RESEARCH ARTICLE OPEN ACCESS

Physical, thermal, optical and spectroscopic properties of lithium diborate glasses containing Bi^{3+} and Er^{3+} ions.

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ABSTRACT

Lithium diobate based bismuth glasses containing erbium oxide were prepared by melt quenching technique. The density found increaseswith the increase of Bi_2O_3 content while the molar volume is decreased. The increase in density is directly linked with the substitution of higher molecular weight of Bi_2O_3 by lower Er_2O_3 content. The structural groups of the glass matrix were analyzed using FTIR spectroscopy. The addition of Er_2O_3 does not cause much to the structure of lithium diborates FT-IR spectrum revealing the absorption bands of BO_3, BO_4. BiO_6 groups. The decrease in glass transition temperature and optical band gap energy with an increase of Bi_2O_3 content has been explained on the basis of an increase in the formation of non-bridging oxygen atoms in the glass network.

Keywords: Optical and thermal properties; Density; Band gap energy; IR spectroscopy;

Date of Submission: 11-04-2022 Date of Acceptance: 28-04-2022

I. INTRODUCTION

Lithium borates are classical glass-forming systems, which have been extensively studied in the literature[1–3]. The ability of boron to exist in both three and four coordinated environments and the high strength of the covalent B–O bonds, imparts borates, the ability to form stable glasses. These alkali borate glasses exhibit excellent physical, thermal, optical, and structural properties.Borate glasses containing heavy metal oxides such as PbO and $Bi_2O_3$are commonly considered as more attractive for radiation shielding material compared to tellurite or phosphate-based glasses.This could be due to the effective shielding properties they possess even under harsh environmental conditions. In order to prevent the possible toxicity of lead oxide, nowadays PbO is replaced by Bi_2O_3.

The vitreous structure of the borate (BO_3 and BO_4 groups) and bismuth (BiO_6 and BiO_3 groups) based glasses, in turn, increases the local field strength of the glass, improving the shielding efficiency. Also, the incorporation of Bi_2O_3 in the oxide glasses enhances the density, thermal stability, high moisture resistance refractive index, third-order non-linearity, and polarizability[4,5].

Borate-based bismuth glasses containing rare earth oxides have attractive optical and structural properties and are promising systems for optoelectronic devices, lasers, and white light applications. Among the rare earth oxides, the erbium (Er^{3+}) ion is one of the most important ones, because of its particular near-infrared (NIR) emission which is attributed to the radiative transition from the first excited state to the ground state. This NIR emission is of great interest for use in telecommunication devices, infrared lasers, optical amplifiers, etc. [6-8].

When a rare earth ion is doped into borate based bismuth glasses, it plays a vital role by possessing desirable physical and optical properties and the doping of these rare-earth ions exhibits a minimum variation in spectroscopic properties. These glasses show good thermal stability, mechanical strength, chemical stability, high refractive index, large polarizability, and higher optical basicity. Hence these glasses have potential applications in the area of optical and electronic devices, [9-13]. These applications stipulate the need of a basic understanding between the structure and property of the oxide glasses.

More recently, the erbium ions doped glasses have been extensively used as mediaof the upconversion laser, waveguide laser, and erbium-doped fiber amplifier which is one of the key elements used in the wavelength-division-multiplexing network system for optical communication. Among the numerous host glasses, bismuth borate glass is widely used due to its low melting temperature and good physical and chemical properties [14,15].Therefore, much attention has been paid to these laser host glasses to explore their strustructure-property relations.

In this work, we present physical, thermal, optical and spectroscopy studies of Er^{3+} doped lithium boro-bismuth glasses. The results are discussed with regard to the structural entitiesof the borate and bismuth glass network.

II. EXPERIMENTAL

Glasses of composition $30Li_2O$-$60B_2O_3$-$(10\text{-}x)Bi_2O_3$-xEr_2O_3 where x = 0, 0.5, 1.0, 1.5 and 2.0 mol% were prepared by melt quenching method, using high purity analar grade chemicals lithium carbonate (Li_2CO_3), boric oxide (B_2O_3), bismuth oxide (Bi_2O_3) and erbium oxide (Er_2O_3). The starting materials were weighed in the required proportions and the components were carefully mixed by grinding together and were heated in ceramic crucibles at 450 ^{0}C for 30 min to get rid of water. During heating, CO_2 gets removed through decomposition. Mixtures of these materials were melted in a crucible at about 1100 ^{0}C to get a homogeneous melt and the homogeneous melt is quenched between brass moulds. A thin bubble-free glass samplewas obtained. All the samples were annealed well below their glass transition temperature for 3 hours and were cooled to room temperature to remove thermal strains developed in the samples during quenching. All the samples obtained are transparent and have good optical quality.

