Structural Analysis of Some Alkali Diborate Glasses

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This manuscript presents a theoretical analysis of the correlation between the computed bulk modulus and the structure of a series of multicomponent sodium diborate based glasses in terms of the bond compression model. The main parameters in the analysis were the computed elastic moduli, the average stretching force constant and the average atomic ring size. These parameters were calculated for every glass series and for every glass composition. The results showed that the average force constant and the elastic moduli of these glasses are sensitive to the decrease in the sodium diborate content. This behaviour was attributed to the increase in the molar volume, and to the role of the different modifiers.

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1. Introduction

The boron atom in borate crystals and glasses is usually coordinated with either three or four oxygen atoms forming [BO$_3$] or [BO$_4$] structural units. These two fundamental units can be arbitrarily combined to form either the so-called super-structure or different B$_x$O$_y$ structural groups like boroxol ring, pentaborate, tetraborate, diborate groups etc. In the alkali borate glass systems, each alkali oxide is associated with a proportional quantity of B$_2$O$_3$; so that, the number of the structural units depends on both the nature and the total concentration of the added modifiers, and can often give rise to tightly organized structures resulting in intermediate order [1–5]. In sodium borate glasses there are three types of structural groupings; namely boroxol rings, tetraborate units and diborate units. All of these groups share two distinct types of boron configurations; BO$_3$ triangles and BO$_4$ tetrahedra with bridging oxygen ions for each type. In high-sodium borate glasses (between 20 and 30 mol% of Na$_2$O), tetraborate groups are partially rearranged, and one Na$_2$O forms two diborate units at the expense of a tetraborate unit, with BO$_4$/(BO$_3$ + BO$_4$) = 0.5. As a result, one Na$_2$O forms two BO$_4$ units, which makes the network structure three-dimensional [6–9]. Kodama [5] analyzed the elastic properties of sodium borate glasses in terms of three structural units defined as B$_3$ ≡ a, M$^+$B$_2$O$^-$ ≡ b and M$^+$B$_4^-$ ≡ c, where represents a bridging oxygen and O$^-$ is a non-bridging oxygen. It is assumed that these structural units have their respective elastic constants defined on the basis of a thermodynamic

equation of deformed body, so the rigidity of the glass will increase with the structural unit c and decreases with the structural unit b. They found that the sound velocity in the sodium-borate glasses shows a single maximum (around $x = 0.34$ mol.%) correlated with the increase in the number of non-bridging oxygens. On the other hand, the MoO$_3$, Nb$_2$O$_5$, PbO, and Bi$_2$O$_3$ oxides appeared as non-conventional network formers because of the participation of MoO$_4$, MoO$_6$, NbO$_4$, PbO$_4$, and BiO$_6$ groups in the formation of the glass network.

Therefore, the analytical structural study of the borate-based glasses correlated with their macroscopic properties presents a challenge in the field of condensed matter physics and chemistry. This correlation helps in the design of materials suitable for specific applications. These glasses are commonly used in the field of opto-acoustical electronics, piezoelectric actuator, and in nonlinear devices for frequency conversion in the ultraviolet region. Meanwhile, these glasses and their crystalline counterparts are considered to be good candidates for the optically induced elastooptoicity [10, 11]. Also, a series of multi-component non-conventional glasses with interesting properties, e.g. low dielectric constant, relatively low dielectric loss, and good radiation shielding for γ-rays can be synthesized [12–15]. These glasses exhibit a high refractive index, widely adjustable in the range from 1.8 to 2.5 by the appropriate glass composition and have high energy gap attributable to the high polarizability of Bi$_2$O$_3$ which allows using them in wide spectra range from UV up to infrared [16, 17].

Inspection of the microstructure and the mechanical properties of the borate glasses were interpreted in terms of collected qualitative or quantitative data from various kinds of characterization techniques. The rigidity

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and the elastic properties of these glasses are very informative about its structure. One way to determine the rigidity is the determination of the sizes of the borate rings, which in turn are influenced by the chemical nature of the modifying oxide. Therefore, the purpose of the present work is to deduce the structural changes of the sodium diborate based glasses upon its modification by non-conditional glass formers like PbO, and Bi_2O_3, MoO_3, and Nb_2O_5. The computation of the elastic moduli based on the data given by Saddeek et al. [18–20] has been calculated in terms of the bond-compression model proposed by Bridge et al. [21].

