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Physical and Elastic Properties of Mixed Alkali Borate Glasses Using Ultrasonic Technique

KEYWORDS: Density, Ultrasonic study, Alkali borate glasses, Pulse-echo technique

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ABSTRACT *The ternary glass system of (50-x) Li2O-50B2O3-xNa2O (where x =10, 15, 20, 25 and 30 mol%) with different composition were prepared by melt-quench technique. The longitudinal and shear ultrasonic velocities were measured for all the glass samples at room temperature at 10 MHz frequency. Density of the samples was measured using relative measurement method. Elastic modulii, Poisson's ratio, acoustic impedance, microhardness, Debye and softening temperature and thermal expansion co-efficient were calculated from velocity and density data and have been used to obtain quantitative details about the structure of these glasses. Compositional dependence of ultrasonic velocities and related parameters are discussed to understand the rigidity and compactness of the glass systems studied.*

1.INTRODUCTION

Among the various experimental methods available for studying the structure-property relations, elastic properties of solid materials are of considerable significance because their measurements yield information concerning the forces between the atoms or ions. This is fundamentally important in interpreting and understanding the nature of bonding in the solid materials. Hence, elastic properties are suitable for describing the glass structure as a function of composition [1].

In Li_2O-B_2O_3 glass system [2], the elastic properties have been discussed in terms of boron coordination. Borate glasses are one of the most popular and excellent glass forming materials. Upon addition of alkali oxides to B_2O_3, the covalent network of amorphous boron oxide causes considerable changes, resulting in the creation of anionic sites that accommodate the modifying alkali cations. Borate glasses containing alkali or alkali earth oxides exhibit high mechanical strength and are relatively moisture-resistant when compared with the pure borate glasses. Some of their applications include phosphors, solar energy converters and optical devices [3].

When two types of alkali ions are introduced into a glassy network, a phenomenon known as mixed alkali effect (MAE) is observed. It represents the non-linear variation in many physical properties associated with the alkali ion movement and structural properties, when one type of alkali ion in an alkali glass is gradually replaced by another, total alkali content in the glass being constant [4] Mixed alkali effect is frequently occurs among properties associated with cation movements such as, ionic conductivity, dielectric loss and alkali diffusion co-efficient [5].

According to Narayana Reddy and Sreekanth Chakradha [6], in borate glasses, the structure of pure vitreous, B_2O_3 consists of a random network of boroxyl rings and BO_3 triangles connected by B–O–B linkage. The addition of alkali oxides modifies the boroxyl rings; complex borate groups with one or two four co-ordinate borate atoms are formed. Fast ion conducting lithium based borate glasses have a variety of technological applications [7].The small size, light weight and highly electropositive character of lithium ions gives rise to high voltage and high energy density micro batteries. Apart from these technological applications, structural studies on these glasses help to understand how the structure of the host glass in which the ions present, influences their mobility. There have been several structural studies, which deal with the structure of lithium based borate glasses [8].

The present study is aimed to investigate the physical and elastic properties of the network structure of mixed alkali effect on ternary (50-x) Li_2O-50B_2O_3-xNa_2O (where x =10, 15, 20, 25 and 30 mol%) glass system, using ultrasonic technique.

2. EXPERIMENTAL TECHNIQUES

2.1. PREPARATION OF GLASSES

The glass samples having the general chemical formula (50-x) Li_2O- 50B_2O_3 _ xNa_2O (where x= 10, 15, 20, 25 and 30mol%) were prepared by melt quench method using the starting materials as Li_2O,B_2O_3andNa_2O of reagent purity grade. The required amount (approximately 15g) in mol% of different chemicals in powder form was weighed using a single pan balance having an accuracy of ±0.0001g.The homogenization of the appropriate mixture of the components of chemicals is effected by repeated grinding using a mortar. The mixtures corresponding to the desired compositions were melted in silica crucible in a muffle furnace. Melting is carried out under controlled conditions at a temperature from 900 to 980 °C. The molten sample is cast into a copper mould having dimensions of 10mm diameter and 6mm thickness. Then the glass samples are annealed for three hours at 300°C to avoid the mechanical strain developed during the quenching process. The samples prepared are chemically stable and non-hygroscopic.

The prepared glass samples are polished and the surfaces are made perfectly plane and smoothened by diamond disc and diamond powder. Thickness of the samples has been measured using digital vernier calipers with an accuracy of 0.0001mm.

2.2 MEASUREMENT OF DENSITY

The density of the glass samples is measured using water as buoyant liquid.The glass samples are weighed both in air and in water at 303 K. The density is calculated using the formula

$$\rho = \frac{W_A}{(W_A - W_B)} \times \rho_B \qquad (1)$$

Where W_A and W_B are the weight of the sample in air and in water. ρ_w is the density of water at 303 K.

2.3. MEASUREMENT OF SOUND VELOCITY

The ultrasonic longitudinal and shear velocities of the specimen have been determined using the conventional pulse echo method at room temperature (303 K) by making use of 10 MHz X-cut and Y-cut transducers. These transducersact as both transmitters and receivers of the ultrasonic pulse.

