

Structural Interpretation of the Results of Investigations into the Influence of Residual Water on the Properties of One-Alkali Borate Glasses

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Abstract—The results obtained in earlier investigations into the influence of water on the viscosity, thermal expansion coefficients, structural relaxation parameters, and fragility parameters of one-alkali borate glasses are analyzed, and schemes of the interaction of water with the glass network are proposed. The variations observed in the properties of glasses are explained in terms of possible changes in the ratio between different borate groups in the structure of the glass with a change in its composition.

INTRODUCTION

In our previous work [1], we investigated a number of structure-sensitive properties of one-alkali borate glasses containing residual water. In order to elucidate the influence of water on the viscosity, thermal expansion, and structural relaxation parameters, we synthesized glasses of the following compositions: $15R_2O \cdot 85B_2O_3$ ($R = Li, Na, K$), $5.5Na_2O \cdot 94.5B_2O_3$, and $25Na_2O \cdot 75B_2O_3$. The water content in glasses was changed by varying the synthesis duration. For the glasses synthesized, we measured the viscosity, thermal expansion, and structural relaxation. The water content in the glasses under study was evaluated using IR absorption spectroscopy.

The purpose of the present work was to analyze the results obtained earlier and to offer their structural interpretation.

As follows from the results presented in [1], structural water even in small amounts (no more than 1 mol %) has a profound effect on the particular properties of borate glasses. It is worth noting that the effect produced on the viscosity by structural water is considerably more pronounced than that observed upon introduction of an alkali oxide into the borate glass. For example, the data obtained in our study indicate that the change in the logarithm of the viscosity by one order of magnitude corresponds to the introduction of approximately 2–3 mol % R_2O or 0.2–0.3 mol % H_2O into the structure of the borate glass. The thermal expansion coefficients of borate glasses are also substantially affected by water. On average, an increase in the water content by 0.2 mol % leads to a change in the thermal expansion coefficient by 10 units. However, this effect is weaker than the effect exerted on this property by the change in the content of alkali oxides. The character of variations in the viscosity and thermal expansion with a change in

the water content depends on the concentration of an alkali oxide entering into the glass composition.

Structural parameters (such as the fragility parameter or the structural relaxation parameter), which depends directly on the content of alkali oxides entering into the glass composition, remain unchanged under variations in the water content in the concentration range covered.

STRUCTURAL INTERPRETATION OF THE RESULTS

According to Vedisheva *et al.* [2], nonbridging oxygen atoms appear in anhydrous alkali borate glasses only at twenty percent of an alkali oxide. Until this content is attained, all oxygen introduced with the alkali oxide is involved in the formation of boron–oxygen tetrahedra, which results in an increase in the connectivity of the glass network. However, there exists another, less common point of view. In particular, Balta and Radu [3] have believed that, if the content of an alkali oxide is less than 25 mol %, only 65% of the oxide introduced is involved in the transfer of boron from a threefold-coordinated state to a fourfold-coordinated state, whereas 35% of this oxide fulfills a destructive function; i.e., it brings about to the disruption of the network connectivity in the glass and the appearance of non-bridging oxygen atoms.

The results of our investigations into the influence of water on the viscosity of alkali borate glasses are in better agreement with the latter point of view. As has already been mentioned, the effect exerted on the viscosity by water is substantially stronger than that observed upon introduction of alkali oxides into the borate glass. This difference can be explained by the fact that only a particular portion of the oxygen atoms introduced with the alkali oxide is involved in the for-

mation of boron–oxygen tetrahedra and, consequently, brings about an increase in the viscosity, whereas the remaining oxygen participates in the formation of non-bridging oxygen atoms, fulfills a function similar to the water function, and leads to a slight decrease in the viscosity. A similar explanation of the temperature dependences of the viscosity was offered earlier by Shartsis *et al.* [4] for the interpretation of the difference in the concentration dependences of the viscosity of anhydrous borate glasses at different temperatures.

