JOURNAL OF MATERIALS SCIENCE **25** (1990) 253–258

Consideration of the boron oxide anomaly

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Densities of $Li_2O-B_2O_3$, $Na_2O-B_2O_3$ and $K_2O-B_2O_3$ glasses have been measured. The density-composition curves are analysed to obtain the volume of both the BO_3 and BO_4 structural units. It is found that the volume changes with the alkali oxide content for the two types of structural unit. A new explanation of the boron oxide anomaly is presented. It is proposed that the volume contraction of the BO_3 units should be responsible for the change of properties of alkali borate glasses with alkali oxide content <16 mol %. For higher alkali oxide concentrations, the interconnection of the spaces associated with the BO_4 tetrahedra should cause the properties to change in the opposite direction.

1. Introduction

Boron oxide is well known as one of the conventional glass formers. B_2O_3 glass is assumed to consist of a random three-dimensional network of nearly flat BO_3 triangles with a comparatively high fraction of six-membered boroxol rings [1, 2] (Fig. 1). Addition of alkali oxide to boron oxide, to form an alkali borate glass, results in transformation of BO_3 triangles to BO_4 tetrahedra. This process takes place in a nearly continuous manner in binary $R_2O-B_2O_3$ systems (R = Li, Na, K, Rb, Cs) up to $R_2O/B_2O_3 \sim 0.5$ [3]. In alkali borate glasses Krogh-Moe [4] proposed that the BO_3 triangles and the BO_4 tetrahedra associate together to form various extended structural groups including boroxol, tetraborate and diborate (Fig. 1). Boroxol and tetraborate groups are assumed to predominate in the region below 20 mol % R_2O, while between 20 and 30 mol % R_2O tetraborate and diborate groups are prevalent.

The change of the relative concentrations of such structural groups with increasing R_2O content should affect the physical properties of the $R_2O-B_2O_3$ glasses. Many physical properties of alkali borate glasses [5–8] change through maximum or minimum at a ratio of $R_2O : B_2O_3$ about 16 : 84. The same is also observed for silver borate glasses [9, 10], alkali borosilicate glasses [6] and more complicated B_2O_3-containing glasses such as alkali alumino-borosilicate glasses [11]. This behaviour is known as the "boron oxide anomaly". The minima of the thermal expansion of alkali borate glasses have been explained [12] by considering the effect as due to competition between the formation of the three-dimensional BO_4 tetrahedra, which decrease the expansion coefficient, and the introduction of the alkali ions, which increase it. Recently [11] it has been assumed that the strengthening of the structure up to 16 mol % Na_2O should be due to formation of BO_4 tetrahedra. For $16 < Na_2O < 33$ mol %, interstices are proposed to form among the BO_4 tetrahedra and this acts in the opposite direction.

Although the structural model of alkali borate glasses given by Krogh-Moe [4] has been supported by studies of nuclear magnetic resonance [13], Raman and IR spectroscopy [14], these techniques are not adequate to detect the formation of interstices in the structure when the fraction of BO_4 tetrahedra increases. The density of the glass should change due to formation of such interstices, and can therefore be used to detect whether the interstices form or not.

The present paper quantitatively analyses the density data of the alkali borate and silver borate glasses. The results should clarify some of the confusion about the boron oxide anomaly.

2. Experimental procedure

The glasses (Table I) were prepared in 100 g batches by mixing the desired amounts of reagent grade Li_2CO_3, Na_2CO_3, K_2CO_3 and H_3BO_3. The melting was carried out using platinum crucibles in air. The melts were maintained in an electric furnace at 1000 to 1200° C, depending on the glass composition, for 2 to 3 h. The melt was frequently stirred to ensure good mixing. After melting was completed, $Na_2O-B_2O_3$ and $K_2O-B_2O_3$ glasses were cast into steel moulds, held for 1 h near the transformation temperature [15] and then cooled at a rate of about $60° C h^{-1}$. Because $Li_2O-B_2O_3$ glasses are easy to devitrify, they were quenched by dipping the bottom of the crucible into water. The specimens were stored in a vacuum desiccator.

