

Influence of glass melting conditions on the viscosity and thermal expansion of alkali borate glasses

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The viscosity and thermal expansion of binary alkali borate glasses containing lithium, sodium and potassium oxides obtained by different glass melting conditions were studied. Glasses of the following compositions were chosen as objects for this study (mol%): $5.5R_2O.94.5B_2O_3$, $15R_2O.85B_2O_3$, where $R = Li, Na, K$ and $25Na_2O.75B_2O_3$. By varying times of melting from 1 up to 4 h and by using remelting under vacuum the glasses of the same composition with different water contents were obtained. Hydroxyl concentrations in studied glasses were estimated by an absorption spectroscopy in near infrared region. Thermal dependencies of viscosity were determined by the beam bending method in the range of viscosity from 10^0 up to 10^{13} dPs. Thermal expansion coefficients in the range of temperatures below and above glass transition and glass transition temperatures at cooling were determined by using the hysteresis dilatometer curves of studied glasses. It was found that the glasses investigated had approximately the same sensitivities of viscosity to the changes in water content independently of type and concentration of alkali oxide. Effect of water content on thermal expansion was found to be dependent on kind and concentration of alkali oxide in glass composition.

Glass melting conditions are very important for the glass composition and consequently for its structure sensitive properties. By using different glass melting conditions such as various temperature and time of melting, bubbling by dry or wet gases through the molten glass and melting under vacuum one can obtain glasses with different contents of both main and admixture components. Water is the most widespread admixture in glass composition. Some part of water is always incorporated in glass structure during melting because of incomplete removal of batch decomposition products and interaction between glass melt and air water.

It is known that even small quantities of water have a definite effect on some properties of glasses.^(1–6) This

problem especially concerns borate glasses. High water absorbing ability and high sensitivity of properties to the water content of these glasses^(4–7) stimulate the researchers to find ways to obtain glasses with minimum water concentration. Changes in glass melting conditions of borate glasses, time or temperature of melting can lead to obtaining glasses with different water content and consequently with different properties.

Borate glasses have been studied for many years. Interest in this glass system can be explained by the peculiarities of structural changes resulting from adding alkali oxides to the glass composition. These peculiarities take place due to the change in boron coordination from three to four and transformation of some part of boron oxygen triangles to the tetrahedrons.^(8,9) It was shown by the nuclear magnetic resonance studies of Bray & co-workers⁽⁹⁾ that the quantity of boron in fourfold coordination depends on the concentration and kind of alkali oxides.

No results have been found in the literature of any results of investigation of influence of water content on the viscosity and thermal expansion of borate glasses containing different alkali oxides. Effect of water content on viscosity and thermal expansion of borate glasses has been studied so far mostly for pure borate and sodium borate glasses.^(4–6) The main task of the present study was to obtain additional information on the effect of the admixture water content on structure sensitive properties, viscosity and thermal expansion for glasses containing lithium, sodium and potassium oxides and to study the influence of glass melting conditions on water concentration.

Experimental procedure

Glass preparation

Reagent boric acid and alkali carbonates were used as raw materials for the preparation of studied glasses. The mixture of batch components was melted in platinum crucible containing 200 g glass in the electrical furnace with air atmosphere. To obtain glasses with different water contents the variation of time of melting from 1 up to 4 h at 1200°C and remelting under vacuum at 1000°C were used. After melting the mol-

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Table 1. Compositions and glass melting conditions of studied glasses

Glass denoted as	Glass compositions, mol% by batch/by analysis				Time of glass melting at 1200°C, h
	B ₂ O ₃	Li ₂ O	Na ₂ O	K ₂ O	
5.5Li ₂ O	94.5/96.4	5.5/3.6	–	–	1
	94.5/96.5	5.5/3.5	–	–	2.5
	94.5/96.5	5.5/3.5	–	–	4
5.5Na ₂ O	94.5/94.6	–	5.5/5.6	–	1
	94.5/94.7	–	5.5/5.3	–	2.5
	94.5/94.7	–	5.5/5.3	–	4
5.5K ₂ O	94.5/94.7	–	–	5.5/5.3	1
	94.5/94.6	–	–	5.5/5.4	2.5
	94.5/94.8	–	–	5.5/5.2	4
15Li ₂ O	85.0/84.7	15.0/15.3	–	–	1
	85.0/84.7	15.0/15.3	–	–	2.5
	85.0/84.9	15.0/15.1	–	–	4
15Na ₂ O	85.0/84.5	–	15.0/15.5	–	1
	85.0/84.8	–	15.0/15.2	–	2.5
	85.0/85.0	–	15.0/15.0	–	4
15K ₂ O	85.0/85.9	–	–	15.0/14.1	1
	85.0/85.9	–	–	15.0/14.1	2.5
	85.0/85.7	–	–	15.0/14.3	4
	85/85.9	–	–	15.0/14.1	1.5*
25Na ₂ O	75.0/75.9	–	25.0/24.1	–	1
	75.0/75.6	–	25.0/24.4	–	2.5
	75.0/75.8	–	25.0/24.2	–	4

