

Influence of europium (Eu^{3+}) ions on the optical properties of silver lead borate glasses

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Abstract. The influence of europium (Eu^{3+}) ions on the optical properties of silver lead borate glasses of the $x\text{Eu}_2\text{O}_3-(1-x)\text{Ag}_2\text{O}-29\text{PbO}-70\text{B}_2\text{O}_3$ ($x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5 mol%) glass system prepared by the conventional melt quenching technique and their physical and optical properties were investigated. The UV absorption spectra were recorded at room temperature in the wavelength range of 200–600 nm. From the absorption edge data, it is found that both the direct and indirect transitions and their values are ranging from 3.19 to 3.54 and 2.50 to 3.07 eV, respectively. The Urbach energy values for these glasses were found to be in the range of 0.39–0.52 eV. The refractive indices have also been evaluated with respect to different molar concentrations of Eu_2O_3 and their calculated values are ranging from 1.598 to 1.654.

Keywords. Optical bandgap; refractive index; Urbach energy.

1. Introduction

Lead borate glasses are important and promising materials for optical fibre, laser hosts, optical filters, photonic devices, X-ray and γ -ray absorbers due to their most significant characteristic features, such as low melting temperatures, high refractive index, thermal stability, wide glass formation regions and being optically transparent from visible to near-infrared range.^{1–3} The study of borate glasses is considerably of much interest because of their structural peculiarities, pure borate glass made up of random network of boroxyl (BO_3) units, the addition of modifier into the glass network produces BO_4 groups and increases the number of non-bridging oxygen (NBO), which leads to the open network structure.^{4,5} Nowadays, there is an emerging trend on silver-containing glasses because of their good optical properties and high ionic conductivity values, which makes potential applications in solid state batteries, biomedical applications, electrochemical devices, etc.^{6–9}

In recent years, rare earth (RE)-doped glasses are having rapid growth in the field of lasers, display devices, photonic and communication applications.^{10–13} Among the other RE elements, trivalent europium (Eu^{3+}) is the most favourable element because of its narrow emission band, producing almost monochromatic light and having long lifetime.^{14–16} The investigation of optical absorption studies gives the crucial information about the band structure and bandgap of the amorphous materials and the meas-

urement of refractive index is one of the most useful tools to examine the polarizability of oxide ion, which provides the evidence for the additive nature of the oxide ion polarizabilities in glass system. It helps us in proper choice of material for optical waveguides, fibres and optical bandgap devices applications.

The objective of the present work is to study in detail the optical properties of europium-doped silver lead borate glasses. Optical properties such as optical bandgap, Urbach energy and refractive index were determined.

2. Experimental

The glasses of composition $x\text{Eu}_2\text{O}_3-(1-x)\text{Ag}_2\text{O}-29\text{PbO}-70\text{B}_2\text{O}_3$ with $x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5 mol% and the raw materials of reagent grade chemicals H_3BO_3 , PbO , Ag_2O and Eu_2O_3 were used to synthesize the samples by the conventional melt quenching method. The appropriate weighed chemicals were taken in porcelain crucible and placed in a muffle furnace set at a temperature of 1100°C for a period of 10 min and stirred regularly for achieving homogeneity in molten liquid. When the melting process was completed, the molten liquid was cast into a brass mould. The sample was annealed at 150°C in a second furnace for 60 min and the prepared samples were cut into appropriate dimensions for the required measurement.

The refractive indices were measured by using Abbe refractometer DR 194A at room temperature and the absorption spectrum was recorded over the wavelength range 300–600 nm by using Perkin-Elmer lambda-30

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spectrophotometer. The optical absorption coefficient $\alpha(\lambda)$ was calculated from the absorbance A and the thickness d of the sample by using the following equation:

$$\alpha(\lambda) = 2.303 \left(\frac{A}{d} \right). \quad (1)$$

3. Results and discussion

X-ray diffraction (XRD) pattern of the glass system was studied by D-8 X-ray diffractometer (Bruker AXS-Model) using $\text{CuK}\alpha$ radiations of wavelength $\lambda = 1.5406 \text{ \AA}$. The obtained typical XRD pattern of the glass system as depicted in figure 1 reveals the absence of discrete or sharp diffracted peaks, but the presence of diffused band in the pattern indicates the amorphous nature.

