*Proc. Fifth Int. Conf. on Borate Glasses, Crystals and Melts  Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B*, August 2006, 47 (4), xxx–yyy

# Structural interpretation of water content effect on the properties of one-alkali borate glasses

*Olga Yu. Golubeva,*[1] *Valerii F. Pavinich & Sergey V. Stolyar*

*Institute of Silicate Chemistry of Russian Academy of Sciences, nab. Makarova, d.2, liter B, St.-Petersburg, 199395, Russia*

*The effect of water content on viscosity of binary sodium and potassium borate glasses is studied. Glasses with different water content were obtained under different melting conditions. The influence of the synthesis conditions on the spectral absorption in the wavelength range 2·5–4 μm, due to the presence of structurally bound water, is investigated. The synthesis under different conditions makes it possible to prepare glasses not only with different water contents but also with different ratios between the so-called free and bonded hydroxyl groups. It is demonstrated that the effect of water on viscosity depends on the ratio between free and bonded hydroxyl groups in glass structure.*

## 1. Introduction

Any glass synthesised in air includes water in different forms. The amount of water formed in the glass in the course of synthesis can vary from hundredths of a percent to a few percents. The amount of water in glasses depends on the melting conditions and can be determined by such factors as purity of batch components, temperature and time of melting, and water vapour partial pressure. According to publications,(1–7) water in glasses can exist in molecular form and in the form of hydroxyl groups. The removal of water in any form from the glass is a rather complex problem.

The investigation into the structural features of glasses with residual water in different forms is especially topical for borate glasses, which are strongly hydroscopic, thus their properties are sensitive to the water content in glass.

As follows from our previous results(8,9) structure sensitive properties of borate glasses depend strongly on water content in the glass structure. It is worth noting that the effect produced on the viscosity by structural water is considerably more pronounced than that observed upon the introduction of an alkali oxide into a borate glass. For example, the data obtained in our study indicate that the change in the logarithm of 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 borate glasses. Thermal expansion coefficients of borate glasses are also substantially affected by water. The character of variations in the viscosity and thermal expansion with a change of the water content depends on the concentration of an alkali oxide entering into the glass composition.

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

The paper presents some new results concerning the structure and properties of water containing alkali borate glasses.

## 2. Experimental

We have studied glasses of compositions $5{\cdot}5R_2O$–$94{\cdot}5B_2O_3$, $15R_2O$–$85B_2O_3$ and $25R_2O$–$75B_2O_3$. The series of binary alkali borate glasses containing 5·5, 15 and 25 mol% $R_2O$, where R=Na and K. Boric acid and carbonates of the corresponding alkali metals were used as initial components. The mixture of batch components was melted in a platinum crucible with a volume of 200 ml in the electric furnace in air.

The melting conditions of studied glasses are presented in Table. The glasses of different compositions were melted at temperatures of 950, 1200 and 1300°C. To obtain glasses with different residual water content, temperature and time of glass melting were varied. For the convenience of further discussion, identical synthesis conditions for glasses of different compositions in Table 1 are designated by identical letters (from A to F).

The chemical analysis of the glasses (performed at the laboratory of analytical chemistry, Institute of Silicate Chemistry) demonstrated that variations in the compositions of glasses synthesised under different conditions are insignificant and do not exceed 1–1·5 mol%.

---

[1] Corresponding author. Email address: olga_isc@mail.ru

*Table 1. Melting conditions of studied glasses*

| Synthesis denotation | Temperature (°C) | Time of heat treatment (h) |
|---|---|---|
| A | 950 | 2 |
| B | 950 | 3 |
| C | 1200 | 1 |
| D | 1200 | 2·5 |
| E | 1200 | 4 |
| F | 1300 | 1 (after 3 h melting at 950°C) |

The viscosity of the samples was measured with a viscometer by the beam bending method in the temperature range corresponding to a change in the viscosity ($\eta$) from $10^{10}$ to $10^{13}$ dPas. The method consists of determining the bending rate of a rod horizontally mounted on two supports under a load applied to the cent of the sample.(10) The root-mean-square error of measurements using this method was equal to $\pm 0{\cdot}04 \lg \eta$.

