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EFFECT OF FLY ASH ON THE Li_2O-B_2O_3 SYSTEM: STRUCTURAL STUDY BY PULSE ECHO TECHNIQUE

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Fly ash obtained from Toshkey project, which in turn was delivered from France, is a valuable source of many oxides such as SiO_2, Al_2O_3, Fe_2O_3, CaO and MgO. These oxides can provide a useful preliminary source for the preparation of glasses. Glass of the system 10 Li_2O – 90 B_2O_3 (wt %) has been prepared. The progressive addition of fly ash to this type of glass was made to study its effect on the chemical and physical properties of the parent glass. Room temperature ultrasonic measurements were performed by pulse-echo method. The densities of the prepared samples were measured to justify the packing arrangements of the constituent oxide. The variations in densities and ultrasonic velocities of the prepared samples containing progressive fly ash contents were correlated and discussed. The values of elastic moduli (including Young's modulus, bulk modulus, shear modulus and Poisson's ratio) were compared with those theoretically calculated in terms of Makishima–Mackenzie model and a model proposed by Rocherulle *et al*.

Key words: Lithium borate glasses, fly ash, elastic properties.

1. Introduction

The burning of coal in thermal power plants produces significant amounts of ashes. A number of methodologies of treatment and recycling have been developed to minimize the harmful effect in the environment caused by the landfill disposal of solid wastes [1–3]. Fly ash is usually a valuable source of useful minerals containing SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO and other oxides [4–5].

The addition of progressive amounts of fly ash to the Li_2O B_2O_3 glass system is believed to have great effect on the structural network. Parent lithium borate glass has only one glass former oxide, B_2O_3, which consists of both BO_3 and BO_4 groups, but the addition of such fly ash will provide some oxides having the ability to form network-forming groups such as SiO_2 besides Al_2O_3 and MgO. These specific oxides are known to strengthen the network structure of the borate glasses by forming strong bonds and superior chemical property [6].

The determination of elastic properties of glass is mostly essential as it involves the mechanical strength for the glass. The various advantages of ultrasonic technique over mechanical and other methods include the determination of the material properties without harming, comparative analysis loading and also, it provides the information about internal arrangements of the constituent oxides. This is possibly due to interaction of ultrasonic waves with macro, micro and sub-microscopic particles during wave propagation into the glasses containing the fly ash.

Therefore, in the present investigation, it is aimed at: (i) to prepare lithium borate samples with different additions of fly ash content, (ii) to study the change in the structure of the prepared glasses with the addition of fly ash content in light of both the measured ultrasonic velocities and density measurements.

2. Experimental work

The fly ash used in this study was obtained from Toshkey project which in its turn was delivered from France. Table 1 shows the chemical analysis of fly ash (wt %).

Table 1. Composition of parent fly ash glass.

Component	SiO_2	CaO	MgO	Al_2O_3	Na_2O	Fe_2O_3	SO_3
Analyzed composition (wt%)	46.38	13.09	12.05	9.22	7.18	4.20	3.50

The glasses having the formula 10 Li_2O – 90 B_2O_3 – x fly ash, $0 \leq x \leq 90$ (wt %), were prepared by mixing the desired amounts of reagent grade Li_2CO_3, H_3BO_3 and fly ash. The components were melted using porcelain crucibles in an electric furnace at a temperature ranging between 1100 and 1150°C, depending on the glass composition, for 3 h before being poured into preheated steel molds. To assure the homogeneity of the glass, the well-mixed components were added in small portions and the melt was swirled frequently. The glasses were annealed at about 350°C for 1 h to relieve the internal stresses and allowed to cool gradually to room temperature at a rate of about 30°C h^{-1}. The corresponding contents of the constituents of the glasses in mol % were tabulated in Table 2. The annealed samples were lapped and two opposite sides were finely polished to be suitable for the ultrasonic velocity measurements. Non-parallelism of the two opposite side faces was less than 0.01 mm.

Table 2. Glass compositions for fly ash lithium borate glasses (mol%).

