Borate glass structure by Raman and infrared spectroscopies*

E.I. Kamitsos and G.D. Chryssikos

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48, Vass. Constantinou Ave., Athens 116 35 (Greece)

(Received 22 January 1990)

Abstract

Raman and infrared spectroscopies have been employed to probe the continuous evolution of borate glass structures as a function of the nature and concentration of alkali oxide modifier. At relatively low alkali contents, the glasses contain covalent networks consisting of interconnected units bearing BO_4^- tetrahedra. Further addition of alkali oxide causes the progressive depolymerization of the network as a result of the formation of non-bridging oxygen atoms. Eventually, complete network disruption into small and highly charged borate units results in "ionic" glasses. The nature of the alkali cation determines the structure of these glasses by affecting several high-temperature isomerization or disproportionation equilibria.

INTRODUCTION

Binary alkali borate glasses $xM_2O(1-x)B_2O_3$ (M, alkali metal) have been extensively studied over the years to elucidate the nature and the relative concentration of the various borate units constituting the glass network. The ultimate goal has been to understand the structural peculiarities of these materials, which are manifested in the non-monotonic variation of most physical properties with x and are widely known as the "boron anomaly effect" [1]. The NMR investigation of Bray and co-workers [2,3] as well as the vibrational work of Krogh-Moe [4] and Konijnendijk and Stevels [5] have been particularly helpful in identifying various boron-oxygen arrangements at different modification levels. These studies have put emphasis on the effect of modifier content (x) on the glass structure, but have provided little or no insight into the possible dependence of the latter on the nature of the particular alkali employed.

Interest in structural studies of borate glasses has been renewed since the discovery of glass compositions with exceptionally high ionic conductivity,

^{*}Dedicated to the memory of Professor George Wilkinson.

which are promising for energy storage and microionics applications [6]. In that respect, binary alkali borate glasses are of special interest since they can be good ionic conductors by themselves [7,8] and may also form the basis of multicomponent fast ionic conductors [6,9,10]. Enhanced ionic conductivity is usually related to high contents of metal oxide modifiers in both binary and multicomponent systems [9,10].

It has been recognized that the limited structural understanding of glasses, inherent to their disordered nature, is the main reason for the lack of a comprehensive theory for the ion transport mechanism in amorphous solids [9–11]. Previous vibrational studies of alkali borate glasses have been limited to compositions with rather low M_2O contents (x < 0.40). Since most of the current interest is focussed on glasses with high M_2O concentrations, it is highly desirable to extend these studies to such materials.

In this paper, we present Raman spectra of sodium borate and caesium borate glasses, with compositions covering a continuous and very broad glass forming range $(0 \le x \le 0.75)$. These spectra will enable the systematic study of the variation of glass network structure with metal oxide content. In addition, Raman spectra of borate glasses with fixed M₂O content will be presented, to demonstrate a possible alkali cation effect on the glass structure.

A thorough understanding of the vibrational characteristics of glassy materials frequently requires a parallel study in the infrared [12] because of the complementary Raman and infrared selection rules. Most of the previous infrared studies on borate glasses were performed on low-M₂O content samples dispersed in a variety of media and cover independently the mid- [4,13–16] and far-infrared [17,18] spectral regions. Some reflectance investigations are reported but most of them are limited to the mid-infrared range [19–21]. By taking advantage of the capabilities of modern Fourier-transform spectrometers we have acquired infrared reflectance data over a wide frequency range (30–4000 cm⁻¹), and obtained the optical and dielectric properties of borate glasses by Kramers-Kronig inversion. This facilitates the simultaneous study of both the glass network structure in the mid-infrared and the cation-network interactions active in the far-infrared. Spectra of characteristic compositions of the system xLi_2O (1-x)B₂O₃ ($0 \le x \le 0.73$) are presented and discussed in relation to the Raman data.

