

Interpretation of mechanical properties and structure of $\text{TeO}_2\text{--Li}_2\text{O--B}_2\text{O}_3$ glasses

Yasser B. Saddeek^{a,*}, H.A. Afifi^b, N.S. Abd El-Aal^b

^aPhysics Department, Faculty of Science, Al-Azhar University, P.O. 71452, Assiut, Egypt

^bUltrasonic Laboratory, National Institute for Standards, Tersa Street, P.O. 136, Giza Egypt

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Abstract

Lithium borate glasses containing TeO_2 as $\text{Li}_{0.6}\text{Te}_x\text{B}_{1.4-2x}\text{O}_{2.4-x}$ have been prepared by the conventional rapid quenching method over a wide range of composition ($x = 0, 0.1, 0.2, 0.3,$ and 0.35). Ultrasonic velocities (longitudinal and shear) were measured in these glasses at room temperature. The elastic moduli, and the Debye temperature, were calculated and discussed quantitatively in terms of the glass transition temperature, the cross-link density, and the packing density. The monotonic decrease in the velocities, the glass transition temperature, and the elastic moduli as a function of TeO_2 modifier content reveals the loose packing structure, which is attributed to the increase in the molar volume and the reduction in the vibrations of the borate lattice. The compositional dependence of these parameters suggested that TeO_2 changes the rigid character of $\text{Li}_{0.6}\text{B}_{1.4}\text{O}_{2.4}$ to a matrix of ionic behavior bonds by breaking down the lithium borate structure. This was attributed to the creation of more and more discontinuities and defects in the glasses.

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1. Introduction

There is a renewed interest in the investigation of the fast ion conducting lithium borate glasses, which have potential as electrolytes for lithium batteries. Glasses with covalent networks often tend to possess open structures and support high ionic conductivities. The investigation of the structures of such materials is essential in order to give a better insight into structure–property relations [1–5]. Stable lithium-modified borate glasses are known to form over wide range of compositions. The role of Li_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 $[\text{BO}_3]$ to $[\text{BO}_4]$. The BO_4 units give rise to tetrahedral network features of the glass [6–10]. A variety of anionic borate species such as penta-, tetra-, tri-, di-, pyro-, and ortho-borates besides structural entities like

boroxol rings with intermediate range order have been identified in modified borate glasses [10,11]. The concentration of the various borate species in the glass structure is determined by the nature and concentration of modifier oxides. This affects the BO_4/BO_3 ratio, for example, the addition of lithium oxide, unlike other alkali oxides, not only modifies the B–O–B bonds but also breaks up the tightly organized diborate units [12,13]. On the other hand, the pure TeO_2 is a conditional glass former, requiring fast quenching to form glass. The presence of TeO_2 into the matrix of alkali borate glasses decreases its hygroscopic nature, improves the glass quality, and enhances the IR transmission [14–16].

The measurement of elastic properties of glasses by ultrasonic pulse-echo methods becomes a more interesting subject, due to the non-destructive nature and the high precision of the technique. This measurement yields valuable information regarding the forces operating between the atoms or ions in a solid. Since the elastic properties describe the mechanical behavior of the materials, so, the study of

*Corresponding author. Tel.: +20 103620536; fax: +20 88325436.

E-mail address: ysaddeek2001@yahoo.com (Y.B. Saddeek).

these properties is of fundamental importance in interpreting and understanding the nature of bonding in the solid state [17–19].

Therefore, in the present investigation, an attempt has been made to complete a previous work [15] and to explore the elastic constants and their influence on the structure and the stability of the lithium borate glasses with different TeO₂ contents employing the ultrasonic studies. Furthermore, the validity of the Makishima and Mackenzie [20–22] model has been examined for the studied glass system.

2. Experimental details

Samples of the vitreous system Li_{0.6}Te_xB_{1.4–2x}O_{2.4–x} with $x = 0, 0.1, 0.2, 0.3,$ and 0.35 were prepared from appropriate amounts of annular grade TeO₂, Li₂CO₃, and H₃BO₃. Calculated quantities of the chemicals were mixed thoroughly in an agate mortar. The powdered mixture was then contained in a ceramic crucible and melted in an electrically heated furnace under ordinary atmospheric condition at temperature depending upon the composition of each sample. These temperatures ranged between 950 and 1050 °C. Better homogeneity of the melt was achieved by removing the crucible from the furnace and swirling several times. The melt was then cast onto preheated stainless-steel mold in the form of a rectangular slab, which was transferred immediately to the annealing furnace adjusted at 275 °C for 1 h. The furnace was switched off and the glass samples were allowed to cool inside until it reached the room temperature. The obtained glasses were lapped and two opposite sides were polished to be suitable for the use in the ultrasonic velocity measurements. Non-parallelism of the two opposite side faces was less than 0.01 mm. The glassy samples were then identified by X-ray diffraction.