Sample	fly ash	Li_2O	B_2O_3
FLB0	0	20.65	79.35
FLB1	9.2	18.7	72.1
FLB2	16.9	17.1	66.0
FLB3	23.4	15.8	60.8
FLB4	28.9	14.6	56.5
FLB5	33.7	13.6	52.7
FLB6	37.9	12.8	49.4
FLB7	39.4	12.5	48.1
FLB8	41.6	12.0	46.4
FLB9	47.8	10.7	41.5

The glassy samples were then examined by X-ray diffraction. The ultrasonic measurements were performed by a pulse-echo method with a Kraütkramer model USM3 pulser /receiver instrument with quartz transducers (both longitudinal and shear) operated at the fundamental frequency of 4 MHz at the room temperature. The velocity measurements were X-cut transducers employed for longitudinal modes and Y-cut ones for shear modes. The pulse transiting time was measured using a Hewlett–Packard model 54502A oscilloscope. Random errors in the measurements were $\pm$ 2% for longitudinal and shear velocities.

The densities of the glass samples were determined at room temperature using the Archimedes method with toluene as a reference immersion liquid. Four samples of each glass were used to determine the density (ρ). The density values were reproducible to ± 50 Kg/m^3. The molar volume (V_m) was calculated using the formula

$$V_m = \sum \frac{x_i M_i}{\rho}, \tag{1}$$

where x_i is the molar fraction for the component (i) and M_i is its molecular weight.

3. Determination of the experimental and theoretical parameters

3.1. The experimentally derived parameters

For isotropic amorphous solids like glasses, the elastic strain produced by a small stress can be described by two independent second-order elastic constants (SOECs), C_{11} and C_{44}. For pure longitudinal waves $C_{11} = \rho v_L^2$, and for pure transverse waves $C_{44} = \rho v_T^2$, where v_L and v_T are the longitudinal and transverse velocity, respectively. The elastic bulk modulus (K_e), Young's modulus (Y), the Debye temperature (θ_D)

and Poisson's ratio (σ) were determined from the measured ultrasonic velocities and the densities of the glasses using the standard relations [7–8]:

$$\sigma = 1/2 - C_{44}/2(C_{11} - C_{44}), \tag{2}$$

$$Y = 2(1+\sigma)C_{44} \qquad \text{(GPa)}, \tag{3}$$

$$K_e = C_{11} - 4/3C_{44} \qquad \text{(GPa)}, \tag{4}$$

$$\theta_D = (h/k)v_D \left[\frac{3q\rho N_A}{4\pi M}\right]^{1/3} \qquad \text{(K)} \tag{5}$$

where v_D is the mean ultrasonic velocity given by $\left[\frac{1}{3}\left(\frac{1}{v_L^3} + \frac{2}{v_T^3}\right)\right]^{-1/3}$, h is Planck's constant, N_A is Avogadro's number, q is the number of vibrating atoms per atomic volume, k is Boltzmann's constant, and M is its molecular weight.

3.2. *The theoretically computed parameters*

MAKISHIMA and MACKENZIE [9, 10] proposed a theoretical model to calculate the elastic moduli of oxide glasses in terms of chemical composition, packing density and the dissociation energy of the oxide constituents. The elastic moduli were represented in terms of these relations:

$$\text{Young's modulus,} \quad Y_{\text{cal}} = 83.6V_t \sum_i G_i x_i; \tag{6}$$

$$\text{Bulk modulus,} \quad K_{\text{cal}} = 100V_t^2 \sum_i G_i x_i, \tag{7}$$

$$\text{Shear modulus,} \quad S_{\text{cal}} = \left[\frac{300V_t^2}{10.2V_t - 1}\right] \sum_i G_i x_i; \tag{8}$$

$$\text{Poisson's ratio,} \quad \sigma_{\text{cal}} = 0.5 - \frac{1}{7.2V_t}, \tag{9}$$

where V_t, G_i and x_i are the packing density, the dissociation energy per unit volume and the mole fraction of the oxide component i, respectively.

$$V_t = \frac{\rho}{M} \sum_i V_i X_i. \tag{10}$$

The packing factor (V_i) of oxide $\mathrm{A}_m\mathrm{O}_n$ having ions A and O with Pauling radii (nm) R_A and R_O is given by:

$$V_i = (4\pi/3)NA[mR_\mathrm{A}^3 + nR_\mathrm{O}^3], \tag{11}$$

where R_A and R_O are the respective Pauling ionic radius of cation and anion. Table 3 presents the values of the density ρ, the effective molecular weight M, the dissociation energy per unit volume G, and the packing factor V_i of each oxide component

Table 3. Density (ρ), molecular weight (M), packing factor (V_i) and dissociation energy (G) of the incorporated oxides in the new glasses.

