STUDY OF PHYSICAL AND ELASTIC PROPERTIES OF LEAD DOPED MIXED ALKALI BORATE GLASSES USING ULTRASONIC TECHNIQUE

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Abstract—The quaternary glass system of xLi_2O - $50B_2O_3$ – (45-x) Na_2O- 05PbO (where x = 20, 25, 30, 35 and 40 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 and 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.

Index Terms— Density, Ultrasonic study, Mixed alkali borate glasses, Pulse-echo technique.

1 INTRODUCTION

An investigation has been made to explore the structural changes, stability and physical properties of mixed alkali borate glasses with PbO using ultrasonic measurements. In conventional glasses, alkali oxides, such as Li_2O, Na_2O, K_2O, Ag_2O, etc. are used as modifiers with network forming oxides like B_2O_3, SiO_2, and P_2O_5.

Alkali metal oxide doped borate glasses are mainly used for applications in solid-state devices, cathode materials for batteries, gas and chemical sensors, electrochemical, electronic and electro-

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optical devices (1, 2). Glasses containing divalent ions such as Mg^{2+}, Zn^{2+} and Pb^{2+} play an important role in modification of physical property and structure (3). For instance it has been observed in alkali borate glasses with divalent ion (Pb^{2+}) that the ions prefer to have network forming as well as modifying positions depends upon the concentration of alkali oxide ie, upto 30 mol% of Li_2O, PbO act as a modifier and for above 30 mol% of Li_2O PbO act as a former. The presence of such divalent ion in glasses forms a covalent bonded open network over awide range of composition and they can be expected to give high ionic conductivities (4). Lead-containing mixed alkali borate glasses (LNBP) have low melting point and have been widely used as good sintering agents (5).B_2O_3 with modifier oxides exhibits unique structural features and is generally present in both three and four coordination of oxygen atoms (6). The proportion of trigonal and tetrahedral boron depends on both the chemistry and concentration of the added modifier oxides. Therefore, the addition of alkali oxide like Li_2O, Na_2O and K_2O to B_2O_3 causes the change of boron atom coordination number from 3 to 4 with the creation of BO_4 tetrahedral including pentaborate, triborate and diborate structural units (7, 8).

2. EXPERIMENTAL STUDIES

2.1 PREPARATION OF GLASSES

The glass samples having the general chemical formula xLi_2O - $50B_2O_3$ – (45-x) Na_2O- 05 PbO (where x = 20, 25, 30, 35 and 40 mol %) were prepared by melt quench method using the starting materials as Li_2O and B_2O_3 of reagent purity grade. The required amount (approximately 15g) in mol% of different chemicals in powder form was weighed using single pan balance having an accuracy of ±0.0001g.The homogenization of the appropriate mixture of the components of chemicals is affected 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 950 to 1000°C. The molten sample is cast into a copper mould having dimensions of 10mm diameter and 6mm length. Then the glass samples are annealed for three hours at 250°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

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

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

$$(V_m) = M/\rho \qquad (3)$$

Longitudinal modulu

$$(L) = \rho U_\ell \qquad (4)$$

Shear modulus

$$(G) = \rho U_s \qquad (5)$$

Bulk modulus

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

Poisson's ratio

$$(\sigma) = \left(\frac{L - 2G}{2(L - G)}\right) \qquad (7)$$

Young's modulus

$$(E) = (1 + \sigma)\, 2G \qquad (8)$$

Acoustic impedance

$$(Z) = U_\ell \rho \qquad (9)$$

Microhardness

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

Debye temperature

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

Where ρ, U_ℓ and U_s are the measured density, longitudinal and shear ultrasonic velocity and h, K, N and V_m are the Planck's constant, Boltzmann's constant, Avogadro's number and molar volume 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)

$$T_s = \left(\frac{M_w}{C\rho}\right) U_s^{\,2} \qquad (12)$$

Where M_w, the molecular weight of the glass and C, is constant equal to 0.5074 × $10^5 cmK^{-1/2}$ s.