2. Theoretical analysis

The structure of oxide glasses can be described in terms of the bond compression model which was first introduced by Bridge et al. [21] for the study of single--component glass, was later developed for multicomponent glasses [22]. 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. Obviously, a sizable part of the volume change is due to a distortion of the network. In order to quantify the treatment of this effect, the model makes several assumptions:

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

$$K_{bc} = \frac{\sum_i x_i n_b r_a^2 f}{9} \quad [GPa], \tag{1}$$

$$f = 5.28 N \left(\frac{X_a X_b}{r_a^2} \right)^{3/4} + 30 \quad [N\ m^{-1}], \tag{2}$$

where x is the mole fraction of the component oxide, n_b is the number of network bonds per unit volume, r_a (nm) is the bond length, N is the bond order (1, 2, or 3), X_a and X_b are the electronegativities of the anion and the cation, respectively.

(ii) 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 atomic ring size is defined as the ring perimeter (number of bonds times bond length divided by π), and is given by the relation

$$l = \left(0.0106 \frac{f}{K_e} \right)^{0.26} \quad [nm], \tag{3}$$

where K_e is the experimental bulk modulus. Therefore, a value of $K_{bc}/K_e \gg 1$ indicates a relatively open (i.e. large ringed) three-dimensional network with ring size tending to increase with K_{bc}/K_e and network bond bending (non-network compression) processes predominate when the glasses are subjected to bulk compression. The authors found that the values of K_{bc}/K_e are 3.05, 3.08,

4.39 and 6.62 for pure SiO_2, P_2O_5, GeO_2 and As_2O_3 glasses, respectively, and the conformable atomic ring size of these glasses is 0.58, 0.567, 0.631 and 0.722 nm, respectively [21].

Moreover, Poisson's ratio σ_{cal} was given according to this model as

$$\sigma_{cal} = 0.28 \left(\overline{n_c} \right)^{-1/4}, \tag{4}$$

$$\overline{n_c} = \left(\frac{1}{\eta} \right) \sum_i x_i (n_c)_i (N_c)_i, \tag{5}$$

where $\overline{n_c}$ is the average cross-link density, n_c is the number of cross-links per unit cation which equals the number of bonds minus 2, N_c is the number of cations per unit glass formula unit and η is the total number of cations per unit glass formula unit given by $\eta = \sum_i x_i (N_c)_i$. The model [21] proposes that for tensile stresses, applied parallel to the chains, the longitudinal strain produced will be the same for all three networks i.e. it is unaffected by the cross links. The ratio of lateral to longitudinal strain (σ) increases with decreasing cross-link density.

3. Results and discussion

The quantitative analysis of the literature data [18–20] in terms of the bond compression model was done using the set of parameters listed in Table I. The set was

TABLE I

The coordination number (N), the cation–anion bond length (r_a), the first order stretching force constant (f), and the electronegativity of the cation (X_a), of the oxides included in this study.

Oxide	N	r_a [nm]	f [N m^{-1}]	X_a
B_2O_3	3	0.1365	450.65	2
Na_2O	4	0.196	145.58	0.93
Bi_2O_3	6	0.240	192.24	2.02
MoO_3	6	0.196	273.9	2.16
Nb_2O_5	6,4	0.170	270.74	1.6
PbO	4	0.214	257.43	2.33

Values of the coordination number, the bond length, the electronegativity of the cation were taken from Refs. [23, 25].

adapted to the crystal structure of each oxide of the studied glass series [23]. These parameters are used in calculating the average stretching force constant F, the number of network bonds per unit volume n_b, the bulk modulus K_{bc}, the average atomic ring size l, and the ratio K_{bc}/K_e. In Table I, one has two entries for the coordination number of Nb_2O_5, $N = 6$ and $N = 4$. Here we follow the work of Mohan et al. [24], which showed that the niobium can be coordinated with either four or six oxygen atoms, depending on the atomic composition. The bond density in Table II was calculated according to their rules.

