

Effect of Doping by Different Transition Metals on the Acoustical Properties of Alkali Borate Glasses

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Longitudinal and shear ultrasonic wave velocities were measured in binary $\text{Li}_2\text{O}-2\text{B}_2\text{O}_3$ glasses doped with different transition metal oxides (TMOs) (where $\text{TMO} = \text{V}_2\text{O}_5, \text{Fe}_2\text{O}_3, \text{Cr}_2\text{O}_3, \text{NiO}, \text{TiO}_2, \text{MnO}_2$ and CuO) using pulse echo technique. Measurements were carried out at 4 MHz frequency and at room temperature. Elastic moduli and some other physical parameters such as acoustic impedance, Debye temperature, thermal expansion coefficient, and latent heat of melting were calculated. Results indicated that these parameters depend upon the TMO modifier i.e., the ionic radius of the transition metal cation. Quantitative analysis has been carried out, in order to obtain more information about the structure of these glasses, based on bond compression model, and the Makishima and Mackenzie model, i.e., the cation-anion bond of each TMO.

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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. Therefore, the choice of the most appropriate material for particular application requires knowledge of its mechanical properties. Hence, elastic properties are suitable for describing the glass structure as a function of composition [1]. There have been studies and reports [2–4] on several binary alkali borate glasses, which show that there is a correlation between elastic properties and borate glass structure. In $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ glass system [4], the elastic properties have been discussed in terms of boron coordination.

Oxide glasses containing transition metal oxides (TMO) are of continuing interest because of their applicability in memory switching, electrical threshold, and optical switching devices, etc. [5–7]. The structural and electronic properties of these glasses as well as their optical, magnetic, and mechanical properties depend on the relative proportions of the different valence states of the TM ions present. In case of borate glasses, the change of some BO_3 to BO_4 takes place with the addition of transition metal oxides [8].

Shelby [9] reported that glass transition temperature (T_g) is strictly related to cross-link density in the glass network, the tightness of packing in the network and the

coordination of the network formers. Mandal et al. [10] studied the (T_g) for $(\text{V}_2\text{O}_5)_{100-x}-(\text{Fe}_2\text{O}_3)_x$ glasses. They observed an increase in T_g with the increase in Fe_2O_3 content in the glass structure, and explained this as due to the higher cross-link density in the iron vanadate glasses than in the vitreous V_2O_5 . El-Alaily and Mohamed [11] have investigated the differential thermal properties and the crystallisation behaviour of binary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ glasses doped with V_2O_5 and Fe_2O_3 oxides. They reported that T_g and crystallisation temperatures (T_c) values of the glass composition doped with Fe_2O_3 are higher than that doped with V_2O_5 .

A series of borate rich metalloborophosphates doped with different transition metals (Fe, Ni, Cu) have been prepared by Tao Yang et al. [12]. Their structures have been solved by single crystal diffraction techniques. The authors reported that the transition metal ions are distorted octahedral coordinated, and the Cu^{2+} octahedrons with $\text{Cu}-\text{O}$ bond lengths are shorter than $\text{Ni}-\text{O}$ bonds which in turn are shorter than $\text{Fe}-\text{O}$ bonds.

Marzouk et al. [13] have investigated the optical properties of binary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ glasses doped with transition metals $\text{V}_2\text{O}_5, \text{Fe}_2\text{O}_3, \text{NiO}, \text{MnO}_2$ oxides. They observed that optical energy gap increases with transition metals as in the following order: $\text{V}_2\text{O}_5 < \text{Fe}_2\text{O}_3 < \text{NiO} < \text{MnO}_2$, which indicates the increase in the connectivity of the glass network structure with the same order.

El-Alaily and Mohamed [14] showed that the refractive index of lithium borate glass as a base glass composition has lower value than that with 2 wt.% of V_2O_5 , which is lower than that with 2 wt.% of Fe_2O_3 . This increase in

refractive index from the base glass composition to that with 2 wt.% of Fe₂O₃, results in the compacting the glass structure.