Thermal expansion coefficient

$$(\alpha_p) = 23.2\ (U_l - 0.57457) \qquad (13)$$

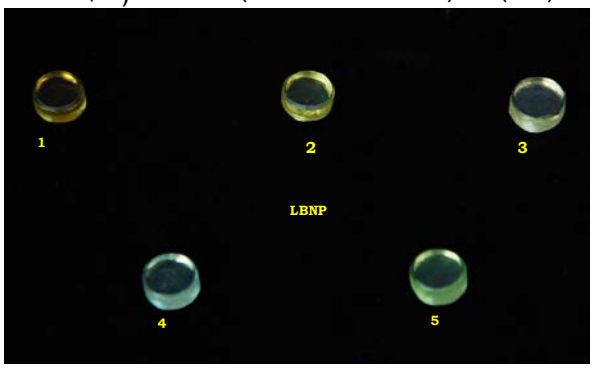

Fig.1Photograph of Glass Specimen

Table 2.1 Nominal composition of LBNP glass samples

	Nominal composition (mol %.)			
Specimen	**Li_2O**	**B_2O_3**	**Na_2O**	**PbO**
LBNP 1	20	50	25	05
LBNP 2	25	50	20	05
LBNP 3	30	50	15	05
LBNP 4	35	50	10	05
LBNP 5	40	50	05	05

X-ray diffraction

The structural study of the glass system can be explained by X-ray diffraction ptteren. The X-ray diffraction pattern of PBCW3 glass is shown in Fig 2. The XRD spectrogram shows no sharp peak which indicates the absence of crystalline nature.It confirms the amorphous nature of the prepared glass system.

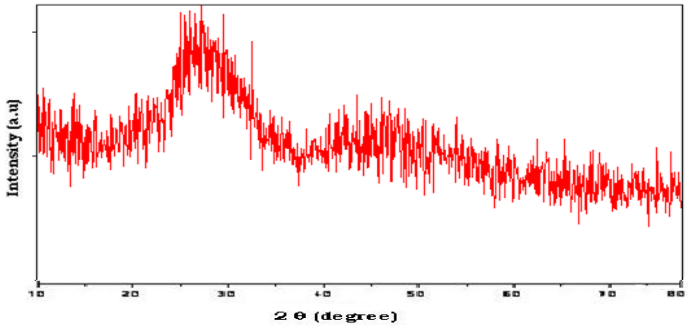

Fig.2 XRD patterns of PBCW3 glass

3. RESULTS AND DISCUSSION

Table 3.1 Values of density (ρ), molar volume (V_m), longitudinal velocity (U_l) andshear velocity (U_s) of LBNPglass 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)
LBNP 1	3.1533	21.387	3696.30	2192.86
LBNP 2	3.3720	19.524	3898.50	2362.86
LBNP 3	3.6813	17.448	4479.11	2614.37
LBNP 4	4.0272	15.550	4678.36	2907.51
LBNP 5	4.3953	13.883	4895.76	3221.47

Density measurement is widely used to study the effect of composition on glass structure (9). This measurement is 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 about different aspects of the glass structure.

The variation of density and molar volume is shown in Table. 3.1. As can be seen from the table that the density values of the present glass system increases with increasing Li_2O content and at the same time the corresponding molecular weight values decrease more rapidly so that the molar volume of the glass decreases. This behavior is attributed to an increase in rigidity and connectivity of the glass network as the lithium content increases, and the formation of three-dimensional covalent bond in the glass network.

The behavior of ultrasonic velocity (Uℓ and Us) and elastic modulii (L, G, E and K) is shown in Tables 3.1 - 3.2. It is observed from the tables that the velocities and all elastic modulii increases with increase in concentration of Li_2O modifier.