Densities of three glass samples of each composition were measured separately, at room temperature, using the suspended-weight method based on the Archimedes principle. Toluene was used as the immersion liquid. The densities obtained were reproducible to $\pm 0.001 g cm^{-3}$. The density data given in Table I represent the average for each composition.

3. Results and discussion

Figs 2 to 4 represent the dependence of density on the alkali content for binary Li_2O–, Na_2O– and $K_2O-B_2O_3$ glasses, respectively. The density changes with composition in a similar manner for both the sodium and potassium borate glasses, whereas the behaviour is different in the case of lithium borate glasses. In

TABLE I Compositions of the glasses studied and the measured densities

Li_2O–B_2O_3		Na_2O–B_2O_3		K_2O–B_2O_3	
Li_2O (mol %)	D (g cm^{-3})	Na_2O (mol %)	D (g cm^{-3})	K_2O (mol %)	D (g cm^{-3})
2.5	1.8801	2.5	1.9189	2.5	1.9222
5.0	1.9112	5.0	1.9693	5.0	1.9773
7.5	1.9432	7.5	2.0173	7.5	2.0220
10.0	1.9774	10.0	2.0645	10.0	2.0571
12.5	2.0132	12.5	2.0974	12.5	2.0853
15.0	2.0501	15.0	2.1331	15.0	2.1109
17.5	2.0863	17.5	2.1614	17.5	2.1261
20.0	2.1230	20.0	2.1908	20.0	2.1472
22.5	2.1571	22.5	2.2297	22.5	2.1713
25.0	2.1892	25.0	2.2748	25.0	2.2047
27.5	2.2195	27.5	2.3237	27.5	2.2421
30.0	2.2450	30.0	2.3458	30.0	2.2711
		32.5	2.3809	32.5	2.2902

Fig. 2 it is shown that the density increases with an increasing rate up to about 15 mol % Li_2O, when the rate begins to decrease. Remarkable changes in the rate of density change are also seen between 15 and 20 mol % Na_2O and K_2O (Figs. 3 and 4). The results, which are in good agreement with those obtained by other investigators [16–23], indicate that there is some structural change in the region of 15 to 20 mol % R_2O.

For a binary borate glass of the type R_2O–B_2O_3 (R can be generalized to be a monovalent cation, to include Ag^+), the density D can be given as

$$D = \frac{N_3 M_3 + N_4 M_4}{N_3 V_3 + N_4 V_4} \qquad (1)$$

where N_3 is the fraction of BO_3 triangles in the structure, M_3 is the mass of the BO_3 triangle and V_3 is its volume. N_4, M_4 and V_4 have the same significance for the BO_4 tetrahedron. The fraction of four-coordinated borons N_4 in a glass of composition $x R_2O \cdot (1 - x) B_2O_3$ can be calculated [3], up to approximately $x = 0.3$, using the relation

$$N_4 = x/(1 - x) \qquad (2)$$

In Equation 1, one may understand V_3 and V_4 as the volume of the corresponding structural unit with its surrounding (associated) space. The masses M_3 and M_4 are to be calculated by considering the ions belonging to the central boron ion of the structural unit. This means that M_3 is considered as the mass of $(B + 1\frac{1}{2}O)$ and M_4 is the mass of $(B + 2O + R)$.

Equation 1 can be used to calculate V_3, when taking $N_4 = 0$, i.e. when dealing with the density of glassy B_2O_3. Using the average density of the B_2O_3 glass as 1.8245 g cm^{-3} [15, 24] one obtains $V_3 = 0.03194\,\mathrm{nm}^3$. Initially, it is assumed that this volume changes as R_2O is added to B_2O_3. To obtain V_3 and V_4 values in a binary R_2O–B_2O_3 glass with a specific R_2O concentration (in mol %), Equation 1 can be solved using two D values corresponding to two R_2O concentrations close to the desired concentration. For example, using the D values corresponding to 7.5 and 10 mol % R_2O, V_3 and V_4 values in the glass with 8.75 mol % R_2O can be obtained.

Only small differences were found between the theoretical and the analysed compositions for alkali borate glasses [25] prepared under similar conditions to those in the present study. Therefore the compositions referred to in the following sections will be the theoretical compositions.