In the light of these observations, the present study was aimed to investigate the influence of doping different types of TMO on the mechanical properties and the network structure of binary Li₂O–B₂O₃ glasses, using ultrasonic pulse-echo technique.

2. Experimental

2.1. Preparation of glasses

Binary Li₂O–B₂O₃ glasses doped with different TMO have been prepared by rapid quenching method. Batches of each glass composition are listed in Table I. The analytical grade materials of purity more than 99.9% of Li₂CO₃, H₃BO₃, and TMO chemicals were used to prepare the glass samples.

TABLE I
Composition of glasses.

Glass	Composition [mol.%]		
	Li ₂ O	B ₂ O ₃	TMO
A	33.38	66.62	0.0
B	33.35	66.55	0.1 (V ₂ O ₅)
C	33.35	66.55	0.1 (Fe ₂ O ₃)
D	33.35	66.55	0.1 (Cr ₂ O ₃)
E	33.35	66.55	0.1 (NiO)
F	33.35	66.55	0.1 (TiO ₂)
G	33.35	66.55	0.1 (MnO ₂)
H	33.35	66.55	0.1 (CuO)

Appropriate amounts in wt.% of chemicals in powder form were weighed using a digital balance (HR-200) having sensitivity of ± 0.0001 g. The homogeneity of the chemicals mixture was achieved by repeated grinding using an agate mortar. The mixture was preheated at 673 K for 60 min (in platinum crucible) to remove H₂O and CO₂. The preheated mixture was then melted in a muffle furnace whose temperature was controlled at 1373 ± 10 K for 120 min, and bubble free liquid was obtained. The mixture was stirred intermediately in order to obtain homogeneous mixture. The molten mixture was then poured in a cuboidal-shaped split mold made of mild steel which had been preheated at about 473 K. Annealing was carried out for a period of 120 min at 623 K. Bulk glass samples of about $1 \times 1 \times 4$ cm³ were therefore obtained.

In order to measure the ultrasonic velocity accurately, each glass sample was first ground on a glass plate using SiC abrasives by setting it in a holder to maintain the two opposite faces parallel. It was then polished with fine alumina abrasive and machine oil on a glass plate. The variation in the sample thickness was found to be ± 25 μ m. The amorphous nature in all glass samples was confirmed using X-ray diffraction (XRD).

2.2. Density measurements

Density (ρ) of all glass samples was measured employing the Archimedes principle at 298 K using toluene as buoyant and applying the relation

$$\rho = \rho_b \left(\frac{W_a}{W_a - W_b} \right), \quad (1)$$

where ρ_b is the density of the buoyant, W_a and W_b are the sample weights in air and the buoyant, respectively. The experiment was repeated three times, and the estimated error in density measurement for all glass samples was found to be ± 5 kg/m³.

2.3. Ultrasonic velocity measurements

The ultrasonic wave velocities were obtained applying pulse-echo technique by measuring the elapsed time between the initiation and the receipt of the pulse appearing on the screen of a flaw detector (USIP20 — Kräutkramer) via standard electronic circuit (Hewlett Packard 54615 B). The velocity was therefore, calculated by dividing the round trip distance by the elapsed time according to the relation

$$U = \frac{2X}{\Delta t}, \quad (2)$$

where X is the sample thickness and Δt is the time interval.

All ultrasonic wave velocity measurements were carried out at room temperature 298 K using Karl Deutsch transducer S12 HB4 with fundamental frequency of 4 MHz to measure longitudinal ultrasonic wave velocity, and Kräutkramer transducer K4KY with fundamental frequency of 4 MHz for measuring shear ultrasonic wave velocity. The estimated error in velocity measurements was ± 21 m/s for longitudinal wave velocity (U_l) and ± 10 m/s for shear wave velocity (U_s).