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

Specimen	Longitudinal modulus ($L \times 10^9$ Nm^{-2})	Shear modulus ($G \times 10^9$ Nm^{-2})	Bulk modulus ($K \times 10^9$ Nm^{-2})	Young's modulus ($E \times 10^9$ Nm^{-2})	Poisson's ratio (σ)
LBNP 1	43.08	15.16	22.86	37.25	0.2284
LBNP 2	51.24	18.82	26.14	45.54	0.2096
LBNP 3	73.85	25.16	40.30	59.96	0.1916
LBNP 4	88.14	34.04	42.75	80.70	0.1853
LBNP 5	105.34	45.61	44.53	102.01	0.1181

In borate glasses, addition of alkali oxides to B_2O_3 network creates $[BO_{4/2}]^-$ units up to 33.3 mol% of modifying oxide, further addition of modifying oxide leads to reconversion of $[BO_4]$ to $[BO_3]$ units and loose structure because of the presence of non bridging oxygen's (NBO's).

These results are already found in ternary

glass system LBN (10).

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 LBNP glass system

Specimen	Acoustic impedance ($Z \times 10^7 kgm^{-2} s^{-1}$)	Micro hardness ($H \times 10^9 Nm^{-2}$)	Debye temperature (θ_D K)	Softening temperature (T_sK)	Thermal expansion coefficient ($\alpha_p \times K^{-1}$)
LBNP 1	1.1655	2.7450	316.66	202.68	11826.321
LBNP 2	1.3145	3.6438	350.99	214.82	12473.361
LBNP 3	1.6488	5.1725	404.63	235.03	14331.313
LBNP 4	1.8840	7.1413	464.71	259.08	14968.913
LBNP 5	2.1518	11.6103	531.21	283.94	15664.593

In the glass system LBNP, if PbO were to be incorporated into the network as a glass modifier, one would have expected decrease in both velocities and elastic modulii when the effective concentration of modifier oxide to exceed 30 mol %. But above 30 mol% of Li_2O the network contains only BO_4 tetrahedral. This strongly indicates that the excess of oxygen supplied by the modifier has been utilized by Pb^{2+} and it is likely to be incorporated into the network as a glass former. So that, the ultrasonic velocities and elastic modulii values are increases above 30 mol% of Li_2O as shown in Tables 3.1 - 3.2.

Poisson's ratio has also been discussed in terms of the dimensionality of glass network. Poisson's ratio (σ) of the glass samples in the present study is found to decrease slowlywith increase in the concentration of Li_2O ($20 \le x \le 40$) as shown in Table 3.2. This composition dependence of Poisson's ratio might be due to the change in the structure of the glass systems.

Table 3.3 shows that, the increase in value of acoustic impedance (Z) and microhardness (H) of the glass system as a function of Li_2O concentration. The addition of Li_2O results in the formation of new network groups in the glass systems, which results in larger impedance for the propagation of ultrasonic waves in the specimens. Thereby, increase in acoustic impedance and decrease in the formation of non-bridging oxygen's (11). Further, the increase in micro hardness (H) strengthens the softening points, as the network modifier content is increased. This cause increases the rigidity of glassy network.

From the Table 3.3, the continuous increase of Debye temperature (θ_D) and softening temperature (T_s) also suggests that increase the compactness of the structure leading to increase in mean sound velocity (12).

Srivastava and Srinivasan (1997) have stated that the thermal expansion coefficient

of materials depends on the strength of bonds. Therefore, the increase in number of bonds per unit volume explains the increase in the values of thermal expansion co efficient as shown in Table 3.3. This indicates the increase in rigidity of the network structure, which confirms increase in elastic modulii.

CONCLUSION

The following are the conclusions drawn from the present study:

The density and elastic properties correlate well with the change in structure and rigidity of the glass network. On comparing the binary (LB) and ternary (LBN) glass systems, the structural compactness and rigidity of glass network is higher in LBNP glass system. This shows the constant addition of PbO increases the rigidity and compactness of the glass network. That is, Pb^{2+} ion prefers network-forming position. Hence PbO leads to tight packing of glass network.

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