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Optical Studies of Eu³⁺ Ion Doped Borate Glasses

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Abstract. Eu³⁺ ion doped borate glasses were prepared by conventional melt quenching technique. Amorphous nature of the prepared glass is confirmed by XRD technique. The physical parameters like density, molar volume, polaron radius, inter-nuclear distance and field strength were calculated. The density, molar volume values were ranging from 4.150 to 4.307 g/cm⁻³ and 26.014 to 27.152 cm⁻³ respectively. The direct, indirect energy band gap and also Urbach energy were calculated. The calculated energy values were range from 3.03 to 3.179eV, 1.461 to 2.771eV and 0.443 to 1.309eV respectively. The optical parameters like refractive index, the molar refraction and polarizability were calculated using Lorentz-Lorentz relation.

INTRODUCTION

Rare earth doped oxide glasses have been synthesised using melt quenching technique. Due to wide applications in various fields, such as solid state lasers, flat panel displays, optical data storage, fibre amplifiers, solid state lasers these glasses have been chosen for detailed investigation¹⁻³. Among the other rare earth ions trivalent europium ion have simple electronic energy level scheme, from this scheme we can study many optical properties⁴⁻⁷. Europium doped borate glasses are widely used for visible laser devices, phosphors and LEDs. They are emitting orange or red colour light having high intensity and mono-chromaticity⁸⁻¹¹.

In this work, the variation of Eu³⁺ ions on physical parameters and optical studies of borate lead lithium glasses has been reported using various characterization techniques.

EXPERIMENTAL

The glass composition of 60B₂O₃-30PbO- (10-x) Li₂O - xEu₂O₃ (where x=0.1, 0.3 & 0.5) were prepared by conventional melt quenching method and the samples are named as BPE, BPE1, BPE3 and BPE5 respectively. The AR grade chemicals were taken and weighed in 8g batches by electric balance. Using an agate and pestle, the chemicals were mixed thoroughly to get homogeneous mixture. The mixture containing crucibles were kept in high temperature furnace and the mixture was melt at 950^oC. The melt was quenched between two smooth surfaced brass molds having thickness about 1 to 2mm in circular shape glasses were obtained. The prepared samples were polished well for the use of optical measurements.

XRD analysis was done by Panalytical X'Pert Pro MPD XRD instrument with Cu K α radiation. To measure the densities of the prepared glass samples Archimedes Principle were employed. The other physical parameters were calculated by using appropriate formulas. For optical absorption spectrum Shimadzu spectrophotometer UV-1800 operated at 220V-240V was used in the range of 200-1100 nm. The optical parameters like refractive index, molar refraction and polarizability of oxide ions were calculated by using Lorentz-Lorentz relation.

RESULTS AND DISCUSSION.

XRD spectra of Eu^{3+} ion doped lead lithium borate glasses were analysed and a typical spectrum is shown in Fig. 1. From the spectrum we can notice that there were no sharp peaks but only a broad hump has been observed. This confirms that the amorphous nature of glass. The calculated density and molar volume values of these glasses were range from 4.150 to 4.307 g/cm^{-3} and 26.014 to 27.152 cm^{-3} respectively. From table 1 we can notice that the density values are non-linear, this may be due to addition of Eu_2O_3 mol% to the glass network and it makes an internal structural rearrangements¹².

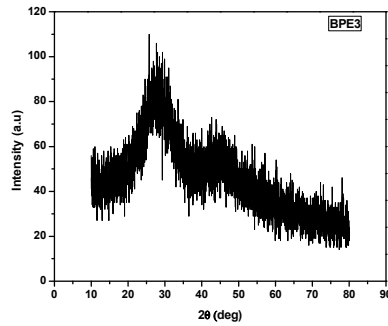


FIGURE 1. A typical XRD spectrum

The variation of molar volume is opposite to that of density as expected. The other physical parameters like concentration of rare earth ions, polaron radius, inter-nuclear distance and field strength were calculated using appropriate formulas are tabulated in table 1. It shows that polaron radius, inter-nuclear distances are decreases with addition of Eu_2O_3 mol%. This indicates that there an increase of Eu-O bond strength and produces strong field strength (i.e., increases in field strength) and the variation of polaron radius and field strength is shown in Fig. 2.

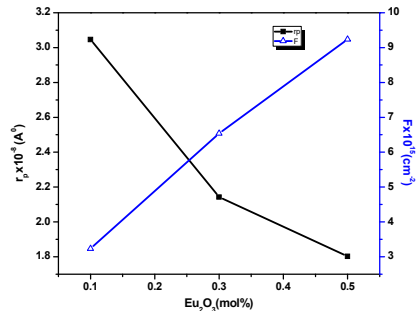


FIGURE 2. Variation of polaron radius and field strength with europium concentration

The typical optical absorption spectrum is shown in Fig. 3. It consists of 3 peaks at 393, 464 and 525 nm, the corresponding transitions are $^5\text{L}_6$, $^5\text{D}_2$ and $^5\text{D}_1$ from $^7\text{F}_0$ respectively. It is found that $^7\text{F}_0 \rightarrow ^5\text{L}_6$ transition is more intense compare to other transition¹³. The spin forbidden $^7\text{F}_0 \rightarrow ^5\text{D}_0$ ground state transition is very weak and hence it is not observed clearly. The intensity for $^7\text{F}_0 \rightarrow ^5\text{D}_3$ transition could not be observed in the spectra as it is not allowed by the selection rule $\Delta J=3$ ¹⁴.

