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Optical Studies of Rare Earths Doped Lead Bismuth Alumina Borate Glasses

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ABSTRACT: Influence of rare earth oxide on structure and glass properties has been investigated in lead bismuth alumina borate (LBAB) glasses doped with Tm_2O_3 and Yb_2O_3 . From the optical absorption spectra it was observed that cut-off wavelength shifts towards the lower wavelength side with the addition of rare earth ions. The absorption spectra exhibited no bands for pure glass and the bands at 658 nm ($^3\text{H}_6 \rightarrow ^3\text{F}_2$), 686 nm ($^3\text{H}_6 \rightarrow ^3\text{F}_3$), 792 nm ($^3\text{H}_6 \rightarrow ^3\text{H}_4$), 1211 nm ($^3\text{H}_6 \rightarrow ^3\text{H}_5$) and 1663 nm ($^3\text{H}_6 \rightarrow ^3\text{F}_4$) due to Tm^{3+} ions and a band at 977 nm ($^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$) is due to Yb^{3+} ions. Optical absorption spectra show that the absorption edge has a tail extending towards lower energies. The edge shifts towards higher energies for all rare earths-doped glasses. The degree of the edge shift was found to be depending on the ionic radius of the rare earths and is mostly related to the structural rearrangement and the relative concentrations of the glass basic units. By increasing the ionic radius of the rare earths, the optical energy gap decreases, while the width of the localized states is increased. Optical band gap (E_{opt}) and Urbach energy (ΔE) values were calculated from the spectra. The FTIR spectra reveals that the glass has BO_4 , BO_3 , AlO_4 and Bi_2O_3 units as the local structure.

KEYWORDS: X-Ray diffraction, Optical absorption, FTIR, Lead borate glasses.

I. INTRODUCTION

In recent times, glasses containing heavy network formers doped with luminescent lanthanide ions have attracted a considerable interest due to their low vibrational frequencies [1], which cause the non-radiative relaxation from the excited states of the dopant ions to be inefficient [2]. This can lead to interesting applications for the development of optical devices requiring high emission quantum yields, such as solid-state lasers and optical amplifiers [3]. On the other hand, glasses containing heavy network formers and/or modifiers can show interesting non-linear optical properties [4]. In the case of Ln^{3+} doped materials, these properties could lead to the possible development of self-frequency-doubling lasers.

According to previous results, lead borate glasses are promising amorphous host matrices to incorporate rare earth ions. In these glasses, lead oxide plays the role of glass former or glass modifier, influencing strongly the structure and optical properties of rare earth ions, which depends on PbO content in the borate glass matrix [5]. In the present study, we have introduced Al_2O_3 and Bi_2O_3 into lead borate glass matrix, because of their special properties such as low phonon energies ($\sim 550 \text{ cm}^{-1}$) and high refractive index (~ 2.3). The low phonon energy and high refractive index could yield low nonradiative decay rates and high radiative emission rates of rare-earth (RE) energy levels [6]. Apart from being used as laser ion hosts, aluminum containing borate glasses are also being widely used as low cost optical connectors, dielectric and sealant materials for solid oxide fuel cells, in actinide immobilization, in optical lenses, seals and as in vivo radiation delivery vehicles because of their high mechanical strength, high electrical resistance and chemical durability [7-9]. Normally, aluminum ions produce greater enhancement on fluorescence of rare-earth ions including Tm^{3+} and Yb^{3+} when incorporated in the glass hosts [10].

According to several previously published results, an increasing interest is observed on rare earth doped glasses from the viewpoint of spectroscopic properties and technological applications [11]. Among various rare earth ions, Tm^{3+} ,

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Yb^{3+} ions are of great interest since they give rich emission in visible and near infrared (NIR) regions in the glass hosts [12]. The aim of this study is to investigate the influence of the rare earth ions on optical band gaps, spectral transitions and infrared spectra of LBAB glasses.

II. EXPERIMENTAL

Lead bismuth alumina borate glasses doped with Tm^{3+} and Yb^{3+} of compositions $[100-x][0.5\text{PbO}-0.25\text{Bi}_2\text{O}_3-0.20\text{B}_2\text{O}_3-0.05\text{Al}_2\text{O}_3]-x\text{R}_2\text{O}_3$ (where $x=0$ for pure sample and $x = 0.2$ mol% for $R = \text{Tm}$ and Yb) were prepared by melt quenching technique. The chemicals used for the preparation of the present glass system were analytical grade reagents (99.9% pure) of PbO , Bi_2O_3 , H_3BO_3 , Al_2O_3 , Tm_2O_3 and Yb_2O_3 . The amounts of oxides were weighed by using digital electronic balance. These chemicals were mixed and thoroughly ground in a mortar to get a homogeneous mixture. The mixed charge was then taken in a crucible and was placed in a vertical furnace. The temperature of the muffle furnace was increased in steps of 50°C . The temperature of the furnace was increased in steps until the mixture melted at about 950°C and the melt was kept at that temperature for thirty minutes to ensure its homogeneity.