EXPERIMENTAL

Sample preparation

Glasses were prepared from reagent-grade powders of anhydrous B_2O_3 and dried metal carbonates, mixed in appropriate amounts and melted in platinum crucibles in an electric furnace. Small replacement of B_2O_3 by Al_2O_3 (about 5 mol%) was necessary to ensure the glass formability of sodium borate glasses

with $0.45 \le x \le 0.55$ [22,23]. Melting times of about 10–30 min, and temperatures in the range 800–1200°C, depending on composition, were employed to obtain clear and bubble-free melts. Glassy samples were then prepared by quenching the melt between two copper blocks. It was observed that preheating these blocks to about 100°C resulted in flat glass samples, with surfaces quite good for infrared reflectance measurements. Such samples were used for both the Raman and infrared measurements without any further treatment. In fact, attempts to improve the surface by polishing often resulted in sample deterioration due to hydrolysis.

Selected glass compositions were checked and found to be X-ray amorphous, while their chemical analysis gave results varying less than 2% from the nominal ones [16], reported in this work. Samples containing small (x < 0.15) or large (x > 0.50) amounts of alkali metal are hygroscopic, and thus special care was taken to avoid hydrolysis by storing them in evacuated desiccators. It should be noted that some carbonate retention could not be avoided in high Na₂O and Cs₂O content glasses, owing to their high melt-basicity [22,23]. Further details of sample preparation and handling have been reported elsewhere [16,24,25].

Spectroscopic measurements

The Raman spectra were measured on a Ramanor HG 2S Jobin-Yvon spectrometer with 90° scattering geometry. Excitation was typically provided by the 488.0 nm line of a Spectra Physics 165 argon ion laser operating at about 500 mW. Glass samples were placed in a vacuum cell fitted with fused silica windows to avoid hydrolysis during spectral recording. Spectral resolution was 5 cm^{-1} or better.

Infrared spectral measurements were performed on a Fourier-transform Bruker 113v vacuum spectrometer, equipped with an 11° reflectance attachment and the appropriate sources, detectors and beam splitters to allow for effective and continuous coverage between 30 and 4000 cm⁻¹. Measurements were made at room temperature and 2 cm⁻¹ resolution. Kramers–Kronig analysis, performed on the reflectance spectra by employing the Bruker HIL programme, yielded the real and imaginary parts of both the refractive index and the dielectric constant. The absorption coefficient, α (cm⁻¹) was then calculated from the relation [26]

$$\alpha = 4\pi \nu k = 2\pi \nu \epsilon''/n \tag{1}$$

where n and k are respectively the frequency-dependent real and imaginary parts of the refractive index, ϵ'' is the imaginary part of the dielectric constant and v is the frequency (cm⁻¹).

RESULTS AND DISCUSSION

Raman spectra of alkali borate glasses

The structure of sodium borate and caesium borate glasses over extended composition ranges

The Raman spectra of sodium borate glasses are shown in Fig. 1 for several compositions with relatively low Na₂O content. The spectrum of glassy B_2O_3 (x=0) is characterized by the strong, sharp and highly polarized band at 806 cm⁻¹. The origin of this band has been the subject of extensive investigations, which have led to its now quite well accepted assignment to the symmetric ring-breathing vibration of the boroxol ring (Fig. 2(1)) [27-32].

Addition of Na₂O to B₂O₃ appears to cause substantial structural changes in the borate network, evidenced by alterations in the Raman vibrational characteristics. The most important effect of increasing x is the rapid decrease of the 806 cm⁻¹ band intensity, with the simultaneous development of a new band at about 770 cm⁻¹. For the glass composition x=0.25 the 806 cm⁻¹ fea-



Fig. 1. Raman spectra of sodium borate glasses, $xNa_2O(1-x)B_2O_3$, in the composition range $0 \le x \le 0.30$.



