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THE STRUCTURE OF BORATE GLASS

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The existing hypotheses on the structure of alkali borate glass were comprehensively analyzed. Their imperfection in explaining the dependences of the properties of the glasses on their composition was noted. Alternative schemes of structural borate complexes which more convincingly explain the characteristics of the change in the properties of this glass are proposed.

The questions concerning the study of the structure of any substances are always pressing, since their solution will allow more accurately predetermining the properties of the synthetic materials being developed. The lack of direct methods of investigating the structure of amorphous substances unfortunately makes it difficult to solve problems on predicting the properties of these materials as a function of a change in their chemical composition. The use of methods of investigating the structure of crystalline to vitreous substances does not give unambiguous answers but on the contrary, many other difficult-to-resolve questions arise in analyzing the data obtained.

For example, according to the data from many researchers, there is no break on the curve of the change in the proportion of four-coordinated boron ions as a function of the alkali oxide content in borate glasses (Fig. 1) in the region of an approximately 16% molar content of these oxides. At the same time, in determining the CLTE of these glasses in the indicated region of concentrations of Na_2O, a sharp change in their values is observed [2] (Fig. 2). These events in alkali borate glasses are attributed to a change in their structure, more precisely, a change in the coordination of the boron ion with respect to oxygen. The impossibility of solving such problems with instrumental methods makes it necessary to use the methods widely used in humanitarian areas of science, where a multitude of versions of interpretations or hypotheses is proposed, and only those that most accurately explain the observed events or processes are selected. We propose using this approach in examining the structure of different glasses, namely, alkali borate glasses.

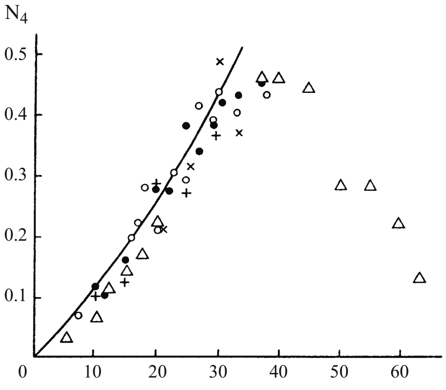

Fig. 1. Proportion of boron atoms in tetrahedral coordination N_4 in alkali borate glasses [1]: ●) Na_2O; ○) K_2O; △) Li_2O; +) Pb_2O; ×) Cs_2O.

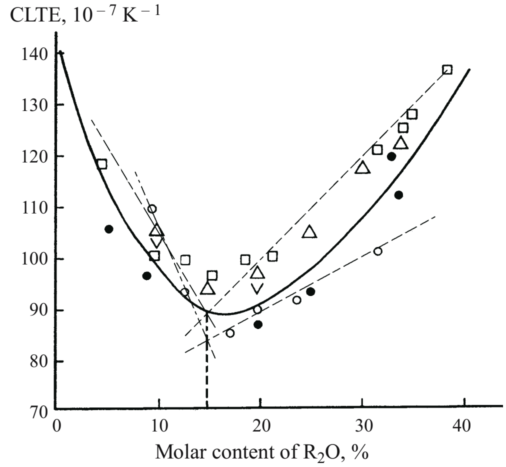

Fig. 2. CLTE of borate glasses as a function of Na_2O content according to data from different investigators [2]: ●) 15 – 100°C; ○) 0 – 120°C; v) 50 – 1150°C; □) 20 – 300 °C; △) 20 – 360°C.

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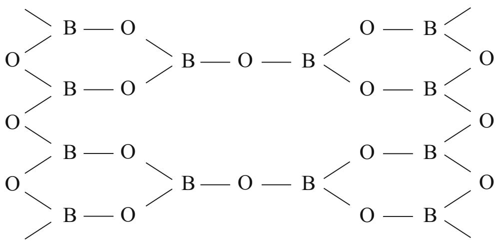

Fig. 3. Diagram of the structure of a layer of $[BO_3]$ groups in borate glass [2].

There are the following published points of view on the structure of borate glasses. In [2], beginning with Krogh-Moe and E. Bray [1, 3] as well as V. V. Tarasova [4], it was indicated that the structure of vitreous B_2O_3 is made up of boroxol rings, each consisting of three $[BO_3]$ triangles joined by a common oxygen atom (Fig. 3).