In order to elucidate the regularities observed and the processes proceeding in the structure of binary borate glasses upon introduction of water into their structure, we will use the structural model proposed by Vedisheva *et al.* [2] for sodium borate glasses. This model accounts for the distribution of threefold- and fourfold-coordinated boron atoms among boroxol, triborate, and diborate groups in borate glasses and melts according to both the calculations performed within the model of ideal associated solutions [2] and the NMR data [5]. It should be noted that this model and other currently available models of the structure of alkali borate glasses are developed for anhydrous glasses and, hence, cannot be used to describe the structure of water-containing glasses. However, from a comparison of the characters of the variations in the structure-sensitive properties of borate glasses upon introduction of alkali metal oxides and water into their structure, one can draw certain conclusions about the structure of the glasses under investigation.

The table presents the results obtained in [2] for the main structural units of sodium borate glasses at different contents of the alkali oxide.

Upon introduction of water into the glass structure, the distribution of coordinated boron atoms among the groups presented in the table should change.

The character of variations in the properties of the studied glasses upon introduction of water into their composition, in particular, a decrease in the viscosity and an increase in the thermal expansion coefficient, indicates that the water does not participate in the formation of boron–oxygen tetrahedra; i.e., the variations observed in the properties occur at a constant ratio between the fractions of fourfold- and threefold-coordinated boron atoms. Therefore, the variations in the properties of glasses with a change in the water content in the glass structure at a constant content of the alkali oxide should be explained either by the appearance of nonbridging oxygen atoms or by the variations in the concentration ratios between different borate groups, i.e., by the change in the medium order.

In the glass structure, the water involved in the form of hydroxyl groups hydrolyzes the B–O bonds, which results in the destruction of the glass network immediately after the first additions of the water. This can be judged from the decrease in the viscosity upon introduction of water into the glass composition and the

Main borate groups in the structure of sodium borate glasses according to the data taken from [2]

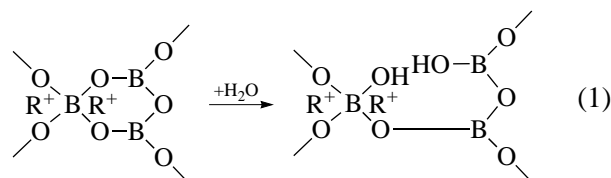
Na ₂ O content, mol %	Structural units, %			
	B ³	T ³	T ⁴	D ^{3,4}
5	80	15	5	–
15	35	12.5	50	2.5
25	4	16	45	20

Note: B³ is the fraction of threefold-coordinated boron atoms; T³ and T⁴ are the fractions of threefold- and fourfold-coordinated boron atoms, respectively, which are distributed among the triborate groups; D^{3,4} is the fraction of threefold- and fourfold-coordinated boron atoms involved in the diborate groups.

presence of the characteristic absorption bands of OH groups in the IR spectrum.

In the glasses containing 5.5 and 15 mol % R₂O, the glass network most probably undergoes hydrolysis at the B–O bond located between the fourfold-coordinated boron atom and the oxygen atom of the tetraborate group, which represents a combination of triborate and pentaborate groups. For glasses of these compositions, the tetraborate group is predominant among the borate groups and, according to the results obtained by Filatov and Bubnova [6], who studied crystalline borates, the aforementioned bond is longest, which makes its breaking easier.

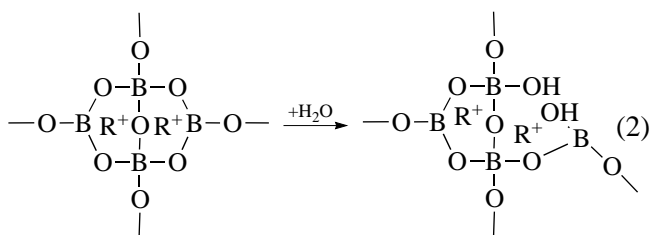
The interaction of water with the network of a borate glass in which the alkali oxide content does not exceed 20 mol % can proceed according to the scheme



The disruption of the network connectivity in the glass brings about a decrease in the viscosity and an increase of the thermal expansion coefficient.

At a higher content of the alkali oxide, the number of diborate groups in the glass structure increases. According to the results of the studies on crystalline borates [6], the B–O bond between the fourfold-coordinated boron atom and the nearest neighbor oxygen atom has a length of 1.481 Å and should most readily undergo breaking due to hydrolysis.

The interaction of water with the network of a borate glass in which the R₂O content exceeds 20 mol % can proceed according to the following scheme:



In this case, the formation of nonbridging oxygen atoms can be accompanied by the destruction of the diborate groups with the formation of triborate-type groups that contain two fourfold-coordinated boron atoms, one of which is bonded to the nonbridging oxygen atom.

