

Effect of Li_2SO_4 on the Structure and Properties of Lithium Lead Borate Glasses Containing Neodymium Ions

K.R.Sardar pasha^{1,2}, V.C. Veeranna Gowda³, N. Hanumantharaju³, C. Narayana Reddy^{1,4}

¹ Research Scholar, Rayalaseema University, Kurnool, Andhra Pradesh-518007

² Government First Grade College, Yelahanka, Bangalore-560064.

³ Maharani Science College for Women, Palace Road, Bangalore-560001.

⁴ Department of Physics, P.E.S. Degree College, Hanumanthanagara, Bangalore-560050.

Abstract.

Neodymium doped lithium sulphate containing lead borate glasses were prepared by melt quenching technique. The distinctive effect of Li_2SO_4 on neodymium doped lithium-lead-borate glasses was studied. The increased density and glass transition temperature with Li_2SO_4 reveals the structural stiffness of the glass network. The marginal increase in molar volume specifying the glasses have open structure. The gradual increase in OPD with Li_2SO_4 content stipulates the creation of more number of bridging oxygen atoms and results in the formation of high cross-link density. The band gap energy found to increase with Li_2SO_4 content. The IR spectra specify that the trigonal boron peak significantly red shifted with lithium sulphate ions and the occurrence of absorption bands consistent with the network structure formed by both lead and borates.

Keywords: Borate glass, Structure, Packing density, Band gap energy

INTRODUCTION

Lithium based borate glasses, due to the light weight and highly electropositive nature of lithium ions, causes significant modifications in the thermal, electrical, optical and spectroscopic properties [1,2]. In view of the structure, property and applications, lithium based borate glasses are deemed to be interesting materials to examine in detail. The structure of borate glass is considered to be pronounced interest due to its ability to coordinate three $[\text{BO}_{3/2}]^0$ ($=\text{B}_3$) and four oxygen atoms $[\text{BO}_{4/2}]^-$ ($=\text{B}_4$) to boron. The stability of the structural conversion among $[\text{B}_3]$ and $[\text{B}_4]^-$ entities in the borate glass depends on the type of modifier oxides added to it [1]. The conversion of B_3 to B_4 units increases the dimensionality and connectivity thereby increases the rigidity of the borate network. The lithium based borate glasses have wide applications such as potential solid electrolytes for lithium batteries, when they are added to lead oxide yields moisture resistant stable glasses over wide range of composition, and these lithium based lead borates doped with rare earth oxides, make the glasses more suitable for lasing materials.

The addition of lead oxide exhibit distinctive effect on the structure of oxide glasses possesses thermal stability to a greater extent [4-10]. PbO in the oxide glasses acts as both glass former and modifier based on its composition present in

the glass. This behaviour of dual role, subject to the type of ionic or covalent bond between lead-oxygen atoms [11-16]. It is found that the incorporation of lithium sulphate to lead borate glasses does not appear to result in any substantial modification of the glass network. But it is considered to be of important in strengthen the glass by providing its sulphate ions for the process of conversion of boron-oxygen coordination.

The structure of leadborate glass consists of boroxyl, pentaborate and diborate with three and four coordinated boron atoms and chain type metaborate groups consists of non-bridging oxygen atoms. It is established that the lead and borate oxides has a larger glass-forming region, good stability, high refractive index and showed strong absorption in the ultraviolet region. The importance of lead borate glasses is further increased due to its possible lasing materials when they are doped with Nd^{3+} , Sm^{3+} , Dy^{3+} rare earth ions. The various study revealed that the optical properties of rare earth ions are affected by varying the composition of the oxide glass.

In the present study, Nd^{3+} rare earth ion doped lithium based lead-borate glasses were investigated. The investigation of structure is essential in order to give a better understanding into structure-property relations. An effort has been made to study the effect of sulphate ion on the network of borate glass by means of its physical, thermal, spectroscopic and optical properties.