Oxide	ρ (kg/m^3)	M (g/mol)	V_i (m^3/mol) $\times 10^{-6}$	G (kJ/m^3) $\times 10^6$
Li_2O	2013	29.88	8	77.9
B_2O_3	2550	69.62	20.8	77.9 (4) 16.4 (3)
SiO_2	2533	60.08	14	68
Al_2O_3	4000	101.96	21.4	119.2
CaO	3340	56.08	9.4	64.1
Na_2O	2270	61.98	11.2	31.9
Fe_2O_3	5250	159.69	21.6	78.5
MgO	3600	40.30	7.6	90
SO_3	1920	80.06	20.8	54.07

presented in the studied glasses according to INABA *et al.* [11], who claimed that the dissociation energy of B_2O_3 had two values, 16.4×10^6 (coordination number 3) and 77.9×10^6 kJ/m^3 (coordination number 4). The computation of these parameters in borate glasses were performed according to SADDEEK [12] including the determination of N_4, the fraction of the 4-coordinated boron in the alkali borates. ROCHERULLE *et al.* [13] used the method of analysis of MAKISHIMA and MACKENZIE [9, 10] to study the glasses which have more than 100 GPa elastic moduli. The authors [13] found that the correlation between the determined experimentally and calculated elastic moduli is not satisfactory, so that some modifications were introduced for the packing factor of an oxide A_mO_n and expressed as:

$$C_i = (4\pi\rho/3M)NA[mR_{\rm A}^3 + nR_{\rm O}^3]. \tag{12}$$

Thus, the elastic moduli and Poisson's ratio will be expressed as

$$Y'_{\rm cal} = 83.6Ct\sum_i G_i x_i, \tag{13}$$

$$K'_{\rm cal} = 100C_t^2\sum_i G_i x_i, \tag{14}$$

$$S'_{\rm cal} = \left[\frac{300C_t^2}{10.2C_t - 1}\right]\sum_i G_i x_i, \tag{15}$$

$$\sigma'_{\rm cal} = 0.5 - \frac{1}{7.2C_t}, \tag{16}$$

$$C_t = \sum_i C_i X_i. \tag{17}$$

4. Results

X-ray diffraction patterns of the studied glass system show no discrete or continuous sharp peaks but the existence of undefined halo of the amorphous solids.

The compositional dependence of both the density and the molar volume for the lithium borate glasses modified by fly ash is shown in Fig. 1. It is observed that as the fly ash content increases, the rate of increase of ρ seems to be a decreasing function from 0 to 45.6 mol % fly ash. On the other hand, the molar volume has an opposite behavior, i.e., it decreases with the increase in the concentration of fly ash. Changes in the rate of the molar volume decrease can be observed after 33.7 mol % fly ash. The values of both ρ and V_m for 0 mol % fly ash are in the same range as those observed earlier by others [14–16].

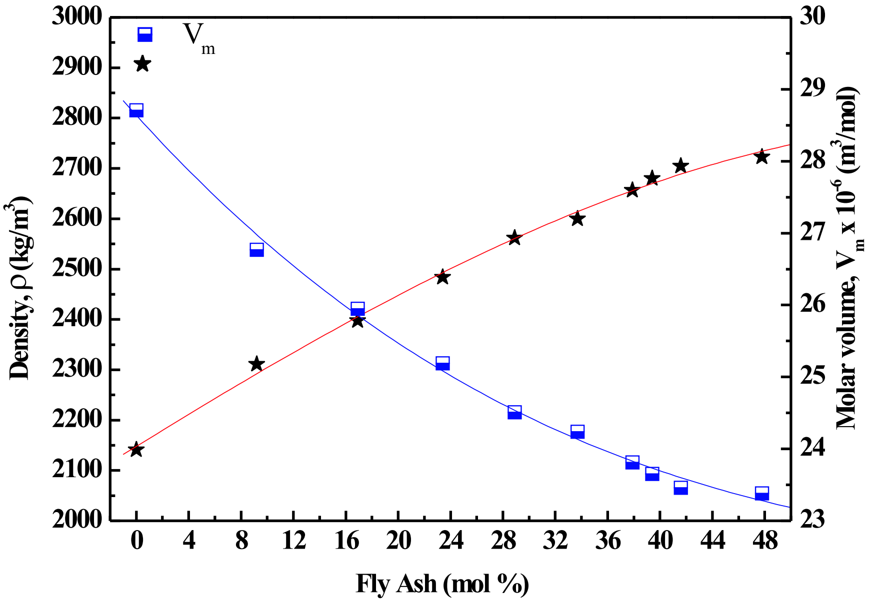

Fig. 1. Dependence of the density and the molar volume of the lithium borate modified by fly ash on the concentration of fly ash. The solid lines represent fitting of the calculated density and the calculated molar volume.