3. Determination of elastic moduli

Elastic moduli (longitudinal L , shear G , bulk K , and Young's E) as well as the Debye temperature (θ_D), softening temperature (T_s), and Poisson's ratio (σ) of binary Li₂O–B₂O₃ glasses doped with different TMOs have been determined from the measured ultrasonic wave velocities and density using the relations [15]:

$$L = \rho U_l^2, \quad G = \rho U_s^2, \quad K = L - \left(\frac{4G}{3} \right),$$

$$E = (1 + \sigma)2G, \quad \sigma = \frac{L - 2G}{2(L - G)}. \quad (3)$$

The Debye temperature of the glass samples was obtained from the relation given by [16] as

$$\theta_D = \left(\frac{h}{k_B} \right) \left(\frac{3\psi N_A}{4\pi V_a} \right)^{\frac{1}{3}} U_m, \quad (4)$$

where h is Planck's constant, k_B is Boltzmann's constant, N_A is Avogadro's number, V_a is the molar volume calculated from the effective molecular weight and density (i.e. M/ρ), Ψ is the number of atoms in the chemical formula, and U_m is the mean ultrasonic velocity defined

by the relation

$$U_m = \left[\frac{1}{3} \left(\frac{1}{U_l^3} + \frac{2}{U_s^3} \right) \right]^{-\frac{1}{3}}. \quad (5)$$

The transmission and reflection of sound energy in the glass sample was determined using the acoustic impedance Z_i given by the relation

$$Z_i = U_m \rho. \quad (6)$$

The latent heat of melting (ΔH_m) as well as the diffusion constant (D_i) are given by the relationships [17]:

$$\Delta H_m = \frac{9M}{128} \left(\frac{\theta_D r_i k_B}{h} \right)^2, \quad D_i = \frac{k_B r_i^2 \theta_D}{96h}, \quad (7)$$

where r_i is the bond length of oxide constituents in terms of chemical composition of prepared glasses.

4. Theoretical models

4.1. Bond compression model

The structure of oxide glasses can be described in terms of the bond compression model which was first introduced by Bridge et al. [18] for the study of single-component glass, and later developed for multi-component glasses [19]. The model assumed two assumptions:

(i) The elastic moduli only depend on the ‘‘connectivity’’ of the network (number of bonds per cation) and the average force constant. The calculated bulk modulus (K_{bc}) according to this model and the first-order stretching-force constant f , can be estimated according to the relations

$$K_{bc} = \frac{\rho N_A}{9M} \sum_i^n x_i (n_f) r_i^2 f_i \quad [\text{GPa}], \quad f_i = 1.7/r_i^3, \quad (8)$$

where x_i is the mole fraction of the i -th oxide, n_f is the number of network bonds per glass formula unit, r_i is the bond length. Accordingly, the average bond stretching-force constant \bar{F} for a three-dimensional poly-component oxide glasses can be estimated [19].

(ii) The ratio between the calculated bulk moduli and the experimental one (K_{bc}/K_{exp}) is assumed to be directly proportional to the atomic ring size (ℓ). The atomic ring size is defined as the ring perimeter (number of bonds times bond length divided by π), and is given by the relation

$$\ell = \left(0.0106 \frac{F_b}{K_{exp}} \right)^{0.26} \quad [\text{nm}], \quad (9)$$

where K_{exp} is the experimental bulk modulus and F_b is the bond bending force constant of the glass, which is proportional to the average bond stretching force constant \bar{F} .

4.2. Makishima and Mackenzie model

Makishima and Mackenzie [20, 21] presented theoretical model to calculate the elastic moduli of oxide glasses in terms of chemical composition, which depends only on packing density (V_t) and dissociation energy (G_t) of the

oxide constituents. The elastic moduli and Poisson’s ratio were given as follows:

$$E_m = 2V_t G_t, \quad k_m = \beta V_t E_m, \quad G_m = \frac{3E_m K_m}{9K_m - E_m},$$

$$\sigma_m = \frac{E_m}{2G_m} - 1, \quad (10)$$

where β is the slope deduced from the linear regression between the experimentally obtained bulk modulus and the product of the packing density multiplied by the experimentally obtained Young modulus.

5. Results and discussions

The density and molar volume of the glass network depend upon many factors such as structure, coordination number, cross-link density, and dimensionality of interstitial spaces [22].