EXPERIMENTAL

The AR grade chemicals Li_2CO_3 , Li_2SO_4 , H_3BO_3 , PbO and Nd_2O_3 were used as starting materials and the glass samples were synthesized by rapidly quenching the homogeneous liquid. The required proportions of the chemicals were grinding in agate bow. The porcelain crucible with 8 gram composition is melted in an electrical furnace. The homogeneous, supercooled liquid was then quenched at 1150 °C. The obtained glasses were annealed just below their glass transition temperature for 2 hours.

X-ray diffraction pattern were measured using JEOL JOX-8P X-ray diffractometer. The transition temperature (T_g) of the glass was recorded using Differential Scanning Calorimeter (Perkin-Elmer, DSC- 2).

The densities of the glasses were measured by Archimedes' principle with acetone as immersion liquid. The precision of the measured densities (ρ) was $\pm 0.001 \text{ g/cm}^3$. The molar

volume, V_m was determined using the formula $V_m = M/\rho$ where M is the molecular weight of the glass system.

The UV-visible absorption spectra were measured using Perkin Elmer Spectrometer (Lambda 35) in the wavelength range of 200 – 900 nm.

The Fourier Transform-Infrared (FTIR) spectra of the samples were measured in the range of 4000 – 400 cm^{-1} . The finely powdered samples were mixed with potassium bromide (KBr). The mixture was made into a pellet for infrared measurements.

RESULTS AND DISCUSSION

X-ray diffraction

The pattern of X-ray diffraction for LLPB samples is shown in Fig. 1. X-ray patterns of the samples did not show any sharp peaks which clearly indicates the amorphous nature of the samples.

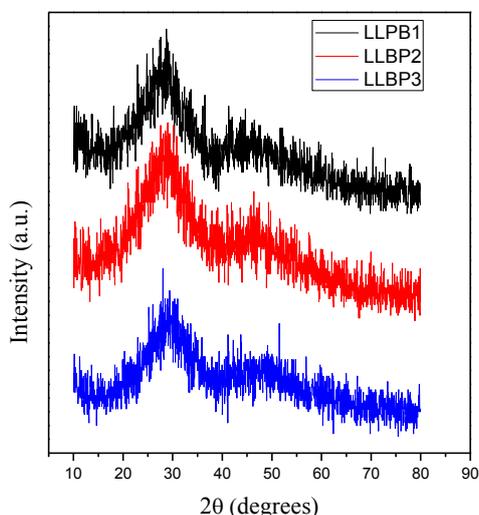
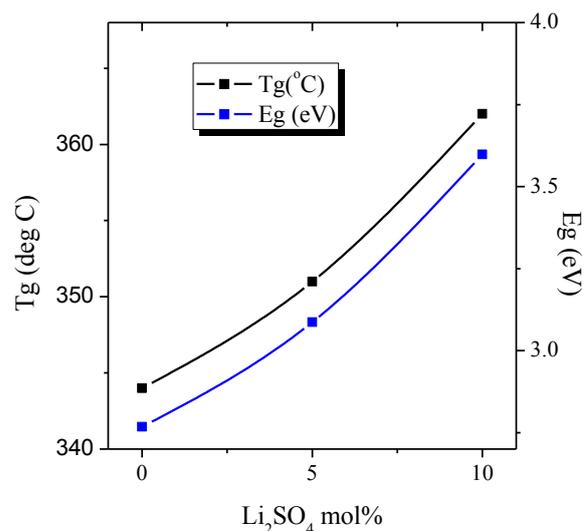


Figure 1: X-ray diffraction pattern of typical LLPB glasses.

Glass transition temperature (T_g)

The transition temperature (T_g) for LLPB glass samples is determined by DSC. The variation of T_g against MnO_2 content is shown in Fig. 2 and the T_g values are given in Table 1. The glass transition increases with increase of Li_2SO_4 content. The increase in T_g leads to structural rearrangement of three coordinated boron (B_3) units to four coordinated tetrahedral boron (B_4) [1]. The formation of four coordinated tetrahedral boron result in strengthening of the glass by forming more number of bridging oxygens, which depicted in the structural stiffness of a glass.