* remelting under vacuum at 1000°C, 1 h

ten glass was poured into an iron mould and put into the annealing furnace which was maintained at the temperatures depending on glass composition.

The compositions of all synthesised glasses were analysed by wet chemical analysis. Table 1 presents the compositions and glass melting conditions of studied glasses. It is seen that the difference in alkali oxides in glass composition by batch and by analysis does not exceed 1 mol%.

The glasses synthesised were stored in a desiccator to prevent water absorption.

Measurements of infrared spectra

To estimate hydroxyl concentrations in studied glasses and absorption spectroscopy measurements in the near infrared region were made. The measurements were performed at room temperature at the device SF-2 developed in the Laboratory of Glass Properties of the Institute of Silicate Chemistry. SF-2 is a double beam spectrophotometer with the working spectral range 0.4–4 μm. The detailed description of the device and method of measurement is given in Ref. 10. The error of the determination of the optical density by this method is ±0.005.

The samples for measurements were polished at the paraffin oil to prevent water absorption. All samples were stored in the desiccator. Every sample was measured several times in different positions in the interval of wavelength from 2.5 up to 4 μm. The absorption coefficient K was determined as described⁽¹⁰⁾ by using the data on optical density and taking into account the losses of the reflection from the boundary sample, air. The value of the refractive index was taken equal to 1.5. This value corresponds to mean value of the refractive index in studied glasses.⁽¹¹⁾

Figure 1 gives the example of the spectrum $K(\lambda)$, where λ is a wavelength, μm, obtained for the 5.5Na₂O glasses.

Reliable spectral data for the 5.5Li₂O and 5.5K₂O

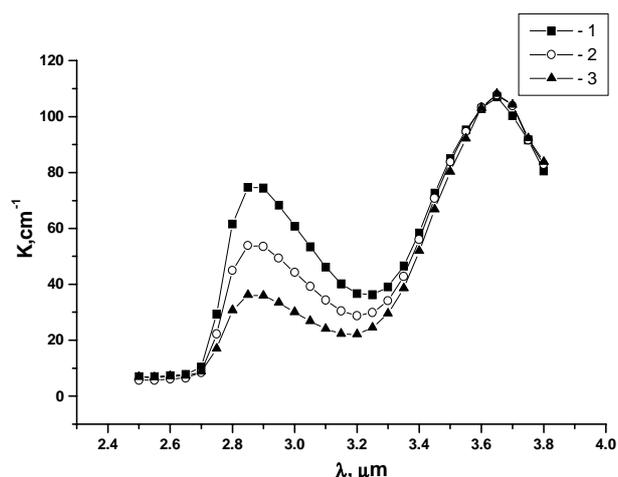


Figure 1. Example of the spectrum for 5.5Na₂O glasses obtained at different times of melting at 1200°C: 1 – 1 h; 2 – 2.5 h; 3 – 4 h

glasses has not been obtained due to the very high water absorption ability of these glasses.

Measurements of thermal dependencies of viscosity

Measurements of viscosity of studied glasses were made by the beam bending method at viscosities from 10¹⁰ up to 10¹³ dPa s. The detailed description of the device and method is given in Ref. 12. The mean square errors of viscosity logarithm determination by this method are not more than ±0.04. The value of error was estimated by measuring the viscosity of SRM glasses of NBS.⁽¹³⁾

The sample temperature was determined by two chromel–alumel thermocouples graduated by means of melting temperatures of pure metals, Pb, Zn, Al. The temperature was maintained constant for several hours with the accuracy ±0.2 K. The experimental results were approximated by the Vogel–Fulcher–Tammann equation.