Fig. 2. Structural groups postulated for borate glasses: (1) boroxol ring, (2) pentaborate unit, (3) triborate unit, (4) diborate unit, (5) metaborate ring, (6) metaborate chain, (7) "loose" BO_4^- tetrahedron, (8) pyroborate unit, (9) orthoborate unit, and (10) boron-oxygen tetrahedron with two bridging and two non-bridging oxygen atoms. Solid circles represent boron atoms, open circles oxygen atoms. Note that Ø indicates a bridging oxygen and O⁻ indicates a non-bridging oxygen.

ture has disappeared, indicating the absence of boroxol rings, while that at 765 cm⁻¹ becomes the dominant Raman band. The latter feature has been observed in the spectra of similar glasses and assigned by Brill [33] to the symmetric ring breathing vibration of six-membered ring arrangements containing one or two $B\mathscr{Q}_4^-$ tetrahedra (\mathscr{Q} , bridging oxygen). Several borate groups of this kind are shown in Figs. 2(2) and 2(3). Thus, the Raman spectra of Fig. 1 indicate that addition of sodium oxide to B_2O_3 causes the progressive transformation of boroxol rings into rings with $B\mathscr{Q}_4^-$ tetrahedra, i.e. a change of boron coordination number from three to four.

Further increasing the Na₂O concentration causes drastic spectral effects, shown in Fig. 3 for the sodium borate glasses with compositions covering the range $0.35 \le x \le 0.55$. These Raman spectra are rather complex and the effect of x on only a few of their bands will be discussed here. More details can be found elsewhere [24]. The band at 630 cm⁻¹, which appears first at x=0.35and develops with increasing x, is of particular interest since it indicates the creation of ring-type metaborate units (Fig. 2(5)). In fact, the 630 cm⁻¹ band originates from the ring-breathing vibration of the latter units [33]. A new band at 820 cm⁻¹ appears in the spectrum of the x=0.45 glass and becomes a dominant feature upon further increasing x. This band and the one at 1210



Fig. 3. Raman spectra of $xNa_2O(1-x)B_2O_3$ glasses in the composition range $0.35 \le x \le 0.55$.

cm⁻¹ are characteristic of the pyroborate units (Fig. 2(8)), and originate from the symmetric stretching vibration of B–O–B bridges and terminal B–O⁻ bonds respectively [24]. Thus, the sequence of the Raman spectra presented in Fig. 3 indicates that, for this particular composition range, addition of Na₂O results in a progressive disruption (i.e. depolymerization) of the borate network, through the formation of non-bridging oxygen-containing borate units. Such representative units are the metaborate rings and the pyroborates, both representing "molecular" type moieties which are completely dismantled from the covalent borate network.

Representative Raman spectra of sodium borate glasses with compositions $0.61 \le x \le 0.75$ are depicted in Fig. 4. It is quite clear that the bands at 630, 755, 820 and 1210 cm⁻¹, as well as the ones at about 550 and 940 cm⁻¹, suffer a systematic intensity decrease upon increasing x. Thus, the borate groups responsible for these bands are progressively destroyed in such high Na₂O-content borate glasses. This is accompanied by the appearance of the 895 cm⁻¹ feature (x=0.61), which increases in intensity with x and eventually becomes the main band of the x=0.75 glass spectrum. We have attributed this band to the symmetric stretching vibration of the planar orthoborate units, BO₃³⁻ (Fig.



Fig. 4. Raman spectra of $x Na_2 O(1-x) B_2 O_3$ glasses in the composition range $0.61 \le x \le 0.75$.

2(9)). In addition the weak band at 1275 cm^{-1} is assigned to the asymmetric stretching of BO₃³⁻, and the one at 588 cm⁻¹ to the in-plane bending mode of the same unit [24]. The weak band observed at 1570 cm^{-1} can be assigned to the overtone of the out-of-plane bending mode of BO₃³⁻, which is infrared active only at 780 cm⁻¹ [34].

In addition to the bands attributed to BO_3^{3-} species, the spectrum of the x=0.75 glass exhibits a sharp band at 1060 cm⁻¹. This can be assigned to the totally symmetric stretching vibration of carbonate species, CO_3^{2-} , which are present in such high basicity borate glasses [25]. The influence of carbonates on the glass structure, their interaction with the glassy environment, and their dependence on melting time, temperature and composition have recently been investigated [36].