The infrared absorption spectra of the glasses were obtained at room temperature with the use of samples in the form of 0·1–0·2 mm thick plates polished in kerosene. The experimental technique and preliminary processing were described in more detail in Startsev & Golubeva.(9)

## 3. Results and discussion

Figure 1 presents the results of viscosity measurements and measurements by infrared absorption method for the four series of studied glasses.

It can be seen from Figure 1 that, for the glasses of the same content of the main components ($B_2O_3$ and $R_2O$), the deviations in the logarithm of viscosity values can reach three orders of magnitude.

According to literature,(11–16) it is believed that the viscosity of glasses reduced on increasing the water in glass structure. The term 'water' usually means the water in the form of free hydroxyl groups. The decrease in viscosity is usually explained by the existence of broken bonds in glass structure due to formation of hydroxyl groups. Other forms of water content are not taken into consideration.

It was shown in our previous work(17) that glass melting conditions can affect the ratio between forms of water content in alkali borate glasses structure. These changes can influence the properties of glasses. Therefore a comparison was made of thermal dependencies of viscosity and infrared absorption spectra of glasses obtained under different glasses melting conditions.

Figure 1(e)–(h) depict the absorption spectra $K(\lambda)$ of studied glasses, where $K$ is the absorption coefficient ($cm^{-1}$) and $\lambda$ is the wavelength (μm). The absorption coefficients were calculated taking into account the losses by reflection from the sample surface.(9)

The wavelength range under investigation contains two bands associated with the stretching vibrations of hydroxyl groups in the glass structure with absorption maxima at 2·8–2·9 and 3·5–3·7 μm. On the basis of the experimental data for a number of oxide glasses, such as alkali silicate glasses and borate glasses containing alkali earth metal oxide, Scholze,(2) Franz(18) and Franz & Scholze(19) attributed the absorption band at 2·8–2·9 μm to nonassociated so called free (not linked by hydrogen bonds) hydroxyl groups, and assigned the band at 3·39–3·63 μm to so called bound hydroxyl groups linked by hydrogen hydrogen bonds in the glass structure. The structures of pure silica glass and vitreous boron oxide involve only free OH groups. The addition of an alkali metal oxide to silicate or borate glasses leads to the appearance of nonbridging oxygen atoms. These atoms and hydroxyl groups can form hydrogen bridging bonds. As a result, the second absorption band at a larger wavelength arises in the infrared spectra.

Different researches revealed other absorption bands associated with water. A number of authors(2,18,19) assign the absorption at 4·25 μm to vibrations of hydroxyl groups linked by very strong hydrogen bonds. Adams(3) rather convincingly justified the assumption that the absorption in this spectral range is attributed to $CO_2$ molecules of atmospheric air rather than to water in glass structure. Ernsberger(5) found the band at a wavelength of 6·1 μm in the spectra of glasses with very high water content. At present, this band is attributed to dissolved molecular water.

Furthermore, there are alternative interpretations of absorption spectra of glasses due to the presence of water. According to Efimov,(20) the infrared absorption spectra of inorganic glasses contain a considerably larger number of associated bands with water in the glass structure. The total number of these bands in the wavelength range from 2·7–6·5 μm can be as large as 15. Among these bands, at least four bands correspond to water in molecular form. Tomozawa(6) showed that, at water content up to 1 wt% in silicate glasses, water is predominantly represented by hydroxyl groups in the glass structure.

It can be seen from Figure 1(e)–(h) that increase in the temperature and time of synthesis (according to Table 1) leads to a decrease in the intensity of the first band (with absorption maximum at 2·8–2·9 μm) for all the glasses. These changes in the intensity indicate a decrease in the content of water in the form of free hydroxyl groups. However, the decrease of water in the form of free hydroxyl groups is not always accompanied by an increase of viscosity. In some cases (Figure 1(b) synthesis *F*, Figure 1(c) synthesis *F*, Figure 1(d) synthesis *F*) one can see a decreased viscosity on decreasing the intensity of fist band.