The number of network bonds per unit volume (n_b), the average cross-link density ($\overline{n_c}$), the experimentally determined bulk modulus (K_e), the bond compression bulk modulus (K_{bc}), the ratio (K_{bc}/K_e), the average force constant (f), the average ring diameter (l) of the sodium diborate glasses.

Composition in [mol%]							$n_b \times 10^{28}$ [m^{-3}]	$\overline{n_c}$	K_e [GPa]	K_{bc} [GPa]	σ	K_{bc}/K_e	f [N m^{-1}]	l [nm]
B_2O_3	Na_2O	Bi_2O_3	MoO_3	Nb_2O_5	PbO	Name								
1.000	–	–	–	–	–	Pure boron	4.77	1.000	13.26	44.76	0.280	3.38	450.0	0.766
0.667	0.333	–	–	–	–	NB	9.25	2.332	45.89	94.64	0.227	2.06	309.6	0.503
0.600	0.300	–	–	–	0.100	NBPb1	8.93	2.316	43.99	93.75	0.227	2.13	304.7	0.507
0.533	0.267	–	–	–	0.200	NBPb2	8.50	2.298	40.93	91.62	0.227	2.24	299.6	0.514
0.467	0.233	–	–	–	0.300	NBPb3	8.08	2.273	40.16	89.23	0.228	2.22	294.8	0.514
0.400	0.200	–	–	–	0.400	NBPb4	7.93	2.250	39.36	89.81	0.229	2.28	289.7	0.515
0.333	0.167	–	–	–	0.500	NBPb5	7.96	2.224	38.56	92.38	0.229	2.40	284.4	0.515
0.267	0.133	–	–	–	0.600	NBPb6	7.75	2.189	36.69	92.17	0.230	2.51	279.4	0.519
0.200	0.100	–	–	–	0.700	NBPb7	7.44	2.154	32.00	90.69	0.231	2.83	273.9	0.535
0.133	0.067	–	–	–	0.800	NBPb8	7.15	2.113	28.61	89.25	0.232	3.12	268.4	0.548
0.633	0.317	0.025	0.025	–	–	NBBiMO1	9.10	2.40	48.10	95.40	0.225	1.98	306.7	0.496
0.600	0.300	0.050	0.050	–	–	NBBiMO2	8.95	2.46	48.40	95.89	0.224	1.98	303.9	0.494
0.567	0.283	0.075	0.075	–	–	NBBiMO3	8.59	2.53	49.30	93.99	0.222	1.91	301.1	0.490
0.533	0.267	0.010	0.010	–	–	NBBiMO4	8.63	2.60	50.30	96.27	0.221	1.91	298.2	0.486
0.500	0.250	0.125	0.125	–	–	NBBiMO5	8.36	2.67	50.70	95.02	0.219	1.87	295.7	0.484
0.467	0.233	0.150	0.150	–	–	NBBiMO6	8.26	2.74	51.00	95.49	0.218	1.87	293.2	0.483
0.433	0.217	0.175	0.175	–	–	NBBiMO7	8.12	2.81	51.10	95.40	0.216	1.87	290.6	0.481
0.400	0.200	0.200	0.200	–	–	NBBiMO8	8.13	2.89	51.80	97.07	0.215	1.87	288.3	0.479
0.633	0.317	0.025	–	0.025	–	NBBiNb1	8.11	2.42	43.7	84.65	0.225	1.94	304.8	0.507
0.600	0.300	0.050	–	0.050	–	NBBiNb2	7.38	2.50	43.3	78.39	0.223	1.81	300.2	0.507
0.567	0.283	0.075	–	0.075	–	NBBiNb3	6.90	2.58	41.4	74.40	0.221	1.80	295.7	0.511
0.533	0.267	0.010	–	0.010	–	NBBiNb4	6.60	2.67	44.2	72.33	0.219	1.64	291.1	0.500
0.500	0.250	0.125	–	0.125	–	NBBiNb5	6.25	2.75	44.4	69.49	0.217	1.57	286.9	0.497
0.467	0.233	0.150	–	0.150	–	NBBiNb6	6.08	2.83	46.2	68.54	0.216	1.48	282.9	0.491

