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THE THERMAL EXPANSION OF ALKALI BORATE GLASSES AND THE BORIC OXIDE ANOMALY

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A brief review is presented of the major theories for the so-called "boric-oxide anomaly" in alkali borate glasses, and a comparison is effected with recent published information on the structure of B_2O_3 and alkali borate glasses. These indicate serious shortcomings in current theories. An experimental study is reported of the mean linear thermal expansion coefficients between 25 °C and −196 °C of a series of glasses, prepared at composition intervals of 2 mole % alkali oxide, in all five alkali borate systems. The thermal expansion versus composition relations are characterized by broad, flat minima, with no single composition being uniquely identifiable with the minimum. It is concluded that the compositional variation of the thermal expansion coefficient of alkali borate glasses is not truly anomalous, but rather seems to vary with structural variations in a generally predictable manner. It is suggested that the term "anomaly" be reserved for the more serious problem of explaining the change in boron coordination with composition.

1. Introduction

In many glasses containing boric oxide, striking variations or "anomalies" are observed in some of the property versus composition relations. The term "anomaly" as applied to borate glasses has primarily been used to describe phenomena which cannot readily be explained by any obvious structural mechanism; the classic example of this is the minimum in the thermal expansion coefficient originally reported at about 15 mole% Na_2O–B_2O_3 [1]).

The purpose of this paper is to review briefly the major attempts to explain anomalous behavior in borate glasses; to collect and discuss a considerable body of recent structural data; to report a study of the thermal expansion behavior of glasses in all five alkali borate systems; and to indicate that, although a number of basic questions remain unanswered, the thermal ex-

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pansion characteristics of alkali borate glasses are not "anomalous" but simply vary with structural variations in a generally predictable manner.

2. Theories of the boric oxide anomaly

Many explanations of "anomalous" property variations in borate glasses deal with the well established coordination change of boron as alkali or alkaline earth oxides are added to B_2O_3. For example, the minimum in the thermal expansion coefficient was initially associated[2, 3]) with changes in coordination of the boron atoms. The structure of B_2O_3 was pictured as a random network of BO_3 triangles; on adding Na_2O, the additional oxygen atoms were thought to be taken up initially by boron atoms changing from triangular to tetrahedral coordination. This change was associated with a change in bonding character from 2-dimensional to 3-dimensional, with an attendant increase in the tightness of the structure and a decrease in the expansion coefficient. The fraction of 4-coordinated borons, N_4, was expected to vary, up to some concentration limit, as

$$N_4 = x/(1-x), \tag{1}$$

where x represents the mole fraction of alkali oxide. With further additions of Na_2O, the added oxygens were pictured as no longer completely taken up by borons changing to tetrahedral coordination, but some were thought to be bonded to only one boron atom. These singly-bonded oxygens were regarded as weak links in the boron–oxygen network, whose presence would loosen the structure and increase the thermal expansion coefficient.

On this view, the minimum in the expansion coefficient reported at about 15% Na_2O was attributed to a cessation in the process whereby as many as possible of the boron atoms are changed to tetrahedral coordination. The location of the minimum was related to a simple structural model[3]); and the plausibility of the picture, together with the results of X-ray diffraction studies (refs. 2–4, e.g.) led to wide acceptance of the suggested interpretation.

Abe[5]) and Huggins and Abe[6]) described a geometric model in which tetrahedra were formed by added alkali oxide up to a composition $M_2O \cdot 5\ B_2O_3$. At this point a 3-dimensional network, made up of tetrahedra surrounded by 4 triangles, would be possible. Further M_2O additions would create non-bridging oxygens and a corresponding looseness of the structure. The application of various structural "rules" led to the prediction that N_4 should remain constant beyond the composition $M_2O \cdot 5\ B_2O_3$. Zhdanov[7]) has discussed the changes in structure of alkali borate glasses in terms of the interaction of boron–oxygen tetrahedra. Properties were qualitatively linked to the degree to which the tetrahedra, with their associated alkali ions, could avoid each other. At about 30 mole% alkali oxide, the charged tetrahedra must unavoidably contact each other. To prevent this, the boron–oxygen tetrahedra "dissociate" in an undescribed manner. Property changes near 30 mole% alkali oxide were qualitatively explained by this process.