Experimental values of density, molar volume, and ratio of the molar volumes $V_m(\text{BO}_4)/V_m(\text{BO}_3)$ which was calculated according to Kodama et al. [23] using fractions of BO_4 units (N_4) values (almost equals 0.5) calculated theoretically according to Inaba et al. [24] are tabulated in Table II. The density value of pure lithium borate glass composition (sample A) is 2230 kg/m³. In addition, the values of the densities of doped glasses with transition metals (samples from B to H) are slightly increased till they reach the value of 2253 kg/m³ for the glass composition doped with CuO as seen in Fig. 1. This is due to

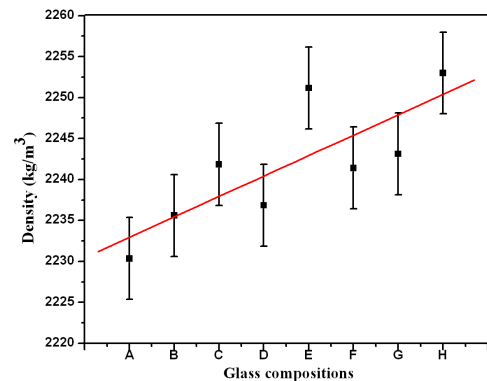


Fig. 1. Variation of density with glass compositions.

the direct addition of 0.1 mol.% of transition metals to the pure composition. On the other hand, the values of molar volume of the studied glasses are slightly decreased from 25.2673 m³/(kg mol) for the pure glass composition (sample A) to 25.0236 m³/(kg mol) for sample H. This decrease in the molar volume of the present glasses may be attributed to the increase in ionic radii of the TMO ions from vanadium to copper which fill the interstices of the glass network structure. Furthermore, the values of the ratio of the molar volumes $V_m(\text{BO}_4)/V_m(\text{BO}_3)$ were found to change slightly from 0.335 to 0.322 indicating that BO_4 units are preferentially included in the six-membered rings of pentaborate groups which are transformed from boroxol rings [23].

TABLE II

Variation of density ρ , molar volume V_a , ratio $V_m(\text{BO}_4)/V_m(\text{BO}_3)$, longitudinal velocity U_1 , shear velocity U_s .

Glass	ρ [kg/m ³]	V_a [m ³ /(kg mol)]	$\frac{V_m(\text{BO}_4)}{V_m(\text{BO}_3)}$	U_1 [m/s]	U_s [m/s]
A	2230±5	25.267±0.002	0.335	6059±21	3702±10
B	2236±5	25.264±0.002	0.335	6263±21	3732±10
C	2242±5	25.184±0.002	0.331	6328±21	3742±10
D	2237±5	25.237±0.002	0.333	6342±21	3747±10
E	2251±5	25.042±0.002	0.323	6428±21	3801±10
F	2241±5	25.153±0.002	0.329	6632±21	3848±10
G	2243±5	25.137±0.002	0.328	6796±21	3863±10
H	2253±5	25.024±0.002	0.322	7155±21	3990±10

Values of ultrasonic wave velocities (longitudinal and shear), elastic moduli, and Poisson's ratio of the investigated glasses are also listed in Table II. Both longitudinal (V_1) and shear (V_s) wave velocities increased from 6059 and 3702 m/s to 7155 and 3990 m/s, respectively, for pure composition (sample A) and those doped with 0.1 mol.% of different (TMO) ions from samples B to H as given in Table II and shown in Fig. 2. This means that the values of the measured wave velocities of the studied samples doped with TMO are in the following order: 33.38 Li₂O – 66.62 B₂O₃ – 0.1 V₂O₅ < 33.35 Li₂O – 66.55 B₂O₃ – 0.1 Fe₂O₃ < 33.35 Li₂O – 66.55 B₂O₃ – 0.1 Cr₂O₃ < 33.35 Li₂O – 66.55 B₂O₃ – 0.1 NiO < 33.35 Li₂O – 66.55 B₂O₃ – 0.1 TiO₂ < 33.35 Li₂O – 66.55 B₂O₃ – 0.1 MnO₂ < 33.35 Li₂O – 66.55 B₂O₃ – 0.1 CuO. In general, the increase of ultrasonic wave velocity is related to the increase in connectivity of the glass network. This increase in ultrasonic wave velocities can be explained by the decrease in molar volume (i.e. the decrease in the inter-atomic spacing) which means that the TMO ions with octahedral coordination are involved in the glass network as modifiers by occupying the interstitial positions which cause the increase in the average number of the network bonds per unit volume. Therefore, it can be suggested that the TMO modification leads to an increase in the network connectivity of the studied glasses with the mentioned order, supporting the preliminary works [10–14] on lithium borate glasses doped with different transition metal oxides.