One oxygen atom binding two neighboring boroxol rings results in the formation of significantly weakened intermolecular bonds between them. In addition, these rings form planar networks joined by weak van der Waals bonds. Due to the presence of weak bonds between the structural complexes and planar networks, boron oxide has a much lower melting point.

According to the data in [4], vitreous boron anhydride consists of chain-layer motifs with the boron atoms in the three-coordinated state. The composition of the unit of the nascent chain-layer structure corresponds to B_6O_9 stoichiometry. The entire structure can be divided into repeating $2B_2O_3$ units.

There is also the hypothesis advanced by K. Fajans and S. Barber [5] concerning the possibility of formation of glass from small molecules of B_4O_6 composition, which also ensures a low melting point of this material. However, this is not sufficient for explaining the low melting point of such glasses. In addition to the observations of S. L. Strong [6] based on x-ray structural analysis, it was concluded that the basic structural elements of anhydrous crystalline boron oxide are trigonal BO_3 pyramids which in his opinion should also persist in vitreous material.

Diagrams of the structural formations in borate glasses consisting of basic structural elements and superstructural groups were presented in [7]; it should be noted that the groups which can only form with a significant content of four-coordinated boron atoms were graphically interpreted.

As for the interpretations in [2], in our opinion, there is some disagreement between the proposed schematic structure of vitreous boron anhydride (see Fig. 3) and the text. It was concluded that based on the text, the structure of vitreous boron anhydride is composed of molar formations of B_6O_9 composition which are better represented as the model (group of two coupled boroxol rings) shown in Fig. 4 and not the diagram shown in Fig. 3. The statement in [2] that one oxygen atom binding two adjacent boroxol rings will cause formation of significantly weakened intermolecular bonds between them is incomprehensible. If we recall that this bond is an intermolecular bond and is essentially covalent, the question then arises: why will it weaken the intermolecular bonds?

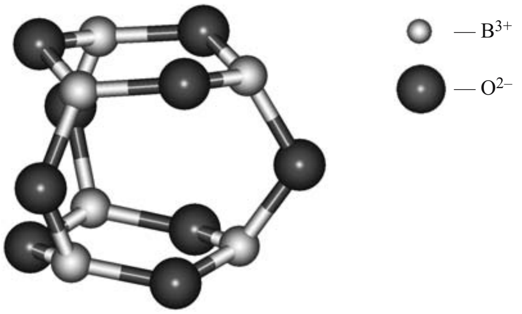

Fig. 4. Hypothetical diagram of the structure of a group of two coupled boroxol rings.

The data from Strong's x-ray structural studies [6] support our representation of the structure of borate glasses to some degree, while according to the diagram shown in Fig. 3, all atoms in the boroxol ring are located in one plane and for this reason, the BO_3 polyhedrons cannot have a pyramidal structure. The model of the structure (see Fig. 4) of borate glasses allows explaining the observed characteristics of the change in their properties and in particular, the boron anomaly, as well as the low melting point, since despite the greater bonding strength of the boron cation with the oxygen atoms (496 kJ/mole), they are only bound together by weak intermolecular forces.

Bringing up the results, we note the following: if the structure of vitreous B_2O_3 actually consists of the groups shown in Fig. 4, then the causes of the decrease in the CLTE of glasses when 17 – 20% alkali metal oxides are incorporated is not so difficult to understand, since there is a "void" between two boroxol rings in the structure of the model and the bonds between the rings are weaker than the bonds inside the rings. For this reason, when alkali oxides are added to this structure of borate glasses, bonds can only break between boroxol rings and not inside them, and the added alkali cation will reduce the free volume by partially occupying the void.

The alkali metal oxide added to borate glass can break one of the three bonds between boroxol rings in two groups at the same time (Fig. 5), while alkali cations can occupy a site in the "voids" inside the coupled boroxol rings and one bridge oxygen thus appears in each two groups (Fig. 6*a*). The alkali cations can hardly be located in the voids of their own two-ring groups and the spatial models shown in Fig. 6*b*, where the alkali cation can be located in voids between two boroxol rings of neighboring groups (Fig. 6*c*) is more probable in these glasses.