Several attempts have been made to account directly for the variation of N_4 with composition, which is basic to any structural explanation of property variations. Beekenkamp[8]) has written expressions for the equilibria between different assumed boron–oxygen configurations as a function of composition, to produce an expression for the variation of N_4 with composition. Yunitskii and Tarasov[9]) adopted a similar approach, writing equilibrium relations between oxygen ions in different configurations. However, the introduction of several empirical parameters makes their final expression of doubtful value, since almost any value of N_4 can be obtained by suitable adjustment of these parameters.

Many other models besides the random network structure of boron–oxygen triangles and tetrahedra have been suggested for the structure of glassy B_2O_3 and the binary borates. According to one of these models[10]), for example, boric oxide glass was thought to be composed of molecular units, presumably B_4O_6 molecules; according to another[11,12]), the coordination of the boron atoms in B_2O_3 was thought to be a hybrid between 3-fold and 4-fold, with the structure consisting of BO_3 triangles having 4th oxygens, at somewhat greater distances than those in the triangles, near the boron atoms. The latter model was also discussed in terms of the tetrahedral boron–oxygen configuration suggested[13]) for the low-density crystalline modification, and was used in attempting to describe the properties of B_2O_3 and binary borates (and, in particular, to describe the boric oxide anomaly). Block and Piermarini[14]) have noted that the known structures of anhydrous crystalline borates often involve boron–oxygen ring structures, and have speculated that the properties of borate glasses depend not only on the tetrahedral coordination of boron, but also on the degree to which the 6-, 8-, or 12-member ring structures are retained in the glassy state after fusion of the crystals. Krogh-Moe[15]) has presented a group model involving combinations of 4 borate molecular groups, containing 3 to 5 borons each, which interpenetrate to some extent over the alkali borate region from B_2O_3 to 33 mole% alkali oxide; some infrared data were interpreted in the light of this model.

None of these latter theories have proven satisfactory for describing all available experimental data; the structural theories described first have come considerably closer to describing actual structural variations with composition, as discussed in the next section, but must also be regarded as unsatisfactory at the present time.

3. The structure of borate glasses

The early X-ray diffraction studies of borate glasses[2-4]) indicated a change in boron coordination from 3-fold to 4-fold, but uncertainties in the experimental data (associated principally with termination effects and Compton scattering) as well as in the technique employed in analyzing the data (in particular, the "proportionality of scattering factors" approximation) limited the conclusions which could be drawn.

3.1. PURE B_2O_3

Two high-precision X-ray diffraction studies of glassy B_2O_3 have recently been carried out[16,17]). In both cases, care was taken to eliminate experimentally the Compton modified scattering; and in one case[17]), a recent, more exact treatment[18]) which eliminates the "proportionality of scattering factors" approximation was employed in analyzing the data. The results of both studies support the BO_3 planar triangle configuration originally suggested by Warren and his co-workers, and are at variance with any picture based on 4-fold coordination of the boron atoms.

In one of the diffraction studies[16,19]), a radial distribution function was also obtained for the low-density crystalline modification (B_2O_3I). The form of this distribution indicated that the previously-suggested[13]) tetrahedral B–O configuration was in error, and suggested that the actual configuration consisted of BO_3 triangles*. A more recent structure determination[21]), carried out with more appropriate single-crystal data, has confirmed this suggestion and indicated a structure based on planar ribbons of BO_3 triangles joined at common oxygen vertices. Two closely similar but crystallographically distinct types of boron–oxygen triangles were noted in the structure.

The results of a nuclear magnetic resonance study of crystalline B_2O_3I[22]) are consistent with those of the diffraction studies, and indicate that the boron atoms reside in a single type of site**, characterized by a quadrupole coupling constant in the same range found for crystalline compounds known to contain the BO_3 planar triangle configuration. A similar study of glassy B_2O_3[22]) indicated a strong response characterized by the same coupling as crystalline B_2O_3I, as well as a weak response at the characteristic frequency expected for boron atoms in 4-fold coordination. These results indicate that, in the B_2O_3 sample investigated, nearly all the boron atoms are in BO_3

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* Only in the high density (high pressure) form of B_2O_3 (B_2O_3 II) is a tetrahedral B–O configuration found[21]); and even in this form, the tetrahedra are highly irregular, having one short B–O distance (1.375 Å) and three long B–O distances (1.503, 1.504 and 1.514 Å).

