtain thermal and structural stability. The glass samples were cut into appropriate dimensions, polished and were used to characterize various experimental techniques.

X ray diffraction pattern was recorded using Panalytical X'Pert Pro MPD with Cu Kα radiation XRD. Archimedes technique was employed to measure the densities of the glass samples at room temperature. Shimadzu spectrophotometer UV-1800 operated at 220V-240V was used to record the optical absorption spectra in the wavelength range from 200-1100 nm. Refractive index was measured using Abbe refractometer DR 194A at sodium wavelength (589.3 nm) with 1-bromonaphthalin as contact liquid. Polaron radius (r_i), internuclear distance (r_p), field strength (F) and polarizability of oxide ions (α) of the glasses were calculated using appropriate formulae [23]. Photoluminescence spectra were recorded from Horiba fluorolog spectrofluorometer with 450W xenon arc lamp as a source. Luminescence color of the glass system was categorized by CIE (Commission International de l'Eclairage de France) 1931 chromaticity diagram.

3. Results and discussion

Typical X-ray diffraction spectra of the prepared EP1 glass sample is shown in figure 1. A broad hump observed around 2θ=15° to 35° due to the scattering of X-rays and the absence of narrow peaks confirms the amorphous nature of the glass samples.
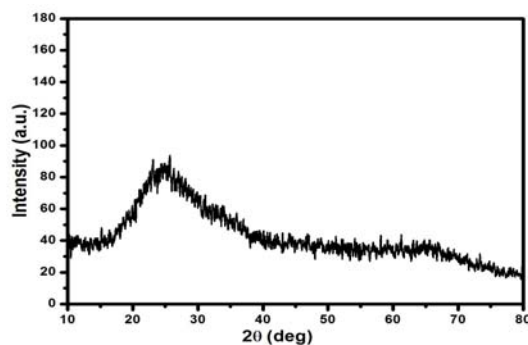

Figure 1. Typical X-ray diffraction pattern of europium doped lithium zinc phosphate glass.

All the measured and calculated physical parameters are presented in table 1 and table 2. Density and molar volume values are ranging from 3.152 to 3.353 g/cm^3 and 29.67 to 31.15 cm^{-3}, respectively. The variation of density values is the result of structural rearrangements that take place in the glass network on adding Eu_2O_3 and the variation of molar volume is found to be exactly opposite to that of the variation observed in density values. It is observed that the polaron radius and internuclear distance values decrease with increasing rare earth ions concentration which shows that there is an increase in Eu-O bond strength producing stronger field strength around Eu^{3+} ions.

Figure 2 shows UV-Visible absorption spectrum of EP5 glass. It consists of four absorption peaks at 362, 393, 464 and 525nm corresponding to the transitions, $^7F_0\rightarrow^5D_4$, $^7F_0\rightarrow^5L_6$, $^7F_0\rightarrow^5D_2$ and $^7F_0\rightarrow^5D_1$ respectively. It is found that $^7F_0\rightarrow^5L_6$ transition is more intense, although it is not allowed by the ΔS and ΔL selection rules, it is permitted by the ΔJ selection rule [24]. The spin forbidden $^7F_0\rightarrow^5D_0$ transition is very weak and hence not observed and the intensity for $^7F_0\rightarrow^5D_3$ transition could not be observed in the spectra as it is not allowed by the selection rule $\Delta J=3$ [25].
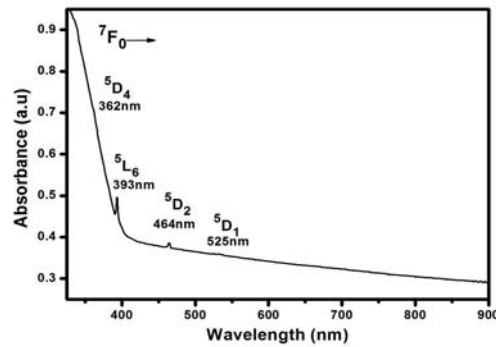

Figure 2. Optical absorption spectrum of EP5 glass in the UV-Vis region.

The optical bandgap defined as the energy (direct and indirect) difference between the valence band and conduction band of the glass samples can be measured using the optical absorption spectra. It is an important tool to describe the nature of the material. The direct and indirect energy bandgaps were evaluated from $(\alpha h\nu)^2$ *vs.* $h\nu$ and $(\alpha h\nu)^{1/2}$ *vs.* $h\nu$ plots (Tauc's plots) respectively, which are represented in figure 3(a) and (b), respectively. The values for direct bandgap ($n = 1/2$) lie between 3.167 and 4.23 eV, whereas for indirect bandgap ($n = 2$) they lie between 2.08 and 3.02 eV.

Table 1. Density (ρ), molar volume (V_m), direct (E_{opt}) and indirect (E'_{opt}) band gap, refractive index (n) and polarizability of oxide ions (α_m) of Eu^{3+} doped lithium zinc phosphate glasses.