The room temperature infrared absorption spectra of the glass systems in the region from 400-4000 cm^{-1} were recorded on a Perkin Elmer (PE 580) Spectrometer by KBr pellet technique. The optical spectra were recorded in Perkin Elmer Lamda 35, a UV-Visible Spectrometer in the wavelength range of 300– 1100 nm at room temperature.

III. RESULTS AND DISCUSSION

The codes, composition density, molar volume, glass transition temperature,and band gap energy values are given in Table 1.

Glass transition temperature

The glass transition temperature values calculated using the heat capacity plots are given in Table 1. The glass transition temperature (Tg) of LDBE glass samples was found to decrease with the increase of Bi_2O_3 concentration. It is clearly manifested from the literature that Er-O bond linkages have higher bond strength of 611 kJ/mol compared to that of Bi-O linkages which are 343 kJ/mol. The changes in the strength of the bond linkages of Bi-O and Er-O bonds with the changes in the concentration reflected the decrease in the glass transition. This decrease in the glass transition is due to an increase in the number of weaker Bi-O linkages with stronger Er-O linkages [16].The variation of glass transition temperature with Bi_2O_3 content is shown in **Figure 1**. The variation of heat capacity value with temperature is shown asan inset in **Figure 1**.

Table 1: The code, composition, density, molar volume, glass transition temperature (T_g), and direct band gap energy.

Sl No	Composition in mol%				Density (g/cm^3)	Molar Volume (CC)	T_g (^oC)	Direct Band gap energy (eV)
	Li_2O	B_2O_3	Bi_2O_3	Er_2O_3				
LDBE1	30	60	10	0	3.341	29.13	353	2.745
LDBE2	30	60	9.5	0.5	3.254	29.78	357	2.659
LDBE3	30	60	9.0	1.0	3.178	30.35	361	2.528
LDBE4	30	60	8.5	1.5	3.064	31.37	365	2.463
LDBE5	30	60	8.0	2.0	2.994	31.95	370	2.309

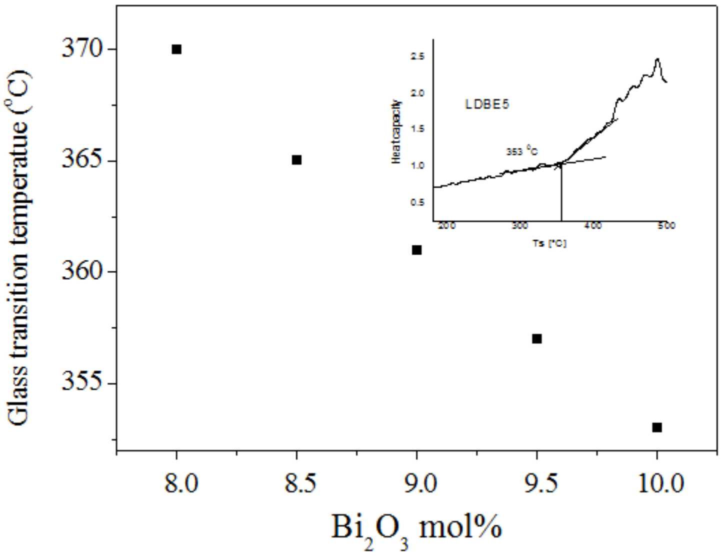

Figure 1: Variation of T_g with Bi_2O_3 mol% (inset: Typical plot of the variation of heat capacity with temperature.