Incorporation of alkali oxides in borate glasses thus causes "crosslinking" of the two indicated groups, which results in polymerization of the structural groups in so-

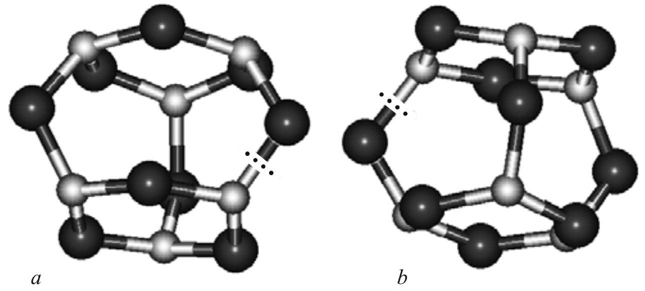

Fig. 5. Diagram of sites of possible bond breaking (**....**) in two borate glass structural groups.

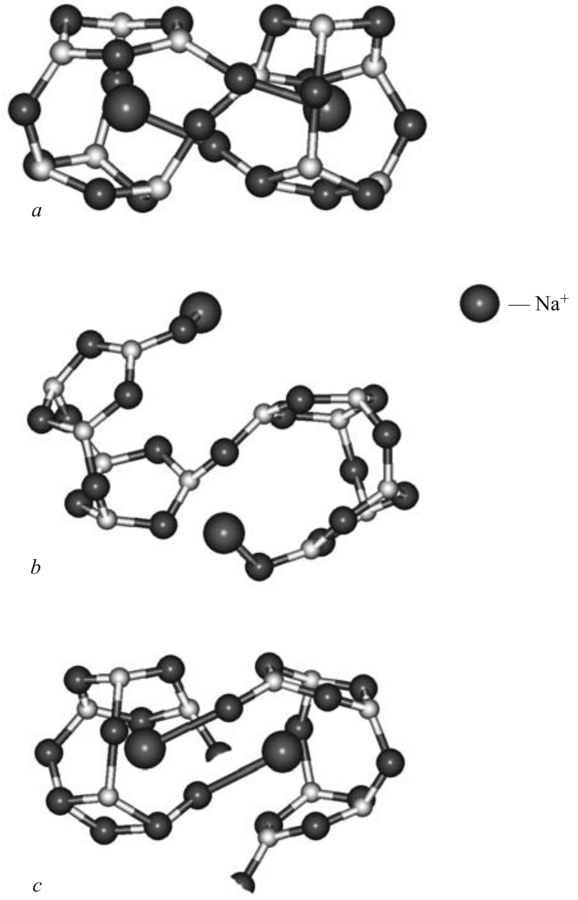

Fig. 6. Diagram of possible positioning of alkali cations in sodium-borate glass in strengthening of its structure.

dium-borate glass. The increase in the infusibility of alkali borate glasses (Fig. 7) in this case is in complete agreement with Tamman's hypothesis of the structure of the glasses in [8] and also the rule used in macromolecular organic chemistry: the greater the length of the polymer chain, the higher the melting point of the substance.

The possible existence of the groups shown in Fig. 6 explains the causes of the observed inflections in the curves of the properties of sodium-borate glasses as a function of the

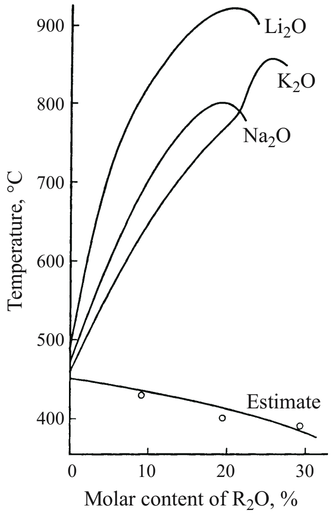

Fig. 7. Position of liquidus curves in the high-borate region of alkali-borate systems [2].

composition and indicates the unconvincing nature of the conclusions that when the molar R_2O content increases more than 18 – 20%, a second $[BO_4]$ group appears in each boroxol ring and the $[BO_4]$ groups positioned alongside in one ring are subject to important repulsive forces between them due to the very high value of the ionic potential of the boron cations [2]. Calculation shows that the second $[BO_4]$ group in the boroxol ring can only appear when the alkali oxide content is greater than 25%.