Such behaviour of viscosity can be explained by the changes in the ratio between free and bonded hydroxyl groups. As can be seen from Figure 1(e)–(h), simultaneously with the changes in the intensity of

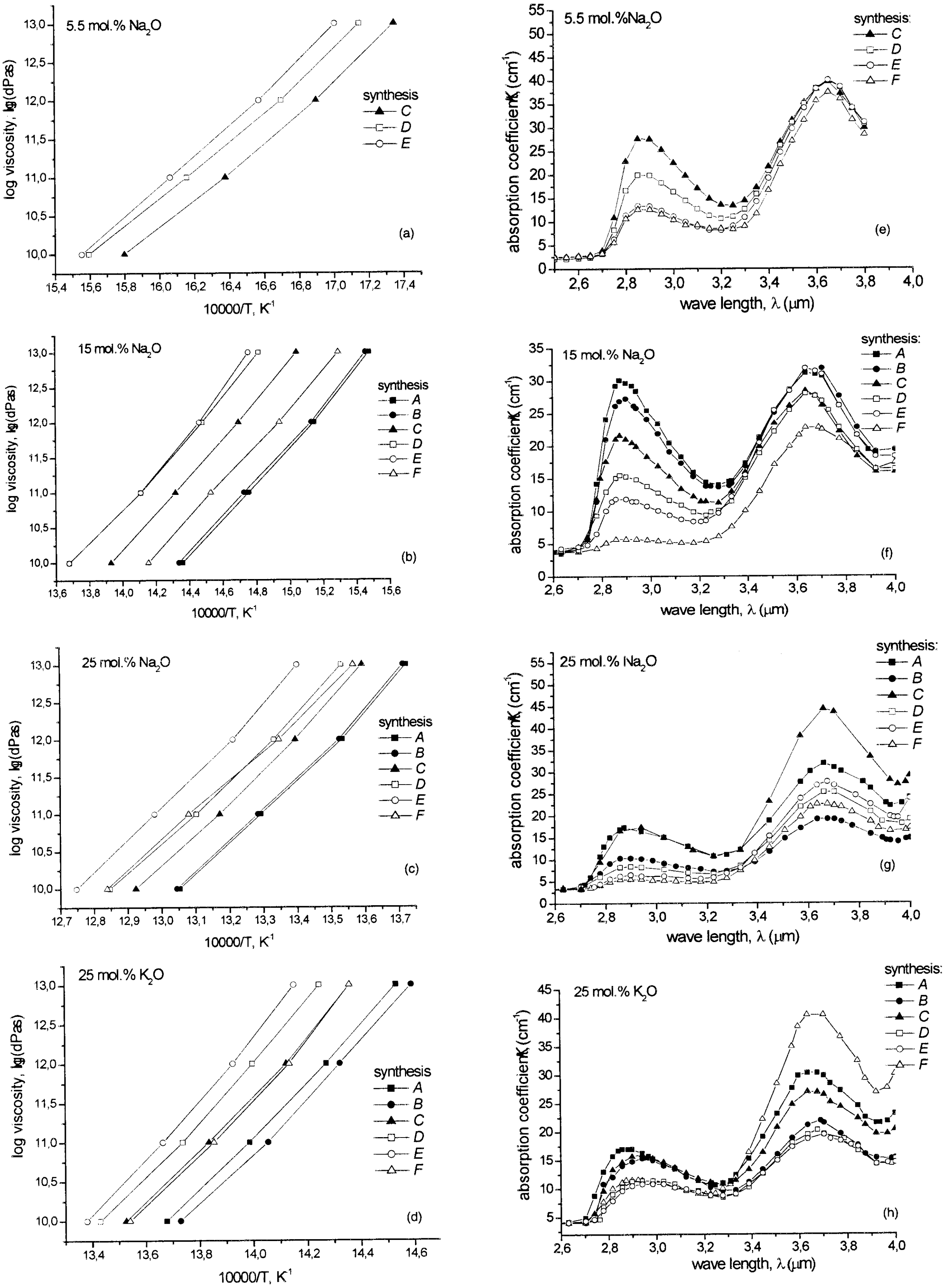

*Figure 1. Temperature dependencies of viscosity and infrared absorption spectra of alkali borate glasses obtained under different glass melting conditions (according to Table 1)*

the first band in absorption spectra, a variation in glass melting conditions leads to a change of the second band (with absorption maximum at 3·7 μm). However, this change in the intensity does not necessarily correlate with the change in the intensity if the first absorption band. Actually, in some cases, an increase in the intensity of the first band is accompanied by a decrease in the intensity of the second band. This tendency tendency is clearly seen in Figure 1(f) (synthesis conditions *D*, *F*) and Figure 1(g) (synthesis conditions *B*, *F*). It is especially pronounced in Figure 1(h), which shows the infrared absorption spectra of the glasses containing 25 mol% $K_2O$.

The spectrum of this glass, prepared at 1300°C (synthesis conditions *F*), is characterised by the lowest intensity of the first band (in addition to the glasses synthesised under conditions *D* and *E*) among the spectra of other glasses that have the same compositions but are synthesised under different conditions. This fact suggests a minimum water content in the sample under consideration, and consequently the highest values of viscosity in this series of glasses. However, as can we see from the Figure 1(d) the viscosity of the sample obtained under synthesis conditions *F* is lower than for glasses obtained under synthesis conditions *D* and *E*. As can be seen from the Figure 1(h) the intensity of the band with absorption maximum at 3·7 μm for this sample is highest compared to those for the other glasses of the series. Therefore, the inference that the water content in this sample is lowest cannot be made unambiguously. As a result, the viscosity values of this glass sample are rather higher than that should be expected form the consideration only the first absorption band.