Ultrasonic velocity is calculated using the relation

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$$U = \frac{2d}{t} \qquad (2)$$

where U is the velocity of the specimen (ms^{-1}), d is the thickness of the specimen(mm) and t is the transit time(μ_s).
Various parameters of the glass specimen are calculated using the standard expressions given below:

Molar volume $(V_m) = \frac{M}{\rho}$ (3)

Longitudinal modulus (L) $= \rho U_\ell^2$ (4)

Shear modulus (G) $= \rho U_s^2$ (5)

Bulk modulus (K) $= L - \left(\frac{4}{3}\right)G$ (6)

Poisson's ratio (σ) $= \left(\frac{L - 2G}{2(L - G)}\right)$ (7)

Young's modulus (E) $= (1 + \sigma)\, 2G$ (8)

Acoustic impedance (Z) $= U_\ell \rho$ (9)

Microhardness(H) $= (1 - 2\sigma)\frac{E}{6(1+\sigma)}$ (10)

Debye temperature (θ_D) $= \frac{h}{K}\left(\frac{9N}{4\pi V_m}\right)^{1/3} U_m$ (11)

Where M, ρ,$U_\ell$and $U_s$are the average molecular weight, measured density, longitudinal and shear ultrasonic velocity and h, K andN are the Planck's constant, Boltzmann's constant and Avogadro's number of the sample respectively.

The mean sound velocity U_m is given by

$$U_m = \left[\frac{1}{3}\left(\frac{2}{U_s^3} + \frac{1}{U_\ell^3}\right)\right]^{-1/3}$$

Softening temperature $T_s = \left(\frac{M}{C\rho}\right)U_s^2$ (12)

Where C, is a constant equal to 0.5074 × $10^5 cmK^{-1/2}$ s.

Thermal expansion coefficient (αp)= 23.2 (Uℓ – 0.57457) (13)

Table 2.1 Nominal composition of LBN glass samples

Nominal composition (mol %.)			
Specimen	Li_2O	B_2O_3	Na_2O
LBN 1	40	50	10
LBN 2	35	50	15
LBN 3	30	50	20
LBN 4	25	50	25
LBN 5	20	50	30

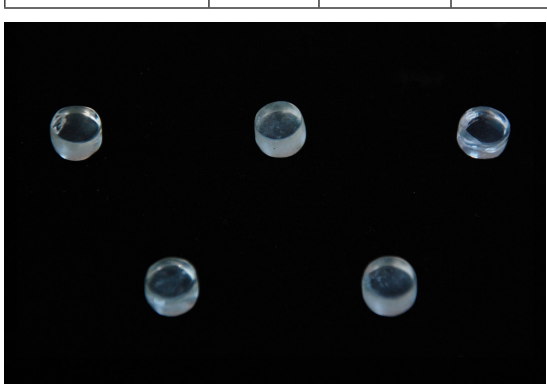

Fig. 2.1 Glass samples of LBN system

3. RESULTS AND DISCUSSION

The experimental values of density (ρ), molar volume (V_m) longitudinal ultrasonic velocity (U_l) and shear ultrasonic velocity (U_s) of the different glass specimen with respect to the change in the mol% of Li_2O are listed in Table 3.1.The calculated longitudinal modulus (L), shear modulus (G), bulk modulus (K), Young's modulus (E) and Poisson's ratio (σ) are also reported in Table 3.2.The acoustic impedance (Z) and micro hardness (H) Debye temperature (θ_D), softening temperature (T_s) and thermal expansion coefficient (α_p)are reported in Table 3.3.

Density measurements are widely used to study the effect of composition on glass structure [9]. These measurements are usually employed to control the homogeneity of glass, but the value of density itself is not a useful structural parameter. On the contrary, the determination of molar volume from density data can provide information on different aspects of the glass structure.

From Table 3.1, it is observed that the density and molar volume show a non-linear variation with increase ofNa_2O content but oppositely directed. The density values initially increase up to 15 mol % of $Na_2O$and decrease to minimum at x = 20mol%and then increases with the increase in Na_2O concentration, whereas the molar volume values initially decrease with increase in Na_2O mol%, then increase to maximum at x = 20mol % and thereafter they decrease due to MAE. According to Doweidar, *et al*. [10],in pure alkali borate glasses, the decrease in density due to MAE was noticed within the composition.

The non-linear variation of ultrasonic wave velocities and elastic moduli can be explained on the basis of the structural consideration of borate network. In lithium borate glasses of the composition xLi_2O-(1-x)B_2O_3,[11] reported that the structural unit $BO_3$is converted in to BO_4 only in the compositional range 0≤ x ≤ 0.20 and this conversion caused an increase in velocity of sound.

In the present glass system, the addition of alkali oxide to B_2O_3 network creates [BO_4] units up to 15 mol% (as modifying oxide), this leads to increase in the network dimensionality and connectivity. Hence both velocities and elastic moduli increases up to x=15mol% of Na_2O. Further addition of modifying oxide leads to reconversion of [BO_4] to [BO_3] units [12] and loose structure because of the presence of non-bridging oxygen (NBOs) and mixed alkali effect (MAE). The formation of NBO will decrease the connectivity and rigidity of the glass system [13]. This leads to decrease the velocities and elastic moduli at x=20 mol%.