Circular brass discs of 2 mm thickness and having hole of diameter 1.5 mm at the center was used to get the glass samples of uniform shape. The melt solidifies quickly producing a circular disc of transparent glass sample. The samples were found to be non-hygroscopic. Since, the cooling of the homogeneous melt was a rapid one, internal stresses may develop during solidification of the liquid phase to the glassy phase. In order to avoid these internal mechanical stresses, the glass samples prepared were annealed at about 300°C , for about four hours and were cooled to room temperature gradually. After annealing, both surfaces of the samples were first polished with fine silicon carbide powder and then with fine grade emery paper. Glass samples of thickness about 1.5 mm and diameter 1 mm with parallel plane surfaces were thus obtained.

The glass samples are labeled as LBAB, LBABT and LBABY as given in Table 1. LBAB stands for pure sample means without dopants, LBABT stands for glass sample doped with 0.2 mol% of thulium and LBABY stands for glass sample doped with 0.2 mol% of ytterbium.

Table 1. Composition of glass samples and labelling.

S.No.	Glass composition		Labels
	x (mol %)	R	
1	0.0	-	LBAB
2	0.2	Tm	LBABT
3	0.2	Yb	LBABY

III. RESULTS AND DISCUSSION

X-Ray Diffraction

The X-ray diffraction analysis was carried out using Rigaku miniflex table top diffractometer with $\text{Cu K}\alpha$ radiation (40 KV x 25 mA) and a graphite monochromator with 2θ (θ being Bragg angle) from 10° to 80° . XRD spectra of glass samples is shown in Fig. 1. The absence of Bragg peaks confirms the amorphous nature of the prepared glass samples.

Optical absorption spectra

The absorption spectra were obtained with the JASCO Model V-670 UV-VIS-NIR spectrophotometer from 350–2000 nm with a spectral resolution of 0.1 nm. Figure 2 shows the absorption spectra of LBAB glass and that doped with Tm^{3+} and Yb^{3+} ions.

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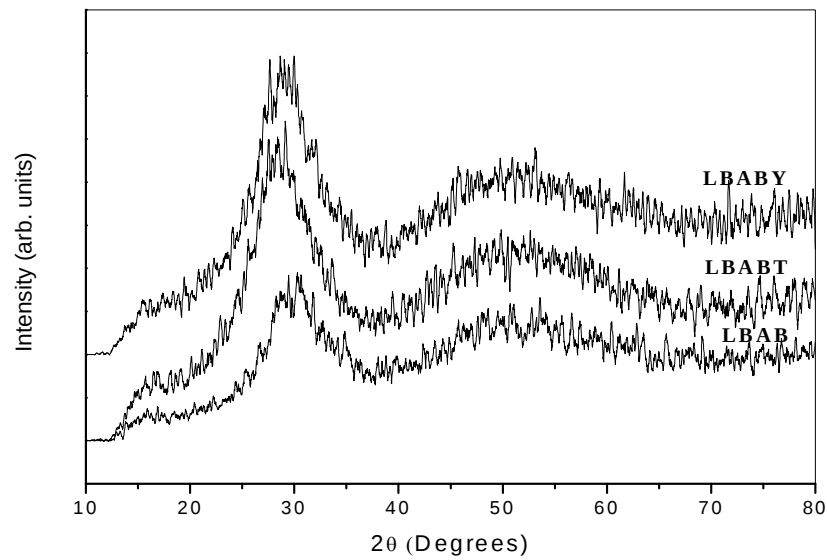


Fig. 1 X-Ray diffraction patterns of LBAB glass and that doped with Tm^{3+} and Yb^{3+} .

