

# Elastic properties of Li<sup>+</sup> doped Lead Zinc Borate Glasses

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**Abstract.** Glasses in the system 0.25PbO-(0.25-x) ZnO-0.5B<sub>2</sub>O<sub>3</sub>-xLi<sub>2</sub>O have been prepared by the melt quenching technique. Elastic properties, DSC studies have been employed to study the role of Li<sub>2</sub>O in the present glass system. Elastic properties and Debye temperature have been determined using pulsed echo ultrasonic interferometer operating at 10MHz. Sound velocities V<sub>l</sub>, V<sub>t</sub> and elastic moduli decrease up to 5 mol% and then gradually increase with increase in Li<sub>2</sub>O concentration. Debye temperature and the glass transition temperature decreases with increase in Li<sub>2</sub>O. Densities remains almost constant up to 15 mol% Li<sub>2</sub>O concentration and increases monotonically while the molar volume decreases with the increase of Li<sub>2</sub>O concentration. The results are discussed in view of the borate structural network and dual role of Zn and Pb in these glasses

**Keywords:** Borate glass, Elastic moduli, Glass transition, Debye temperature.

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## INTRODUCTION

ZnO-B<sub>2</sub>O<sub>3</sub> glasses exhibit low melting point and therefore they are of special interest owing to their applications in different fields of electronic products [1-2]. This is due to the fact that the higher the polarizability of an ion, the lower the melting temperature of the substance. Moreover, the compounds containing cations with an outer electron shell of 18 (Zn<sup>2+</sup>) or 18 + 2 electrons (Pb<sup>2+</sup>) have lower melting temperatures [3-5]. Divalent oxides, such as MO (where M= Zn, Pb, Mg etc.) when used as modifiers, the cations can produce several complex structural effects due to their higher valence than alkali cations[6]. In our previous work we have shown these glasses (PbO-ZnO-B<sub>2</sub>O<sub>3</sub>) doped with rare-earth show good optical response [6]. The present work involves study of elastic properties in ZnO/Li<sub>2</sub>O modified PbO-B<sub>2</sub>O<sub>3</sub> based glass.

## EXPERIMENT

Glasses in the system 0.25PbO-(0.25-x) ZnO-0.5B<sub>2</sub>O<sub>3</sub>-xLi<sub>2</sub>O have been prepared by the melt quenching technique starting from analar grade lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>), lead oxide (PbO), Zinc oxide (ZnO) and orthoboric acid (H<sub>3</sub>BO<sub>3</sub>). The required quantities of the above materials were thoroughly mixed and melted in a crucible at about 1150°C to get a homogeneous melt. All the samples were annealed below their glass transition temperature. The glassy state of the samples was confirmed using X-ray diffraction technique. The room temperature ultrasonic measurements were

carried out at 10MHz using x-cut and y-cut quartz transducers. A pulse superposition method was employed using ultrasonic interferometer (System dimensions, Bangalore). Phenylsalicilate (Salol) was used to bond the transducers to the samples. Longitudinal and transverse sound velocities were determined by pulse superposition method using a Hewlett-Packard model 54600 B oscilloscope. Using Mckimin's Δt criteria, the round trip delay time (τ) has been calculated [7]. By measuring the thickness of the sample (d), longitudinal (V<sub>l</sub>) and transverse (V<sub>t</sub>) velocities were calculated using the relation  $V = 2d/\tau$ . In an amorphous solid, elastic strain produced by low stress can be described by two independent elastic constants, C<sub>11</sub> and C<sub>44</sub>. The Cauchy relation  $2C_{44} = C_{11} - C_{12}$  allows one to determine C<sub>12</sub>. Elastic Elastic moduli were calculated using the following standard relations.

$$\text{Longitudinal modulus, } C_{11} = L = \rho V_l^2 \quad (1)$$

$$\text{Shear modulus, } C_{44} = G = \rho V_t^2 \quad (2)$$

$$\text{Bulk modulus, } K = L - (4/3) G \quad (3)$$

$$\text{Young's modulus, } E = (1+\sigma)2G \quad (4)$$

$$\text{Poison's ratio, } \sigma = (L-2G)/2(L-G) \quad (5)$$

$$\text{Debye temperature, } \theta_D = \frac{h}{K} \left( \frac{3\rho q N_A}{4\pi M} \right)^{\frac{1}{3}} V_m \quad (6)$$

Where ρ is the density and M is the molecular weight of the corresponding samples, q is the number of atoms in the unit formula. N<sub>A</sub> is the Avogadro number. The mean sound velocity V<sub>m</sub> in the Eq. 4.13 is estimated by the following defined relation

$$3/V_m^3 = 1/V_l^3 + 2/V_t^3 \quad (7)$$

## RESULTS AND DISCUSSION

### Physical properties:

The variation of molar volume and density is as shown in the Fig.1. As can be seen from fig.1 that the density remains almost constant up to 15 mol% of  $\text{Li}_2\text{O}$  concentration and then increases monotonically while the molar volume decreases with the increase of  $\text{Li}_2\text{O}$  concentration. Although the effective modifier concentration is same, but when Li is inter-substituted for Zn. It is likely that with increase  $\text{Li}_2\text{O}$  has direct bearing on the structural borate network. Presumably, the added oxygen of the Li is taken up for the conversion of  $\text{BO}_3$  to  $\text{BO}_4$  groups leading compactness in the structure resulting increase the density and a decrease in molar volume [8].