In Figs 5 to 10 the dependence of V_3 and V_4 on R_2O content is shown, using the density data of the present work and those given by other investigators [9, 16–23, 26]. Except in the case of Li_2O– and Ag_2O–B_2O_3 glasses (Figs 5 and 10, respectively) V_3 decreases to a minimum value at about 15 mol % R_2O, increases to a maximum

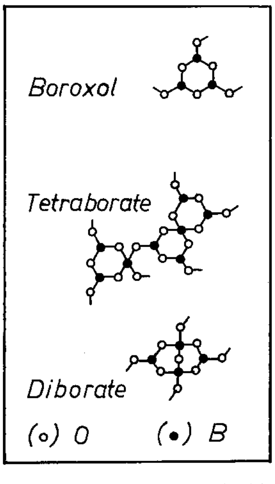

Figure 1 The proposed structural groups in binary borate glasses containing up to 30 mol % R_2O [4].

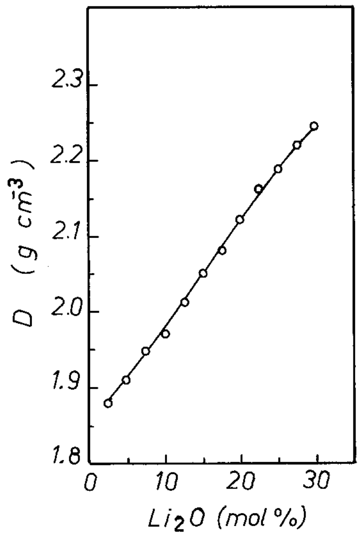

Figure 2 Change of density of Li_2O–B_2O_3 glasses with Li_2O content.

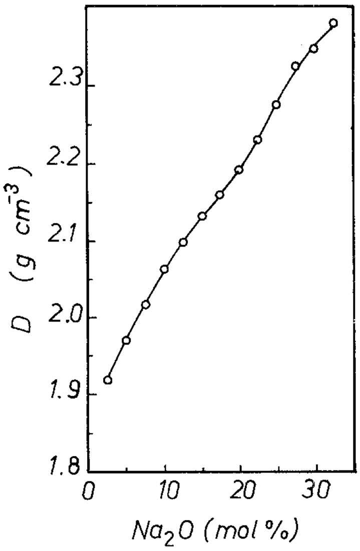

Figure 3 Change of density of $Na_2O-B_2O_3$ glasses with Na_2O content.

at R_2O between 24 and 27.5 mol % and then decreases. On the other hand, V_4 changes oppositely with R_2O showing a maximum at about 15 mol % R_2O and a minimum at R_2O between 24 and 27.5 mol %. This behaviour is found for binary $R_2O-B_2O_3$ glasses containing Na_2O, K_2O, Rb_2O and Cs_2O (Figs 6 to 9).

In binary $Na_2O-B_2O_3$ glasses the activation energy for electric conductivity increases, reaching a maximum at about 16 mol % Na_2O [11]. Higher Na_2O concentrations cause the activation energy to decrease. This behaviour was attributed to the strengthening of the structure due to formation of three-dimensional BO_4 tetrahedra up to 16 mol % Na_2O. At higher alkali oxide conents, vacancies are assumed to form among the formed BO_4 tetrahedra, which causes a decrease of activation energy.

The increase of V_4 up to about 15 mol % R_2O (Figs 6 to 9) contradicts the previous assumption. The net volume of a polyhedron (without its surrounding space) should comprise its internal space plus the volume of the contributing ions. The B–O distance changes from 0.139 nm in an $Na_2O \cdot 5B_2O_3$ glass to 0.145 nm in an $Na_2O \cdot 2B_2O_3$ one [27]. This may lead one to neglect the volume of the internal space of the

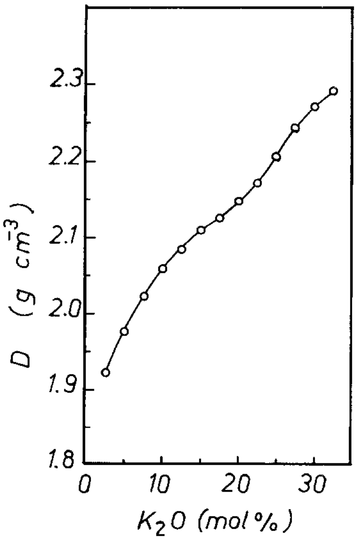

Figure 4 Change of density of $K_2O-B_2O_3$ glasses with K_2O content.