The thermal properties of these glasses as a function of TeO₂ were determined by the standard Shimadzu differential thermal analyzer system (DTA 50). The 15 mg powdered glass sample was placed in a platinum crucible and examined up to 1000 °C in argon medium with a heating rate 10 K/min. The powdered alumina was used as a reference material. The accuracy in the measurements of T_g is ± 2 K.

The density (ρ) of the glass samples was determined using Archimedes technique by using toluene as the worked fluid. The accuracy was about ± 5 kg/m³. The molar volume, V_m , has been determined as M/ρ , where M is the molar weight of the glass calculated by multiplying x times the molecular weights of the various constituents. The mean atomic volumes were also calculated as V_m/q , where q is the number of atoms in the unit formula.

Room temperature ultrasonic measurements were performed by a pulse-echo method with a Krautkramer model USM3 pulsar/receiver instrument with a quartz transducer. X-cut transducers were employed for longitudinal modes and Y-cut ones for shear modes. The operated frequency

was adjusted to 4 MHz. The pulse transiting time was measured using a Hewlett-Packard model 54502A oscilloscope. Random errors in the measurements were $\pm 2\%$ for longitudinal (v_L) and shear (v_T) velocities. The two velocities besides the density were utilized in determining the two independent second-order elastic constants (SOECs), namely, the longitudinal (C_{11}) and shear (C_{44}) moduli. C_{11} and C_{44} described the elastic strain produced by a small stress in an isotropic amorphous solids like glasses. For pure longitudinal waves $C_{11} = \rho v_L^2$, and for pure transverse waves $C_{14} = \rho v_T^2$. The elastic bulk modulus (K_e), Young's modulus (Y), the Debye temperature (θ_D), and Poisson's ratio (σ) can be determined using C_{11} and C_{44} according to the standard relations adopted elsewhere [23].

3. Results and discussion

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

3.1. Density and molar volume

The density is an intrinsic property capable of casting the light on the short-range order structure of a solid like glass. It is known that, B₂O₃ in its glassy form is a laminar network consisting of boron atoms three-fold coordinated with oxygen. Upon modification with an alkali oxide, the additional oxygen, obtained by the oxide dissociation, causes a conversion from the trigonal boron atoms BO₃ into four-fold BO₄-coordinated boron atoms. Each BO₄ 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 be varied with a change in the composition. Thus, the density clearly reflects the underlying atomic arrangements in a quantitative manner and lends support to the ideas of Krogh-Moe [24]. In a structural study on Li₂O–B₂O₃ glass system by Kodama et al. [9], the density and the connectivity of the network were found to increase linearly with the addition of Li₂O to the borate network. However, in the present study, the substitution of TeO₂ having high-density value (5101 kg/m³) [14] for Li_{0.6}B_{1.4}O_{2.4} having low-density value (2266 kg/m³) [25] lead to a linear increase in the density (Table 1), as the TeO₂ content increases. These values are greater than the density of pure B₂O₃ glass (1839 kg/m³) [9].

Generally, it is expected that the molar volume and the density should show opposite behavior to each other, but in the present investigated glasses the behavior is different. However, this anomalous behavior between the density and the molar volume was reported earlier for many glass systems, for example, LiBO₂–TeO₂ [5], Li₂O–Tl₂O₃–B₂O₃

Table 1

The density (ρ), the ultrasonic longitudinal velocity (V_l), the ultrasonic transverse velocity (V_s), the oxygen molar volume (V_o), the average force constant (F), the dissociation energy (G_i), the packing density (V_t), and computed elastic moduli [bulk modulus (K_m), and the shear modulus (S_m)] of the glass system $\text{Li}_{0.6}\text{Te}_x\text{B}_{1.4-2x}\text{O}_{2.4-x}$