The experimental values of the ultrasonic velocities (both longitudinal and transverse), and elastic moduli of the glass samples at room temperature are given in Table 4.

The behavior of the ultrasonic velocities with the addition of fly ash, shows one maximum at 27.1 mol % and two minima at 21.8 and 39.4 mol % of fly ash. Ultrasonic velocities can be utilized in computing Poisson's ratio and Debye temperature according to Eqs. (2) and (5). The values of Poisson's ratio show a decreasing trend as the fly ash content increases, while the Debye temperature shows a similar behavior

Table 4. The ultrasonic longitudinal velocity (v_L), and the ultrasonic transverse velocity (v_T), Poission's ratio (σ), the Debye temperature (θ_D), the cross-link density (n_c), the number of network bonds per unit volume n_b, the experimentally determined moduli (bulk, K_e; Young, Y; and C_{12}), the fugacity (f_g), and the ratio (d) of the studied glass system.

Sample	v_L	v_T	σ	θ_D	n_c	$n_b\times 10^{28}$	K_e	Y	f_g	d	C_{12}
	m/s	m/s		K		m^{-3}	GPa	GPa			GPa
FLB0	5926	3305	0.27	502.5	1.4	7.17	44	59.6	0.021	2.1	28.41
FLB1	5972	3439	0.25	527.9	1.5	7.97	45.98	68.43	0.027	2.4	27.76
FLB2	6020	3446	0.26	529.9	1.6	8.47	48.94	71.55	0.026	2.3	29.95
FLB3	5919	3419	0.25	526.4	1.6	8.95	48.31	72.57	0.028	2.4	28.95
FLB4	6292	3602	0.26	556.1	1.7	9.38	57.11	83.52	0.026	2.3	34.95
FLB5	5990	3410	0.26	525.4	1.7	9.66	52.98	76.2	0.025	2.3	32.82
FLB6	5900	3364	0.26	518.7	1.8	9.9	52.4	75.72	0.025	2.3	32.35
FLB7	5597	3302	0.23	506	1.8	10.18	44.99	72.06	0.034	2.6	25.51
FLB8	5865	3417	0.24	523.1	1.9	10.37	50.94	78.52	0.030	2.5	29.88
FLB9	5981	3511	0.24	535.8	1.9	10.52	52.65	83.05	0.033	2.6	30.27

to the compositional dependence of the velocity with the increase in the concentration of fly ash.

The amorphous structure of a glass can be described by two parameters [17–21], one of them is the ratio (d), defined as the degree of the dimensionality of amorphous structure. HWA *et al.* [20] proposed that this ratio should be equal to 4 C_{44}/K_e. This ratio is 3 for the three-dimensional tetrahedral coordination polyhedron (e.g. pure vitreous SiO_2), while two-dimensional layer structures have $d = 2$. The second parameter given by CHEN *et al.* [21] is the ratio C_{44}/C_{12}, $C_{12} = C_{11} - 2C_{44}$. The authors [21] claimed that this ratio is considered as an indicator of the character of the force field. It was observed that $C_{44}/C_{12} = 1$ when the type of the forces is central (the case of our glasses) and $C_{44}/C_{12} \neq 1$ if the type of forces is non-central. It was found that, as the ratio of C_{44}/C_{12} approaches unity, the central force field may reduce the fraction of the broken bonds in the glass structure. The values of the experimentally determined elastic moduli were listed in Table 4. Figure 2 shows the compositional dependence of the ring diameter and Young's modulus on the fly ash content. The average atomic ring diameter was calculated according to BRIDGE *et al.* [8] as:

$$\ell = \left(\frac{0.0106\,\bar{F}}{K_e}\right)^{1/3.84}, \tag{18}$$

$$\bar{F} = \frac{\sum\limits_i x n_f \bar{f}}{\sum\limits_i x n_f}, \tag{19}$$

$$\bar{f} = 5.28\,\mathrm{O}\left[\frac{X_a X_b}{r^2}\right]^{3/4} + 30, \tag{20}$$

where x is the mole fraction, n_f is the number of network bonds per unit glass formula F is the average stretching force constant in Nm^{-1}, $\bar{f}$ is the first-order stretching-force constant, r is the bond length expressed in nanometers, O is the bond order (1, 2, or 3), X_a, and X_b are the electronegativities of the anion and the cation, respectively.