The additionofBi$_2$O$_3$ toB$_2$O$_3$ glasses causes structural changes and leads to the formation of mixed bonding in the network structure [17].The addition of Bi_2O_3content leads to induce breaking up of the basic diborate units. This would lead to the formation of mixed bonding through the creation of B–O–B, Bi–O–Bi,Bi–O–B linkages, during glass formation which causes a decrease in its glass transition temperature. Hence the decrease in glass transition temperature with an increase of Bi_2O_3concentration can be also attributed to the possible substitution of Stronger Er–O bond strengths (611 kJ/mol) by weaker Bi–O bonds (343 kJ/mol) [18].

Density and molar volume

The densities of glasses were measured using toluene as immersion liquidby the buoyancy method based on the Archimedes principle. (density of toluene is 0.86 g/cm3 at 25 ^{0}C). The molar volumes, $V_m$was calculated using the relation$^M/_\rho$, where M is the molecular weight and ρ is the density of the corresponding glass samples. The densities and molar volumes of all the glasses investigated are given in Table 1. The densities determined in these measurements are accurate to ±0.005 g/cc. The variation of density and molar volume of the investigated samples are shown in **Figure 2**.

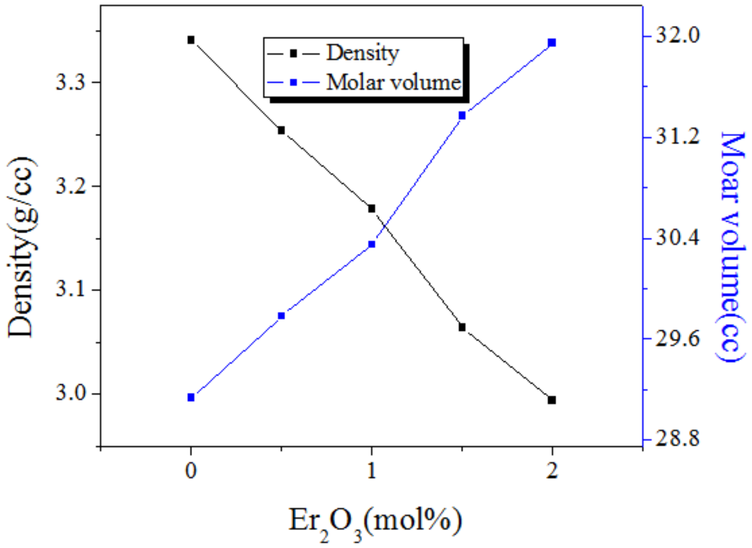

Figure 2: Variation of density and molar volumewith Bi_2O_3 mol%.

The density of glass increases gradually with the increase of Bi_2O_3. The increase in density is due to the high relative molecular mass of Bi_2O_3 (465.96 g/mol).The molecular mass of Er_2O_3 is 382.56 g/mol.The Bi_2O_3 content is increased in the glass matrix at the expense of Er_2O_3, this would lead to an increase in the density. The molar volume of the glass decrease monotonically with an increase of Bi_2O_3 and the rate of decrease is about 8.83% (from 31.95 cc to 29.13 cc). The decrease in the molar volume also indicates more compactness in the structure and Bi^{3+}has a contracting effect leading to an increase in density [19].

Infrared Spectroscopy:

FTIR absorption spectra of LDBE glasses are shown in **Figure 3.**The absorption band lies between the region 1200–1400 $cm^{-1}$and is assigned to the symmetrical stretching vibrations of B–O bonds in $[BO_3]$ units. The absorption band between 850 - 1100 cm^{-1} is attributed to stretching modes of $[BO_4]^-$ tetrahedral boron coordination in borate glasses. The characteristic peaks of $[BO_3]^-$ and $[BO4]^-$band frequencies are resolved well. The absorption band around 700 cm^{-1} is attributed to B-O-B bending vibrations [20,21]. The broad absorption band appearsin the region of 500 cm^{-1} attributable to Bi-O bond vibrations in distorted $[BiO_6]$ units [22-24]. The intensities of the peak do not change much with the variation of Bi_2O_3 concentration.