Modifier content (mol. %)	ρ	V_l	V_s	$V_o \times 10^{-6}$	F	$G_i \times 10^6$	V_t	K_m	S_m
X	(kg/m ³)	m/s	m/s	(m ³ /mol)	Nm ⁻¹	kJ/m ³		(Gpa)	(Gpa)
0	2266	6400	3590	10.6	386	51.29	0.666	54.62	26.45
0.10	2613	5869	3341	11.1	368.7	52.56	0.641	51.76	26.24
0.20	2900	5400	3159	11.9	351.9	53.97	0.603	47.11	25.63
0.30	3190	5000	2950	12.6	335.6	55.52	0.570	43.28	25.19
0.35	3300	4714	2752	13.2	327.7	56.35	0.549	40.69	24.79

[6], and $\text{TeO}_2\text{-Na}_2\text{O-B}_2\text{O}_3$ [15]. The increase in the molar volume may be attributed to the following:

- (i) The density values of the present glass system increase with increasing TeO_2 content and at the same time the corresponding molecular weight values increase more rapidly so that the molar volume of the glass increases.
- (ii) The effect of the so-called open structure, discussed earlier by El-Egili and Oraby [6] and Krins et al. [26]. They consider that the presence of Li_2O creates non-bridging oxygens (NBOs), which opens the structure of the glass. Therefore, the tellurium ions cannot be accommodated in the voids associated with BO_4^- units upon its introducing as modifiers, without any expansion of the glass matrix, i.e., the molar volume increases. This is attributed to the larger radii of tellurium ions than the radii of the other ions in the present glasses (radii according to Shannon [27] were considered).

3.2. Thermal properties

It is known that the glass transition temperature (T_g) is affected by the alteration of the glass structure, and the structure of the thermally stable glasses is close packed one [28,29]. DTA curves for the studied glass samples with different TeO_2 contents have been obtained. Fig. 1 shows a typical DTA curve for $\text{Li}_{0.6}\text{Te}_{0.1}\text{B}_{1.2}\text{O}_{2.3}$ glass, in which the single endothermic peak is related to the glass transition temperature (T_g), followed by the onset crystallization temperature (T_x), while the exothermic peak is attributed to the full crystallization temperature (T_c). The single peak of T_g reveals the good homogeneity of the prepared glasses. The T_g dependence on the molar volume, as shown in Fig. 2, clarifies that the increase in TeO_2 content causes an increase in the molar volume, and a decrease in T_g values. The role of Li_2O in the studied glasses can be explained as part of it associates with B_2O_3 and the other part associates with TeO_2 . This association transforms the main structural units of $\text{Li}_{0.6}\text{B}_{1.4}\text{O}_{2.4}$ glass from BO_4 to BO_3 and also the structural unit TeO_4 characteristic of TeO_2 into TeO_3 . This behavior creates NBOs and expands the glass structure, as observed before [30]. Thus, the

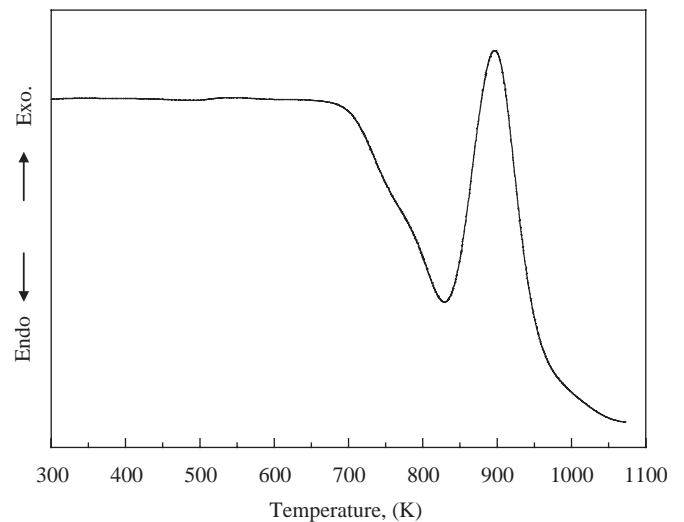


Fig. 1. DTA curve for $\text{Li}_{0.6}\text{Te}_{0.1}\text{B}_{1.2}\text{O}_{2.3}$ glass.

