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Structural and Elastic Properties of Li^{+} and W^{6+} Metal Ions Doped With Sodium Borate Glass Using Pulser – Receiver Technique

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Abstract: ***Longitudinal, shear ultrasonic velocities and attenuation were measured in different compositions of the glass systems of 20Na_2O-(80-x) B_2O_3-x Li_2O and 20Na_2O-(80-x) B_2O_3-xWO_3 (where x = 0 to 10 in steps of 2 mol%) at room temperature by using Pulser - receiver technique at 5 MHz. The glass samples were prepared by conventional melt-quenching method. The amorphous nature of the samples was ascertained using X-ray diffractometry (XRD). The density of the glass samples were measured by relative measurement method. The measured experimental values are utilized to evaluate elastic moduli, Poisson's ratio, acoustic impedance, internal friction, microhardness, Debye temperature, and thermal expansion coefficient. Trends of the coordination number, cross-link density, mechanical and thermal stability for the systems are discussed in terms of the structural changes taking place due to variations in composition.***

Keywords: Ultrasonic velocity, Attenuation, X-ray diffractometry, Elastic moduli, Microhardness.

1. Introduction

Elastic properties of solids are very significant, because their measurement gives information regarding the forces that are acting between the constituent atoms of a solid. This is important in interpreting and understanding the nature of bonding in the solids and non-destructive nature of the technique. Hence, elastic properties are suitable for describing the glass structure as a function of composition [1]. The role of Na_2O in the B_2O_3 network is to modify the host structure through the transformation of the structural units of the borate network from [BO_3] to [BO_4]. Tungsten-containing glasses have been studied for the favorable properties of tungsten ions, such as high electro-negativity, polarizability, large ion radius, and changeable valance [2, 3]. A review of literature indicates that attempts have been made to study the structural and physical properties of xLi_2O-(30-x)Na_2O-10WO_3-60B_2O_3 through IR [4] however, to the best of our knowledge, no ultrasonic study has been made on this kind of sodium borate glasses at room temperature. Therefore the objective of the present ultrasonic-based investigation has been made.

2. Materials and Methods

The glass samples of the formula 20Na_2O-(80-x)B_2O_3-xLi_2O and 20Na_2O-(80-x) B_2O_3-xWO_3 (where x = 0 to 10 in steps of 2 mol%) have been prepared by the conventional melt-quenching technique. Required quantities of analytical grade of Na_2CO_3, B_2O_3, Li_2CO_3 and WO_3 were obtained from E-Merck, Germany and Sd-Fine chemicals, India. The mixture is melted in alumina crucible at about 1053K for 45 minutes to homogenize the melt. Then the glass samples were annealed at 573K for two hours to avoid the mechanical strains developed during the quenching process. The amorphous nature of glass samples was confirmed by X-ray diffraction technique using an x-ray diffractometry Density (ρ), at room temperature was measured by following Archimedes principle. The ultrasonic wave (longitudinal and shear) velocities and attenuation of the glass specimens were measured using ultrasonic high energy Pulser receiver (PANAMETRICS – 5800 PR) technique at room temperature by making use of X-cut and Y-cut transducers at 5 MHz The attenuation coefficient a of the sample in neper per unit length is obtained from the relation

I= Io$e^{-\alpha t}$

Where, t is the thickness of the sample, I_o and I are the ratios of amplitude of the two successive echoes.

3. Theory and Calculation

The elastic and thermal properties of the glass specimens were calculated at room temperature by using the measured values of density (ρ), longitudinal velocity (U_l), shear velocity (U_S) and attenuation (α).

(i) Longitudinal modulus (L)

$$L = \rho U_l^2 \quad (1)$$

(ii) Shear modulus (G)

$$G = \rho U_S^2 \quad (2)$$

(iii) Bulk modules (K)

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

(iv) Poisson's ratio (σ)

$$\sigma = \left(\frac{L-2G}{2(L-G)}\right) \quad (4)$$

(v) Young's modulus (E)

$$E = (1+\sigma)\, 2G \quad (5)$$

(vi) Acoustic impedance (z)

$$Z = U_l \rho \quad (6)$$

(vii) Internal friction (Q^{-1})

$$Q^{-1} = \frac{\alpha}{8.66\pi f U_l} \qquad (7)$$

Where, α - attenuation coefficient and f -frequency of the quartz crystal

(viii) Microhardness (H)

$$H = (1-2\sigma)\frac{E}{6(1+\sigma)} \qquad (8)$$

(ix) Debye temperature (θ_D)