Glass code	ρ g/cm^3	V_m cm^{-3}	E_{opt} (direct) eV	E'_{opt} (indirect) eV	n	α_mx10^{-24} cm^3
EP0	3.161	30.96	4.23	3.02	1.568	4.016
EP1	3.152	31.15	3.167	2.08	1.588	4.156
EP3	3.234	30.56	3.179	2.15	1.585	4.061
EP5	3.353	29.67	3.35	2.22	1.572	3.870

Table 2. Concentration of Eu^{3+} ions (N_{RE}), polaron radius (r_p), inter nuclear distance (r_i) and field strength (F) of Eu^{3+} ions doped lithium zinc phosphate glasses.

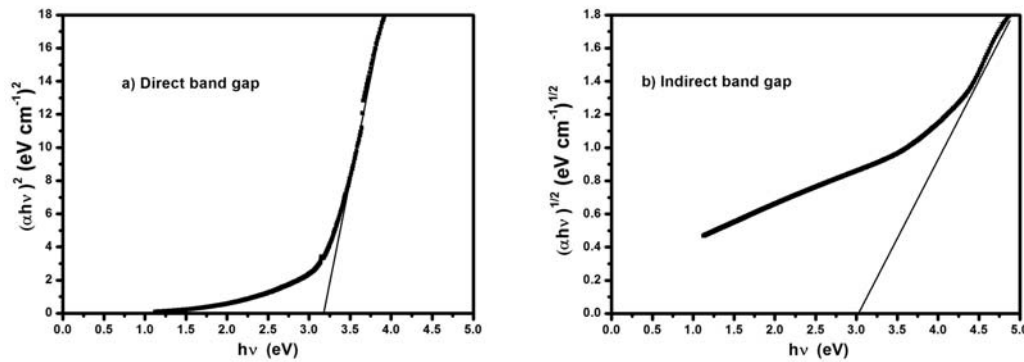| Glass code	N_{RE}x 10^{21} atoms/cm^3	r_p Å	r_i Å	Fx10^{15} cm^{-2}
EP1	1.932	3.235	8.029	2.866
EP3	5.910	2.228	5.531	6.043
EP5	10.07	1.866	4.630	8.615

Figure 3(a). Plots of $(\alpha h\nu)^2$ versus $h\nu$ (direct bandgap) and **(b)** $(\alpha h\nu)^{1/2}$ versus $h\nu$ (indirect bandgap).

The variation observed in the direct bandgap and indirect bandgap values with Eu_2O_3 concentration is shown in figure 4. It is observed that, there is a decrease in both direct and indirect band gap energies at 0.1 mol% of Eu_2O_3 which is the result of generation of more number of non-bridging oxygen. With increasing Eu_2O_3 concentration up to 0.5 mol% and decreasing Li_2O concentration, an increase in the optical bandgap is observed, which attributes to some changes that have been occurred in bonds [26].

It is well known that the addition of divalent oxides depolarizes the glass forming system, which alters the oxygen bonding in the network and any such variations of oxygen bonding occurred in the network changes the absorption characteristics. Shifting of the absorption band to higher energies corresponds to the less number of non-bridging oxygen in the network making the structure more compact [27]. This explains the variation of density and band gap (direct and indirect) values. The measured refractive index and polarizability of oxide ions of these glasses are ranging from 1.568 to 1.588 and 3.926 to 4.157 cm^3 respectively, and their variation with Eu_2O_3 concentration is exactly opposite to the variation of optical bandgap values with respect to Eu_2O_3 concentration.
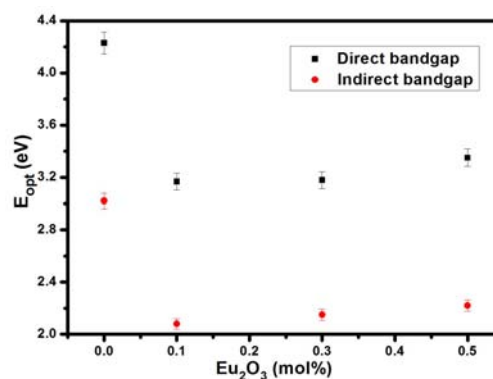

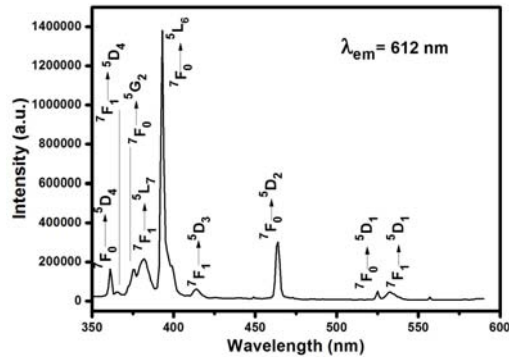**Figure 4.** Variation of direct and indirect bandgap w.r.t Eu_2O_3 mol%.