** The two crystallographically-distinct types of boron sites in the B_2O_3I structure[21]) have closely-similar BO_3 triangular configurations, which are not distinguished in the NMR results.

triangular configurations but that some (perhaps 1%) may exist in BO_4 tetrahedral units. It has been noted, however, that such tetrahedral units may be associated with residual OH from the H_3BO_3 starting material, and may not be present in "dry" B_2O_3.

3.2. Binary borates

NMR studies of alkali borate glasses[23]) have confirmed the earlier suggestion of Warren and his co-workers[2,3]) that addition of alkali oxide to B_2O_3 results in a change of boron coordination from 3-fold to 4-fold. In more detail, as shown in fig. 1, the fraction of boron atoms in tetrahedral coordination was found to increase with increasing alkali oxide content, up to about 30–35 mole% alkali oxide. In this low-alkali range, the observed fraction of 4-coordinated borons in most systems lies close to – but perhaps somewhat below – the curve (shown in fig. 1) representing the assumption that each added oxygen converts two boron atoms from triangular to tetrahedral configurations. Beyond about 35–40 mole% alkali oxide, the fraction of 4-coordinated borons decreases continuously, and goes to zero in the composition range about 65–75 mole% alkali oxide.

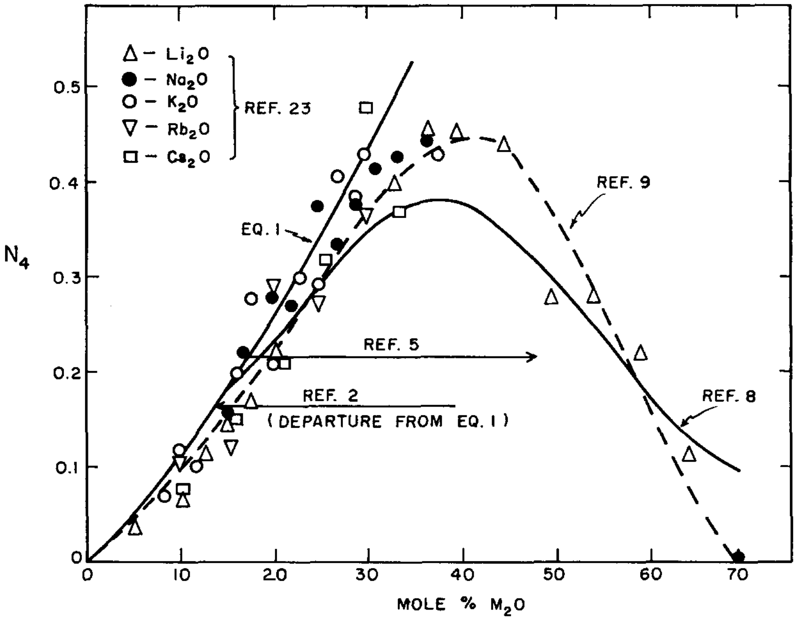

Fig. 1. The fraction N_4 of boron atoms in fourfold coordination compared with theories of alkali borate glass structure.

Fig. 1 also compares the structural theories described in the preceding section with the data. It is evident that agreement of theory with experiment is good only for the curve of Yunitskii and Tarasov; however, this good agreement is the result of careful curve-fitting by means of their disposable parameters, as discussed earlier, which leaves the interpretation still open to question. For the other cases, the generally poor agreement indicates again the current lack of an adequate theory.