The probability of the changes in ratio between free and bonded hydrogen groups in borate glass structure increases on the increasing alkali oxide content. This probability should correlate with the probability of forming hydrogen bonds in glass structure which depends on the number of the nonbridging oxygen atoms. It is well known that in borate glasses the introduction of alkali oxides into the network does not result in a drastic increase in the number of nonbridging oxygen atoms, because a number of boron atoms transform the three-fold coordinated state to the four-fold coordinated state.(21–23) Oxygen introduced into the glass with the alkali metal oxide is used for enhancing the network connectivity and is not accompanied by the appearance of nonbridging oxygen atoms. According to the data of different authors (for example Krogh-Moe(21)), this process only partially occurs, beginning with a content of 25–39 mol% $R_2O$. A part of oxygen atoms introduced with the alkali metal oxide then transforms bridging oxygen atoms into nonbridging oxygen atoms. However, at lower oxide contents, a few alkali metal atoms most likely fulfil a destructive function – lead to the breaking of the network and the appearance of nonbridging oxygen atoms.(24)

For glasses with small alkali oxide content (5 mol%) the number of nonbridging atoms is very low. As a result there is a direct connection between content of free hydroxyl groups in glass structure and viscosity. Further increases in alkali oxide content to 15–25 mol%, and increases in the number of nonbridging oxygen atoms in the structure of borate glasses, are accompanied by an increase of the bonded hydroxyl groups. These two types of hydroxyl groups have a double effect on the glass structure and properties. On the one hand, free hydroxyl groups decrease the connectivity of the network and decrease the viscosity, on the other hand, bonded hydroxyl groups by the formation the hydrogen bonds increase the connectivity of the network and increase the viscosity. When the content of bonded hydroxyl groups is high, the second effect becomes the main one. In the case of glasses with rather high alkali oxide contents (25 mol%), the effect of water content on properties is more complicated because of the more complicated glass structure. The network of these glasses is formed by different borate groups – boroxol groups, tri- and diborate groups. On increasing the water in glass structure, the double effect described above may be accompanied by the effects connected with the destruction or transformation of borate groups.