The above results demonstrate the effectiveness of Raman spectroscopy in probing the continuous variation of the borate network structure upon Na₂O addition. Thus, at low modification levels ($x \le 0.30$), Na₂O causes the formation of four-coordinated boron atoms, which provide additional crosslinks to the borate network through the oxygen bridges. At higher Na₂O contents ($0.35 \le x \le 0.55$) the glass network becomes depolymerized upon the formation

of non-bridging oxygen containing units, (ring metaborates and pyroborates). At even higher sodium contents, the latter are decomposed in favour of small and highly charged orthoborate moieties. Thus, a return to a boron coordination number of three is effected at such high x values.

The Raman spectra of caesium borate glasses have recently been reported for composition in the range: $0 \le x \le 0.50$ [37]. It has been observed that for small values of x, the caesium glass spectra were quite similar to the corresponding ones of sodium borate glasses. The cation dependence of the borate glass network is consequently rather small at low modification levels, but becomes progressively very significant as x increases towards the metaborate stoichiometry. Thus, the spectrum of the x = 0.50 caesium borate glass exhibits pronounced differences from that of the sodium glass of the same alkali concentration. It should be kept in mind that the spectrum of sodium metaborate is that of a pseudo-binary glass containing about 5 mol% Al₂O₃. The aluminafree sodium melt is not glass-forming, in contrast to the corresponding caesium melt and this illustrates even better the role of the modifying cation in determining the structure of borate networks. This led us to further extend the glass-forming region of the Cs₂O-B₂O₃ system [25] and study the structure of the obtained glasses.

The Raman spectra of caesium borate glasses with compositions $0.50 \le x \le 0.75$ are depicted in Fig. 5. The metaborate composition (x=0.50) is



Fig. 5. Raman spectra of $xCs_2O(1-x)B_2O_3$ glasses $(0.50 \le x \le 0.75)$.

characterized by sharp bands at 606 and 545 cm⁻¹ which have been attributed respectively to metaborate rings and "loose" BO_4^- tetrahedra [37]. The former groups are also responsible for the 370, 463 and 1400–1600 cm⁻¹ features. The latter units (Fig. 2(7)) are boron-oxygen tetrahedra isomeric to the metaborate triangles BO_2O^- , and connect various segments of the glass network without participating in specific borate arrangements. The 900 cm⁻¹ band is assigned to the asymmetric vibration of "loose" BO_4^- tetrahedra; that at 1040 cm⁻¹ is indicative of the presence of some undissociated carbonates [37].

At higher Cs₂O contents all spectral features related to the aforementioned boron-oxygen units appear to decrease in intensity, indicating that those units are no longer favoured. Instead, the spectral activity is progressively enhanced around 675 cm⁻¹ and 345 cm⁻¹. These features maintain fixed relative intensities regardless of the extent of their coexistence with bands that characterize the metaborate glass, and finally dominate the spectrum of the orthoborate composition (x=0.75). It is argued, on the basis of the similarity between the spectrum of the x=0.75 caesium borate glass and those of calcium orthoaluminate and orthogallate, that the new features at 675, 377 and 345 cm⁻¹ denote the existence of BØ₂ O₂³⁻ units (Fig. 2(10)) [25]. These are boron-oxygen tetrahedra with two bridging (Ø) and two non-bridging (O) oxygen atoms. Such units are recognized for the first time in highly modified borate glasses, though similar tetrahedra are common in phosphate and silicate amorphous and crystalline networks [38].

The majority of crystalline orthoborate compounds are formed by isolated triangular orthoborate units, BO_3^{3-} , which were also found to constitute the "network" of the x=0.75 sodium borate glass. However, such units are not present in the corresponding caesium borate glass, but are replaced by isomeric $BØ_2O_2^{3-}$ species. Thus, it appears that the structure of the borate glass network is a function of both the content and the nature of the metal oxide present. The effect of the nature of the alkali metal is examined in more detail in the following section.