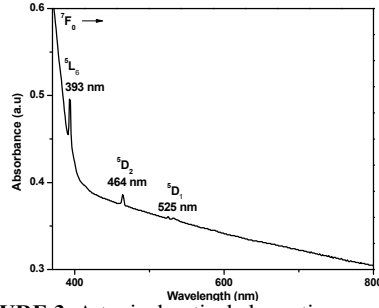


FIGURE 3. A typical optical absorption spectrum

Tauc plots $(\alpha h\nu)^2$ V/s $h\nu$ and $(\alpha h\nu)^{1/2}$ V/s $h\nu$ are shown in Fig. 4(a) & 4(b) the direct and indirect energy band gaps were calculated and tabulated in table 1. The direct and indirect energy band gap values were ranging from 3.03 to 3.179 eV and 1.461 to 2.771 eV respectively. The values are not varying linearly with addition of Eu_2O_3 mol% this may be due to the photon-lattice interaction and also due to the presence of Eu-O bonds¹⁵. The optical parameters like refractive index, molar refraction and polarizability were calculated by using Dimitrov and Sakka and Lorentz-Lorentz relation^{16, 17}. The calculated refractive index and polarizability of oxide ions of synthesised glasses were lies between 2.337 to 2.389 and 6.209 to 6.580 cm^3 respectively. The refractive index and polarizability variation with Eu_2O_3 mol% is exactly opposite to the variation of optical band gap values.

TABLE 1. Density (ρ), molar volume (V_m), $E_{g(\text{direct})}$, $E_{g(\text{indirect})}$, Urbach energy (E_{tail}), concentration of rare earth ions (N), polaron radius (r_p), inter-nuclear distance (r_i), Field strength (F), refractive index (n), molar refraction (R_m) and polarizability of oxide ions (α_m) of europium doped borate lead lithium glasses

Glass series code	BPE	BPE1	BPE3	BPE5
Density (g/cm^3)	4.269	4.307	4.150	4.205
Molar volume (cm^3)	26.167	26.014	27.152	26.951
$E_{g(\text{direct})}$ (eV)	3.158	3.116	3.03	3.179
$E_{g(\text{indirect})}$ (eV)	2.771	1.839	1.461	2.250
E_{tail} (eV)	0.443	0.985	1.309	0.695
$N \times 10^{21}$	--	2.315	6.655	11.174
$r_p \times 10^{-8}$ (A^0)	--	3.046	2.142	1.802
$r_i \times 10^{-8}$ (A^0)	--	7.559	5.316	4.473
$F \times 10^{15}$ (cm^{-2})	--	3.233	6.538	9.238
n	2.337	2.366	2.389	2.350
R_m (cm^3/mol)	15.648	15.742	16.583	16.203
$\alpha_m \times 10^{-24}$ (cm^3)	6.209	6.247	6.580	6.429

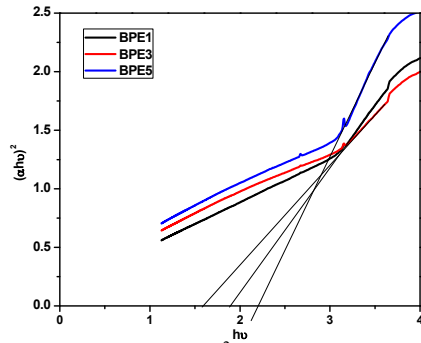


FIGURE 4(a). $(\alpha hv)^2$ V/s hv of europium doped borate lead lithium glasses.

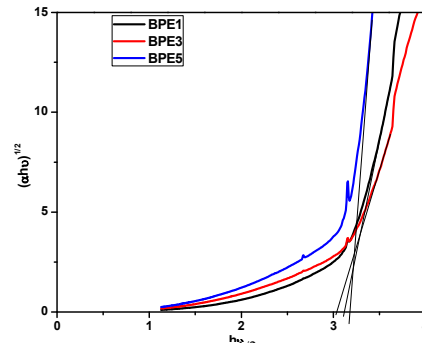


FIGURE 4(b). $(\alpha hv)^{1/2}$ V/s hv of europium doped borate lead lithium glasses.

CONCLUSION

Lithium lead borate glasses doped with europium trioxide have been successfully prepared by conventional melt quenching technique. The prepared glasses are amorphous in nature. The physical parameters were calculated using appropriate formulae; the values were well agreed with the energy band gap values. The studied glasses show some non-linear variation in both direct and indirect energy band gap values; this may be due to some structural rearrangements taking place in glass network with the addition of Eu_2O_3 to the host glass. This leads to the significant changes to the optical properties and these glasses are suitable for display device applications.

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