It should be noted that if the amount of alkali oxides necessary for complete conversion of boron oxide into the groups represented in Fig. 6 is calculated, we can see that the molar content of alkali metal oxides at which there should be an extremum of the properties will be 14.28%. Even if these values differ slightly from those in [2, 9], they are not so far apart for the curves for the CLTE of borate glasses shown in Fig. 2. At the same time, having hypothesized that the dependences of the properties both before and after the "critical" concentration of alkali oxides will be linear in character, the point of intersection can be obtained in the region of 14 – 15% Na_2O (see Fig. 2).

Incorporation of more than 14.28% alkali oxides in borate glass in our opinion will also lead to breaking of a bond between two groups formed by bound boroxol rings (Fig. 8), which will in turn cause large structural complexes to break down and the CLTE of the glasses to increase.

Our hypotheses for explaining the structure of alkali-borate glasses in the form of the models presented are totally acceptable, since other complexes of more complicated composition can also be present in the glass. Nevertheless, these models, in our opinion, allow revealing the physical essence of the processes that take place and for this reason can be totally used as the basic elements of the structural network of alkali-borate glass at the indicated concentrations of oxides.

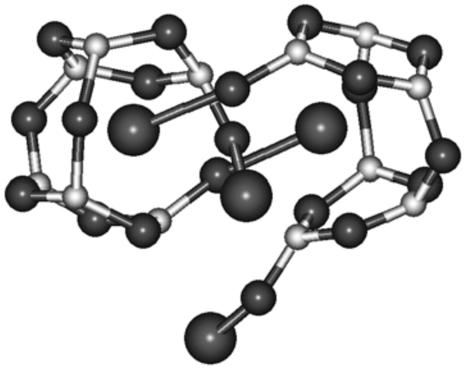

Fig. 8. Model of breakdown of structural complexes.

The proportion of four-coordinated boron ions in the glasses can absolutely increase with an increase in the amount of alkali oxides in them. The inflection on the composition – property curves (see Fig. 2) is observed when the nature of some of the boroxol groups, and not the coordination number, changes.

These studies and the analysis of the published data on the characteristics of the change in the properties of alkali-borate glasses and the proportion of four-coordinated boron as a function of their composition with consideration of the reduced structural fragments demonstrates the validity of the following statements:

the question of coupling of [BO_4] tetrahedrons through a common apex between two neighboring groups of the structural network of alkali-borate glasses is still debatable;

there is no direct correlation between the character of the change in the physicochemical properties of the glasses and the coordination of the constituents of their cations (in particular, the proportion of four-coordinated boron in alkali-borate glasses);

the proposed models of the structural elements and their modifications in alkali-containing compositions make it possible to reveal and explain the dependences of the physicochemical properties on the type of borate groups formed, which also determine the coordination of the constituent cations;

the sodium-borosilicate groups in the structural network of such glasses can interpenetrate each other, since the alkali cation bound through an oxygen with a boron ion of one group can be located in the void of the boroxol rings of two neighboring groups.

REFERENCES

1. P. J. Bray, “Study of the structure of glass by nuclear magnetic resonance,” in: *The Glassy State* [in Russian], Nauka, Moscow – Leningrad (1965), pp. 237 – 251.
2. N. M. Bobkova, “Thermal expansion and structure of binary borate glasses,” *Fiz. Khim. Stekla*, **29**(5), 695 – 703 (2003).
3. J. Krogh-Moe, “The structure of vitreous and liquid boron oxide,” *Non-Cryst. Solids*, **1**(3), 269 – 284 (1969).
4. V. V. Tarasov, *Problems in the Physics of Glass* [in Russian], Stroiizdat, Moscow (1979).
5. K. Fajans and S. W. Barber, “Properties and structures of vitreous and crystalline boron oxide,” *J. Am. Chem. Soc.*, **74**(5), 2761 – 2768 (1952).
6. S. L. Strong and R. Karlow, “The structure of crystalline B_2O_3,” *Acta Cryst.*, **24B**(8), 1032 – 1036 (1968).
7. B. Z. Pevzner, “Interpretation of the image of the structure of borate glasses,” *Fiz. Khim. Stekla*, **29**(5), 704 – 710 (2003).
8. M. V. Artamonova, M. S. Aslanova, I. M. Buzhinskii, et al., *Chemical Engineering of Glass and Sitals: A University Textbook* [in Russian], Stroiizdat, Moscow (1983).
9. H. Rowson, *Inorganic Glass Forming Systems*, Academic Press, London (1967).