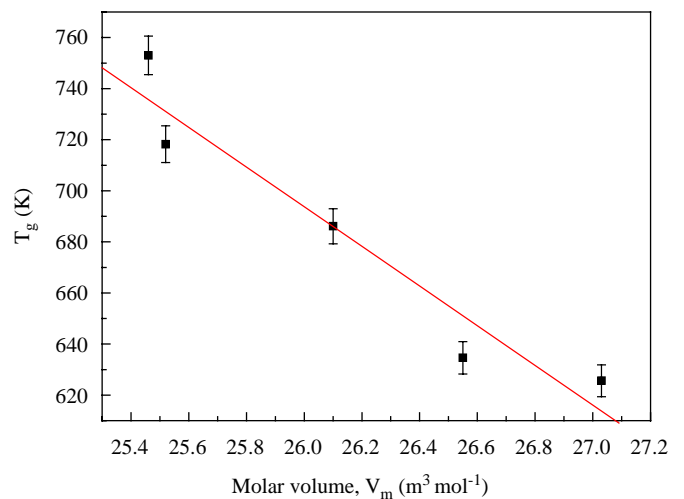


Fig. 2. Dependence of the glass transition temperature on the molar volume for the glass system $\text{Li}_{0.6}\text{Te}_x\text{B}_{1.4-2x}\text{O}_{2.4-x}$. The lines are drawn for guides to the eye.

variation in the T_g values indicates that the increase in TeO_2 content weakens the network structure by disrupting the Li-O-B bonds and forming new bonds such as Te-O-B or Te-O-Li bonds. Also, T_g may be attributed to the

cross-link density and the tightness of the packing in the network [31]. Roy [32] proposed that the cross-link density and the molar volume have greater effects on T_g than the bond strength. Cross-link density was calculated according to Bridge et al. [33,34]. In this study, the cross-link density is constant (1.6 ± 0.1) so the variation in the trend of T_g may be attributed to the variation in the molar volume.

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

The experimental values of ultrasonic velocities of all $\text{Li}_{0.6}\text{Te}_x\text{B}_{1.4-2x}\text{O}_{2.4-x}$ glasses are presented in Table 1. The compositional dependence of both the ultrasonic velocity and Debye temperature (Fig. 3) shows a monotonic decrease with an increase in the TeO_2 content. With the change in TeO_2 content, the values of Poisson's ratio remain almost constant to be about 0.25.

The observed continuous decrease in velocity with addition of TeO_2 is ascribed to the change in the coordination number. When TeO_2 is added to the rigid framework glasses $\text{Li}_{0.6}\text{B}_{1.4}\text{O}_{2.4}$, distorted TeO_4 units followed by creation of regular TeO_3 sites will be formed, besides the transformation of BO_4 into BO_3 . This ionic character bond results in a monotonic decrease in velocity (Table 1). The observed difference between higher values at low TeO_2 content ($x = 0$) and lower values at high TeO_2 content ($x = 0.35$) in the velocity confirms a substantial change in the glass structure. The value of the velocity (both longitudinal and shear) at $x = 0$ is in good agreement with Kodama et al. [9]. Thus, the direct replacement of one B_2O_3 by one TeO_2 diminishes the amount of oxygen atoms by merely one atom while the amount of boron decreases by two atoms. This means that the ratio of oxygen to boron atoms (O/B) or by other words the oxygen molar volume must increase (Table 1), and the number of BO_4 units (packed one) decrease while BO_3 units increase (loosed

packed). This behavior is confirmed by the results of the molar volume– T_g relation.

It is known that Poisson's ratio is affected by the changes in the cross-link density of the glass network. This means that as reported by Rajendran et al. [35,36], that high cross-link density structure has Poisson's ratio in the order of 0.1–0.2, while a low cross-link density structure has Poisson's ratio between 0.3 and 0.5. In the present system, Poisson's ratio is almost constant (0.25 ± 0.01) with almost constant cross-link density (1.6 ± 0.1), as the TeO_2 content is increased as $0 \leq x \leq 0.35$. The observed decrease in the Debye temperature supports the claim that addition of TeO_2 will loose the packed structure of the $\text{Li}_{0.6}\text{B}_{1.4}\text{O}_{2.4}$ glass which reduce the vibrations of the lattice of the formed glasses, as observed earlier by Bridge and Higazy. [34].

3.4. Elastic moduli determined experimentally

As stated by Rajendran et al. [37], Young's modulus is sensitive for any changes in the nature of the chemical bond and its strength, which characterize the glass structure, while, the bulk modulus is more sensitive in exploring the changes in the cross-link density and the bond stretching force constant. The elastic moduli of $\text{Li}_{0.6}\text{Te}_x\text{B}_{1.4-2x}\text{O}_{2.4-x}$ glasses show (Fig. 4) a decreasing trend similar to that of the velocities, with TeO_2 addition. The observed decrease in the elastic moduli with increasing TeO_2 content can be attributed to the increase of the molar volume which is expected if one takes into account that the values of bond lengths of Li_2O and TeO_2 are 1.59 nm [38] and 1.99 nm [14], respectively, while their cations were coordinated with four oxygens. In other words, TeO_2 changes the packed structural units BO_4 and TeO_4 into loose-packed units BO_3 and TeO_3 , which reduces the rigidity of the glass.