It is interesting to note that the fraction of 4-fold coordinated borons in these alkali borate glasses ceases increasing well below the metaborate composition ($M_2O \cdot B_2O_3$) where all the boron atoms can be converted to the tetrahedral configuration; and indeed, when this composition is reached, the fraction of tetrahedrally-coordinated borons has decreased to about 0.3. The composition range where singly-bonded oxygens begin to be formed in appreciable concentrations is presently the subject of some discussion. While the data shown in fig. 1 must be regarded as insensitive to the presence or absence of some singly-bonded oxygens, it is apparent from the figure that the first marked departure of the experimental data from the relation of eq. (1) occurs in the composition range about 30 mole% alkali oxide.

By comparison, X-ray diffraction studies of crystalline alkali pentaborates[24]), tetraborates[25]) triborates[26]) and diborates[27]) have indicated that up to the diborate composition, the maximum possible (for the composition) number of borons are in tetrahedral coordination. In contrast to the glasses, however, all of the boron atoms in crystalline anhydrous alkali metaborates are apparently in triangular coordination[28-30]), albeit in some cases rather distorted triangles.

It seems apparent that the energetic differences between 3-fold and 4-fold coordinations may in many cases be slight, with the actual configuration being determined by relatively small factors. An interesting example of this is provided by the crystalline metaboric acids (HBO_2), where all the boron atoms are in tetrahedral coordination in the cubic form[31]), only one-third are 4-coordinated in the monoclinic form[32]) and all seem to be in 3-fold coordination in the orthorhombic form[33])*.

On another scale of structure, a recent study[37]) has located metastable miscibility gaps in all five alkali borate systems. The scale of the typical submicrostructures ranged from about 50 to a few hundred Å; and in contrast to the alkali silicates, this scale was found to increase in the order $Li < Na < K < Rb < C_s$. An evaluation of the effect of phase separation on the properties of simple glasses[38]) has indicated that the "anomalous"

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* The conclusions of these X-ray diffraction studies are again supported by NMR investigations[34-36]).

thermal expansion behavior is not associated with phase separation. The existence of miscibility gaps does, however, indicate that corrections to the theories of the preceding section are required.

4. The properties of borate glasses

It is apparent from the above discussion that the minimum in the expansion coefficient, reported [1-4]) to occur at about 15 mole% alkali oxide, cannot

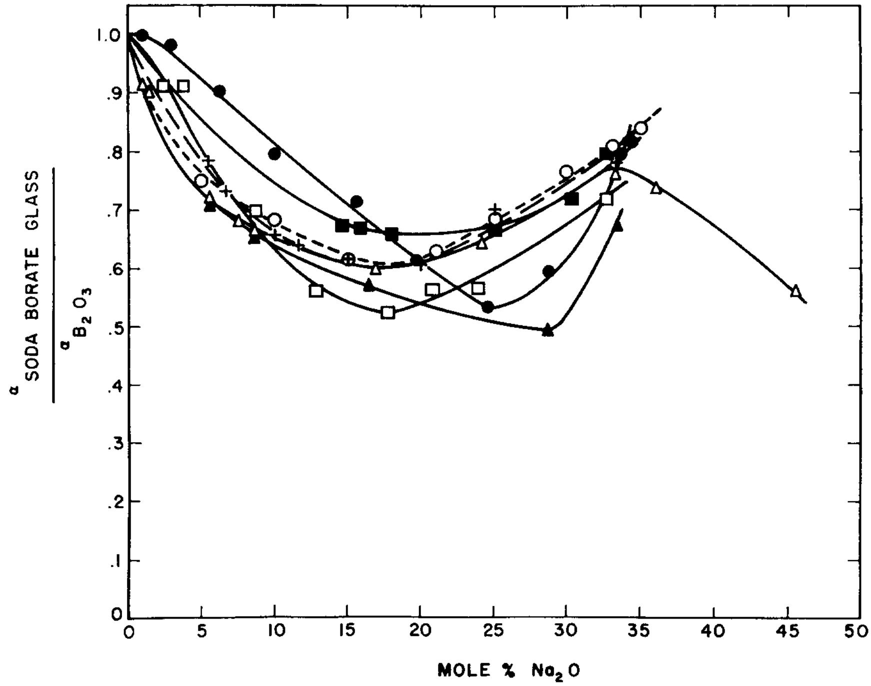

Fig. 2. Normalized thermal expansion coefficients of sodium borate glasses reported by different investigators. (●) ref. 39; (▲) ref. 40; (□) ref. 1; (○) ref. 41; (■) ref. 42; (+) ref. 43; and (△) ref. 44.

be explained by the original Warren hypothesis. As shown in fig. 1, the fraction of 4-coordinated borons increases continuously through the composition range of the reported thermal expansion minimum. The apparent problem then exists of explaining a pronounced minimum in the expansion coefficient in a range of composition where the local cohesion of the network is continuously increasing.