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

where, h, k, N, V_m and U_m are the Planck's constant (6.626×10^{-34}JS), the Boltzmann's constant ($1.38\times10^{-23}JK^{-1}$), the Avogadro's number ($6.023\times10^{23}mol^{-1}$), the molar volume and mean sound velocity of the sample respectively

where $U_m = \left[\frac{1}{3}\left(\frac{2}{U_S^3} + \frac{1}{U_l^3}\right)\right]^{-1/3}$

(x) Thermal expansion coefficient (α_p)

$$\alpha_p = 23.2\ (U_l - 0.57457) \qquad (10)$$

4. Result and Discussion

The experimental values of density (ρ), longitudinal ultrasonic velocity (U_l), shear ultrasonic velocity (U_s), and attenuation (α) of the sodium borate glasses with respect to the change in mol percentage of Li_2O and WO_3 used as network modifier (NWM) are listed in the Table 1. The related computed parameters are presented in the Tables 2-3. The X-ray diffraction patterns (Fig. 1) of the studied glass systems reveals the absence of any discrete or continuous sharp crystalline peaks, but show homogenous glassy characters.

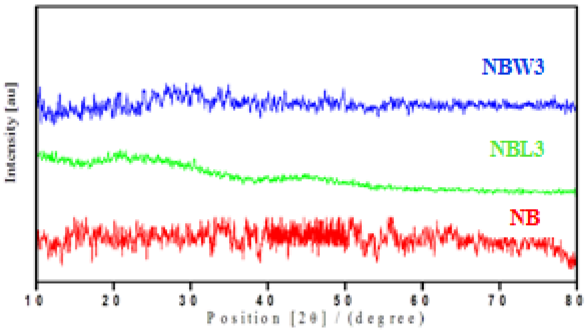

Figure 1: The powder XRD pattern of glass samples of NB, NBL3, and NBW3 at room temperature

The density is a powerful tool capable of exploring the changes in the structure of glasses. The density values (Table 1) were found to decrease with direct substitution of Li_2O and WO_3 by B_2O_3, Na_2O. The density values of NBL glass system are much higher than that of NBW glasses. Further, it is observed from the above table, the values of longitudinal velocity (U_l) and shear velocity (U_s) are increasing with increasing of Li_2O contents, and the same has decreased with increasing of WO_3 contents, but the rate of increase of U_l is greater than that of U_s. The increase of ultrasonic velocities is related to the decrease in the number of non-bridging oxygen and consequently the increase in connectivity of the glass network [5]. Further, the elastic moduli and attenuation explores more information about the structural changes and stability of the glass network [6]. Table-1 shows the values of attenuation are increasing with increasing of Li_2O concentrations, and it decreases with increasing of WO_3 concentrations which confirms the strengthening nature of these glasses as suggested from the composition dependence ultrasonic velocities [7].

The variation of longitudinal, shear, bulk and Young's moduli (Table 2) increases with increase in concentration of Li_2O and, it decreases with increasing of WO_3 concentrations. The obvious decreases in elastic moduli are due to the continuous reduction in the rigidity of glass samples [8]. In the studied glass system, the values of Poisson's ratio (Table 2) are increases with increasing of Li_2O and it reverses in WO_3 glasses. Further, these values are varying from 0.2 to 0.3. The decrease in Poisson's ratio is due to making of network linkages and formation of smaller structural units in the glass samples [9]. Further, an increase in cross-link density leads to a decrease in Poisson's ratio and vies-versa. Further, the increase in acoustic impedance and internal friction (Table 3) is due to the increase in compactness and rigidity of the structure of the Li_2O compared to WO_3 glass. The continuous decrease in microhardness, Debye temperature and thermal expansion coefficient observed in WO_3 glasses (Table 3) reveals the presence of Non-bridging oxygen ion (NBO) and this causes the formation of soft glassy network [10,11].

Table 1: Composition, measured values of density (ρ), longitudinal velocity (U_l), shear velocity (U_s) and attenuation (α) Of NB, NBL, and NBW glasses at room temperature.

Sample Label	Composition (mol %)	Density $\rho/(\times kg.m^{-3})$	Ultrasonic Velocity $U/(m.s^{-1})$		Attenuation α/(nepers.unit length^{-1})
			Longitudinal (U_l)	Shear (U_s)	
Na_2CO_3-B_2O_3 (NB)					
NB	80-20	1353.6	5209.30	2786.06	44.88
System 1 : Na_2CO_3-B_2O_3-Li_2CO_3 (NBL)					
NBL 1	20-78-2	1323.0	5485.44	2942.70	50.88
NBL 2	20-76-4	1309.9	5756.10	2994.92	51.58
NBL 3	20-74-6	1302.5	6020.94	3026.16	52.56
NBL 4	20-72-8	1204.7	6084.66	3074.87	71.00
NBL 5	20-70-10	1184.9	6250.00	3108.10	72.85

System 2 : Na_2CO_3-B_2O_3-WO_3 (NBW)					
NBW 1	20-78-2	1322.2	4919.15	2947.37	65.99
NBW 2	20-76-4	1261.0	4869.57	2879.58	57.91
NBW 3	20-74-6	1252.4	4695.65	2833.33	50.82
NBW 4	20-72-8	1224.9	4675.21	2813.57	38.39
NBW 5	20-70-10	1155.2	4641.35	2790.87	35.20

Table 2: Values of elastic moduli and Poisson's ratio of NB, NBL and NBW glasses at room temperature.