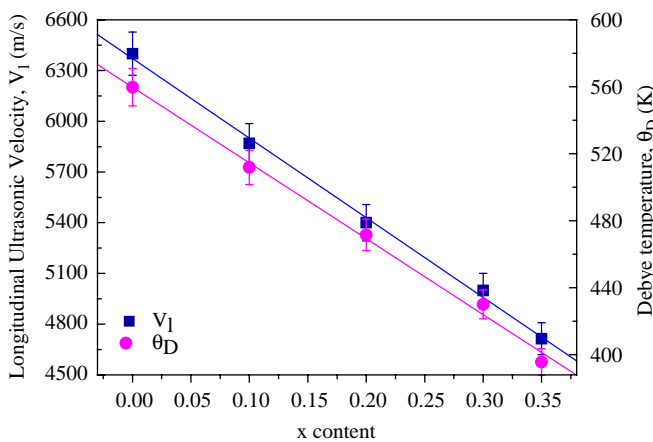


Fig. 3. Composition dependence of the ultrasonic velocity and Debye temperature in $\text{Li}_{0.6}\text{Te}_x\text{B}_{1.4-2x}\text{O}_{2.4-x}$ glasses with change in TeO_2 content. The lines are drawn for guides to the eye.

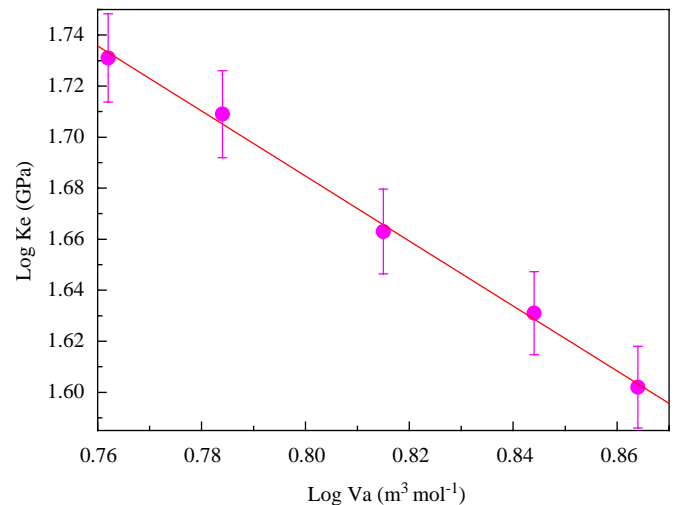


Fig. 4. Variation of the bulk modulus with the values of the mean atomic volume of the glass system $\text{Li}_{0.6}\text{Te}_x\text{B}_{1.4-2x}\text{O}_{2.4-x}$ in (log-log) representation. The lines are drawn for guides to the eye.

The bulk modulus (K_e) and the mean atomic volume (V_a) are related by the relation: $K_e V_a^m = C$ [39], where C is a constant. As stated earlier, the value of m for oxide glasses is 4 [35], and the variation of m in the bulk modulus–volume relationship is determined by the nature of the bonding and the coordination polyhedra. When the volume change occurs without change in the nature of the bonding or change in the coordination polyhedra, $\log(K_e)$ – $\log(V_a)$ plots generally are linear, as shown in Fig. 4. From the above results, it is noted that the increase in the volume should lead to a decrease in the bulk modulus with increasing TeO_2 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 observed decrease in the bulk modulus is associated with the decrease in the glass transition temperature. The compositional dependence of the bulk modulus may be discussed in terms of the glass structure as the addition of TeO_2 results in a decrease of the network rigidity (the bulk modulus decreased). 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. 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. Weakening the cation field strength will decrease the packing density due to the local expansion of the network around such a cation together with the effects of decreasing the bulk modulus.

3.5. The theoretically computed parameters

The computation of the structural parameters according to the bond compression model of the borate glasses was explained elsewhere [33,34,40]. The model is based on the observation that the measured bulk modulus K_e of oxide glasses is always markedly smaller than K_{bc} , the bulk modulus calculated under the assumption that each covalent bond experiences the linear contraction of the whole sample. The model assumes that the elastic moduli depend only on the “connectivity” of the network (number of bonds per cation) and on the average force constants. Also, the ratio between the calculated elastic moduli and the experimental one (K_{bc}/K_e) is assumed to be directly proportional to the atomic ring size (l).