The pure LBAB glass sample exhibited no bands and Tm^{3+} doped glass exhibited bands at 658 nm ($^3\text{H}_6 \rightarrow ^3\text{F}_2$), 686 nm ($^3\text{H}_6 \rightarrow ^3\text{F}_3$), 792 nm ($^3\text{H}_6 \rightarrow ^3\text{H}_4$), 1211 nm ($^3\text{H}_6 \rightarrow ^3\text{H}_5$) and 1663 nm ($^3\text{H}_6 \rightarrow 3\text{F}_4$). Yb^{3+} doped glass exhibited a band at 977 nm ($^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$) [13, 14]. These bands are due to forbidden transitions involving the 4f levels, and these 4f orbitals are very effectively shielded from interaction with external fields of the hosts by $5s^2 5p^6$ shells.

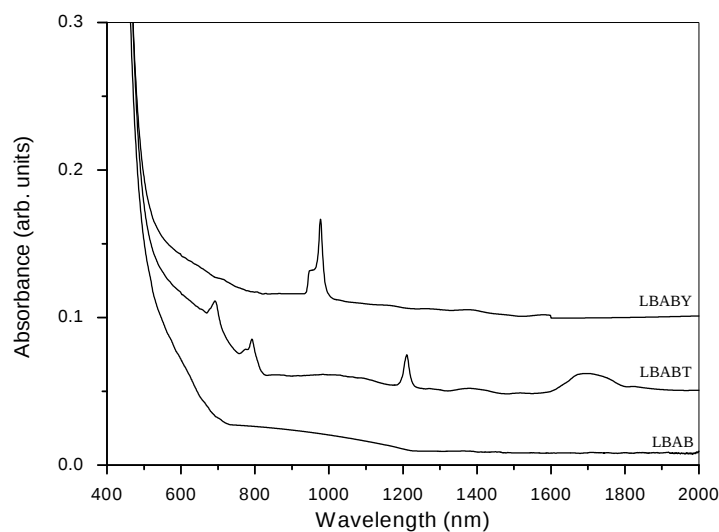


Fig. 2 Optical absorption spectra of LBAB glass and that doped with Tm^{3+} and Yb^{3+} .

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Hence, the states arising from the various 4f configurations are only slightly affected by the surrounding ions and remain practically invariant for a given ion in various compounds. Reisfeld [15] proposed that the rare earth ions in glass occupy the center of a distorted cube, which is made of four tetrahedra of phosphate, silicate, borate, and germanate glasses. Each tetrahedron contributes two oxygens to the coordination of the rare earth ions. The overall coordination number is 8, the most common coordination number of the rare earth oxides.

From the Figure 2 it is clear that there is no sharp absorption edge and this is the characteristic of glassy state. Generally, the absorption edge of these glasses is determined by the oxygen bond strength in the glass forming network. Any change of oxygen bonding in the glass network, for instance, the formation of nonbridging oxygen, changes the characteristic absorption edge. The position of the fundamental absorption edge shifts to lower energy (higher wavelength) with increasing the ionic radius of the rare earth ions in LBAB glasses. This is due to the fact that Al^{3+} ions (like any other III A group elemental ions), isolate the rare earth ions from RE-O-RE bonds and form Al-O-RE bonds, which reflected in the absorption spectra by a significant shifting of the absorption edge to shorter wavelengths (higher energy). The shifts of the absorption edge are most likely related to the structural rearrangement of the glass and the relative concentrations of the various fundamental units. From the inspection of the absorption spectra of the studied glasses doped with rare earth oxides; we found that, the absorption spectra of the rare earth ions in glasses differ from that of rare earths in crystals. The broadening of the absorption bands is due to the multiplicity of rare earth sites in the glass.

Using the optical absorption data a graph is plotted between $(\alpha h\nu)^{1/2}$ and $h\nu$ to calculate optical band gap (Fig. 3). The optical absorption at the fundamental edge in terms of the theory given by Davis and Mott can be written in the general form and given by:

$$\alpha(\nu) = \frac{B}{h\nu} (h\nu - E_{\text{opt}})^n \quad (1)$$

where B is a constant and $h\nu$ is the photon energy, E_{opt} is the optical band gap. Values of n are 1/2 and 2 for direct and indirect forbidden transitions, respectively. Both these band gaps obtained from the above relations are interband transitions, but the later involves the phonon interaction.