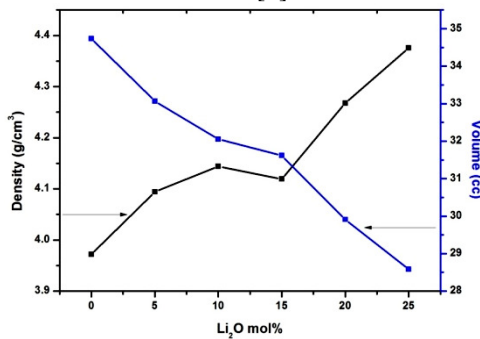


Fig. 1. Variation of Density, Volume versus  $\text{Li}_2\text{O}$  mol%

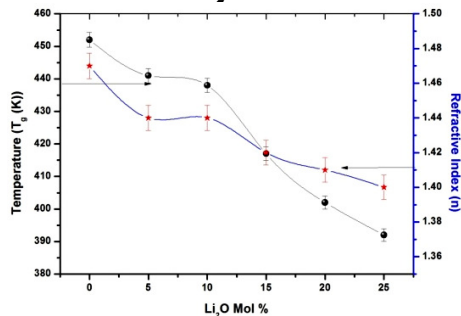


Fig. 2. Variation of  $T_g$ ,  $n$  versus  $\text{Li}_2\text{O}$  concentration.

The glass transition  $T_g$  give us the information on structural degradation, Figure.2 shows the variation for both  $T_g$  and refractive index ( $n$ ) and it is found to decrease with increase in  $\text{Li}_2\text{O}$  concentration. In a binary alkali borate glass,  $T_g$  increases with increase in alkali concentration indicating the conversion of  $[\text{BO}_{3/2}]^0$  to  $[\text{BO}_{4/2}]^-$ . However, in the present glass system the presence of Pb and Zn both are known for dual nature, bring interesting structural defects. As Li concentration is increased there is conversion of  $\text{B}_3$  to  $\text{B}_4$  as stated above but at the same time there is rupture of  $\text{ZnO}_4/\text{PbO}_4$  groups leading to decrease in the connectivity's. Thus the  $T_g$  would decrease continuously as exhibited in Fig 2. The results are consistent with density variation.

### Ultrasonic studies:

Fig. 3. Shows the variation of longitudinal sound velocity ( $V_l$ ) and transverse sound velocity

( $V_t$ ) and Fig. 4 shows the variation of the various elastic moduli as a function of  $\text{Li}_2\text{O}$  concentration. As can be seen from Figs. 3 and 4 that both  $V_l$ ,  $V_t$  and elastic moduli decreases upto 15 mol% and then show gradual increase with  $\text{Li}_2\text{O}$  concentration. In general the velocities as well as the moduli show the same trend with increase in Li concentration.

The substitution of  $\text{Li}_2\text{O}$  at the expense of ZnO and other PbO oxides in the glass network do not alter the ratio of oxygen to boron atoms ( $\text{O/B} = 2.0$ ). Addition of  $\text{Li}_2\text{O}$  in expense of ZnO content will lead to formation of  $\text{BO}_3$  units to  $\text{BO}_4$  units until a ratio  $\{([\text{PbO}]-[\text{Li}_2\text{O}] + [\text{ZnO}])/[\text{B}_2\text{O}_3]\} \approx 0.5$  is reached. This ratio corresponds to 'borate anomaly' when the ratio increases beyond 0.5 that leads to transformation of  $\text{BO}_4$  to  $[\text{BO}_3]^-$  creating NBOs. As shown in the fig.4 that the rate of change of elastic moduli is more pronounced in L and least in case of G. This indicates resistance to the deformation and it is most probably due to presence of large number of covalent bonds [3, 9-10]. In the present system we notice decrease in bulk modulus (K) upto 15 mol%  $\text{Li}_2\text{O}$  glass samples. In these glasses the network connectivity decreases as the ratio  $\{([\text{PbO}]-[\text{Li}_2\text{O}] + [\text{ZnO}])/[\text{B}_2\text{O}_3]\} > 0.5$  corresponding to borate anomaly and then gradually increases with increase in  $\text{Li}_2\text{O}$  content.