The increase in TeO_2 content transforms some of TeO_4 into TeO_3 groups, similar to the formation of BO_4 and BO_3 groups in the borate glasses as reported by Kashchieva et al. [41]. So, the increase in the density leads to a change in K_{bc} values congruent with a change in the ring diameter. The values of the two parameters approach those of the ring diameter and of the ratio (K_{bc}/K_e) of the tellurite-based glasses as observed by El Mallawany [14]. Depending on a study by Kodama et al. [9], it is found that the average force constant of lithium borate glasses (386 N/m) is larger than the corresponding value of TeO_2 (314 N/m) [14], i.e., the average force constant will decrease while both the ring

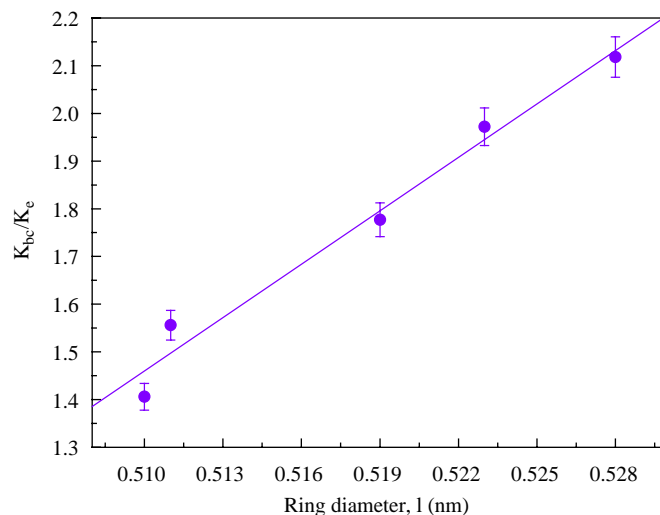


Fig. 5. Dependence of the ratio K_{bc}/K_e on the ring diameter of the glass system $\text{Li}_{0.6}\text{Te}_x\text{B}_{1.4-2x}\text{O}_{2.4-x}$. The lines are drawn for guides to the eye.

diameter and the ratio K_{bc}/K_e increase, as shown in Fig. 5. Generally, the ratio (K_{bc}/K_e) is a measure of the extent to which bond bending is governed by the configuration of the network bonds, i.e., this ratio is assumed to be directly proportional to the ring diameter. The values of the ring diameter and the ratio (K_{bc}/K_e) for pure B_2O_3 are 0.764 nm and 3.33, respectively [39], while for pure TeO_2 they are 0.53 nm and 2.3, respectively [14]. Thus, the continuous addition of TeO_2 results in an increase of the discontinuity of the glass network.

It is important to demonstrate the applicability of Makishima and Mackenzie’s theory [20–22] for the present glasses. Makishima–Mackenzie suggested that the elastic moduli are function of both the packing density (ionic radii of elements) and the average strength (dissociation energy) of the chemical bonds in the glass. The details of the computation of the elastic moduli for the borate glasses according to this model were explained elsewhere [40]. According to Inaba et al. [42], the values of the packing factors for Li_2O and TeO_2 are considered to be 8×10^{-6} and $14.7 \times 10^{-6} \text{ m}^3/\text{mol}$, respectively, while the dissociation energy for both oxides are 77.9×10^6 and $54 \times 10^6 \text{ kJ/m}^3$, respectively. The dissociation energy of B_2O_3 has two values, 16.4×10^6 (coordination number 3) and $77.9 \times 10^6 \text{ kJ/m}^3$ (coordination number 4). Rocherulle et al. [22] modifies the expression of the packing density to agree the computed elastic moduli fairly with the determined experimentally moduli. The values of these moduli according to the modification of Makishima–Mackenzie model [20–22] for all glass samples are given in Table 1. Fig. 6 shows the relation between the computed (according to Rocherulle et al. [22]) and the experimentally determined Young’s modulus.