Measurements of thermal expansion

Measurements of thermal expansion were made in a silica dilatometer. The description of the device is given in Ref. 14. The construction of the dilatometer allows to obtain the dilatometer curves in the range of temperatures covering the glass transition interval of studied glasses and even above this range. The temperature of sample was measured by a chromel–alumel thermocouple graduated by means of the melting temperatures of pure metals. The error of the determination of thermal expansion coefficients by this device is ±1 × 10⁻⁷ K⁻¹. The precision of the dilatometer was determined by measuring the corundum standard over the 200–500°C temperature range.

Hysteresis dilatometer curves of studied glasses at cooling and heating with the temperature rates 2 and 3 K/min were obtained. Thermal expansion coefficients (TEC) in the ranges of temperatures below (α_g) and above (α_l) glass transition interval as well as glass transition temperatures (T_g) at cooling were determined.

Figure 2 shows the example of the dilatometer curve of 15Li₂O glass and the scheme of determination of α_g , α_l and T_g .

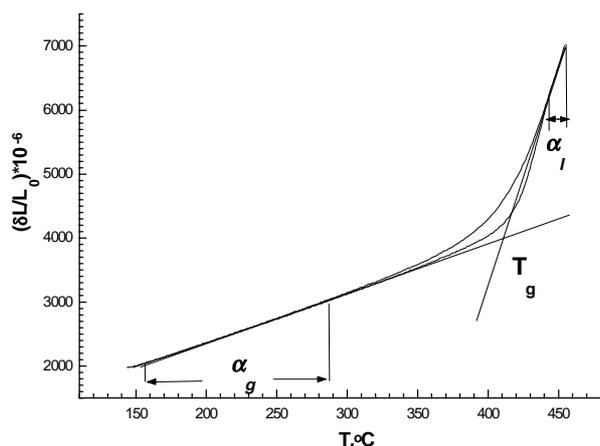


Figure 2. Scheme of determination of thermal expansion coefficients below (α_g) and above (α_l) glass transition interval and glass transition temperatures T_g (as an example dilatometer curve of $15\text{Li}_2\text{O}$ glass is shown)

Treatment of the spectroscopic data

Infrared analysis is considered to be the most suitable method for the study of water in glasses. It should be noted here that water can exist in glasses as either molecules or hydroxyl. According to the number of works^(15,16) water in glasses containing not more than 1 wt% water exist rather in the form of hydroxyl groups (OH). The scheme of interaction between water and glass network can be written in the following form^(7,15,16)



Hydroxyl groups are incorporated in glass structure in different ways dependent on glass composition. OH groups in glass structure can be divided into so called 'free' and 'bound' groups.

Only free OH groups are present in pure vitreous silica and boron oxide glasses with the absorption band around $2.8 \mu\text{m}$. To the extent that nonbridging oxygens are produced through introduction of network modifiers, the OH groups form hydrogen bridging bonds through which the band of higher wavelength arises at around $3.5 \mu\text{m}$.

Although the infrared analysis is very fast and rather simple there are some difficulties in treatment of the results obtained. Quantitative analysis of OH groups by means of spectroscopic data is based on the Beer-Lambert Law

$$C_{\text{OH}} = \frac{1}{\epsilon d} \lg\left(\frac{1}{T}\right) \quad (1)$$

where C_{OH} is the concentration, mole/l, d the thickness of sample, cm, T the transparency, %, ϵ the extinction coefficient, $\text{l}/(\text{mol cm})$.

Therefore, qualitative analysis is impossible until a value of the extinction coefficient has been determined experimentally by other method. The determination of the extinction coefficient is difficult.

We found two published methods for water content determination in borate glasses by spectroscopic data suggested by Franz⁽⁷⁾ and Eagan & Bergeron⁽¹⁸⁾ which can be used without experimental determination of the extinction coefficient.

Franz⁽⁷⁾ has calculated the extinction coefficients from the hydroxyl absorption band at around $2.8 \mu\text{m}$ for the alkali borate glasses as function of composition. On calculating Franz assumed that the water concentration c is proportional to the integral extinction I and that the total integrated intensity I of the hydroxyl band is independent of glass composition. Using the spectra of alkali borate glasses with different water content Franz showed by the difference spectrum that there was only one hydroxyl band at $2.9 \mu\text{m}$. Therefore, extinction coefficients of Franz are concerned only with the free hydroxyl groups in glass structure.