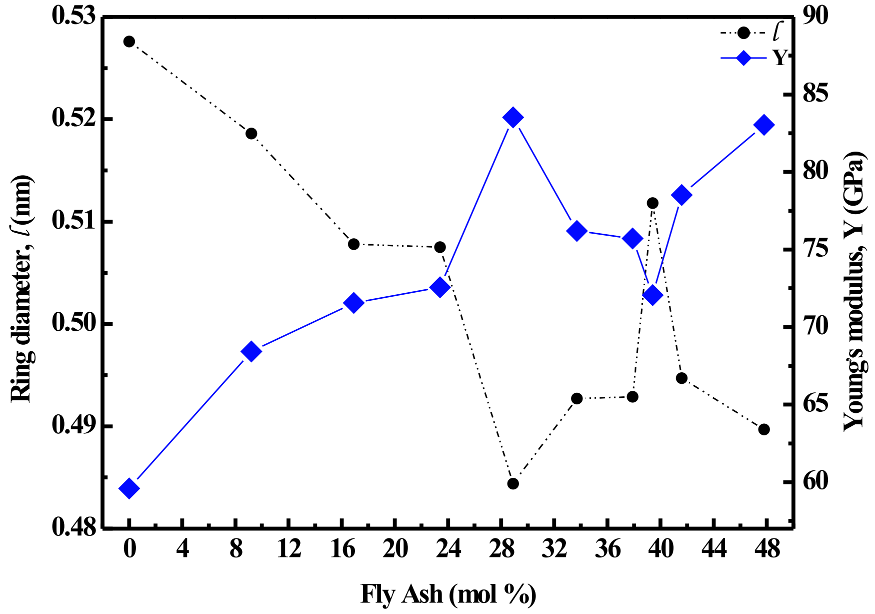

Fig. 2. Dependence of the average ring diameter and Young,s modulus of the lithium borate glass system modified by fly ash on the concentration of fly ash.

There is an inverse relation between these two parameters, e.g. for the sample FLB4, in Young's modulus behaviour, there is one maximum at 27.1 mol % fly ash in correspondence to a minimum in the behavior of the ring diameter.

Table 5 collects the values of the elastic moduli according to the models proposed by MAKISHIMA–MACKENZIE [9, 10] and by ROCHERULLE [13]. Figures 3, 4 show the relation between the experimentally determined elastic moduli and the theoretically computed elastic moduli according to the last two proposed models.

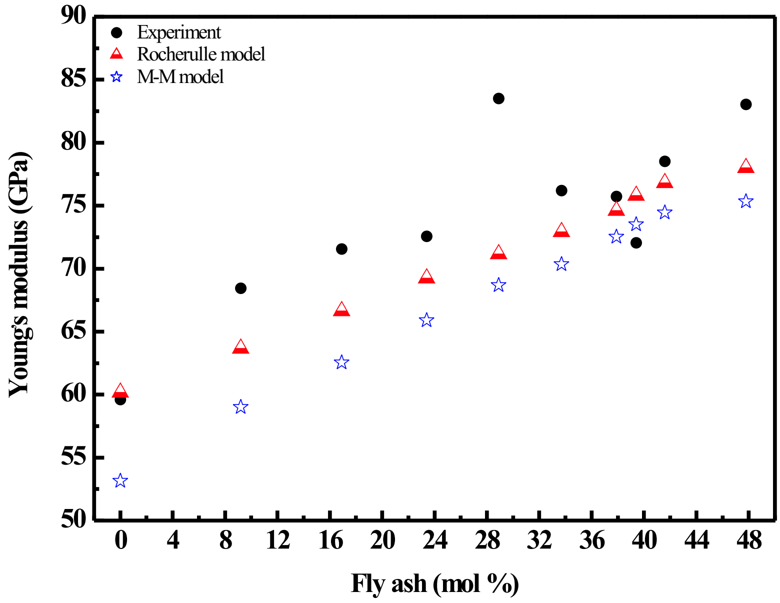

Fig. 3. Agreement between the experimental and theoretically calculated values of Young's modulus for the lithium borate glass system modified by fly ash.