The evaluation of the elastic moduli according to the model reveals that the values of the elastic moduli are lower

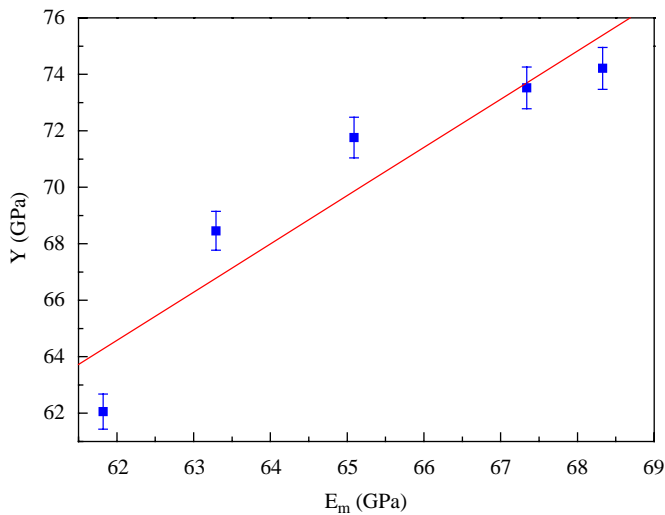


Fig. 6. Agreement between the experimental and theoretically calculated values of Young's modulus of the glass system $\text{Li}_{0.6}\text{Te}_x\text{B}_{1.4-2x}\text{O}_{2.4-x}$. The lines are drawn for guides to the eye.

than those measured experimentally. These lower values may be attributed to the decreasing packing density and the increasing molar volume of the studied glass. Addition of TeO_2 with a packing factor $14.7 \times 10^{-6} \text{ m}^3/\text{mol}$ will reduce the packing density as the packing factor of $\text{Li}_{0.6}\text{B}_{1.4}\text{O}_{2.4}$ glass is $16.96 \times 10^{-6} \text{ m}^3/\text{mol}$. On the contrary, the dissociation energy of the borate glasses modified with TeO_2 increases with the increase in the TeO_2 content, as the dissociation energy per unit volume of TeO_2 is higher than the dissociation energy per unit volume of the $\text{Li}_{0.6}\text{B}_{1.4}\text{O}_{2.4}$ glass or of B_2O_3 itself. This contradiction with the decrease in the stretching force constant was referred to the proposal of the model, which considered the covalent bonds only. Therefore, the elastic moduli of the glass system will decrease as the rigidity, the packing density, and the vibrations of the system decrease.

4. Conclusions

- The increase in the density is ascribed to the replacement of the low-density $\text{Li}_{0.6}\text{B}_{1.4}\text{O}_{2.4}$ glass by the high-density TeO_2 . The increase in the molar volume is attributed to the open structure resulting from the introducing of Te^{4+} with larger radii than the radii of the other ions in the present glasses.
- The decrease in the ultrasonic velocities and the Debye temperature with increasing TeO_2 content, is attributed to the increase in the oxygen molar volume and to the decrease in both the rigidity and the vibrations of the glass network.
- The elastic moduli (determined experimentally or computed theoretically) and the force constant decrease, while Poisson's ratio shows a constancy congruent with constant cross-link density. This was

attributed to the progressive transformation from the rigid character of $\text{Li}_{0.6}\text{B}_{1.4}\text{O}_{2.4}$ glasses into a matrix of ionic behavior bonds, which results in loose packing of the glass network.