While there is no simple relation between thermal expansion coefficient and cohesion, it does seem highly plausible to expect distances normal to the planar BO_3 groups to increase readily with thermal motion of the atoms, and to expect the resulting large thermal expansion coefficient to decrease as the boron-oxygen configuration changes from triangles to tetrahedra on adding alkali. Even allowing for some positive contribution to the expansion coefficient associated with the presence of the alkali ions, it is difficult to anticipate the occurrence of a pronounced minimum in expansion in a composition range where the fraction of 4-coordinated borons is continuously increasing. Further, even if some number of singly-bonded oxygens were formed in this composition range, the presence of a small number of such oxygens would not be expected to affect strongly the expansion behavior of the glasses.

It should be noted, however, that while different investigators agree on the occurrence of minima in expansion coefficient vs. composition relations for alkali borate glasses, they often do not agree on their location. This is illustrated in fig. 2, which compares the results obtained by different investigators on Na_2O–B_2O_3 glasses. To facilitate comparison, the results of each investigator were normalized on the expansion value reported for B_2O_3. It is clear that appreciable variability apparently exists among the different results, with the location of the apparent minimum ranging anywhere from about 15 to 30 mole% Na_2O depending on the investigator. Similar remarks apply to the relative magnitudes of the minima.

Much of the variation seen in fig. 2 is very likely associated with variations in experimental procedure, sample purity, composition intervals selected and the temperature range of the measurements. As examples of this last variation, it might be noted that the expansion coefficient of B_2O_3 increases by about an order of magnitude as the glass transition region is approached and traversed 45, 46) and that the apparent minimum in expansion coefficient in the Na_2O–B_2O_3 system is not found in the molten range 39). It can also be noted from fig. 2 that, within the sensitivity and accuracy of the thermal expansion measurements, a fairly broad minimum can be sketched through the data points in some cases. In others, an apparently sharp minimum is defined by a single datum point. The location of this minimum is, however, quite different among different investigators.

In the hope of elucidating this question, the mean linear thermal expansion coefficients between 25 °C and −196 °C were measured for a series of glasses, prepared at composition intervals of 2 mole% alkali oxide, in all 5 alkali borate systems. The low temperature region was chosen to avoid possible high temperature effects on the expansion behavior. It was found that the lower temperature interval itself did not significantly affect the relative values of the expansivities for different compositions, although the absolute values were lower for all compositions.

5. Experimental procedure

5.1. SAMPLE PREPARATION

Sodium borate glasses were prepared from either reagent grade anhydrous sodium borate ($Na_2B_4O_7$) or reagent grade sodium carbonate mixed with appropriate amounts of reagent grade boric acid. Glasses in all other alkali borate systems were prepared from the appropriate alkali carbonates and reagent grade boric acid.

The melting and forming conditions used in preparing glasses for this study are similar to those described elsewhere[37]). Glasses in the Na_2O–B_2O_3 system were prepared at 1 or 2 mole% composition intervals up to 40 mole% Na_2O. Glasses in all other systems were prepared at 2 mole% intervals.

The compositions to be reported in this study are nominal compositions calculated from the batch. Chemical analyses of eleven Na_2O–B_2O_3 glasses indicated actual compositions well within the suggested limits of ± 1 mole% alkali oxide from the nominal values.

Both X-ray and electron diffraction were used to check many of the samples for crystallinity. Both indicated that any specimen which was white, powdery, opaque, or translucent had strong crystalline diffraction peaks, while clear specimens had only the broad, diffuse patterns associated with amorphous substances.