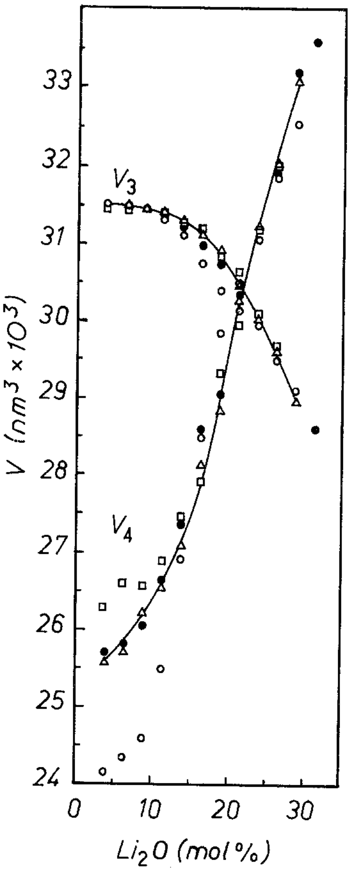

Figure 5 Dependence of V_3 and V_4 on R_2O content in $Li_2O-B_2O_3$ glasses. Density data are taken from (□) [18], (○) [21, 22], (●) [23] and the (△) present work.

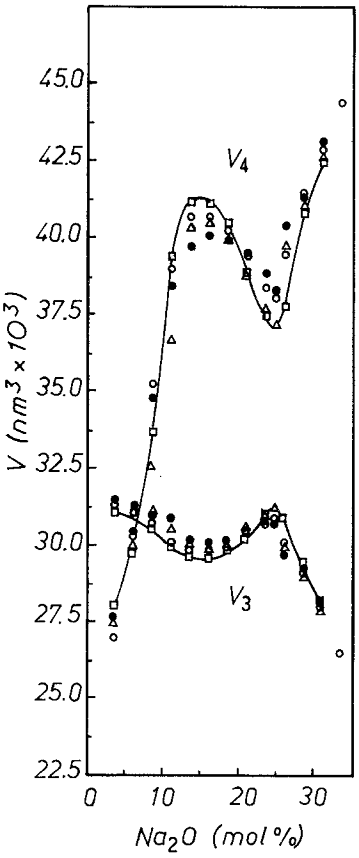

Figure 6 Dependence of V_3 and V_4 on R_2O content in $Na_2O-B_2O_3$ glasses. Density data are taken from (○) [16], (●) [17] (△) [21, 22] and (□) the present work.

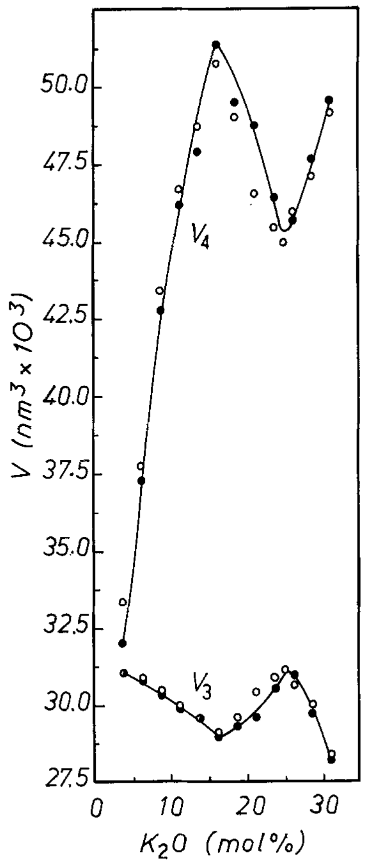

Figure 7 Dependence of V_3 and V_4 on R_2O content in K_2O–B_2O_3 glasses. Density data are taken from (○) [17–19, 21, 22] and (●) the present work.