The addition of PbO also plays significant role in the variation of T_g in lithium borate glasses. In lithium lead borate glasses when PbO is at low percentage, it acts as a network modifier alike any alkali oxides [4,17]. Hence when PbO behaves like a glass modifier, the structural variation can be characterized by the reaction as, $\text{PbO} \rightarrow \text{Pb}^{2+} + \text{O}^{2-}$. But when the content of PbO is larger ($> 20\%$), it results in the formation of a $[\text{PbO}_4]^{2-}$ unit. The lead-oxygen polyhedral also competes with boron to acquire oxygen atoms available from the modifier oxide such as $\text{Li}_2\text{O}/\text{Li}_2\text{SO}_4$. This depends on the electronegativity of B_2O_3 and PbO atoms. The



electronegativity (χ) of $[\text{BO}_{3/2}]^0$ is 2.71 much higher than the PbO ($\chi = 2.31$) [18]. Therefore, initially oxygen atoms

Figure 2: Variation of density and molar volume with Li_2SO_4 content.

available from lithium for the modification are utilized by B_2O_3 to convert $[\text{BO}_{3/2}]^0$ to $[\text{BO}_{4/2}]^{-1}$ units. The electronegativity of $[\text{BO}_{4/2}]^{-1}$ is 1.96 [18]. As the modification continues, the group electronegativity (B_3 connected to B_4 groups) becomes smaller than the electronegativity of PbO . Then lead atoms have a tendency to form four coordinated $[\text{PbO}_{2.2}\text{O}_2]^{2-}$ units. Thus PbO enters into the glass as network former. When PbO entered into the network as glass former, the added lead oxide interrupts borate glass structure by breaking the chain structure of B_3 connected to B_4 units. This is consistent with the role of PbO and its effect of modification in the glass. The formation of covalently bonded $[\text{PbO}_{2.2}\text{O}_2]^{2-}$ units enters into the network structure and would result in the formation of denser packing of the components of the glass structure. Hence the glass transition temperature found to increase with Li_2SO_4 concentration.

Density and Molar Volume

Molar volume of the glass is considered to be sensitive to structure and bonding arrangement in the glass system. Its influence can be easily reflected in the variation of density and transition temperature of the glass. The change in molar volume and density of LLPB glasses is shown in Fig. 3 and are found to increase with Li_2SO_4 content. The increase in density is explained by considering the molecular weight of the glass components. In the investigated glasses, the molar content of B_2O_3 , PbO and Nd_2O_3 are kept constant. Li_2O is replaced by Li_2SO_4 . The molecular weight of Li_2O is 29.94 g/mol and that of Li_2SO_4 is 109.94 g/mol. The increase of Li_2SO_4 at the expense of Li_2O increases the density. The increase in density is also explained by considering the formation of compact packing of the components of the glass structure as explained in the glass transition temperature.

The increase in Li_2SO_4 composition results in marginal increase in molar volume indicating that the glasses have open structure. In order to examine the effect of Li_2SO_4 on the glass molar volume, the molar volume of the crystalline state is found to be comparable to that of glass molar volume. This indicates that the addition of lithium salts to the borate glass network appear to be simply dissolved in the glass matrix [19-20].

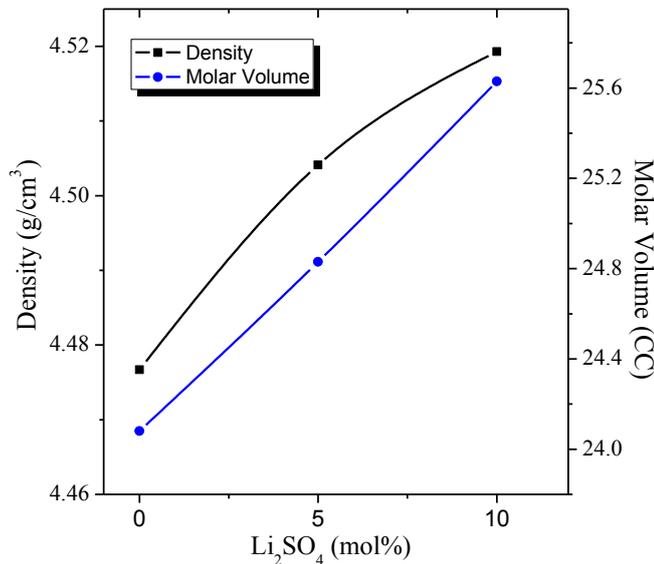


Figure 3: Variation of density and molar volume with Li_2SO_4 content.