5.2. THERMAL EXPANSION MEASUREMENTS

The mean linear thermal expansion coefficient was determined in all glass systems between room temperature and $-196\,^{\circ}C$ by means of a sensitive capacitance dilatometer. In this instrument, the thermal displacement of the sample was transmitted by a fused silica pushrod-and-sleeve assembly to a large capacitor which formed part of the LC circuit of a Colpitts radio-frequency oscillator, where L was the variable inductance of a tunable coil. The variable output of the Colpitts circuit was beat against a fixed 7.098 megacycle crystal oscillator by means of a mixer, whose output corresponded to the difference frequency, usually in the audio range. The difference frequency was directly proportional to the thermal displacement, and was measured with an electronic counter.

Samples were prepared by grinding flats on opposite faces, which did not necessarily have to be parallel. After measuring the initial length, the sample was centered in the fused silica assembly, and the end of the assembly was immersed in liquid nitrogen to a depth of about $\frac{5}{8}$ inch. The sample, sleeve, and pushrod ordinarily reached equilibrium in about 20 sec. After 30 sec, an average difference frequency was obtained by electronic counting. The assembly was warmed to room temperature and cleaned with acetone and ethyl ether baths if condensation of moisture occurred. About 6–10 min were required per run.

6. Results

The mean linear thermal expansion coefficients between 25 °C and − 196 °C for all alkali borate glasses are summarized in fig. 3.

As shown in the figure, at a given alkali oxide concentration, the coefficients of thermal expansion increase with increasing cation size – i.e., in the order from Li to Cs. The range of coefficients is quite large, ranging from a minimum of about $4 \times 10^{-6}\,\mathrm{deg}^{-1}$ in the lithium borates to a maximum of about $18 \times 10^{-6}\,\mathrm{deg}^{-1}$ in the cesium borate glasses. No evidence is found for the maximum in thermal expansion in the system Na_2O–B_2O_3, suggested by Sampsoen[44]) to occur at about 33 mole% Na_2O.

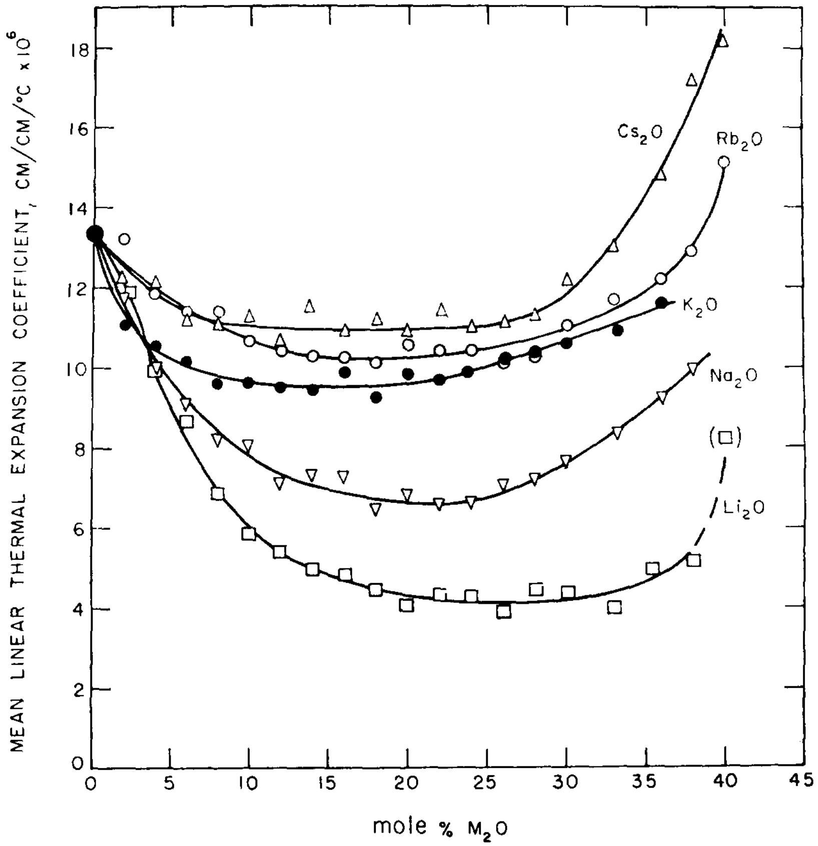

Fig. 3. Thermal expansion coefficients of alkali borate glasses as a function of composition.