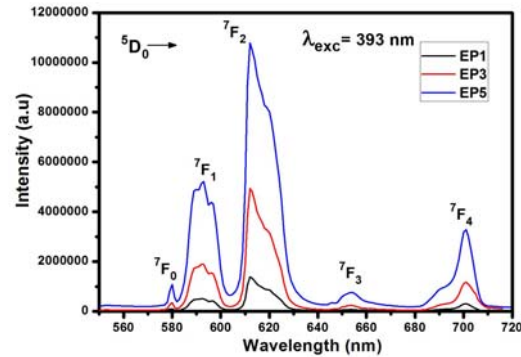**Figure 5.** Excitation spectrum of Eu^{3+} doped lithium zinc phosphate glass (EP5).

Figure 6. Emission spectra of Eu^{3+} doped lithium zinc phosphate glasses.

The excitation spectra for different concentrations of Eu^{3+} doped lithium zinc phosphate glasses have been recorded at an emission wavelength of 612nm. The obtained excitation spectrum of EP5 glass is shown in figure 5. There are nine excitation peaks at 362, 367, 377, 381, 393, 414, 464, 524, and 532nm assigned to the transitions $^7F_0 \rightarrow ^5D_4$, $^7F_1 \rightarrow ^5D_4$, $^7F_0 \rightarrow ^5G_2$, $^7F_1 \rightarrow ^5L_7$, $^7F_0 \rightarrow ^5L_6$, $^7F_1 \rightarrow ^5D_3$, $^7F_0 \rightarrow ^5D_2$, $^7F_0 \rightarrow ^5D_1$ and $^7F_1 \rightarrow ^5D_1$ respectively. Among all the excitation peaks, intensity of 393nm ($^7F_0 \rightarrow ^5L_6$) is relatively stronger and also characteristic doublet nature at 532nm can be observed. As the excitation transition $^7F_0 \rightarrow ^5L_6$, is more strong the emission measurements are done by exciting at 393nm using xenon arc lamp. Emission spectra of the glasses with different concentrations of Eu^{3+} is shown in figure 6, it exhibits five emission transitions such as $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_3$ and $^5D_0 \rightarrow ^7F_4$ with energies at 580, 592, 612, 654 and 701nm respectively. Characteristic emission with an intense and most prominent red emission (612 nm), which is credited to $^5D_0 \rightarrow ^7F_2$ transition, can be observed in the luminescence spectra. Luminescence transition between 4f levels of rare earth ions are mainly due to the electric and magnetic dipole interactions. The presence of transition $^5D_0 \rightarrow ^7F_0$ specifies that the Eu^{3+} ions are in a higher asymmetrical environment [28]. The emission transitions $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_J$ (J= 2,4) are allowed by magnetic and forced electric dipole interactions, respectively. The $^5D_0 \rightarrow ^7F_1$ transition follows the selection rule $\Delta J=1$ and the transition $^5D_0 \rightarrow ^7F_2$ is hypersensitive to the local environment which follows the selection rule $\Delta J=2$ [29].
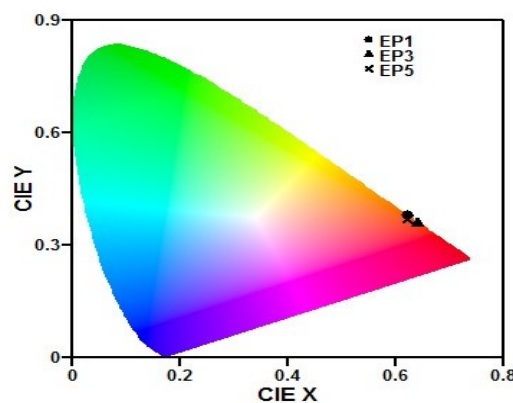

Figure 7. CIE 1931 diagram for different concentrations of Eu^{3+} doped glasses.

The color chromaticity coordinates are evaluated from the emission spectra for different concentrations of Eu^{3+} doped lithium zinc phosphate glasses and are represented in the chromaticity diagram which is shown in figure 7. The coordinates of the emissions for EP1, EP3 and EP5 glasses excited at 393nm are found to be (0.62,0.38), (0.62, 0.37) and (0.64, 0.36), resulting to be in the reddish orange region, which is close to the standard (0.67, 0.33) of the National Television System Committee for the red phosphor.

4. Conclusion

Eu^{3+} doped lithium zinc phosphate glasses have been successfully prepared and their physical, optical and luminescence properties have been studied. Variation of refractive index, direct and indirect bandgap values are due to the creation of non-bridging oxygen and the structural rearrangement that take place on adding Eu_2O_3 to the host glass matrix, causing significant modifications in the optical characteristics of the glasses. Emission spectra of the glasses have been recorded by exciting at a wavelength of 393nm. The most prominent and intense luminescence peak observed at 612 nm suggests that the glasses are potential materials for red emission. The CIE chromaticity coordinates are found to be in the reddish orange region, which confirms that Eu^{3+} doped lithium zinc phosphate glasses can be used as red emitting materials. The overall results observed indicate the significant effect of Eu_2O_3 on the glass matrix.

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