Optical packing density (OPD)

The oxygen packing density provides the information about density and glass transition temperature in oxide glasses, which is a degree of compactness of oxygen atoms in the network. The oxygen packing densities of the glasses were calculated using standard Equation 1 [21]:

$$OPD = \frac{n \times 1000}{V_m} \quad (1)$$

Where ‘n’ is the number of oxygen atoms in the oxide glass. The calculated OPD values are given in Table 1. The OPD values increases from 79.24 to 86.15 (about 8%). The increase in OPD with Li_2SO_4 concentration specifies the formation of more number of bridging oxygen atoms. This results in the formation of high cross-link density. Therefore, in LLPB glasses the density and glass transition temperature found to increase with Li_2SO_4 content.

UV-Visible absorption spectroscopy

The band gap energy values obtained from Tauc's plot is reliable with the values determined from the absorption edge using the Equation 2 given below:

$$E_g = \frac{hc}{\lambda} \quad (2)$$

Where λ is the cut-off wavelength in the optical absorption spectra. The band gap energy found to increase with Li_2SO_4 content.

The addition of PbO to diborate glass structure provides additional bonded oxygen coordination. When PbO percentage is greater than 20 mol%, Pb atoms may enter into the glass as tetrahedral $[\text{PbO}_4]^{2-}$ units [17]. This resulted in the formation of three dimensional connectivity of the lead borate glass system. In the present glass system, Nd^{3+} ions sits in the vicinity of lead-borate glass network. The absorption band is shifted towards higher energy, indicates the formation of more number of bridging oxygen atoms.

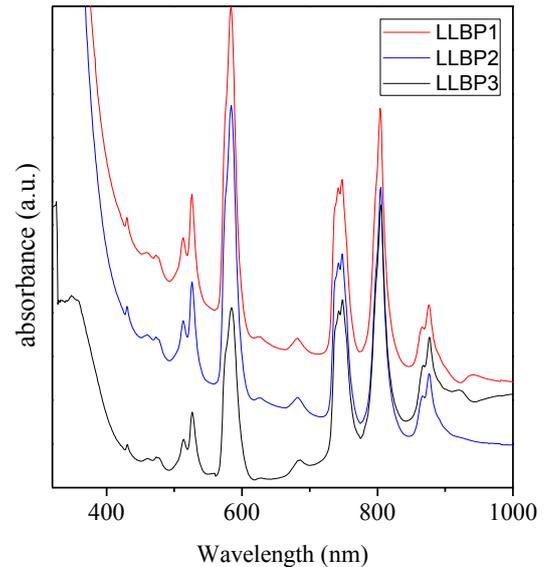


Figure 4: Optical absorption spectra of LLBP glasses.

Table 1: The code and composition of glass components.

Code	Composition (mol%)				
	Li_2SO_4	Li_2O	B_2O_3	PbO	Nd_2O_3
LLBP1	0	25	44.4	29.6	1
LLBP2	5	20	44.4	29.6	1
LLBP3	10	15	44.4	29.6	1

Table 2: The code, density (ρ), molar volume (M_v), OPD, T_g and activation energy (E_a).