Alkali cation dependence of the borate glass structure

As noted above, differences between the spectra of alkali borate glasses of the same x value are mainly manifested at high alkali concentrations. Nevertheless, a careful examination of the Raman spectra of glasses with relatively low M₂O content has also revealed the dependence of the network structure on the particular alkali employed [39]. Figure 6 illustrates the Raman spectra of borate glasses with x=0.70. This particular composition was chosen because it lies roughly halfway between the pyroborate (x=0.67) and orthoborate (x=0.75) compositions, and thus it should in principle correspond structurally to a mixture of the corresponding isolated moieties (Fig. 2(8) and 2(9)). Indeed, the spectrum of the lithium glass exhibits bands characteristic of ortho-



Fig. 6. Raman spectra of alkali borate glasses of composition $0.70M_2O0.30B_2O_3$, (where M is Li, Na, K, Rb, Cs).

borate units (925 cm^{-1}), pyroborate (835, 1250 cm^{-1}) units, and six-membered rings with BO_4^- tetrahedra (763 cm⁻¹). The same network-building units are evident in the spectrum of the corresponding sodium glasses. They are also present in the potassium glasses, as manifested by their corresponding Raman bands, which now coexist with a number of new features. For instance, we can deduce the presence of metaborate rings (608 cm^{-1}) and chains (740 cm^{-1}) in addition to orthoborate triangles (865 cm^{-1}) and pyroborates $(810 \text{ and } 1180 \text{ cm}^{-1})$ cm^{-1}) [37]. The formation of $BØ_2O_2^{3-}$ tetrahedra is also evident from the presence of the 680, 395 and 350 cm^{-1} bands. These features grow mainly at the expense of the band characteristic of orthoborate triangles (865 cm^{-1}). which suffers a significant loss in relative intensity from sodium to potassium. The spectra of the rubidium and caesium glasses recover their simplicity in a way that bears no similarity to those of lithium and sodium glasses. Thus, the predominant network unit appears to be the four-coordinated $BO_{2}O_{2}^{3-}$ species (675, 377 and 345 cm⁻¹), while some "loose" BO_4^- tetrahedra (545 cm⁻¹) and metaborate rings ($\approx 600 \text{ cm}^{-1}$) are also present.

On the basis of the Raman spectra discussed above the formation of highly modified borate glasses seems to be associated with the existence of the following set of high-temperature equilibria

Stoichiometry

meta-: $x = 0.50$,	$(BO_2^-) BØ_2O^- \rightleftharpoons BØ_4^-$	(2)
---------------------	--	-----

pyro-: $x = 0.67$,	$(BO_{2.5}^{2-})$	$2B\emptyset O_2^{2-} \rightleftharpoons (BO_3^{3-}) + (BO_2^{})$	(3)
---------------------	-------------------	---	-----

ortho-:
$$x = 0.75$$
, $(BO_3^{3-}) BO_3^{3-} \rightleftharpoons B\emptyset_2 O_2^{3-}$ (4)

It is obvious that the above equilibria are strongly cation dependent. For example, eqns. (3) and (4) are shifted to the left for lithium and sodium. The potassium analogue, whose spectrum is the most complex of all, favours the coexistence of all reactants and products in eqns. (2)-(4). In rubidium and caesium glasses of high M₂O content (x=0.70), the Raman spectra indicate that all three equilibria are shifted to the right, resulting in network tetrahedra with none or two non-bridging oxygen atoms.

Quenching the above equilibria accounts for the observed dependence of borate glass structures of a given stoichiometry on the modifier. It should also be relevant to the glass-formability of the corresponding melts and this finds support in the devitrification data recently available for selected glasses [40,41].

Infrared spectra of lithium borate glasses

Infrared absorption spectra of lithium borate glasses were calculated by Kramers-Kronig analysis of the reflectance spectra and are shown in Fig. 7 for several compositions spanning the region $0 \le x \le 0.73$. It is obvious that addition of Li₂O to B₂O₃ results in significant spectral changes, which illustrate the progressive structural variation of the borate network. The measured infrared spectra appear more complex than the Raman ones (Figs. 1, 3, and 4), due to the presence of a large number of broad and extensively overlapping bands. Nevertheless, three spectral regions can be distinguished in the midinfrared: 1200–1450 cm⁻¹ (B–O stretching vibrations of trigonal BO₃ units), 850–1200 cm⁻¹ (B–O stretching vibrations of the borate network) [4,16]. Absorption in the far-infrared region (50–600 cm⁻¹) increases progressively with x, and results in a broad asymmetric band with frequency at a maximum and a relative intensity that increases with Li₂O content. This far-infrared