Table III gives the experimentally estimated values of the elastic moduli: longitudinal modulus L , shear modulus G , Young's modulus E , bulk modulus K . As seen from Table II, all elastic moduli values showed that the lowest values are for the pure lithium borate glass composition. These parameters have the values of 81.9 GPa, 30.6 GPa, 73.5 GPa, and 41.1 GPa, respectively. Doping with 0.1 mol.% of TMO ions from V₂O₅ to CuO will cause an increase in elastic moduli to 115.9 GPa, 35.9 GPa, 91.4 GPa, and 67.5 GPa, respectively, as shown in Table II. Rajendran et al. have investigated the mechanical properties of P₂O₅–Na₂O–

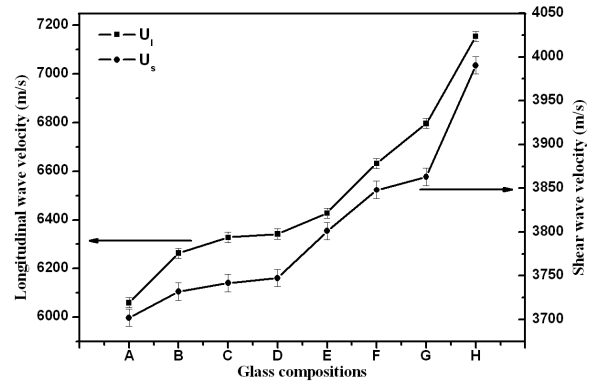


Fig. 2. Variation of (longitudinal and shear) ultrasonic wave velocities with glass compositions.

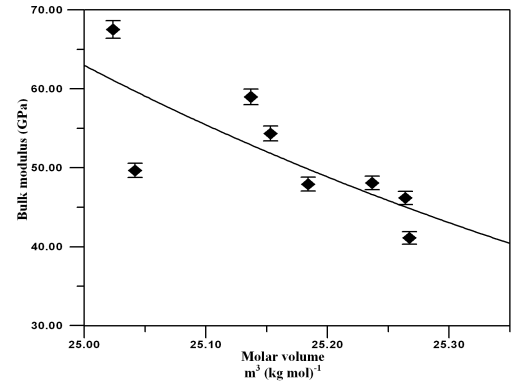


Fig. 3. Plot of bulk modulus with molar volume.

CaO–TiO₂ glasses [25]. The authors reported that the transition metal ions enter the glass network in a position which create a cross-linking between the phosphate tetrahedra (TM–O–P instead of P–O–P), and consequently improve the stability and mechanical properties of the glass [25].

Figure 3 shows the variation of bulk (K) modulus with the molar volume of glass compositions doped with different TMOs. From this figure it is noted that a decrease in volume should lead to an increase in bulk modulus with changing the type of TMO doped in the lithium borate glasses. 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, and the decrease in bulk modulus is associated with the change in the number of bonds per unit volume and coordination of the glass network [26]. Therefore, it is clear why the elastic moduli behaviours of the present glass system have increased in the same order as the ultrasonic wave velocities as well as the number of bonds per unit volume increases from 1.033×10^{28} to $1.044 \times 10^{28} \text{ m}^{-3}$ (see Table IV) which consequently means the increase in the connectivity of the network structure.

TABLE III

Variation of longitudinal modulus L , shear modulus G , Young's modulus E , bulk modulus K , ratio G/C_{12} , Poisson's ratio σ of all glass compositions.