Code	ρ (g/cm ³)	M_v (CC)	OPD (g-atom/ltr)	T_g (°C)	E_a (eV)
LLBP1	4.4767	24.08	79.24	344	2.768
LLBP2	4.5041	24.83	82.88	351	3.089
LLBP3	4.5193	25.63	86.15	362	3.598

FT-IR spectroscopy

The Infrared spectra reveal the structural information and the groups that occur in the glass. It is noticed from the IR spectra that vibrational modes of the borate network consists of three typical absorption bands. The absorption band between 1200 and 1400 cm^{-1} corresponds to borate units in which the boron atom is connected to three oxygen atoms

$[\text{BO}_{3/2}]^0$ [22-24]. The bands in the region between $850 - 1100 \text{ cm}^{-1}$ were attributed to the B-O stretching vibrations of boron atom in tetrahedra coordination $[\text{BO}_{4/2}]^-$ [22-24]. The B-O-B bending vibrations visible in the lower frequency region between 600 and 800 cm^{-1} [22-24]. These absorption bands are found to be consistent with the values reported in the literature. The relative intensities of these peaks undergo changes with Li_2SO_4 content. The trigonal boron peak at 1347 cm^{-1} is significantly red shifted as the concentration of sulphate ions increases.

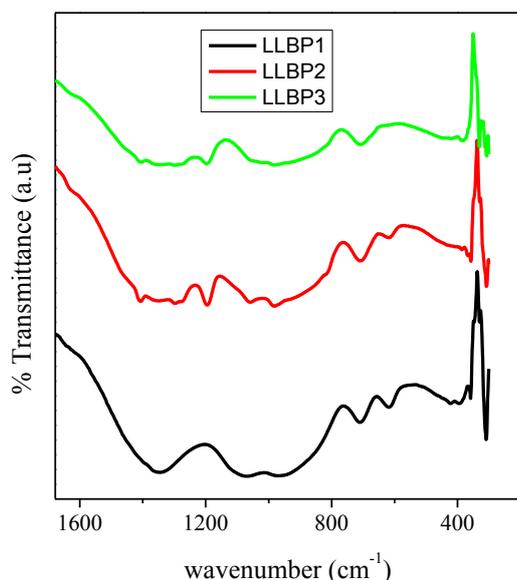


Figure 5: FT-IR spectra of LLBP glasses.

The absorption band correspond to tetrahedral boron becomes broaden with the increase of Li_2SO_4 concentration. There is also a characteristic limit of the maximum concentration of $[\text{BO}_{4/2}]^-$ structural groups. If it exceeds the maximum concentration, the reconversion of $[\text{BO}_{4/2}]^-$ units to $[\text{BO}_{3/2}]^-$ and $[\text{BO}_{3/2}]^{2-}$ units (boron with one and two non-bridging oxygen atoms) would have been occurred. The creation of non-bridging oxygen atoms would leads to weakening the glass resulted in decrease of its density and glass transition temperature. Therefore, in the present study it is expected that PbO converts into $[\text{PbO}_{4/2}]^{2-}$ units through simultaneous conversion of $[\text{BO}_{3/2}]^0$ to $[\text{BO}_{4/2}]^-$ units by preventing the reconversion of tetrahedral $[\text{BO}_{4/2}]^-$ borons into $[\text{BO}_{3/2}]^-$ or $[\text{BO}_{3/2}]^{2-}$ units. The IR spectra of the investigated glasses are consistent with the presence of network structure formed by both lead and borates. The absence of distinctive absorption band at 806 cm^{-1} reveals that the structure of borate glass does not consists of boroxol ring [25]. The absorption band around 440 cm^{-1} ascribed to Nd-O stretching vibrations and is consistent with theoretical value of Nd-O absorption bond occurs at 450 cm^{-1} [26].

CONCLUSION

Neodymium doped lithium-lead-borate glasses containing sulphate ions have been investigated by melt quenching method. The addition of PbO to diborate glass structure provides additional bonded oxygen coordination. The formation of covalently bonded $[\text{PbO}_{2.2}\text{O}_2]^{2-}$ units enters into the network structure and would result in the formation of denser packing resulting an increase in the glass transition temperature with. The effect of Li_2SO_4 on the molar volume indicates that the addition of lithium salts to the borate glass network appear to be simply dissolved in the glass matrix. The band gap energy values obtained from Tauc's plot is reliable with the values determined from the absorption edge.

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