The compositions of the series NBPb were according to [18], NBBiMO were according to [19], NBBiNb were according to [20].
The values of n_b, K_{bc}, K_{bc}/K_e, f, l, and n_c for pure B_2O_3 were according to [26].

The determination of the average cross-link density was based on the computation of both the coordination number of the modifiers and the former on one hand, and on the N_4, the ratio of four-to-three-coordinated boron in the borate glass, on the other hand. Also, it was found that the average force constant (F) is governed by the reciprocal of the bond length. The bond lengths for BO_3 and for BO_4 are 0.1365 nm and 0.1475 nm, respectively. Thus, according to the results of the model, the structure of the stoichiometry sodium diborate glass is more rigid than that of the pure vitreous B_2O_3. The latter is less cross-linked, has a large ring and high K_{bc}/K_e value than those of the former. Previously [21] it has been argued that the high value of the ratio K_{bc}/K_e more than 3 indicates that network bond bending (or non-network bond compression) processes predominate when these materials are subjected to bulk compression. The rigidity of the stoichiometry sodium diborate glass network is maximized according to some former studies [5, 26]. Thus, analysis of the computed elastic moduli according to the bond-compression model may be achieved of these glass series [18–20] as follows.

3.1. NBPb series

Modification of the sodium diborate glasses with PbO having 4 coordination number and 0.214 nm bond length results in an increase in the molar volume [18], decrease in the number of bonds per unit volume (n_b) and a decrease in the cross-links (Fig. 1) in the glass system with decreasing the sodium diborate content. The decrease in n_b and the average cross-link density is attributed to both the decrease in the total number of cations per unit glass formula unit [21, 22] and the increase in molar volume confirming the creation of non-bridging oxygens NBOs as the oxygen molar volume (V_O) increases from 12.8×10^{-6} to 26.9×10^{-6} m^3/mol [18] with the increase of PbO content which expands (opens up) the structure of the tightly network of $Na_2B_4O_7$ (NBO) glass. Therefore, the number of network bonds per unit volume will decrease (Fig. 2) from 9.25×10^{28} to 7.15×10^{28} m^3. According to Table II, the K_{bc} (Fig. 3) decreases, the packing density, and the experimentally determined bulk modulus K_e [18] decrease as the sodium diborate content decreases. Thus, the structure will be less linked and the network of these glasses becomes weaker as the average bond stretching
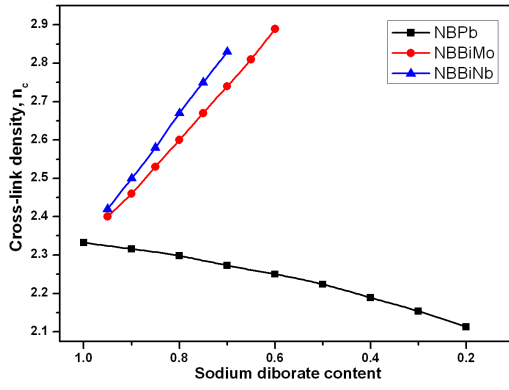
Fig. 1.   The compositional dependence of the cross-link density on the sodium diborate content.
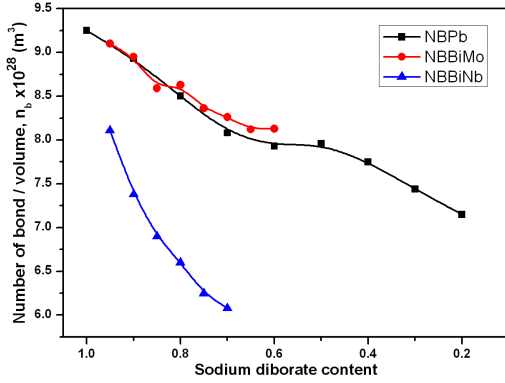