Perhaps the most striking feature of the present data is the absence of sharp minima in the thermal expansion versus composition relations. As shown in fig. 3, these relations seem rather to be characterized by broad, spread-out minima, with no single composition uniquely identifiable with the minimum.

It is interesting to note that the pronounced increase in thermal expansion occurs in the same range of composition (around 30 mole% alkali oxide or so) where NMR results indicate a cessation in the process of nearly each added oxygen converting two boron atoms from BO_3 to BO_4 configurations. Beyond this range, singly-bonded oxygens are presumably formed in appreciable concentrations; and their presence in large numbers seems likely to be associated with a decrease in the coherence of the network and an increase in the thermal expansion coefficient.

7. Discussion and conclusions

The preceding sections may be summarized as follows. In the case of B_2O_3, the structure seems to be composed of planar BO_3 triangles, with perhaps one percent BO_4 tetrahedra. In the alkali borates, up to about 30 mole% alkali oxide or so, nearly all the added oxygen seems to be used in converting boron atoms from triangular to tetrahedral coordination. Beyond about 40% alkali oxide, the fraction of 4-fold coordinated boron atoms decreases with increasing alkali oxide concentration. In the composition range below 20 to 25 mole% alkali oxide, all alkali borate systems exhibit the phenomenon of liquid–liquid immiscibility, and normally-cooled glasses are heterogeneous on a scale of 50 to a few hundred Å.

While no single structural model can be uniquely supported by experimental data, the available information on B_2O_3 seems to be consistent with the familiar random network model. In contrast, because of the large difference in properties between glassy and crystalline B_2O_3, a crystallite model (even a distorted crystallite model) does not seem highly plausible for this material. Because of the occurrence of phase separation, the structure of many binary borate glasses is not well described by the random network model as originally advanced; nevertheless the model may still represent a useful description of the structure of the individual phases into which the system separates.

A careful consideration of the minima in the expansion coefficients for the alkali borates shows that there is no one composition characteristic of any minimum, and that the expansion coefficient begins to increase sharply in a manner consistent with the variation of N_4 with composition. While the observed variation cannot be predicted in any detail from our present knowledge of structure and interatomic forces in these materials, it can be related qualitatively to certain structural characteristics.

In such qualitative terms, the broad minima shown in fig. 3 may well reflect a competition between two processes: the formation of BO_4 tetrahedra, tending to decrease the expansion coefficient*, and the introduction of modifying cations, tending to increase it. The larger the size of the cation, the larger its effect on the expansion coefficient. This effect of the cations might physically be related to the filling of holes in the B–O network of triangles and tetrahedra and to the interaction between the ions. With the reduction in the formation of additional tetrahedrally-coordinated borons in the composition range about 30 mole% alkali oxide, the effect of the cations begins to predominate; and this effect is enhanced by the introduction of singly-bonded oxygens in significant numbers.

As yet, little is known about the location and environments of the modifying cations in the glass structure – and this lack of structural knowledge renders difficult a discussion of properties which are highly sensitive to structural detail. In the case of properties which depend primarily on structural cohesiveness, the smaller cations with higher field strengths seem to produce tighter, more strongly bound structures than the larger cations, and the smaller-cation glasses are generally characterized by larger moduli, smaller expansion coefficients, etc.

In any event, in light of the absence of pronounced minima seen in the data of fig. 3, it seems rather questionable to refer to the thermal expansion behavior of alkali borate glasses as "anomalous". Rather, the observed behavior might well be anticipated from direct structural considerations. It seems preferable to associate the "anomaly" in the thermal expansion of alkali borate glasses (if, indeed, there is one) with the variation of N_4 with composition, since this seems to represent the most fundamental, poorly understood problem at the present time.

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* It is interesting to speculate whether the absence of any minimum in the expansion coefficient in molten sodium borates $^{32)}$ may indicate a smaller tendency toward the formation of four-coordinated borons in this temperature range. This suggestion may readily be investigated by NMR techniques.

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