Glass	L [GPa]	G [GPa]	E [GPa]	K [GPa]	G/C_{12}	σ
A	81.9±0.9	30.6±0.2	73.5±0.3	41.1±0.9	1.473±0.006	0.202±0.006
B	87.7±0.9	31.1±0.2	76.3±0.3	46.2±0.9	1.225±0.006	0.225±0.006
C	89.8±0.9	31.4±0.2	77.3±0.3	47.9±0.9	1.163±0.006	0.231±0.006
D	90.0±0.9	31.4±0.2	77.4±0.3	48.1±0.9	1.158±0.006	0.232±0.006
E	93.0±0.9	32.5±0.2	80.1±0.3	49.7±0.9	1.163±0.006	0.231±0.006
F	98.6±0.9	33.2±0.2	82.7±0.3	54.3±0.9	1.030±0.006	0.246±0.006
G	103.6±0.9	33.5±0.2	84.5±0.3	59.0±0.9	0.913±0.006	0.261±0.006
H	115.3±0.9	35.9±0.2	91.4±0.3	67.5±0.9	0.823±0.006	0.274±0.006

TABLE IV

Values of B–O bond lengths in BO_3 and BO_4 units, theoretical bond compression bulk modulus K_{bc} , K_{bc}/K_{exp} ratio, average ring diameter ℓ , average stretching force constant F , number of bonds per unit volume N_b , and packing density V_t of all glass compositions.

Glass	B–O (BO_3) [nm]	B–O (BO_4) [nm]	K_{bc} [GPa]	K_{bc}/K_{exp}	ℓ [nm]	F [N/m]	N_b $\times 10^{28}$ [m^{-3}]	V_t [m^3 / mol]
A	0.1289	0.1579	115.53	2.809	5.503	391.4	1.033	0.688
B	0.1289	0.1579	115.52	2.502	5.339	391.3	1.033	0.689
C	0.1288	0.1577	115.96	2.420	5.291	392.2	1.036	0.691
D	0.1289	0.1579	115.70	2.406	5.282	391.1	1.035	0.689
E	0.1286	0.1575	116.77	2.352	5.246	393.4	1.043	0.694
F	0.1288	0.1577	116.15	2.248	5.188	392.1	1.038	0.691
G	0.1287	0.1577	116.24	2.248	5.188	392.4	1.039	0.692
H	0.1285	0.1574	117.00	2.071	5.076	394.0	1.044	0.695

TABLE VI

Comparison of experimentally estimated elastic moduli (longitudinal L , bulk K , and Poisson's ratio σ) with those obtained theoretically using theoretical models.

Glass	L_{exp}^a [GPa]	L_{th}^b [GPa]	L_m^c [GPa]	K_{exp}^a [GPa]	K_{th}^b [GPa]	K_m^c [GPa]	σ_{exp}^a	σ_{th}^b	σ_m^c
A	81.9	85.3	86.7	41.1	45.2	47.1	0.202	0.227	0.239
B	87.7	96.3	88.3	46.2	51.0	48.9	0.225	0.227	0.249
C	89.8	100.1	89.0	47.9	53.0	49.7	0.231	0.227	0.252
D	90.0	100.4	88.9	48.1	53.2	49.7	0.232	0.226	0.253
E	93.0	103.8	91.0	49.7	55.0	51.7	0.231	0.227	0.261
F	98.6	108.3	92.1	54.3	57.3	53.2	0.246	0.227	0.269
G	103.6	108.3	93.1	59.0	57.3	54.4	0.261	0.227	0.273
H	115.3	118.7	97.5	67.5	62.8	59.1	0.274	0.227	0.291

^a Experimental.

^b Calculated using bond compression model.

^c Calculated using Makishima and Mackenzie model.

An important parameter describing the dimensionality of the glass system investigated is the ratio G/C_{12} given by Chen et al. [27], where $C_{12} = L - 2G$. The authors claimed that this ratio is considered as an indicator of the character of the force field. It was observed that $G/C_{12} = 1$ when the type of the forces is central, and $G/C_{12} \neq 1$ if the type of forces is non-central. Moreover, it was found that as the ratio of G/C_{12} approaches to unity, the central force field may reduce the fraction of the broken bonds in the glass structure. Therefore, the decrease of the ratio G/C_{12} from 1.473 for the pure glass composition to 0.823 for the glass composition doped with 0.1 mol.% of CuO (see Table III) indicates that the types of forces are non-central and also confirms the increase in the connectivity of the network structure.