The optical absorption spectra of $(1-x)\text{Ag}_2\text{O}-29\text{PbO}-70\text{B}_2\text{O}_3$ glass with $x = 0.5 \text{ mol\%}$ of Eu_2O_3 is as shown in figure 2. The obtained absorption spectrum consists of seven absorption peaks, located at 394, 414, 464, 525, 531, 578 and 585 nm corresponding to the electronic transition of ${}^7\text{F}_0-{}^5\text{L}_6$, ${}^7\text{F}_1-{}^5\text{D}_3$, ${}^7\text{F}_0-{}^5\text{D}_2$, ${}^7\text{F}_0-{}^5\text{D}_1$, ${}^7\text{F}_1-{}^5\text{D}_1$, ${}^7\text{F}_0-{}^5\text{D}_0$ and ${}^7\text{F}_1-{}^5\text{D}_0$, respectively, as reported in the literature.¹⁷ The optical bandgap E_{opt} , which defines the direct and indirect energy difference between valence and conduction band of glasses, is obtained from the following expression:

$$\alpha h\nu = B(h\nu - E_{\text{opt}})^m, \quad (2)$$

where α is the absorption coefficient, $h\nu$ the incident photon energy, B the electronic transition constant and the index m values are 1/2 and 2 for direct and indirect allowed transitions, respectively. Both direct and indirect bandgaps obtained from the above relation (2) are inter-band transitions, but the latter involves the phonon

interaction. The direct and indirect bandgaps were determined from the tangential drawn to the curves of $(\alpha h\nu)^2$ vs. $h\nu$ and $(\alpha h\nu)^{1/2}$ vs. $h\nu$ plot at $(\alpha h\nu)^2 = 0$ and $(\alpha h\nu)^{1/2} = 0$, respectively, which are shown in figures 3 and 4, respectively. The obtained E_{opt} values for direct transition ($n = 1/2$) lies between 3.19 and 3.54 eV, whereas for indirect transition ($n = 2$) they lie between 2.50 and 3.07 eV.

The variations of direct and indirect bandgap values vs. Eu_2O_3 mol% are shown in figure 5. It is found that, the decrease in both direct and indirect bandgaps to lower energies at 0.1 mol% of Eu_2O_3 probably may be due to the generation of more number of non-bridging oxygens and also the increasing optical bandgap with increasing Eu_2O_3 concentration upto 0.5 mol% was observed,¹⁸ which attributes to some changes that might have

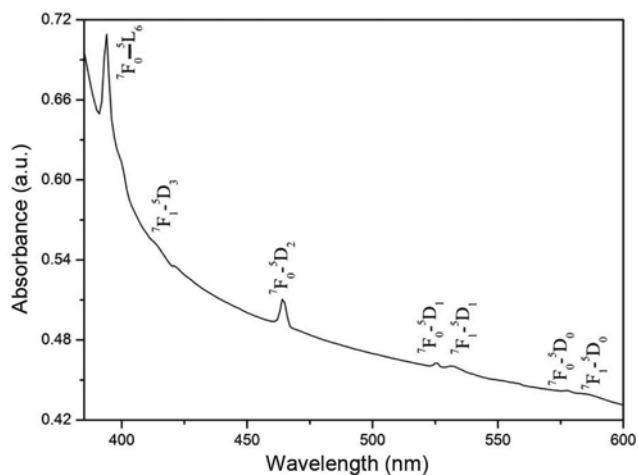


Figure 2. Typical optical absorption spectra of $(1-x)\text{Ag}_2\text{O}-29\text{PbO}-70\text{B}_2\text{O}_3$ with $x = 0.5 \text{ mol\%}$ of Eu_2O_3 .

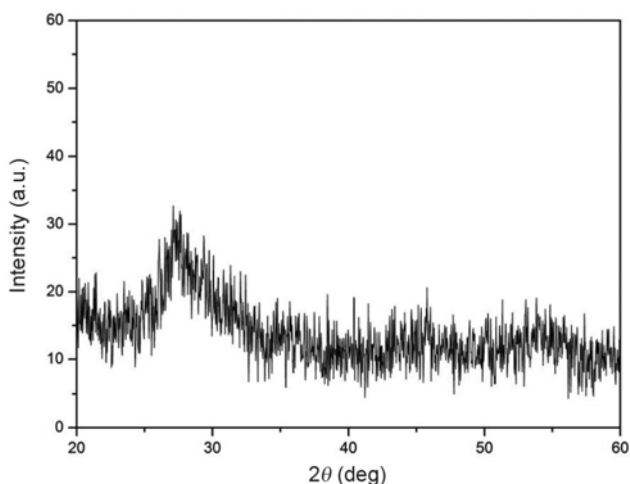


Figure 1. Typical XRD pattern of $\text{Eu}_2\text{O}_3-\text{Ag}_2\text{O}-\text{PbO}-\text{B}_2\text{O}_3$ glass system.