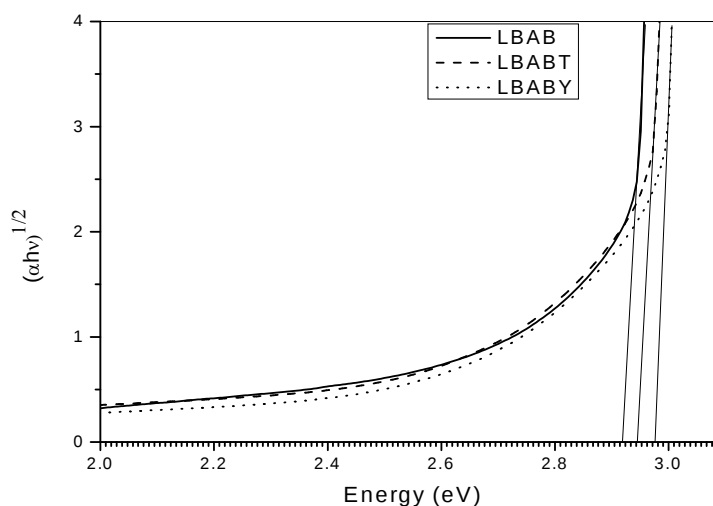


Fig. 3. Dependence of $(\alpha h\nu)^{1/2}$ on photon energy ($h\nu$) for LBAB glass and that doped with Tm^{3+} and Yb^{3+} .

The E_{opt} values were determined from the curves representing $(\alpha h\nu)^{1/2}$ as a function of photon energy $h\nu$ by extrapolation of the linear region of the plots to $(\alpha h\nu)^{1/2} = 0$. The validity of the equation (1) between $(\alpha h\nu)^{1/2}$ and $h\nu$, points out that the optical band gap is caused by amorphous optical absorption edge. This indicates the fact that the disordered amorphous glass materials have prevailing the direct transitions between the valence band and the

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conduction band and the absence of the indirect inter-band transitions like in the case of the crystals (i.e. the transitions in the different points of the Brillouin zone). Some deviations observed from this dependence are understood due to trapping of some disordered states within the energy gap.

From the data (Table 2) it was observed that optical band gap values are decreasing with the increase of ionic radius of the rare earth ions. The increase in the optical band gap with the addition of rare earth ions is due to decrease of the degree of depolymerization or concentration of bonding defects and non-bridging oxygens (NBO) in the glass network. In the case of rare earth doped LBAB glasses the aluminium ions may take network forming positions with AlO_4 structural units and alternate with BO_3 units. Such linkages may cause a increase in the rigidity of the glass network and leads to the increase in the optical band gap as observed.

The lack of crystalline long range order in amorphous/glassy materials is associated with a tailing of the density of states into the normally forbidden energy band [16]. The exponential absorption tails (referred as the Urbach energy, ΔE) depend on temperature, induced disorder, static disorder, and strong ionic bonds and on average phonon energies. The absorption coefficient $\alpha(\omega)$ of the optical absorption near the band edge show an exponential dependence on photon energy $h\nu$ and obey the empirical relation due to Urbach [17].

$$\alpha(\omega) = \alpha_0 \exp\left(\frac{h\nu}{\Delta E}\right) \quad (2)$$

where α_0 is constant and ΔE is the width of the band tails of localized states in the normally forbidden band gap, which are associated with the amorphous nature of the materials. This relation was first proposed by Urbach to describe the absorption edge in alkali halide crystals at high absorption levels when $\alpha(\omega) > 10^4 \text{ cm}^{-1}$. The relation was found to hold for many amorphous or glassy materials at lower ranges of the absorption edge, while for higher absorption values a relationship proposed by Tauc and Zanini [18] and deduced in more form that is general by Davis and Mott in equation (1). The origin of the exponential dependence of absorption coefficient on photon energy, $h\nu$, in Urbach equation in both crystalline and amorphous semiconductors is not clearly known. Tauc and Zanini [18] suggested that it arises from electron transitions between localized states where the density of localized states is exponentially dependent on energy. Davis and Mott [19] reported that this explanation is not valid for all disordered materials since the slope of the observed exponential behavior remains unchanged for many crystalline and non-crystalline materials. Dow and Redfield [20] suggested that it might be arise from random fluctuations of the internal fields associated with structural disorder in many amorphous solids. One possible reason suggested by them is that the slopes of the observed exponential edges obtained from Urbach equation are very close to each other in many semiconductors. In the present study, an exponential dependence of the absorption coefficient on photon energy is observed, suggesting that the Urbach rule is obeyed.

Table 2.Values of cut off wavelength, optical band gap (E_{opt}) and Urbach energy (ΔE) of LBAB glass and that doped with Tm^{3+} and Yb^{3+} ions.