Fig. 7. Infrared spectra of $x \text{Li}_2 O(1-x) B_2 O_3$ glasses for selected compositions in the range $0 \le x \le 0.73$.

feature was previously assigned to vibrations of Li^+ cations against their network sites. The relatively large bandwidth of the far-infrared band has been associated with the broad distribution of similar anionic sites that characterize the glassy state [18]. While the borate network dynamics contribute mostly to the mid-infrared absorption profile, these lithium cation motions dominate the low frequency spectral region.

The most obvious effect of adding Li_2O to B_2O_3 is the growing of a multiple band in the 800-1200 cm⁻¹ region, attributed to $BØ_4^-$ absorptions. This envelope exhibits a maximum relative intensity for x=0.40, and then it decreases upon further increasing x. Such behaviour is indicative of the initial creation of $BØ_4^-$ tetrahedra-containing groups, followed by their subsequent destruction in favour of non-bridging oxygen-containing units (x>0.40). This is in accordance with the findings of NMR spectroscopy for this and similar glass systems [42].

Careful comparison of the spectra of Fig. 7 with those of crystalline borate

compounds of similar compositions [4,43] suggests that the initially created BO_4^- tetrahedra are found in pentaborate (Fig. 2(2)) groups, which are then replaced by diborate arrangements (Fig. 2(4)) with maximum concentration at x=0.40. The subsequent destruction of the latter groups is due to the creation of non-bridging oxygen atoms as suggested by the appearance of the 1240 cm⁻¹ band (x>0.40). This is a characteristic feature of the infrared spectrum of crystalline α -Li₂O·B₂O₃, known to consist of metaborate chains (Fig. 2(6)) [43]. In addition, the 1135 cm⁻¹ band developing at the high frequency side of the BO₄⁻ absorption envelope denotes the formation of pyroborate units. This feature is due to the asymmetric stretching of B–O–B bridges in B₂O₅⁴⁻ units, and is one of the main bands in the spectrum of crystalline lithium pyroborate, $2\text{Li}_2\text{O}\cdot\text{B}_2\text{O}_3$ [43].

The dominant absorption of the x=0.73 glass spectrum is at 1300 cm⁻¹, observed originally as a shoulder to the 1250 cm⁻¹ band. Crystalline lithium orthoborate $(3\text{Li}_2\text{O}\cdot\text{B}_2\text{O}_3)$ gives its strongest absorption at this frequency, as a result of the infrared active asymmetric stretching vibration of BO₃³⁻ units [43]. Thus, the borate network of the x=0.73 lithium glass appears to be built up mainly of orthoborate units and a minor concentration of pyroborates (1130 cm⁻¹), as well as groups with BØ₄⁻ tetrahedra (1040, 960 cm⁻¹). The second-strongest feature of the mid-infrared spectrum of this glass is at 775 cm⁻¹, and can be assigned to the out-of-plane bending vibration of BO₃³⁻ units, while the in-plane bending mode gives rise to the 650 cm⁻¹ shoulder of the lithium motion band [34].

Detailed assignment of all infrared features requires careful deconvolution of the spectra and comparison with analogous crystalline compounds. While the details of the deconvolution will be reported elsewhere [43], we present here the summarized results of this study (Fig. 8), expressed as the relative concentration of various borate units as a function of Li₂O content. This enables the illustration of the network modification scenario upon increasing the amount of modifier oxide (Li₂O). Thus, the relative concentration of borate groups with BO_4^- tetrahedra peaks at x=0.40, with obvious shoulders at x=0.20and x=0.50, while metaborate chains and pyroborate units exhibit their maximum concentration at x=0.50 and x=0.65 respectively. The trigonal orthoborate units are the dominant species in glasses of very high Li₂O content.