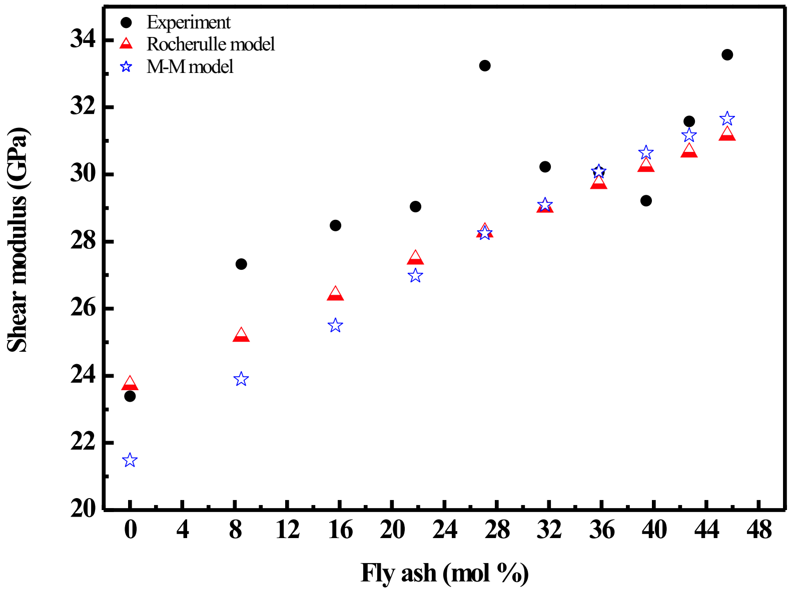

Fig. 4. Agreement between the experimental and theoretically calculated values of shear modulus for the lithium borate glass system modified by fly ash.

Table 5. Theoretically calculated packing density (V_t), new packing density (C_t), Poisson's ratio (σ_{th}), bulk modulus (K_{th}) according to Makishima–Mackenzie model, and Poisson's ratio (σ'_{th}), bulk modulus (K'_{th}) according to Rocherulle model for glasses based on fly ash.

	Calculated parameters according to Makishima–Mackenze model			Calculated parameters according to Rocherulle model		
Sample	V_t	K_{th} GPa	σ_{th}	C_t	K'_{th} GPa	σ'_{th}
FLB0	0.633	33.64	0.2806	0.7166	43.11	0.3062
FLB1	0.663	39.55	0.2905	0.7074	45.03	0.3037
FLB2	0.6705	42.78	0.2929	0.7002	46.65	0.3016
FLB3	0.6795	46.02	0.2956	0.6948	48.1	0.3001
FLB4	0.6878	48.86	0.2981	0.689	49.02	0.2984
FLB5	0.6866	50.22	0.2977	0.6845	49.91	0.2971
FLB6	0.6915	52.38	0.2992	0.6812	50.82	0.2961
FLB7	0.6884	53.07	0.2983	0.677	51.32	0.2948
FLB8	0.687	53.84	0.2978	0.6733	51.72	0.2937
FLB9	0.6843	54.43	0.297	0.6712	52.36	0.2931

5. Discussion

5.1. Density and molar volume

The density is an important measure of the glass; its value stands on its own as an intrinsic property capable of casting the light on the short-range structure. It is known that, boron oxide B_2O_3 in its glassy form is a laminar network consisting of boron atoms 3-fold coordinated with oxygen which can form six-membered boroxol rings (B_3O_6), as reported earlier by KROGH–MOE [22]. When an alkali oxide modifies the pure boron oxide, the additional oxygen, obtained by the oxide dissociation, causes a conversion from the trigonal boron atoms BO_3 into 4-fold BO_4 coordinated boron atoms. Each BO_4 structural group is negatively charged and the four oxygens are included in the network as bridging oxygen. These units are responsible for the increase in the connectivity of the glass network. As a result, the degree of the structural compactness, modification of the geometrical configuration, etc. in the glass network can vary with a change in the composition. Thus, the densities seem to clearly reflect the underlying atomic arrangements in a quantitative manner and lend support to the ideas of KROGH–MOE [22]. In the studied glasses, as shown in Fig. 1, the changes in both the density and molar volume at these concentrations are to be attributed to changes in the glass structure. It is generally accepted that the density increases when the concentration of the third component (fly ash) is increased while the ratio of the other concentrations remains constant ($Li_2O/B_2O_3 \approx 0.26$). The computed average atomic weight of fly ash is about 61. The decrease in the molar volume may be attributed to the creation of bridging oxygens (BOs), which will strengthen the network more and then the spaces in the network will decrease. The values of the density and the molar volume lie in the same range of the borosilicate glasses as reported by DOWEIDAR [23]. Also, it may be assumed that the addition of fly ash introduces extra network-former units giving compactness to the structure.