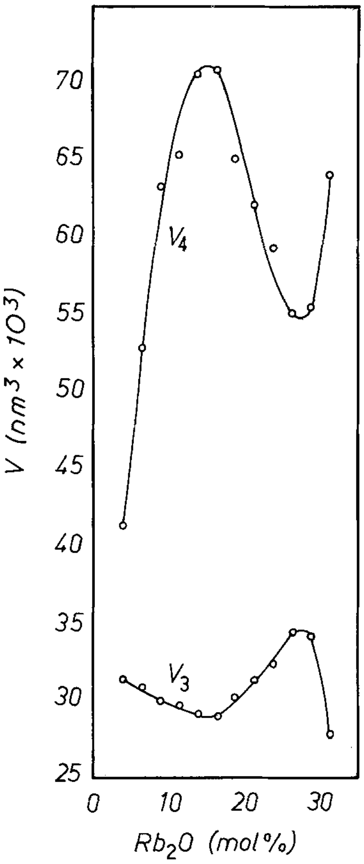

Figure 8 Dependence of V_3 and V_4 on R_2O content in Rb_2O–B_2O_3 glasses. Density data are taken from [21, 22, 26].

polyhedron compared with the volume of its own ions. The net volume V_4' of a BO_4 tetrahedron can therefore be taken as the volume occupied by the ions only, and is given as

$$V_4' = V_{R^+} + 2V_{O^{2-}}, \qquad (3)$$

where V_{R^+} is the volume of the R^+ ion, which belongs to the BO_4 tetrahedron for charge compensation, and $V_{O^{2-}}$ is the volume of the oxygen ion. The volume of B^{3+} is not considered in Equation 3 because of its position within the internal space of the tetrahedron. These considerations should mean that the net volume of a BO_4 tetrahedron remains nearly independent of the R_2O content.

Fig. 6 indicates that the space surrounding each tetrahedron increases up to about 16 mol % Na_2O. If the electric conduction is only dependent on the volume of the space surrounding the BO_4 tetrahedra, then one would expect the activation energy to decrease up to 16 mol % Na_2O, which is not the case. Starting with $V_3 = 0.03194\,nm^3$ in vitreous B_2O_3, Figs 6 to 9 show that at about 15 mol % R_2O there is contraction in the volume of BO_3 units, ranging between 7 and 9% for Na_2O–, K_2O–, Rb_2O– and Cs_2O–B_2O_3 glasses. It seems that the contraction in the space surrounding the BO_3 triangles in that alkali range is responsible for the increase of the activation energy for electric conduction, the decrease of the linear thermal expansion coefficient [28, 29] and the drastic change of other physical properties of such glasses [5–7, 25]. It is also concluded that up to 16 mol % Na_2O there should be no interconnection between the spaces surrounding the BO_4 tetrahedra and, therefore, the motion of the charge carriers will be controlled by the nature of the interconnected BO_3 matrix.

For R_2O concentrations higher than about

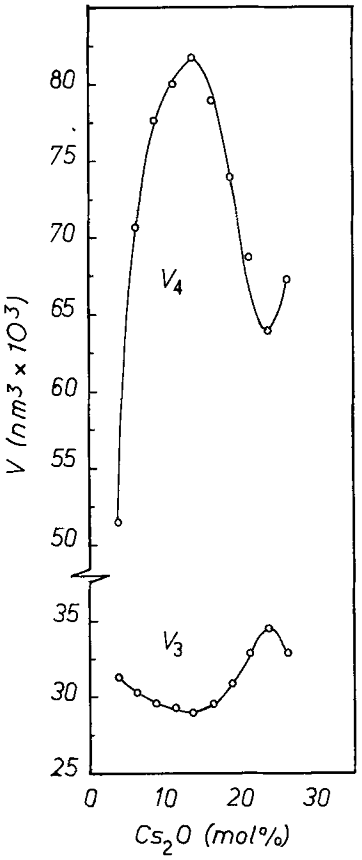

Figure 9 Dependence of V_3 and V_4 on R_2O content in Cs_2O–B_2O_3 glasses. Density data are taken from [21, 22].