The above modification pattern for lithium borate glasses is in general agreement with that deduced from the Raman study of sodium borate glasses. However, it is at pronounced variance with that found for caesium and rubidium borate glasses, especially of high M_2O contents. This is presumably the manifestation of a "preference" of each specific alkali cation for special borate units. This aspect will be further explored by the systematic study of the infrared spectra of the rest of the alkali borate glass systems.



Fig. 8. Compositional dependence of the relative concentration of borate units encountered in $xLi_2O(1-x)B_2O_3$ glasses. $B\emptyset_4^-$ denotes units containing boron-oxygen tetrahedra, and $B\emptyset_2O^-$ denotes chain type metaborates.

CONCLUSIONS

Raman and infrared spectroscopic techniques are powerful tools for providing structural insight into borate glasses. The new results presented in this study, together with the available literature, point to the strong dependence of the network modification on the nature of the cationic modifier. This cation dependence would be most obvious in glasses with high alkali contents and this has now been demonstrated, at least qualitatively. The smallest alkali cations, Li⁺ and Na⁺, seem to favour complete disruption of the borate network into isolated units, because of their high charge density. Correspondingly, the fraction of four-coordinated boron atoms (N_4) after going through a maximum at x = 0.35 is progressively and smoothly reduced towards a limiting value of zero as the glass composition approaches the orthoborate stoichiometry (x=0.75). On the contrary, the large and polarizable alkali cations (Rb^+, Cs^+) do not favour this reversal of boron-oxygen coordination from four to three. Instead, the N_4 value of the 75 mol% Cs₂O glass approaches unity owing to the formation of tetracoordinated boron atoms with two non-bridging oxygen atoms, which are not encountered in their lithium and sodium analogues.

These results are expected to trigger the investigation of high alkali content borates by NMR and other techniques. They also open the way for a detailed study of the devitrification mechanisms of these glasses, to confirm the nature of the high temperature equilibria thought to account for the diversity of the modification schemes. Much will also be gained in terms of understanding the glass-formability of the corresponding borate melts, and the glass transport properties.

ACKNOWLEDGEMENTS

We are grateful to M.A. Karakassides and A.P. Patsis for their valuable assistance. This work was supported by N.H.R.F.