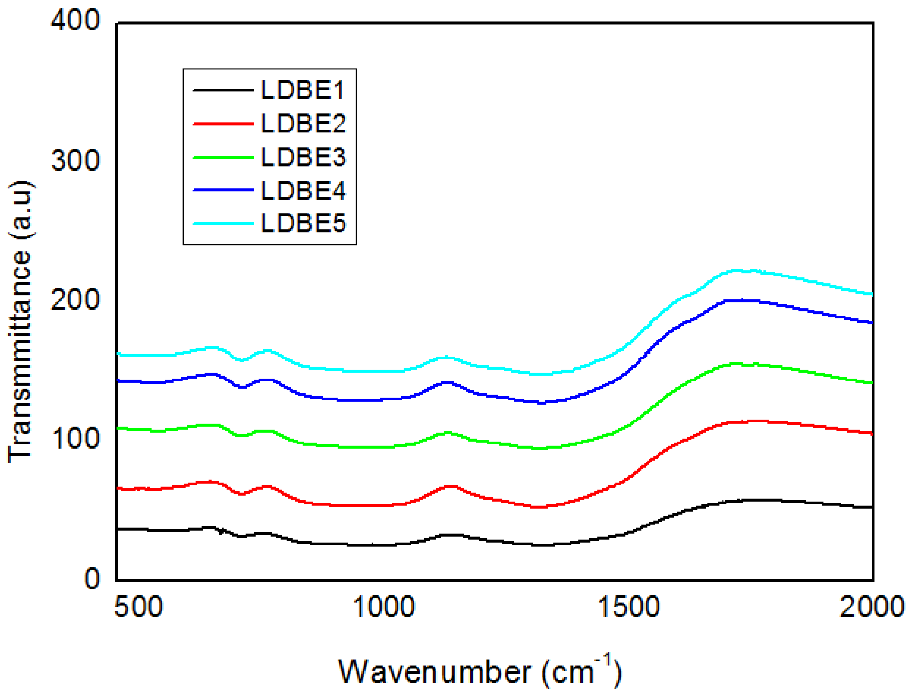

Figure 3: FT-IR Spectra of Er^{3+} ion doped $Li_2B_4O_7$ - Bi_2O_3 glasses

Optical absorption

The typical absorption spectra for LDBE1, LDBE3 and LDBE5 glasses is shown in **Figure 4**. The band gap energies in the oxide glasses were calculated on the basis of absorption spectra in the ultraviolet region. In the case of oxide glasses the absorption edges of the spectra are not sharply defined which is considered to be one of the most characteristic features of amorphous materials. The intensities of the absorption band increases with the increase in Er_2O_3 concentration and this depends on the covalence and asymmetry of Er–O local structure among the host matrices.

Optical band gap energy

The direct optical transitions for amorphous materials is analyzed using the absorption co-efficient $\alpha(\nu)$ as a function of photon energy $(h\nu)$ [25]:

$$\alpha h\nu = B^2(h\nu - E_g)^r$$

where E_g is the optical band gap energy and the index value r has different values (2, 3, 1/2 and 1/3) corresponding to indirect allowed, indirect forbidden, direct allowed and direct forbidden

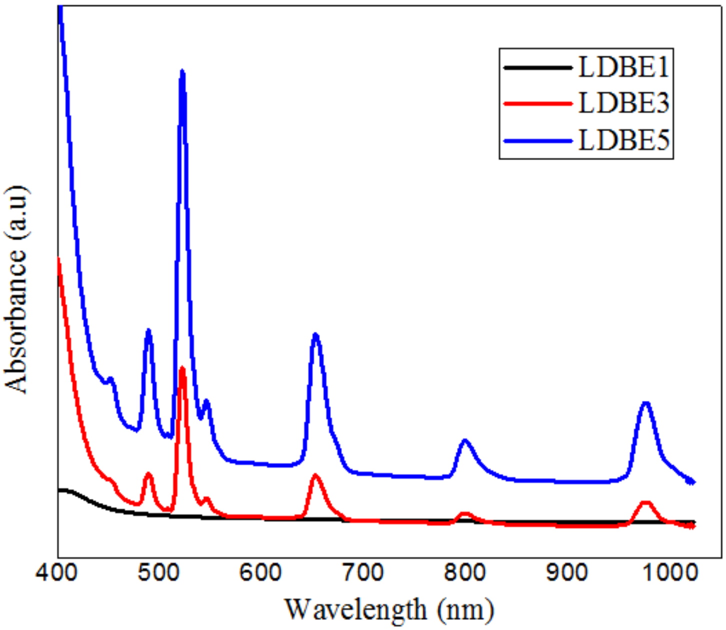

Figure 4: Typical UV-Visible absorption spectra of Er^{3+} doped glasses.

transitions respectively. *B* is a constant called the band tailing parameter and *hν* is the energy of incident photons.