The validity of this scheme is confirmed by the fact that the sensitivity of the logarithm of the viscosity to a change in the water content in the glasses containing 25 mol % Na_2O proves to be somewhat higher than that in the glasses with a lower content of alkali oxides, i.e., in the glasses with a lower degree of fragility.

This result is inconsistent with the conclusions drawn by Jewell *et al.* [7], who revealed a correlation between the character of the influence of water on the viscosity of glasses and the degree of their fragility. In [7], the authors analyzed the temperature dependences of the viscosity of aluminosilicate glasses and made the inference that the structures of the so-called strong liquids, which represent three-dimensional connected networks, undergo a very slow insignificant destruction into smaller structural units with an increase in the temperature. These structures are more sensitive to the breaking of bonds with an increase of the content of hydroxyl groups in the glass structure. On the other hand, the structure of the melts of the fragile substances, which very rapidly decompose into smaller units of viscous flow with an increase in the temperature, is substantially less affected by small amounts of additional broken bonds (observed with an increase of the content of hydroxyl groups) as compared to the structure of strong liquids and, hence, their viscosity changes to a lesser degree with an increase in the water content.

The discrepancy between our results and the data obtained in [7] can be explained by the differences in the objects of investigations. Jewell *et al.* [7] studied the temperature dependences of the viscosity of aluminosilicate glasses in which the water has the only function of disrupting the network connectivity due to the formation of nonbridging oxygen atoms at any content of alkali oxides. In borate glasses, with an increase in the content of alkali oxides, the glass structure becomes more complex due to the appearance of different borate groups. At the same time, the role played by water in the glass structure also becomes more complicated. Upon introduction of water into borate glasses in which the content of alkali oxides exceeds 20 mol %, the ratio between the borate groups can change according to scheme (2).

This inference is also confirmed by the results of the determination of the thermal expansion coefficients for the glasses under investigation. As follows from the data on the thermal expansion studied in [1], an increase in the water content in borate glasses brings about a decrease in the thermal expansion coefficient of the glasses with 25 mol % Na_2O and an increase of the thermal expansion coefficient of the glasses with a lower content of an alkali oxide (5.5 and 15 mol %). The increase observed in the thermal expansion coefficient of the glasses containing 5.5 and 15 mol % R_2O with an increase in the water content is associated with the appearance of nonbridging oxygen atoms according to scheme (1).

The decrease observed in the thermal expansion coefficient of the borate glasses with 25 mol % Na_2O upon introduction of water can be explained in terms of scheme (2) and the dependence of the thermal expansion coefficient of alkali borate glasses on the content of alkali oxides. The concentration dependences of the thermal expansion coefficient of alkali borate glasses, as a rule, exhibit a minimum at approximately twenty percent of an alkali oxide [8, 9]. The presence of minima in the concentration dependences of the thermal expansion coefficient of alkali borate glasses most frequently is explained by the fact that, in this concentration range, the glass is characterized by the lowest content of boroxol groups, the highest content of tetraborate groups, and the formation of diborate groups (see table). Therefore, the ascending branch of the concentration dependence of the thermal expansion coefficient of glasses in which the R_2O content exceeds 20 mol % can be associated with an increase in the number of diborate groups. On this basis, the decrease of the thermal expansion coefficient of sodium borate glasses containing 25 mol % Na_2O with an increase in the water content can be explained by the destruction of part of the diborate groups according to scheme (2).

CONCLUSIONS

The results of investigations of the viscosity, thermal expansion, and structural relaxation and IR spectroscopic measurements of one-alkali borate glasses demonstrated that structural water even in small amounts (no more than 1 mol %) has a profound effect on some properties of borate glasses. The effect exerted on the viscosity by water is considerably more pronounced than that observed upon introduction of an alkali oxide into the borate glass. The change in the logarithm of the viscosity by one order of magnitude corresponds to the introduction of approximately 2–3 mol % R_2O or 0.2–0.3 mol % H_2O into the glass structure. On average, an increase in the water content by 0.2 mol % leads to a change in the thermal expansion coefficient by 10 units. The variations observed in the properties of glasses with a change in the water content can be explained by the possible variations in the ratio

between different borate groups in the structure of the glass with a change in its composition.

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