REFERENCES

- 1 D.L. Griscom, Borate Glass: Structure, Properties and Applications, in L.D. Pye, V.D. Frechette and N.J. Kreidl (Eds), Plenum Press, New York 1978, pp. 11-149.
- 2 A.H. Silver and P.J. Bray, J. Chem. Phys., 29 (1958) 984.
- 3 P.J. Bray and J.G. O'Keefe, Phys. Chem. Glasses, 4 (1963) 37.
- 4 J. Krogh-Moe, Phys. Chem. Glasses, 6 (1965) 46.
- 5 W.L. Konijnendijk and J.M. Stevels, J. Non-Cryst. Solids, 18 (1975) 307.
- 6 H.L. Tuller, D.P. Button and D.R. Uhlmann, J. Non-Cryst. Solids, 40 (1980) 93.
- 7 A. Levasseur, M. Kbala, P. Hagenmüller, G. Couturier and Y. Danto, Solid State Ionics, 9-10 (1983) 1439.
- 8 Y. Ito, K. Miyauchi and T. Oi, J. Non-Cryst. Solids, 57 (1983) 389.
- 9 M.D. Ingram, Phys. Chem. Glasses, 28 (1987) 215.
- 10 H.L. Tuller and P.K. Moon, Mater. Sci. Eng., B1 (1988) 171.
- 11 M.D. Ingram, M.A. Mackenzie, W. Müller and M. Torge, Solid State Ionics, 28-30 (1988) 677.
- 12 J. Wong and C.A. Angell, Glass Structure by Spectroscopy, Marcel Dekker, New York, 1976.
- 13 W.L. Konijnendijk, Philips Res. Rep., Suppl. No. 1 (1975) 1.
- 14 J.T. Quan and C.E. Adams, J. Phys. Chem., 70 (1966) 340.
- 15 E.I. Kamitsos, M.A. Karakassides, G.D. Chryssikos, J. Phys. Chem., 91 (1987) 1073.
- 16 E.I. Kamitsos, M.A. Karakassides and G.D. Chryssikos, Phys. Chem. Glasses, 28 (1987) 203.
- 17 G.J. Exarhos and W.M. Risen, Jr., Chem. Phys. Lett., 10 (1971) 484.
- 18 E.I. Kamitsos, M.A. Karakassides and G.D. Chryssikos, J. Phys. Chem., 91 (1987) 5807.
- 19 N.F. Borelli, B.D. McSwain and G.-J. Su, Phys. Chem. Glasses, 4 (1963) 11.
- 20 M. Irion, M. Couzi, A. Levasseur, J.M. Reau and J.C. Brethons, J. Solid State Chem., 31 (1980) 285.
- 21 M. Massot, C. Julien and M. Balanski, Infrared Phys., 29 (1989) 775.
- 22 S.W. Martin and C.A. Angell, J. Non-Cryst. Solids, 66 (1984) 429.
- 23 M. Shibata, C. Sanchez, H. Patel, S. Feller, S. Stark, G. Sumcad and J. Kasper, J. Non-Cryst. Solids, 85 (1986) 29.
- 24 E.I. Kamitsos and M.A. Karakassides, Phys. Chem. Glasses, 30 (1989) 19.
- 25 G.D. Chryssikos, E.I. Kamitsos, A.P. Patsis and M.A. Karakassides, Mater. Sci. Eng. B, 7 (1990) 1.
- 26 F. Gervais, A. Blin, D. Massiot, J.P. Couture, M.H. Chopinet and F. Naudin, J. Non-Cryst. Solids, 89 (1987) 384.
- 27 J. Goubeau and H. Keller, Z. Anorg. Allg. Chem., 272 (1953) 303.
- 28 L.A. Kristiansen and J. Krogh-Moe, Phys. Chem. Glasses, 9 (1968) 96.
- 29 F.L. Galeener, G. Lucovsky and J.C. Mikkelsen, Jr., Phys. Rev., B22 (1980) 3983.

- 30 C.F. Windisch and W.M. Risen, Jr., J. Non-Cryst. Solids, 48 (1982) 307.
- 31 P.A.V. Johnson, A.C. Wright and R.N. Sinclair, J. Non-Cryst. Solids, 50 (1982) 281.
- 32 A.C. Hannon, R.N. Sinclair, J.A. Blackman, A.C. Wright and F.L. Galeener, J. Non-Cryst. Solids, 106 (1988) 116.
- 33 T.W. Brill, Philips Res. Rep., Suppl. No. 1 (1975) 1.
- 34 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1978.
- 35 J.B. Bates, M.H. Brooker, A.S. Quist and G.E. Boyd, J. Phys. Chem., 76 (1971) 1565.
- 36 E.I. Kamitsos, M.A. Karakassides and A.P. Patsis, J. Non-Cryst. Solids, 111 (1989) 252.
- 37 E.I. Kamitsos, M.A. Karakassides and G.D. Chryssikos, Phys. Chem. Glasses, 30 (1989) 229.
- 38 N. Umesaki, N. Iwamoto, M. Tatsumisago and T. Minami, J. Non-Cryst. Solids, 106 (1988) 77.
- 39 G.D. Chryssikos, E.I. Kamitsos and M.A. Karakassides, Phys. Chem. Glasses, 31 (1990) 109.
- 40 E.I. Kamitsos, M.A. Karakassides, A.P. Patsis and G.D. Chryssikos, J. Non-Cryst. Solids, 116 (1990) 115.
- 41 G.D. Chryssikos, E.I. Kamitsos, A.P. Patsis, M.S. Bitsis and M.A. Karakassides, J. Noncryst. Solids, 126 (1990) 42.
- 42 Y.H. Yun and P.J. Bray, J. Non-Cryst. Solids, 44 (1981) 227.
- 43 E.I. Kamitsos, A.P. Patsis, M.A. Karakassides and G.D. Chryssikos, J. Non-cryst. Solids, 126 (1990) 52.