Fig. 2.   The compositional dependence of the number of bonds per unit volume on the sodium diborate content.
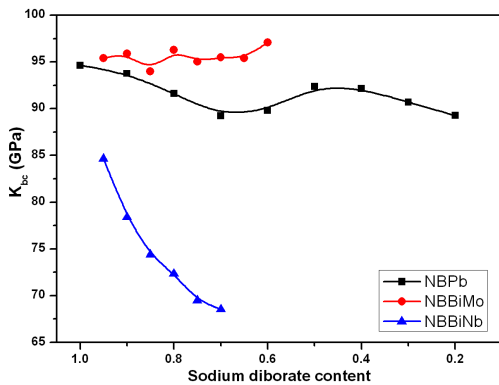

Fig. 3.   The compositional dependence of computed bulk modulus on the sodium diborate content.
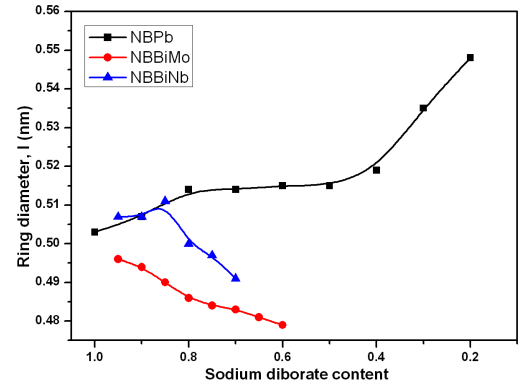

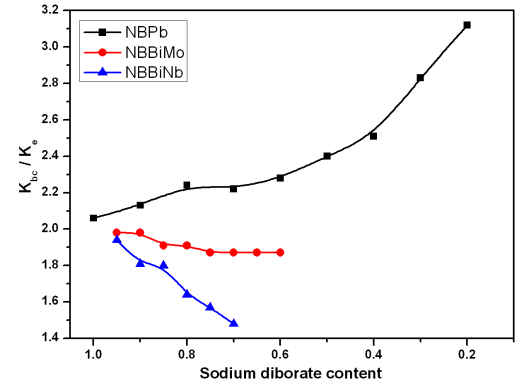Fig. 4.   The compositional dependence of the ring diameter on the sodium diborate content.

Fig. 5.   The compositional dependence of the ratio K_{bc}/K_e on the sodium diborate content.

force constant F decreased (see Table II), and as a direct result the average atomic ring diameter (Fig. 4) increases which correlates with the increase in both molar volume (i.e. inter-atomic spacing) and NBOs. The suggestion by Bridge et al. [21] that the ratio K_{bc}/K_e (Fig. 5) is related to the average size of the rings may be accepted in fully polymerized glasses such as borate glasses, so the relation between K_{bc}/K_e and the average ring size of this type of glasses is straightforward. The computed values of these parameters are in a good agreement with the values given previously by Bridge et al. [21] for pure B_2O_3. As discussed previously, as the value of the ratio K_{bc}/K_e increases to more than unity, so the connections between the structural units will be weaker and the structure will become less stable. In addition, the increase in the values of Poisson's ratio as shown in Table II is mainly due to the decrease in cross-link density confirming the decrease in rigidity with addition of PbO at the expense of the $Na_2B_4O_7$ diborate.