15 mol % (Figs 6 to 9) it is shown that V_3 increases and V_4 decreases up to about 25 mol % for Na_2O, K_2O and Cs_2O, and about 27.5 mol % Rb_2O. Again, the increase of V_3 should act in the direction of decreasing the activation energy for electric conduction and increasing the thermal expansion. The decrease of V_4 should act in the opposite direction, but one must consider that the spaces surrounding the BO_4 tetrahedra should be interconnected for $R_2O > 16$ mol %. The increase of V_4 for $R_2O > 25$ mol % and the interconnection of the spaces associated with the BO_4 tetrahedra can be considered as reasons for the decrease of the activation energy and the increase of the thermal expansion coefficient, in spite of the decrease of V_3 in the same R_2O region.

The maxima of V_3 and the minima of V_4 at about 25 mol % R_2O reflect specific structural changes. Breaks in the plot of both the refractive index and the volume of glass per gram-atom of oxygen, against Na_2O in Na_2O–B_2O_3 glasses, were also recorded at about 16.5 and 28.3 mol % Na_2O [15].

In the case of Li_2O– and Ag_2O–B_2O_3 glasses the change of V_3 and V_4 with R_2O content is different. In Figs 5 and 10 it is shown that V_3 is nearly constant up to about 10 mol % R_2O and then decreases. The absence of maxima and minima of V_3 and V_4 can be connected with the higher tendency of the glasses in these systems to phase separation [9, 29]. However, the maxima or minima of the physical properties of Li_2O– and Ag_2–B_2O_3 glasses at about 16 mol % R_2O can be explained by considering the same effects as those discussed for the other alkali borate glasses.

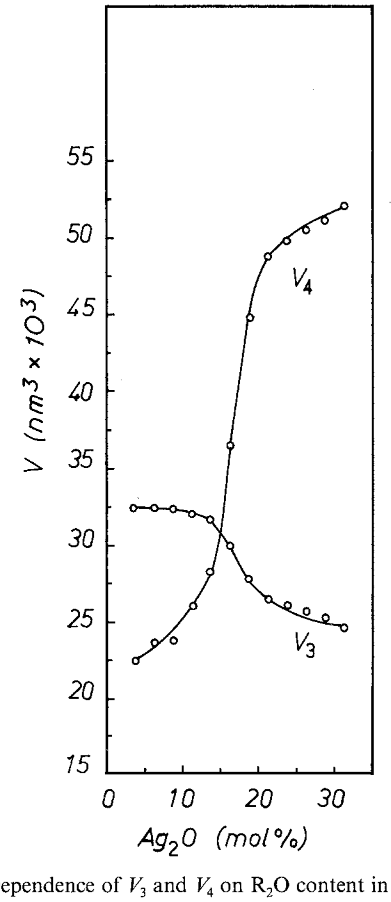

Figure 10 Dependence of V_3 and V_4 on R_2O content in Ag_2O–B_2O_3 glasses. Density data are taken from [9].

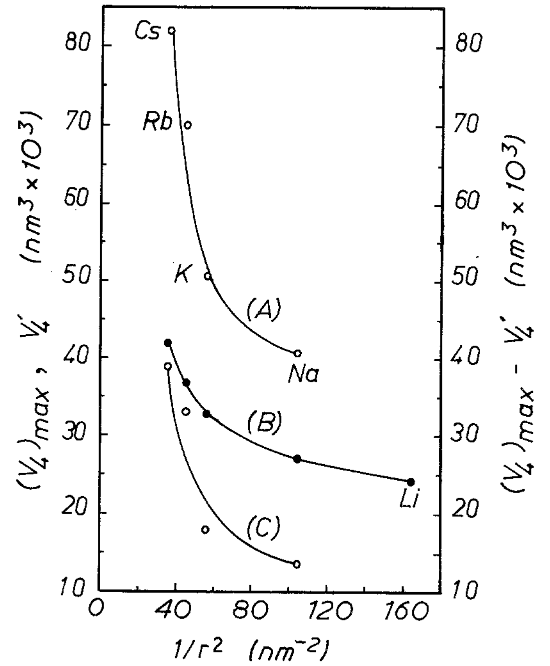

Figure 11 Dependence of $(V_4)_{max}$ (curve A), V_4' (curve B) and $[(V_4)_{max} - V_4']$ (curve C) on the ionic radius r of the alkali cation in binary alkali borate glasses.