References

- [1] S.R. Elliott, *Physics of Amorphous Materials*, Longman Scientific & Technical, Harlow, 1990.
- [2] C. Angell, *Ann. Rev. Phys. Chem.* 43 (1992) 693.
- [3] J. Swenson, L. Börjesson, *Phys. Rev. B* 57 (21) (1998) 13514.
- [4] N. Prasad, K. Annapurna, N. Sooraj Hussain, S. Buddhudu, *Mater. Lett.* 57 (2003) 2071.
- [5] K. Rao, M. Harish Bhat, *Phys. Chem. Glasses* 42 (3) (2001) 255.
- [6] K. El-Egili, A. Oraby, *J. Phys.: Condens. Matter* 8 (1996) 8959.
- [7] J. Krogh-Moe, *Phys. Chem. Glasses* 1 (1960) 26.
- [8] R. Rawson, *Inorganic Glass Forming Systems*, Academic Press, London, 1967.
- [9] M. Kodama, T. Matsushita, S. Kojima, *Jpn. J. Appl. Phys.* 34 (1995) 2570.
- [10] E.I. Kamitsos, M.A. Karakassides, G.D. Chryssikos, *Phys. Chem. Glasses* 30 (1989) 229.
- [11] G.D. Chryssikos, E.I. Kamitsos, M.A. Karakassides, *Phys. Chem. Glasses* 31 (1990) 109.
- [12] U. Selvaraj, K.J. Rao, *Spectrochim. Acta A* 40 (1984) 1081.
- [13] M. Ganguli, K.J. Rao, *J. Solid State Chem.* 145 (1999) 65.
- [14] R. El Mallawany, *Tellurite Glasses Physical Properties and Data*, CRC Press, New York, 2002.
- [15] Y. Saddeek, L. Abd El Latif, *Physica B* 348 (2004) 475.
- [16] T. Rao, R. Reddy, Y. Nazeer Ahmed, M. Parandamaiah, N. Sooraj Hussaina, S. Buddhudu, K. Purandar, *Infrared Phys. Technol.* 41 (2000) 247.
- [17] Y. Saddeek, H. Mohamed, M. Azzoz, *Phys. Status Solidi A* 201 (9) (2004) 2053.
- [18] L. Hwa, K. Hsieh, L. Liu, *Mater. Chem. Phys.* 78 (2002) 105.
- [19] R. El Mallawany, N. El Khoshkhany, H. Afifi, *Mater. Chem. Phys.* 95 (2006) 321.
- [20] A. Makishima, J.D. Mackenzie, *J. Non-Cryst. Solids* 12 (1973) 35.
- [21] A. Makishima, J. Mackenzie, *J. Non-Cryst. Solids* 17 (1975) 147.
- [22] J. Rocherulle, C. Ecolivet, M. Poulain, P. Verdier, Y. Laurent, *J. Non-Cryst. Solids* 108 (1989) 187.
- [23] A. Varshneya, *Fundamentals of Inorganic Glasses*, Academic Press Inc., New York, 1994.
- [24] J. Krogh-Moe, *Acta Cryst.* 15 (1962) 190.
- [25] Y. Saddeek, M.Sc. Thesis, El-Minia University, Egypt, 1997.
- [26] N. Krins, A. Rulmont, J. Grandjean, B. Gilbert, L. Lepot, R. Cloots, B. Vertruyen, *Solid State Ionics* 17 (2006) 3147.
- [27] R. Shannon, *Acta Cryst. A* 32 (1976) 751.
- [28] H. Hirashima, H. Kurokawa, K. Mizobuchi, T. Yoshida, *Glasstech. Ber.* 61 (1998) 151.
- [29] R. Iordanova, V. Dimitrov, Y. Dimitriev, D. Klissurski, *J. Non-Cryst. Solids* 180 (1994) 58.
- [30] R. Cuevas, L. Barbosa, A. de Paula, Y. Liu, V. Reynoso, O. Alves, N. Aranha, C. Cesar, *J. Non-Cryst. Solids* 191 (1–2) (1995) 107.
- [31] A. Vaz de Araujo, I. Weber, B. Santos, B. da Silva, R. de Mello Jr., S. Alves Jr., G. de Sa, C. Donega, *J. Non-Cryst. Solids* 219 (1997) 160.
- [32] N. Roy, *J. Non-Cryst. Solids* 15 (1974) 423.
- [33] B. Bridge, N. Patel, D. Waters, *Phys. Status Solidi A* 77 (1983) 655.
- [34] B. Bridge, A.A. Higazy, *J. Mater. Sci.* 21 (1986) 2385.
- [35] V. Rajendran, N. Palanivelu, B. Chaudhuri, K. Goswami, *J. Non-Cryst. Solids* 320 (2003) 195.
- [36] V. Rajendran, N. Palanivelu, D.K. Modak, B.K. Chaudhuri, *Phys. Status Solidi A* 180 (2000) 467.

- [37] V. Rajendran, A. Nishara, M. Azooz, F.H. EL Batal, *Biomaterials* 23 (2002) 4263.
- [38] A.F. Wells, *Structural Inorganic Chemistry*, fourth ed., Clarendon Press, Oxford, 1975.
- [39] E. Gopal, T. Mukuntan, J. Philip, S. Sathish, A. Pramana, *J. Phys.* 28 (5) (1987) 471.
- [40] Y. Saddeek, *Physica B* 344 (2004) 163.
- [41] E. Kashchieva, M. Pankova, Y. Dimitriev, *Ceramics-Silikaty* 45 (3) (2001) 111.
- [42] S. Inaba, S. Fujino, K. Morinaga, *J. Am. Ceram. Soc.* 82 (12) (1999) 3501.