Table III gives the values of Poisson's ratio σ . They have increased from 0.202 to 0.274 with changing the type of TMO ions from samples A to H. This increase in Poisson's ratio can be explained in terms of ionic bonds that are formed in the glass network. In addition, Bridge and Higazy [28] have suggested a close correlation between Poisson's ratio and cross-link density which is defined as the number of bridging bonds per cation. They reported that the cross-link density of two, one, and zero are related to the values of Poisson's ratio of 0.15, 0.39, and 0.4, respectively.

The Debye temperature (θ_D) is an important parameter of solids, which represents the temperature at which nearly all the vibrational modes are excited. Calculated values of the mean ultrasonic velocity U_m , Debye temperature θ_D , acoustic impedance Z , latent heat of melting ΔH_m , diffusion constant D_i , and thermal expansion coefficient α of the glasses under study are collected in Table V.

TABLE V

Variation of mean ultrasonic velocity U_m , Debye temperatures θ_D , acoustic impedance Z_i , latent heat of melting ΔH_m , diffusion constant D_i , and thermal expansion coefficient α of all glass compositions.

Glass	U_m [m/s]	θ_D [K]	Z_i $\times 10^{-6}$ [kg m ⁻² s ⁻¹]	ΔH_m $\times 10^3$ [J]	D_i $\times 10^9$ [m ² s ⁻¹]	α $\times 10^{-7}$ [1/°C]
A	4088±23	571±3	91.17±0.12	1.528	3.376	92.36
B	4131±23	577±3	92.35±0.12	1.565	3.414	91.78
C	4145±23	580±3	92.92±0.12	1.578	3.428	91.93
D	4152±23	580±3	92.86±0.12	1.581	3.431	91.62
E	4211±23	590±3	94.78±0.12	1.631	3.488	91.57
F	4270±23	597±3	95.71±0.12	1.673	3.533	90.32
G	4295±23	601±3	96.33±0.12	1.694	3.554	90.20
H	4443±23	623±3	100.10±0.12	1.817	3.681	88.67

It can be observed from Table V that the Debye temperature increased from 571 to 623 K, respectively, for glass compositions from A to H doped with 0.1 mol.% of

TMO. The increase in the mean ultrasonic velocity from 4088 to 4443 m/s and consequently the increase in the Debye temperature are mainly due to the increase of the number of bonds per unit volume as a direct effect of insertion of TMO ions into the glass network structure.

The values of the acoustic impedance Z_i were found to increase from 91.17×10^{-6} to 100.10×10^{-6} (kg m⁻¹ s⁻¹) when the glass compositions changed from A to H. The variation of the acoustic impedance indicates that the addition TMO ions (from V₂O₅ to CuO) causes the increase in connectivity of the glass network, thereby increasing the number of bonds per unit volume, resulting in higher impedance to the propagation of ultrasonic waves in the specimens [29].

Furthermore, latent heat of melting ΔH_m , and diffusion constant D_i were found to increase from 1.528×10^3 J and 3.376×10^9 m² s⁻¹, respectively, to 1.817×10^3 J and 3.681×10^9 m² s⁻¹, respectively. This increase with increasing the ionic radius of the TMO ions from vanadium to copper would explain the increase in the Debye and softening temperatures (i.e. the bond distances used in the calculations are taken approximately equal to the sum of the ionic radii of TM and oxygen ions [30]). Also, calculated values of thermal expansion coefficient α of the glasses under study (according to Makishima and Mackenzie [31]) were found to decrease from 92.36×10^{-7} to 88.67×10^{-7} 1/°C. Srivastava and Srinivasan [32] have stated that the thermal expansion coefficient of materials depends on the strength of bonds. Therefore, the increase in the number of bonds per unit volume explains the decrease in the values of thermal expansion coefficient which confirm the increase in experimental elastic moduli.