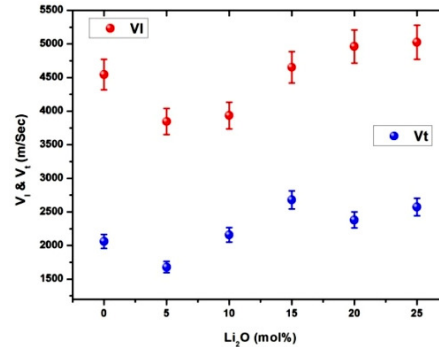


Fig. 3. Variation in  $V_l$  &  $V_t$  with  $\text{Li}_2\text{O}$

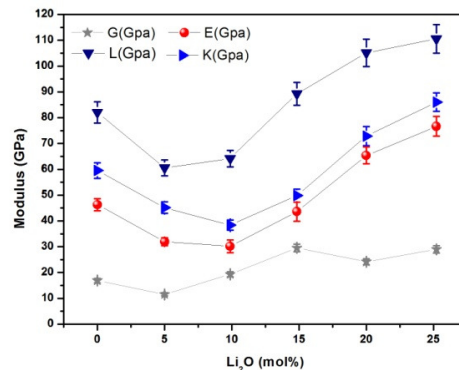


Fig. 4. Variation of Elastic moduli with  $\text{Li}_2\text{O}$

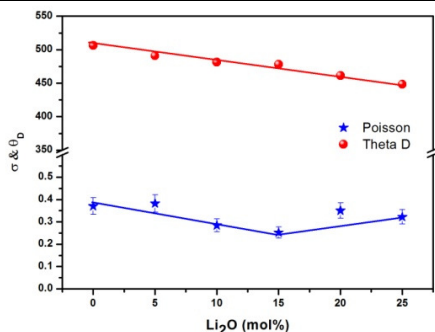
Poisson's ratio is defined as the ratio between lateral and longitudinal strain produced when tensile force is applied or function of the ratio of longitudinal and shear velocities. The variation of Poisson's ratio with composition is shown in Fig. 5 it should be exactly the reverse of the elastic moduli variation

[11]. Poisson's ratio has been also discussed in terms of the dimensionality of glass network and it is

observed that the Poisson's ratio for a three

**Table.1.** The composition, density, elastic constants ( $C_{11}$ ,  $C_{44}$  and  $C_{12}$ ), bulk modulus (K), Young's modulus (E), Poisson's ratio ( $\sigma$ ) and Debye temperature ( $\theta_D$ ).

Composition				$\rho$ (g/cm <sup>3</sup> )	$C_{11}$ (Gpa)	$C_{12}$ (Gpa)	$C_{44}$ (Gpa)	K (Gpa)	E (Gpa)	$\sigma$	$\theta_D$ (in K)
PbO	ZnO	Li <sub>2</sub> O	B <sub>2</sub> O <sub>3</sub>								
25	25	0	50	3.971	82.04	48.28	16.88	59.52	46.28	0.3704	506.3
25	20	5	50	4.094	60.55	37.45	11.55	45.15	31.94	0.3821	490.8
25	15	10	50	4.143	64.16	25.50	19.33	38.38	30.14	0.2843	481.4
25	10	15	50	4.119	89.22	30.10	29.56	49.80	49.80	0.2522	477.8
25	05	20	50	4.267	105.12	56.74	24.19	72.86	65.35	0.3505	461.3
25	0	25	50	4.375	110.53	52.55	28.99	86.01	76.66	0.3222	448.4



**Fig. 5.** Variation of Poisson's ratio & Debye temperature versus Li<sub>2</sub>O mol%.

dimensional network is less than that of a two dimensional structure, which in turn is less than that of a one dimensional structure. This has been attributed due to the fact that the concentration of bonds resisting a transverse deformation decreases in that order [12]. The decrease in Poisson's ratio when ZnO increased (Li<sub>2</sub>O decreased) from 0 to 10 mol% (i.e., R6, R5, R4 samples) may be referred to as the increase in covalent cross-linking between Li<sub>2</sub>O [13] as discussed in previous section, the increase in Poisson's ratio values above 15 mol% is due to the fact that the presence of Pb<sup>2+</sup>. It is clear from the above results that the type of bonding in the network structure plays a dominant role in deciding the rigidity of these glass structures. This is due to the fact that the increase of Li<sub>2</sub>O content affects the glass network structure based on its network-modifying/forming role with respect to ZnO intersubstitution. The variation of calculated acoustic Debye temperature with Li<sub>2</sub>O concentration is shown in Fig. 5. As can be seen in figure Debye temperature decreases with increase in mole fraction of Li<sub>2</sub>O. The decrease in Debye temperature results in a monotonic decrease in the total vibrational energy of the system. This is because any of the conceivable vibrational units resulting from the substitution will be of lower energy. Debye temperature plays an important role in solid materials in the determination of elastic moduli and atomic vibrations.  $\theta_D$  represents the temperature at which all the high frequency lattice vibrational modes are excited. The continuous decrease of Debye temperature also suggests the structural

degradation which is reflected in the glass transition as discussed in sec 1.1.

## CONCLUSIONS

Ultrasonic properties of lead zinc borate doped with lithium glasses have been investigated. Both  $V_L$ ,  $V_T$  and elastic moduli decrease upto 10 mol% of Li<sub>2</sub>O and then gradually increase with increase in Li<sub>2</sub>O concentration, this variation is similar to density variation observed. Debye temperature and glass transition temperatures decreases with varying Li<sub>2</sub>O concentration indicating their structural degradation. The analysis clearly indicates Li<sub>2</sub>O acts as a modifier, whereas PbO and ZnO acts as intermediates.

## ACKNOWLEDGEMENT

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