Sample Label	Longitudinal Modulus L/($\times10^{10}$ N.m^{-2})	Shear Modulus G/($\times10^{10}$ N.m^{-2})	Bulk Modulus K/($\times10^{10}$ N.m^{-2})	Young's Modulus E/ ($\times10^{10}$ N.m^{-2})	Poisson's Ratio (σ)
Na_2CO_3-B_2O_3 (NB)					
NB	3.6732	1.0507	2.2723	2.7311	0.2997
System 1 : Na_2CO_3-B_2O_3-Li_2CO_3 (NBL)					
NBL 1	3.9808	1.1457	2.4534	2.9740	0.29880
NBL 2	4.3401	1.1749	2.7735	3.0886	0.3144
NBL 3	4.7218	1.1928	3.1314	3.1752	0.3310
NBL 4	4.4602	1.1390	2.9415	3.0264	0.3285
NBL 5	4.6285	1.1447	3.1023	3.0579	0.3357
System 2 : Na_2CO_3-B_2O_3-WO_3 (NBW)					
NBW 1	3.1990	1.1486	1.6675	2.8023	0.2199
NBW 2	2.9902	1.0456	1.5960	2.5746	0.2311
NBW 3	2.7614	1.0054	1.4209	2.4528	0.2198
NBW 4	2.6773	0.9697	1.3844	2.3584	0.2161
NBW 5	2.4886	0.8998	1.2888	2.1898	0.2168

Table 3: Values of acoustic impedance (Z), internal friction (Q^{-1}), microhardness (H_v), Debye temperature (θ_D) and thermal expansion coefficient (α_p) of NB, NBL and NBW glasses at room temperature.

Sample Label	Acoustic Impedance Z /($\times10^7$kg. m^{-2}s^{-1})	Internal Friction (Q^{-1}) /($\times10^{-11}$ dB.s^{2}m^{-2})	Micro Hardness H_v/($\times10^9$ N.m^{-2})	Debye Temperature θ_D/(K)	Thermal Expansion Coefficient α_p/($\times10^2$ m.s^{-1})
Na_2CO_3-B_2O_3 (NB)					
NB	0.7051	2.1683	1.4032	296.60	1208.42
System 1 : Na_2CO_3-B_2O_3-Li_2CO_3 (NBL)					
NBL 1	0.7257	3.4110	1.5431	298.62	1273.49
NBL 2	0.7540	3.2954	1.4538	303.44	1335.28
NBL 3	0.7843	3.2103	1.3439	306.67	1396.73
NBL 4	0.7330	4.2912	1.3021	309.00	1411.51
NBL 5	0.7406	4.2865	1.2536	322.92	1449.87
System 2 : Na_2CO_3-B_2O_3-WO_3 (NBW)					
NBW 1	0.6504	4.9333	2.1448	292.34	1141.11
NBW 2	0.6141	4.3734	1.8742	227.90	1129.61
NBW 3	0.5881	3.9801	1.8780	268.85	1089.26
NBW 4	0.5727	3.0197	1.8353	261.86	1084.52
NBW 5	0.5362	2.7890	1.6986	260.75	1076.66

5. Conclusion

The elastic moduli of the $20Na_2O$-(80-x) B_2O_3-xLi_2O and $20Na_2O$-(80-x)B_2O_3-xWO_3 glass systems show many enhancements with the progressive addition of Li_2O and WO_3. The enhancements were attributed to the increase in the cross link density, and the rigidity of the glass network. The decrease in density of the glass specimens show that it depends on the atomic weight of the metal atom in the network modifier (NWM). The decreasing elastic moduli indicate a reduction in network rigidity of the glass samples. It is generally accepted that lithium and tungsten ion enter the glass structure originally in one valance state viz., Li^+ and W^{6+}. The estimated acoustical, elastic and mechanical properties of the lithium and tungsten doped with sodium borate glasses throw light on the rigidity and compactness in structural network. However the NBL series of glass possess higher rigidity, strength and compactness of the glass network over the NBW glasses.

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