It is interesting to interpret the variation in the experimental elastic behaviours observed in this study with the bond compression model put forward by Bridge et al. [18] which extended by Abd El-Moneim et al. [33, 34], and Makishima and Mackenzie model [20, 21] for predicting the compositional dependence of elastic moduli of poly-component oxide glasses. Table IV gives the values of theoretical bond compression bulk modulus K_{bc} , ratio of K_{bc}/K_{exp} , atomic ring diameter (ℓ), average stretching force constant F , average cross-link density \bar{n}_c , and packing density V_t . It is quite clear from Table IV that the values of the bond compression bulk modulus K_{bc} (calculated employing the theoretically obtained B-O bond lengths in BO₃ and BO₄ units using the model proposed by Hager and El-Hofy [35]) are slightly increased from 115.53 to 117 GPa, for all glass compositions under study. Moreover, addition of very small amounts of TMO ions to the pure composition (sample A) causes the increase in the average stretching force constant F from 391.4 N m⁻¹ (for sample A) to 394.0 N m⁻¹ (for sample H). Therefore, the increase in the values of K_{bc} and F explains the increased elastic properties of the glasses network structures.

In general, the ratio K_{bc}/K_{exp} is a measure of the extent to which bond bending is governed by the con-

figuration of the network bonds, i.e. this ratio is assumed to be directly proportional to the ring diameter and inversely proportional to the experimentally determined elastic moduli. The values of K_{bc}/K_{exp} ratio and ℓ were found to decrease from 2.809 and 5.503 nm to 2.071 and 5.076 nm, respectively, as shown in Fig. 4. These increases in K_{bc}/K_{exp} and ℓ confirm the increase in elastic moduli and therefore the network structure becomes more compact. This is due to the increase in the number of bonds per unit volume from 1.033×10^{28} to $1.044 \times 10^{28} \text{ m}^{-3}$ as a direct effect of addition of 0.1 mol.% of TMO from V_2O_5 to CuO for glass samples A to H. Furthermore, the calculated values of the packing density V_t of the present glass compositions were found to increase slightly from 0.688 to 0.695 m^3/mol describing the increase in the rigidity of the network structure.

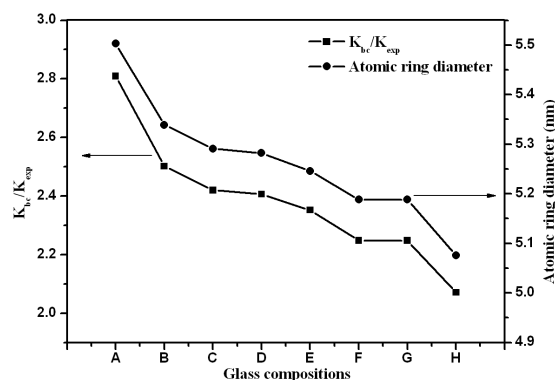


Fig. 4. Plot of the ratio (K_{bc}/K_{exp}) and atomic ring diameter (ℓ) against glass compositions.

Theoretically estimated values of elastic moduli (longitudinal L , bulk K , and Poisson's ratio σ) obtained using theoretical models were collected in Table VI. It is clearly noted that there is good agreement between the experimentally estimated elastic moduli and those theoretically estimated.

6. Conclusions

The density, ultrasonic wave velocities, and elastic properties of binary $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ glasses doped with different TMO from V_2O_5 to CuO have revealed the following conclusions:

1. The densities of the glass system studied were found to be slightly increased, while the molar volumes decreased.
2. Ultrasonic velocities (both longitudinal and shear), and the Debye temperature values increased with addition of small amounts of different TMO from V_2O_5 to CuO, which is interpreted as due to the increase in connectivity of the network structure.
3. Elastic moduli and Poisson's ratio increased, calculated values of thermal expansion coefficient de-

creased and number of bonds per unit volume increased, indicating the increase in rigidity of the network structure.

4. Theoretical values of elastic moduli and Poisson's ratio were calculated using theoretical model of bond compression and Makishima and Mackenzie's theory, and showed good agreement with the experimental ones.

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