In Figs 6 to 9 it is shown that the minimum value of V_3, $(V_3)_{min}$, obtained at about 15 mol % R_2O, is nearly constant and lies between 0.029 and 0.030 nm^3. This means that $(V_3)_{min}$ is not greatly affected by the type of alkali ion added to the glass. The maximum V_4. $(V_4)_{max}$, at about 15 mol % R_2O, changes markedly with a change of alkali ion. Fig. 11 (curve A) shows that $(V_4)_{max}$ decreases as the ionic field strength increases. Fig. 11 (curve B) also shows that the net volume V_4' of the BO_4 groups, calculated from Equation 3, changes similarly with the ionic field strength. The change of V_4' is expected, since a change of V_4' should arise from the change of V_{R^+}. Curve C (Fig. 11) indicates that the difference $[(V_4)_{max} - V_4']$ increases as the ionic field strength decreases. This difference should represent the volume of space surrounding the BO_4 tetrahedron at about 15 mol % R_2O. The decrease of $[(V_4)_{max} - V_4']$ with an increase of ionic field strength suggests that there is some electrostatic attraction between the alkali ion and the surrounding oxygen ions, which belong to other polyhedra. This conclusion is in agreement with the proposed weak heteropolar bond between the alkali ion and the boron ion in the BO_4 tetrahedra [30].

Fig. 12 (curve A) shows that $(V_4)_{max}/V_4'$ changes from about 1.5 for Na_2O– and K_2O–B_2O_3 glasses to about 1.9 for Rb_2O– and Cs_2O–B_2O_3 glasses. On the other hand, it is found that $V_4(3.75\,R_2O)$, the volume of the BO_4 tetrahedron at 3.75 mol % R_2O, nearly equals the net volume V_4' as calculated using Equation 3. This indicates that at such an alkali concentration the BO_4 tetrahedra formed are introduced into the structure nearly with their net volume, i.e. without surrounding space. The surrounding space should increase with R_2O to reach its maximum at about 15 mol %.

Shibata *et al.* [31] studied the density of lithium borate glasses and proposed that for $Li_2O < 28.57$ mol %,

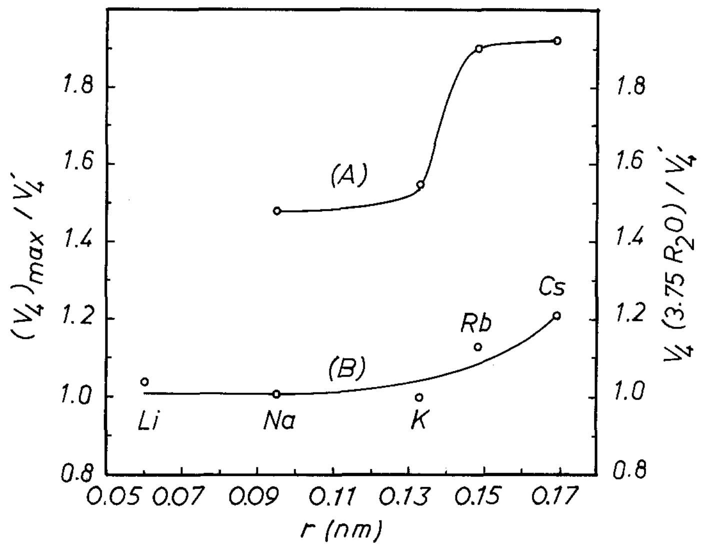

Figure 12 Change of both the ratio $(V_4)_{max}/V_4'$ (curve A) and the ratio $V_4(3.75R_2O)/V_4'$ (curve B) with the ionic radius r of the alkali cation in binary alkali borate glasses.

$V_4 = 0.84 V_3$. In their article they assumed V_3 to be constant ($V_3 = 0.032\,nm^3$). They treated the change of density as due to the change of N_3 and N_4 (the fractions of the three- and four-coordinated borons, respectively). The present study indicates that the model given by Shibata *et al.* [31] should be extended to include the change of V_3 and V_4 too.

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Received 4 August 1988
and accepted 14 April 1989