Above the value, x=20mol % of Na_2O the conversion of BO_3 coordinated state to BO_4 coordinated state increase the connectivity the glass network [14] resulting in a progressive and pronounced compact glass structure.

Finally the presence of BO_4 with bridging oxygen in (50-x) Li_2O-50B_2O_3-xNa_2O glass system increases the rigidity of the glasses for higher concentration of Na_2O, causes an increase in the value of ultrasonic velocities and elastic moduli.

Table 3.2 shows the compositional dependence of Poisson's ratio as a function of Na_2O concentration. Poisson's ratio is the ratio of the transverse and linear strains for a linear stress. Poisson's ratio has also been discussed in terms of the dimensionality of glass network. As it can be seen from Table 3.2 that the Poisson's ratio is varied non-linearly with increase in concentration of alkali modifier, these composition dependence of Poisson's ratio might be due to the change in the structure of the glass network and the Poisson's ratio value is found to decrease when the concentration of modifier at x= 20 mol %, this suggests that there is no formation of BO_3 groups with NBOs.

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Table 3.1.Values of density (ρ), molar volume (V_m), longitudinal velocity (U_l) and shear velocity (U_s) of LBN glass system

Specimen	Density ($\rho \times 10^{-3}$ kg m^{-3})	Molar volume ($V_m \times cm^3$/mol)	Ultrasonic Velocity (U) ms^{-1}	
			Longitudinal velocity (U_l)	Shear velocity (U_s)
LBN 1	2.410	21.94	4895.8	2580.8
LBN 2	2.638	20.67	5089.9	2722.1
LBN 3	2.483	22.61	4858.7	2523.6
LBN 4	2.699	21.39	5117.7	2876.7
LBN 5	2.995	19.81	5489.9	3110.8

Table 3.2 Values of longitudinal (L), shear (G), bulk (K) Young's modulus (E) and Poisson's ratio (σ) of LBN glass system

Specimen	Longitudinal modulus (L × 109 Nm-2)	Shear modulus ($G \times_2 10^9$ Nm^{-2})	Bulk modulus ($K \times_2 10^9$ Nm^{-2})	Young's modulus ($E \times 10^9$ Nm^{-2})	Poisson's ratio (σ)
LBN 1	57.77	16.05	36.36	41.98	0.307
LBN 2	68.35	19.55	42.29	50.82	0.299
LBN 3	58.61	15.81	37.53	41.59	0.315
LBN 4	70.70	22.34	40.91	56.7	0.269
LBN 5	90.29	28.99	51.63	73.26	0.263

Table 3.3 Values of acoustic impedance (Z), microhardness (H), Debye temperature (θ_D), softening temperature (T_s) and thermal expansion coefficient (α_p) of LBN glass system

Table 3.3 shows the acoustical impedance of the glass system as a function of Na_2O concentration. In the case of sodium silicate glasses containing K_2O or Li_2O, it has been reported [15] that the addition of alkali oxide causes splitting of the glass network thereby increasing the formation of non-bridging oxygen's which results in lowering of the impedance to the propagation of ultrasonic waves.

In the present study, the acoustic impedance value decrease at x = 20% of Na_2O, this may due to the presence of non-bridging oxygen. Above the value x≥20% of Na_2O,the acoustic impedance increases in the glass system attributed to the presence of bridging oxygens and increase in rigidity of the glass structure. Similar trend is observed by Raghavaiah and Veeraiah[16].

It is seen from Table 3.3 that the microhardness changes non-linearly with increase of Na_2O content indicating the changes occurring in the glass rigidity. The results are further confirmed by other parameters, Debye temperature and softening temperature obtained directly from the measured velocity. The Debye temperature and softening temperature values obtained are given in Tables 3.3.

Debye temperature (θ_D) is a useful parameter to understand the change in structure and plays an important role in solid materials in the determination of elastic moduli and atomic vibrations. The softening point is the temperature at which viscous flow changes to plastic flow. The observed increasing and decreasing value of θ_D and Ts are related to the changes occur in compactness, thermal stability and cross-link density of the glass network.

Srivastava and Srinivasan [17], have stated that the thermal expansion coefficient of materials depends on the strength of bonds. In the Table 3.3thethermal expansion coefficient (α_p) of the glass system shows an anomalous behavior due to the presence of mixed alkali effect (MAE).

CONCLUSION

The density and molar volume for lithium-sodium-borate glasses show an anomalous behavior due to the presence of mixed alkali effect (MAE).

The ultrasonic study of LBN glasses shows a non- linear variation in velocities, elastic moduli and other parameters due to the presence of MAE.

It is observed that, the velocities, elastic moduli and other parameters decreases at x = 20 mol% of Na_2O and above the value x ≥ 20 mol% of Na_2O,the velocities, elastic moduli and other parameters increases. This result strongly indicate that, the compactness and rigidity of the glass system decreases at x = 20 mol% of Na_2O and then increased for higher concentration of Na_2O.

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