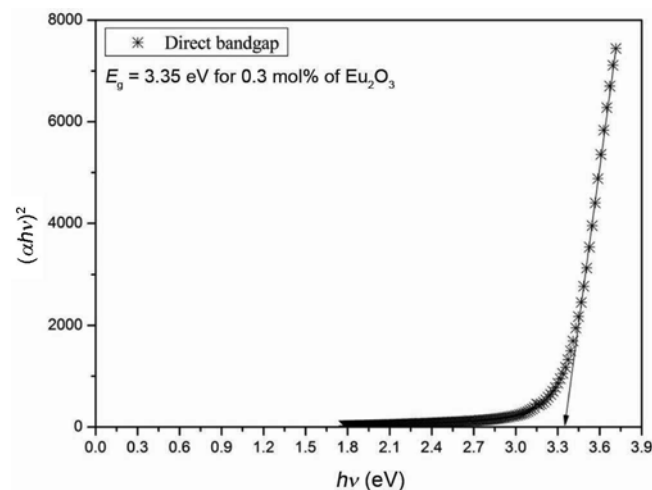


Figure 3. Typical plot of $(\alpha h\nu)^2$ vs. $h\nu$ for direct bandgap measurement in $x\text{Eu}_2\text{O}_3-(1-x)\text{Ag}_2\text{O}-29\text{PbO}-70\text{B}_2\text{O}_3$ glass with $x = 0.3 \text{ mol\%}$.

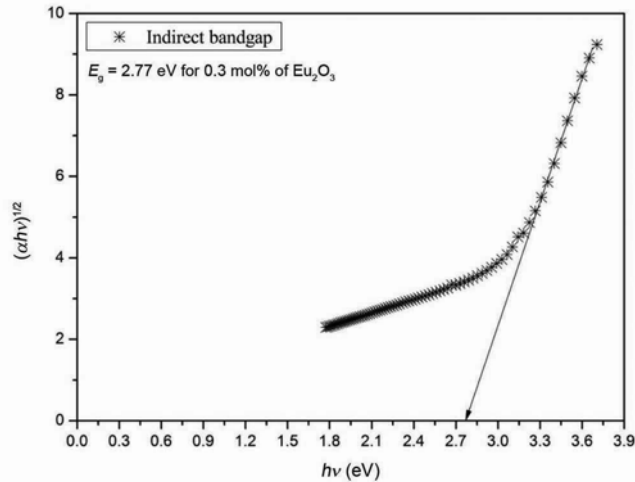


Figure 4. Typical plot of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ for indirect bandgap measurement in $x\text{Eu}_2\text{O}_3-(1-x)\text{Ag}_2\text{O}-29\text{PbO}-70\text{B}_2\text{O}_3$ glass with $x = 0.3$ mol%.

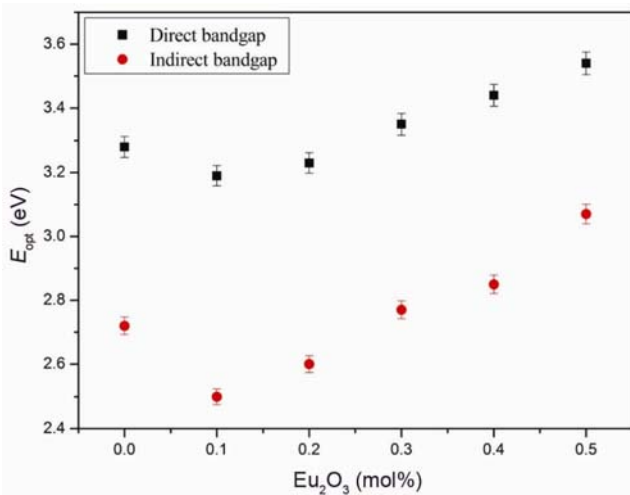


Figure 5. Variation of direct and indirect bandgap as a function of Eu_2O_3 mol%.

occurred in bonds and also may be due to the photon-lattice interaction.⁶ Shifting of the absorption band to a higher energy can be related to the formation of less number of non-bridging oxygen making the structure more compact. This can be interpreted as the reduction of the compactness of the glass network due to the occupation of europium ions in the free space regions in the glass network. The increase in optical bandgap with decreasing Ag_2O mol% was also observed. According to the author,¹⁹ the addition of divalent oxides depolarizes the glass-forming network. We know that absorption edge depends on the oxygen bond strength in the glass-forming network. This process changes the oxygen bonding in the glass-forming network, and any change of oxygen bonding in glass network such as the formation of non-bridging oxygen changes the absorption characteristics. This explains why the absorption edges, and hence E_{opt} moves