Eagan & Bergeron⁽¹⁸⁾ have suggested another method for calculation of water content in lead borate glasses from spectroscopic data. They have pointed out that the integrated intensity I of the hydroxyl groups fundamental vibration changes on amount ΔI in the proportion to the frequency shift, $\Delta\nu_s$, of the maximum absorption. Increase in the integrated intensity was attributed to an increase in the strength of the hydrogen bonding of hydroxyl groups in the glass structure on adding the alkali oxides.

In order to calculate the concentration of water in borate glasses, Eagan & Bergeron determined the theoretical integral extinction of the hydroxyl groups absorption for a pure vitreous boric oxide which was found to be equal $25.6 \times 10^3 \text{ l}/(\text{mol cm}^{-1})$. The theoretical integral extinction for a lead or any other binary borate glass is equal to the sum of this value and the enhancement ΔI due to hydrogen bonding. Knowledge of this value allows one to calculate the hydroxyl groups concentration by the equation suggested by Eagan & Bergeron. This method can be used for any binary borate glasses.⁽¹⁹⁾

Water content of studied glasses in this paper was estimated by means of both methods described above. On treating the initial spectrum was deconvoluted into Gaussian bands and only the band at the higher frequency was taken into account. Finally water content of studied glasses was calculated from the following equation.⁽¹⁹⁾

$$C_{\text{H}_2\text{O}} = \frac{C_{\text{OH}} M_{\text{OH}}}{2\rho} \frac{100}{1000} = \frac{0.85 C_{\text{OH}}}{\rho} \quad (2)$$

where M_{OH} is the molecular weight of OH, 17 g/mol and r the value of glass density, g/cm^3 , taken from Ref. 11.

Table 2 presents the results of water concentration calculation.

Results

Water content determination

It is seen from the Table 2 that both methods of water content determination applied here give approximately the same results for glasses $5.5\text{Na}_2\text{O}$. Using the extinction coefficients suggested by Franz we obtained the higher values of water concentration in glasses containing 15 and 25 mol% R_2O than by using the method suggested by Eagan & Bergeron. It can be connected with the fact that at low level of alkali oxides concentrations (up to 5 mol%) hydrogen bonding has no noticeable effect on the absorption spectrum. On the following add-

Table 2. Water contents in studied glasses determined by methods suggested by Franz⁽⁷⁾/Eagan & Bergeron⁽¹⁸⁾

Glass composition	Water content (mol%)			
	Electric furnace, 1200°C 1 h	2.5 h	4 h	Vacuum 1 h
5.5Na ₂ O	0.53 / 0.50	0.38 / 0.38	0.27 / 0.31	–
15Li ₂ O	0.49 / 0.28	0.28 / 0.21	0.14 / 0.11	–
15Na ₂ O	0.61 / 0.34	0.46 / 0.23	0.30 / 0.19	–
15K ₂ O	0.54 / 0.36	0.32 / 0.20	0.28 / 0.16	0.16 / 0.12
25Na ₂ O	0.23 / 0.11	0.15 / 0.07	0.07 / 0.03	–

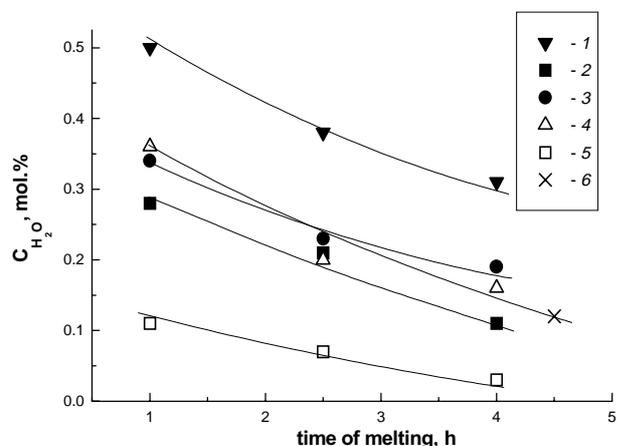
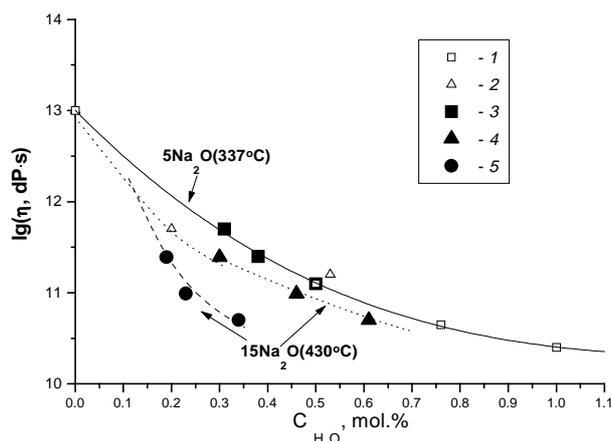
ing of alkali oxides the quantity of hydrogen bonding increases and the integrated intensity changes. That is why the method of Franz, in which he assumed the independence of integrated intensity on glass composition, gives the higher values of water content.