5.2. Ultrasonic velocity, Poisson's ratio and Debye temperature

It is well established that alkali oxides introduce non-bridging oxygen into the silica tetrahedra group in silicate glasses. As in borate glasses, the addition of alkali to borosilicate glasses causes the formation of four-coordinated BO_4 groups, which competes with non-bridging oxygen formation in the glass structure [24]. In fact, the structure of alkali borosilicate glasses [25] is composed of SiO_4 units with zero, one, or two non-bridging oxygens, boroxol rings consisting of BO_3 triangles and six-rings with one or two non-bridging BO_4 groups [23].

KODAMA [14] studied the binary glass system Li_2O–B_2O_3, and found that addition of Li_2O to the borate network will increase the density, and the connectivity of the network increases as Li_2O increases up to 28.1 mol % linearly. MAIA *et al.* [26], studied the electrical conductivity of lithium borosilicate glasses, and found that the addition of B_2O_3 up to 0.3 mol % will increase the electrical conductivity of the silica-rich to the boron-rich glass network, with no evidence of a former mixed effect. The authors [26] observed the borate anomaly and attributed it to the possibly structural modifications introduced by the substitution of SiO_2 by B_2O_3.

The compositional dependence of the ultrasonic velocity (longitudinal and shear) on the concentration of fly ash shows one maximum at 27.1 mol % and two minima at 21.8 and 39.4 mol % of fly ash respectively. The observed difference between higher and lower values in the velocity confirms a substantial change in the glass structure. The observed increase in the ultrasonic velocity for the sample FLB-4 implies a possible mechanism of the structural change for the role of SiO_2, CaO, and Al_2O_3 in the glasses. Also, the structure of this sample may contain less non-bridging oxygens. Addition of fly ash causes the values show constancy of Poisson's ratio to be about 0.26 from 0 to 35.8 mol % of fly ash and then decrease to be about 0.24 from 35.8 to 45.6 mol % of fly ash. It is known that Poisson's ratio is affected by the changes in the cross-link density of the glass network. Therefore, RAJENDRAN *et al.* [27], and BRIDGE *et al.* [8], proposed that a high cross-link density should have Poisson's ratio in the order of 0.1 to 0.2, while a low cross-link density has Poisson's ratio between 0.3 and 0.5. In the present system, Poisson's ratio decreases from 0.27 to 0.24 with increasing cross-link density (changes from 1.4 to 1.9, Table 4), when the fly ash content is increased. This supports the previous postulates. The observed variation in the Debye temperature, Table 4, supports the claim that addition of fly ash from 0 to 27.1 mol % creates BOs and then non-bridging oxygens (NBOs) will be created as the borate network is partly mixed with silicate network.

5.3. Elastic moduli determined experimentally

The changes in the nature of the chemical bond and the bond strength in the glass structure are normally incorporated in Young's modulus which has the ability to determine the fracture behaviour involved in the glasses. On the other hand, the bulk modulus is more sensitive in exploring the changes in the cross-link density and the bond stretching force constant, as stated by RAJENDRAN *et al.* [28]. In general, the elastic moduli decrease when the density or the ultrasonic velocity decreases. In this study, the elastic moduli have a similar trend as the compositional dependence of the velocity [Table 4]. Addition of fly ash causes the d-value to increase slightly from 2.1 to 2.6, i.e., the structure seems to be transformed slightly from two-dimensional layers to three-dimensional structure, with more cross-link density which characterizes the introduced silicate network by fly ash additions. Also, the type of the predominant forces is central as $C_{44}/C_{12} \approx 1$. This ratio is 1.8 for pure SiO_2 as deduced by HWA *et al.* [20]. This result agrees with the results of the cross-link density and Poisson's ratio.