## 4. Conclusions

While studying the effect of water content on the borate glasses properties, it is necessary to take into account the existence of water in glass structure in the form of free and bonded hydroxyl groups. The correlation between free and hydrogen bonded groups on glass structure depends on the glass melting conditions. These two forms of water in glass structure exert a double effect on glass structure – free OH-groups decrease the connectivity of glass network while the hydrogen bonded OH-groups increase the connectivity of the network. As a result, changes in the ratio between free and bonded hydroxyl groups have an effect on structure sensitive properties of borate glasses.

## Acknowledgments

The work was supported by the Russian Foundation for basic research (project no. 03-03-32269) and by Russian Science Support Foundation.

## References

1. Sholze, H. *Glass. Nature, structure and properties*. New York, 1991.
2. Scholze, H. *Glastech. Ber.*, 1959, **32**, 81–88, 278–281, 314–320, 381–386.
3. Adams, R. V. *Phys. Chem. Glasses*, 1961, **2** (2), 39–49.
4. Tomlinson, J. W. *J. Soc. Glass. Tech.* 1956, **40**, 25–31T.

5. Ernsberger, F. M. *J. Am. Ceram. Soc.* 1977, **60** (1–2), 91–2.
6. Tomozawa, M. *J. Non-Cryst. Solids.* 1985, **73** (1–3), 197–204.
7. Shelby, J. E. *Handbook of gas diffusion in solids and melts.* ASM Int., 1992, 240 ps.
8. Golubeva, O. & Startsev, Y. *Phys. Chem. Glasses,* 2002, **43C**, 471–6.
9. Startsev, Y. & Golubeva, O. *Glass Phys. Chem.*, 2002, **28** (3), 159–69.
10. Kluev, V. P. & Totesh, A. S. *Methods and Instruments for Testing the Viscosity of Glasses,* Moscow, VNIESM, 1975 (in Russian).
11. Visser, Th. J. *Rheological Properties of Alkali Borate Glasses.* Thesis. Eindhoven, Netherlands. 1971. 88 ps.
12. Hetherington, G. & Jack, K. H. *Phys. Chem. Glasses,* 1962, **3** (4), 129–33.
13. Hetherington, G., Jack, K. H. & Kennedy, J. C. *Phys. Chem. Glasses.* 1964, **5** (5), 130–6.
14. Kimura, T. *Jpn. J. Appl. Phys.* 1969, **8 (12)**, 1397-1403.
15. Jewell, J. M. & Shelby, J. E. *J. Non-Cryst. Solids.* 1988, **102** (1–3), 24–9.
16. Jewell, J. M. & Shelby, J. E. *J. Am. Ceram. Soc.* 1992, **75** (4), 878–83.
17. Golubeva, O. Yu. & Pavinich, V. F. *CD Proc. XX Int. Congress of Glass.* 2004. Kyoto (Japan). P-07-062.
18. Franz, H. *J. Am. Ceram. Soc.* 1966, **49** (9), 473–7.
19. Franz, H. & Scholze, H. *Glastech. Ber.* 1963, **36** (9), 347–56.
20. Efimov, A. M. *J.Non-Cryst. Solids.* 1985, **43C**, 165–75.
21. Krogh-Moe, J. *Phys. Chem. Glasses.* 1962, **3** (1), 1-6.
22. Bray, P. J. & O'Keefe, J. G. *Phys. Chem. Glasses.* 1963, **4** (2), 37–46.
24. Zhong, J. & Bray, P. J. *J. Non-Cryst. Solids.* 1989, **111** (1), 67–76.
25. Balta T. & Radu, D. *Phys. Chem. Glasses,* 2000, **41** (5), 278–81.