Both methods are based on many assumptions which have not been proved and can be used only for the approximate estimation of water content in alkali borate glasses. Further, unless specially mentioned we will use the results obtained by the method suggested by Eagan & Bergeron because it takes into account structural changes on adding alkali oxides and has better correlation with the results of measurements of temperature dependencies of viscosity of studied glasses.

Figure 3 illustrates the results obtained on the effect of glass melting conditions on water content of alkali borate glasses. It is seen from Figure 3 that at the same glass melting conditions, glasses with lower content of alkali oxide kept higher water concentrations. On increasing time of melting from 1 up to 4 h water content in glasses containing 5.5 and 15 mol% R₂O decreases approximately by half. Increasing time of melting for glasses with higher alkali oxide concentration (25Na₂O) leads to the reduction of water content to a lesser extent.

Viscosity

The only paper concerned with the effect of water content on the viscosity of alkali borate glasses was the data obtained by Visser⁽⁶⁾ for sodium borate glasses containing 5.5 and 15 mol% Na₂O. The author determined the water content in glass structure by measurements of pressure of water vapour above the glass melt. Viscosity measurements were made by a

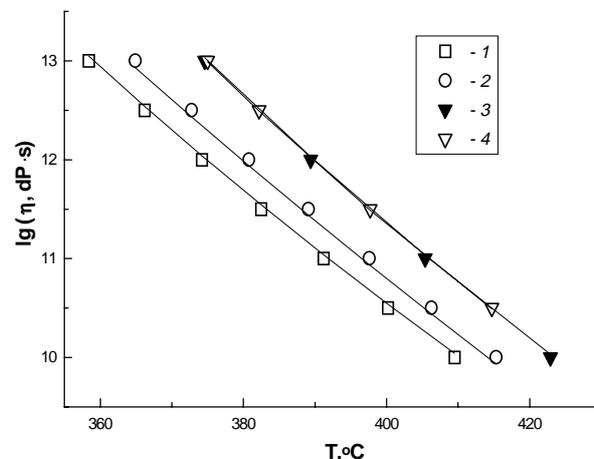
**Figure 3.** Influence of glass melting conditions on water concentrations in studied alkali borate glasses 1 – 5.5Na₂O; 2 – 15Li₂O; 3 – 15Na₂O; 4 – 15K₂O; 5 – 25Na₂O; 6 – 15K₂O (after vacuum treatment)**Figure 4.** Comparison of dependencies of logarithm of viscosity on water contents with published data: 1, 2 – data obtained by Visser⁽⁶⁾ for 5.5Na₂O and 15Na₂O respectively; 3 – our results for 5.5Na₂O; 4, 5 – our results for 15Na₂O with water calculation made by methods suggested by Franz⁽⁷⁾ and by Eagan & Bergeron,⁽¹⁸⁾ respectively

Pochettino viscometer. Figure 4 presents the comparison of our results with the data of Visser for glasses with the same composition.

It is seen that our results and data of Visser lie on the one curve for glasses with 5.5 mol% Na₂O. Our results for glasses containing 15 mol% Na₂O do not coincide with the data of Visser. It should be noted that the method for the water content determination in glasses used by Visser has some weak points connected with the possibility of evaporation on melting some other admixtures (e.g. carbon dioxide).