Another important parameter in this study is the fluctuation free volume (fugacity f_g) which plays an important role in the molecular kinetic process in liquids. FERRY [29] reported that the proportion of free volume at the glass transition temperature (fugacity) characterizes the degree of rigidity of the glass network. Thus, the fugacity of the inorganic glasses and their structural features can be described using the mathematical formulation proposed by FERRY [29] as:

$$f_g \ln(1/f_g) = \frac{(1-2\sigma)^2}{2\,(1+\sigma)}, \tag{21}$$

where σ is Poisson's ratio. It is observed from Table 4 that the values of the fugacity increase as the fly ash content increases. The values of the fugacity for pure vitreous TeO_2, B_2O_3, and SiO_2 are 0.034, 0.018, and 0.078, respectively. Calculation of this parameter for Li_2O–B_2O_3 glasses [14] reveals an increase from 0.019 to 0.022. This variation in the values of the fugacity trend can be correlated to the slight transformation from two-dimensional layers to three-dimensional structure.

From the above results it is noted that the decrease in the molar volume should lead to an increase in the bulk modulus with increasing fly ash content. It is clear from the above results that the type of bonding in the network plays a dominant role in determining the bulk modulus rather than the volume (i.e. density). The bulk modulus of a covalent network is determined by the bond density (number of bonds in a unit volume), and by the stretching force constant [8]. The force constant is related to the cation field strength of the modifier, i.e. high field strength cations polarize their environment strongly and enhance the ion-dipole interaction. Increasing the cation field strength will increase the packing density due to the local contraction of the network around such a cation, together with the effects of increasing the bulk modulus. The observed variation in the bulk modulus is associated with an increase in the number of bonds per unit glass formula unit, with high values of the cross-link density and with a variation in the average atomic ring diameter. Thus, the change in dimensionality of the glasses will increase the rigidity of the network and decrease the average ring diameter, Fig. 2. The values of the calculated average ring size of these glasses confirm these results. The average ring diameter for pure SiO_2 is 0.58 nm [30].

5.4. Elastic moduli computed theoretically

The values of the experimentally determined elastic moduli of the studied glasses are compared with the theoretically calculated values from both the MAKISHIMA and MACKENZIE's model [9, 10], and ROCHERULLE's model [13] in Figs. 3–4. There is some kind of agreement of the values computed theoretically and determined experimentally of both Young's modulus and the shear modulus obtained for most of the studied glasses. The reason may be due to the cross-link density, number of bonds per unit volume, the fugacity, and the fractal bond connectivity models suggest a three-dimensional structure for these glasses. The disagreement between the experimental and the theoretically calculated results are in the range of 1–18% for Young's modulus. For the FLB4 glass the experimental value is significantly higher than that obtained from the models, while for the sample FLB7 the experimental value is lower than the values calculated from the models. The reason for the disagreement in the values of the two samples may be due to the existence of six-fold coordinated [AlO_6] structural unit, while the two models [9, 10, 13] used the packing density of four-fold coordinated [AlO_4] to do the calculation. In the used fly ash, the ratio of Al_2O_3 to CaO is about 0.7. HWA *et al.* [20] noticed a similar discrepancy in his study on low silicate content glasses containing Al_2O_3 and CaO (their ratio is 0.66). Therefore, one can claim that at this ratio, there is some disagreement between the values (computed theoretically and determined experimentally) of elastic moduli of these two samples. Other reasons may be the existence of borate anomaly and the dimensionality variation upon the transformation from the borate to silicate-rich structures, i.e, transformation from two-dimensional network to three-dimensional network.

6. Conclusions

Density and ultrasonic velocity measurements at room temperature of the studied glass system demonstrate that:

a) The density increases with increasing fly ash content. This is explained when the concentration of the third component (fly ash) is increased while the ratio of the other concentrations remain always constant (Li_2O / B_2O_3 $\approx$ 0.26). The molar volume will decrease due to the formation of BOs, which decreases the distances between the structural groups of the studied glass system and as a result, the packing density increases.

b) The variation of the ultrasonic velocities, and that of the Debye temperature with increasing fly ash content, is attributed to the transformation from pure borate structure to mixed borate and silicate networks.

c) The variation in the compositional dependence of the elastic moduli, the ratios d, and C_{44}/C_{12}, the fugacity, and Poisson's ratio on the fly ash content is attributed to the progressive transformation from the borate-rich structure to a matrix of covalent bonds (BOs), which characterizes the silicate glasses and results in more packing of the glass network. Also, the ring diameter will behave in inverse relation to Young's modulus.

d) There is a good agreement between the elastic moduli determined experimentally and that computed theoretically according to Rocherulle's model than the calculated moduli according to Makishima–Mackenzie model.

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