S.No	Sample	Cut-off Wavelength (nm)	Band gap (eV)	ΔE
1	LBAB	422	2.91	0.31
2	LBABT	418	2.94	0.27
3	LBABY	414	2.97	0.34

FTIR Studies

Fig. 4 shows the FTIR spectra of LBAB glass sample and that doped with Tm^{3+} and Yb^{3+} ions in the range $1600\text{-}600 \text{ cm}^{-1}$. The FTIR spectra shows characteristic bands corresponding to the different vibration modes of the various functional groups present in the glass system. Absorption bands and their assignments are presented in Table 3 [21, 22]. A band cited in the region $\sim 700\text{-}705 \text{ cm}^{-1}$ is identified due to vibrations of B-O-B linkages and also due to network forming AlO_4 tetrahedral groups. It was found that with addition of rare earths ions this band shift towards higher wavenumber. The band around 902 cm^{-1} is attributed due to stretching vibrations of B-O bands in BO_4 units. There is no significance shift is observed in this band. The band cited around $\sim 1217 \text{ cm}^{-1}$ is identified due to stretching modes of borate triangles BO_3 and BO_2O^- units. There is no significance shift is observed in this band.

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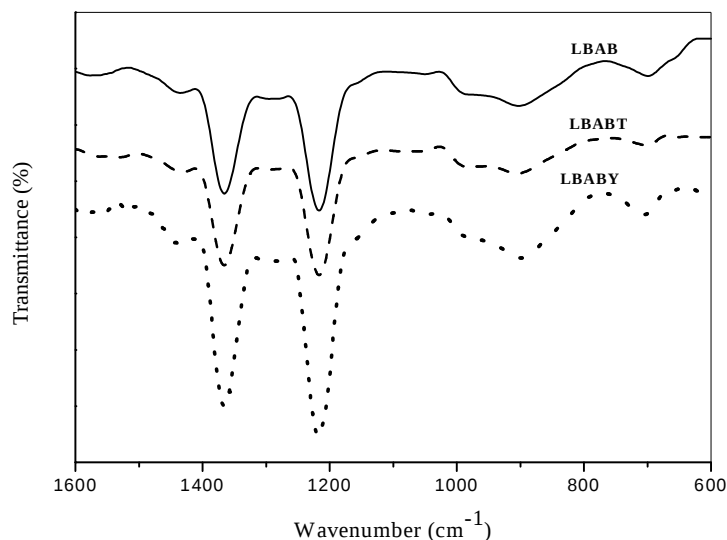


Fig. 4. FTIR spectra of LBAB glass and that doped with Tm^{3+} and Yb^{3+} ions.

Table 3. Absorption bands and their assignments for FTIR spectra

Wavenumber (cm^{-1})	IR assignments
~700-705	Vibrations of B-O-B linkages and due to AlO_4 structural
~902	Stretching vibrations of B-O bands in BO_4 units
~1217	Stretching modes of borate triangles BO_3 and BO_2O^- units

IV. CONCLUSIONS

Lead bismuth alumina borate glasses doped with Tm^{3+} and Yb^{3+} ions have been fabricated and characterized. The FTIR spectra reveals that the glass has BO_4 , BO_3 , AlO_4 and Bi_2O_3 units as the local structure. Quantitative justification of some of the absorption bands for pure and rare earth doped glasses was done. The theoretical wavenumber agree reasonably well with the experimental values for all bonds stretching vibrations. In the present investigation, the dependence of the absorption coefficient $\alpha(\omega)$ on photon energy suggests that, the studied glass system obey the Urbach rule.

From the absorption spectra it was found that the absorption edge shifts towards the lower wavelength and optical band gap (E_{opt}) value increases with decrease in the ionic radius and with increase in the atomic number of the rare earth ions. The dependence of E_{opt} on the type of RE ions is most likely related to structural rearrangement in the glass network. The increase in the optical band gap with the addition of rare earth ions suggests decreasing degree of depolymerization or concentration of bonding defects and non-bridging oxygens (NBO) in the glass network. This is due to the fact that Al^{3+} ions (like any other III A group elemental ions), isolate the rare-earth ions from RE-O-RE bonds and form Al-O-RE bonds. Such declustering effect which seems to be dominant in the glasses containing higher

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concentrations of rare earth ions and leads to the larger spacing between RE ions and contributes for the enhancement of fluorescence emission. Hence LBAB glasses are suitable hosts for rare earth ions. The observed higher E_{opt} values indicate the suitability of these glasses for optical device applications.

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