Besides, on estimating water content in studied glasses we took into consideration only the band at around 2.8 μm connected with 'free' hydroxyl groups. The second band at around 3.5 μm connected with the existence of 'bound' hydroxyl groups was not examined. This fact could lead to the deviation in results obtained by different methods.

It was noted for all studied glasses that viscosity had the tendency to reduction as the water content increased in glass structure. Figure 5 shows the example of tem-

**Figure 5.** Example of temperature dependencies of viscosity for 15K₂O glasses with different water contents, mol%: 1 – 0.36 (1200°C, 1 h); 2 – 0.20 (1200°C, 2.5 h); 3 – 0.16 (1200°C, 4 h); 4 – 0.12 (1000°C, 1 h). Lines are the results of experimental data approximation by the Vogel-Fulcher-Tammann equation

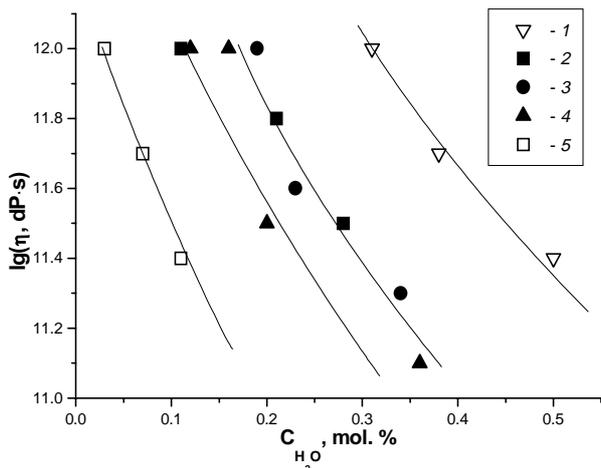


Figure 6. Isothermal dependences of logarithm of viscosity of studied glasses on water contents: 1 – 5.5Na₂O at 331°C; 2 – 15Li₂O at 437°C; 3 – 15Na₂O at 420°C; 4 – 15K₂O at 389°C; 5 – 25Na₂O at 481.5°C

perature dependences of viscosity of 15K₂O glasses obtained containing different water contents.

As is seen from Figure 5 the temperature dependences of viscosity for 15K₂O glasses obtained by melting in an electric furnace for 4 h (0.16 mol% H₂O) and by remelting under the vacuum for 1.5 h (0.12 mol% H₂O) approximately coincide. This result corresponds to the results of water content determination in these glasses.

The studied glasses had approximately the same sensitivities of viscosity to the changes in water content independently of the kind and concentration of alkali oxides, Figure 6. On the average additions of 0.1 mol% water corresponds to 0.3 order of magnitude reduction in logarithm of viscosity.

Thermal expansion

It was found for all studied glasses that the glass transition temperatures decreases on increasing water content, Figure 7.

Figure 8 shows the dependences of thermal expansion coefficients (TEC) of studied glasses below (a) and above (b) glass transition interval on water contents. Values of coefficients are shown with their error bars.