3.2. NBBiMo series

According to Table II, the cross-link density, and the K_{bc} increases while the number of network bonds per unit volume, and the ring diameter decrease as the sodium diborate content decreases. Also, the molar volume increases, oxygen molar volume increases and the packing density [19] decreases of these glasses with the decrease in the sodium diborate content. The increase in the average cross-link density is attributed to the replacement of both bismuth and molybdenum ions with higher

coordination numbers at the expense of diborate content. On the other hand, the decrease in the number of network bonds per unit volume (Fig. 2) from 9.10×10^{28} to 8.13×10^{28} m^3 is attributed to the increase in molar volume and oxygen molar volume [19] which means the increase of NBOs with addition of bismuth and molybdenum oxides at the expense of Na$_2$B$_4$O$_7$ content. In this series n_c increases markedly than the latter series which may be due to the effect of the higher coordination number of Bi$_2$O$_3$ and MoO$_3$ than PbO. The computed values of these parameters are in a good agreement with the values given previously [21]. Incorporation of Bi$_2$O$_3$ and MoO$_3$ in the sodium diborate glass network increases the concentration of MoO$_6$ and BiO$_6$ structural units, as their coordination numbers are higher than B$_2$O$_3$, and hence leads to the increase in cross-link density and consequently the increase in K_{bc} and K_e values as seen in Table II. Therefore, the decrease in the values of the ratio K_{bc}/K_e and average ring diameter confirm the increased rigidity of these glasses. Moreover, the decrease in the values of Poisson's ratio confirms the increased rigidity and cross-link density of these glasses through the change in the type of bonds from covalence to ionic, since the replacement of B$_2$O$_3$ (with strong B–O bonds and lower coordination number) by Bi$_2$O$_3$ and MoO$_3$ oxides (with weaker Bi–O and Mo–O bonds and higher coordination numbers) would lead to the increase in the ionic cross-links (i.e. increase in rigidity) and the decrease in the average bond stretching force constant F as seen in Table II. Therefore, the increase in the elastic moduli of these glasses along with the increase in molar volume indicates the change in the type of bonding [27].

3.3. NBBiNb series

Incorporation of Bi$_2$O$_3$ and Nb$_2$O$_5$ in the sodium diborate network results in a markedly increase in the molar volume and a decrease in the packing density [20] than the two former series. This incorporation will increase the average cross-link density and causes a constancy in the total number of cations per unit glass formula unit [21, 22], so the number of network bonds per unit volume strongly decreases (Fig. 2) from 8.11 to 6.08×10^{28} m^3. In this type of glass, more polymerization will be created as the sodium diborate content decreases, and as a result both the average ring diameter and K_{bc}/K_e will decrease and the relation between them is straightforward. The behaviour of the last parameters with the decrease in the sodium diborate content is attributed to the dual role of Nb$_2$O$_5$ as a modifier/former [20]. This behaviour was noticed elsewhere [28] in a theoretical analysis of low silicate content glasses and was attributed to the dual role of La$_2$O$_3$. Moreover, the decrease in the values of Poisson's ratio confirm the increased rigidity and cross-link density of these glasses through the formation of bonds with high ionic character which would lead to the increase in the ionic cross-links (i.e. increase in rigidity) and the decrease in the average bond stretching force constant F as seen in Table II.

It is inferred that modification of the sodium diborate glasses (the three series) will increase the molar volume, the average cross link density and decrease the packing density, the average force constant, and the number of bonds per unit volume, while the K_{bc} is very sensitive to the rate of increase of the molar volume. Accordingly, the relation between the average ring diameter and K_{bc}/K_e is depending on the polymerization or depolymerization of the sodium diborate network. Also, it is worth mentioning that there is an intrinsic correlation between fragility of a liquid and bulk modulus of its glass. Jiang and Dai [29] found that there is a linear correlation between the fragility and the bulk-shear modulus ratio exists strictly at either absolute zero temperature or very high frequency. Their further analyses [29] indicate that a real flow event in bulk glasses either metallic or nonmetallic is shear dominant, and fragility is in inverse proportion to shear-induced bulk dilatation.

4. Conclusions

The average atomic ring size and the elastic moduli can be calculated theoretically for sodium diborate based glasses from the indicative structural parameters. The theoretical bulk modulus K_{bc} of these glasses is governed by the forces interlocking the network, and is increased or decreased by placing transition metal ions of high or low field strengths in the interstices of the sodium diborate network. The behavior of the sodium diborate based glasses is dependent upon the kind of glass modifier. The average ring diameter of these glasses has been calculated and it has been found that is depends upon the kind of the modifier.

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