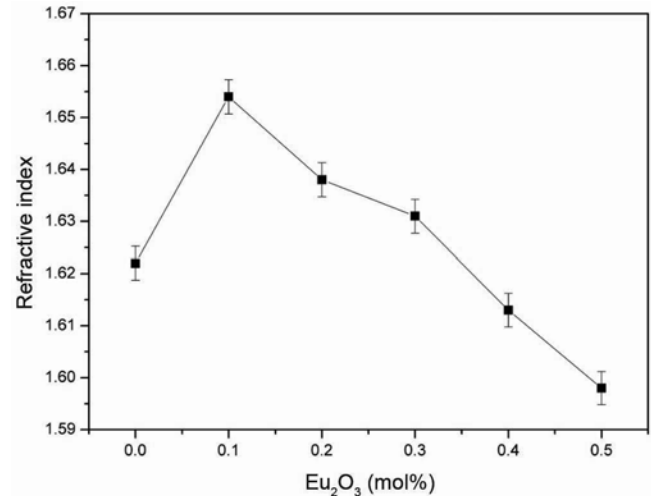


Figure 6. Variation of refractive index as a function of Eu_2O_3 mol%.

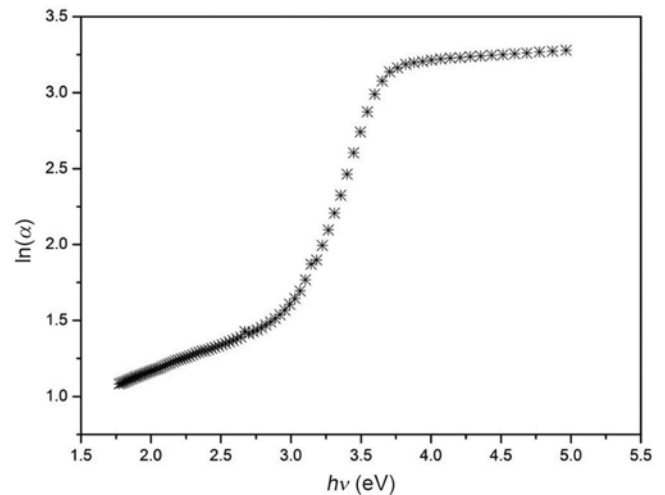


Figure 7. Typical plot of $\ln(\alpha)$ vs. $h\nu$ for Urbach energy measurements in $\text{Eu}_2\text{O}_3-\text{Ag}_2\text{O}-\text{PbO}-\text{B}_2\text{O}_3$ glass system.

towards higher energies. The refractive indices (shown in figure 6) of the studied glass samples were exactly opposite to the values of optical bandgap because non-bridging oxygens also have an effect on the refractive index, the polarity of the non-bridging oxygens is higher than that of bridging oxygens.²⁰

In glass and amorphous materials, Urbach assumed that the absorption coefficient at the photon energy below the optical gap is the tail absorption that depends exponentially on the photon energy.²¹ The extent of band tail in forbidden energy bandgap can be estimated by using the equation

$$\alpha(\nu) = B \exp\left(\frac{h\nu}{E_{\text{tail}}}\right), \quad (3)$$

where B is a constant and E_{tail} the width of the band tails in electronic states. The values of the Urbach energy were

calculated by taking the reciprocal of the slopes of the linear portion of the $\ln(\alpha)$ vs. $h\nu$ curves in the lower photon energy regions; its typical plot is shown in figure 7. The obtained values of E_{tail} vary between 0.39 and 0.52 eV and these values are well matched with the amorphous semiconductors (0.046–0.66 eV) as reported in the literature,²² and the obtained values of E_{tail} measures the degree of defects in the glass network.

4. Conclusion

In summary, the optical properties of silver lead borate glass system were studied with respect to small concentration of europium ions, and the amorphous nature of the glass system was confirmed by XRD study. The values of refractive indices, direct and indirect bandgaps show the variation at 0.1 mol% of Eu_2O_3 because of the creation of more number of non-bridging oxygens at 0.1 mol% of Eu_2O_3 . It was not only due to the presence of Eu^{3+} ions, but also due to the addition of divalent oxides that depolarize the glass-forming network (B_2O_3). These results show the significant changes that occurred in the optical properties of europium-doped silver lead borate glasses.

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