The typical $(\alpha h\nu)^2$ versus $(h\nu)$ for direct allowed transitions (called Tauc's plot) have been plotted to find the values of optical band gap energy E_g. The values of E_g are obtained by extrapolating the linear region of the curve to the $(h\nu)$ axis, i.e. $(\alpha h\nu)^2 = 0$. The linear dependence is more pronounced indirect optical band gap clearly suggests that the transitions occurring in the present glass samples are all of the direct types.The variation of band gap energy with Er_2O_3 content is shown in **Figure 5**.

The incorporation of bismuth atoms to diborate structural entity results in the openness of the glass network, the opened network structure provides additional non-bonded oxygen coordination. When the non-bridging oxygen coordination is formed due to the strong polarizability of bismuth ions, results in the shifting of the absorption edge to a shorter wavelength region and it is attributed to a decrease in the optical band gap energy.
The high polarizability of Bi^{3+}cations may exist in the glass network as $[BiO_3]$ pyramidal units and results inasymmetric coordination of oxygen atoms when the diborate network structure is interrupted and leads to the formation of non-bridging oxygen atoms.

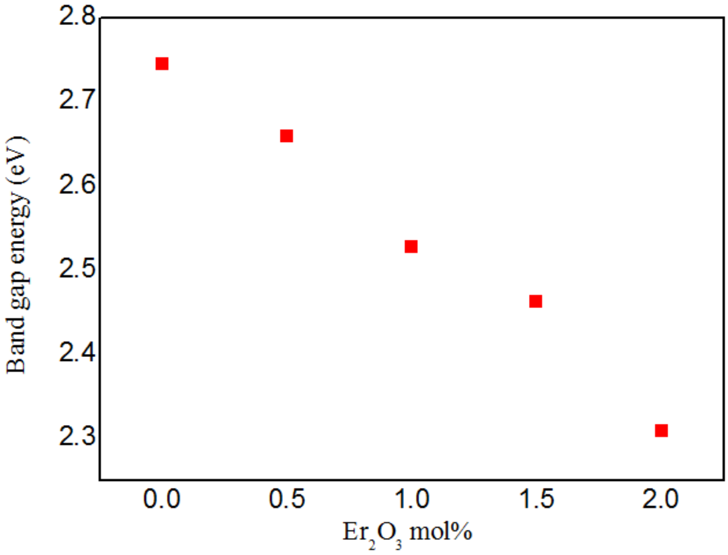

Figure 5: Variation ofoptical band gap energy with Er_2O_3 content.

IV. Conclusion

Glasses of the system $30Li_2O$-$60B_2O_3$-(10-x) Bi_2O_3-xEr_2O_3 were prepared by melt quenching method with erbium concentration varied from 0 to 2 mol%.The addition of $Bi_2O_3$to B_2O_3 glass induces the breaking up of the basic diborate structural units. This would lead to the formation of mixed bonding such as B–O–B, Bi–O–Bi, Bi–O–B linkages, which causes a decrease in its glass transition temperature. The decrease in glass transition temperature in the glass network can be also attributed to the possible substitution of Stronger Er–O bond strengths by weaker Bi–O bonds. The density of glass increases gradually with the increase of Bi_2O_3. The increase in density is due to the replacement of the high relative molecular mass of $Bi_2O_3$with a lower molecular mass of Er_2O_3. The decrease in the molar volume indicates more compactness in the structure and Bi^{3+} has a contracting effect leading to an increase in density.

The FT-IR spectral analysisreveals the existence of structural entities of oxide glasses which are made up of three coordinated boron atoms [BO_3], tetrahedral coordination of borons [BO_4], and octahedral coordination of [BiO_6] structural entities. The incorporation of Er_2O_3 causes a conversion of [BiO_3] and [BO_3]$^-$ units leading to the formation of non-bridgingoxygen atoms in the glass structure. The formation of non-bridging oxygen coordination is could be due to the possible strong polarizability of bismuth ions, results in the shifting of absorption edge to shorter wavelength region which in turn decrease in the optical band gap energy.

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