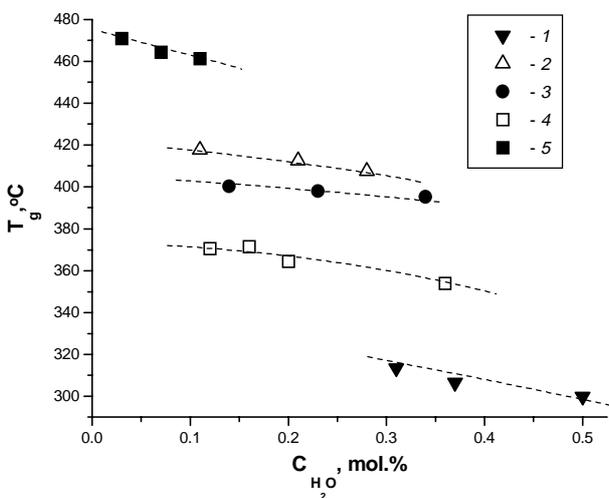
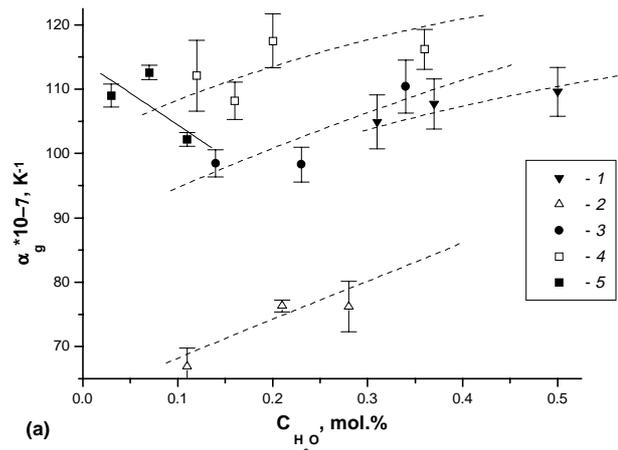
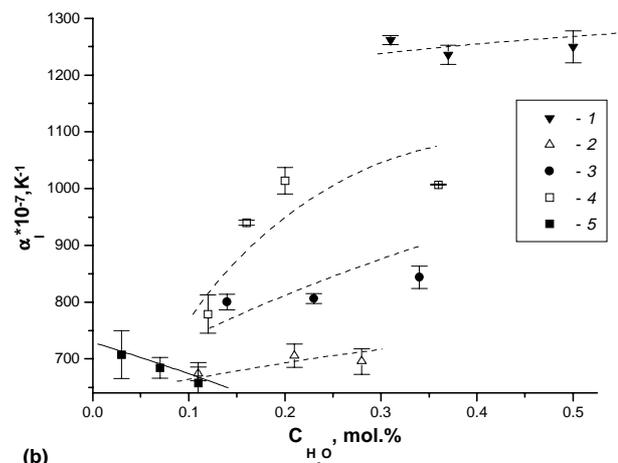


Figure 7. Dependences of glass transition temperatures of studied glasses on water contents: 1 – 5.5Na₂O; 2 – 15Li₂O; 3 – 15Na₂O; 4 – 15K₂O; 5 – 25Na₂O



(a)



(b)

Figure 8. Dependences of thermal expansion coefficients below (a) and above (b) glass transition interval on water contents in studied glasses

Bars show the mean square errors of measured values.

No distinct effect was found of water content on glasses with 5.5 mol% Na₂O. TEC of glasses containing 15 mol% alkali oxides have the tendency to increase on increasing water content in glass composition. Glasses containing 25 mol% Na₂O reveal the reverse tendency—TEC decreases on increasing water content.

Therefore, the influence of glass melting conditions and water content on thermal expansion of alkali borate glasses depends on the concentration of alkali oxides.

The results obtained should be connected with the structural changes in alkali borate glasses on adding alkali oxides. According to the NMR of Bray & coworkers⁽⁹⁾ there is the maximum of fourfold coordinated boron in alkali borate glass structure at around 30–40 mol% of alkali oxides. However, the curves of thermal expansion versus composition of alkali borate glasses demonstrate the existence of a clear minima at around 20 mol% R₂O.^(20,21) Shelby⁽²¹⁾ related this minimum to the maximum in concentration of tetraborate groups and the disappearance of boroxol and appearance of diborate groups. The difference in manner of the effect of water content for glasses with different concentrations of alkali oxides can also be related to the existence of different types of borate groups in glass structure (Figure 9, Ref. 21). To give a more exact answer we need to make further study of glasses containing more than 20 mol% alkali oxides.

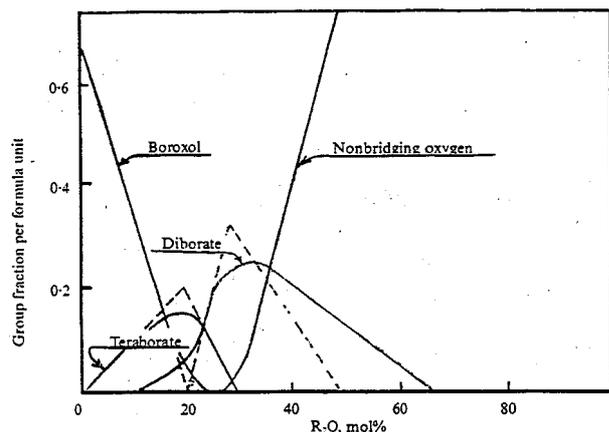


Figure 9. Simple model of alkali borate glasses based on the work of Krogh-Moe & Bray⁽²¹⁾

Conclusions

The viscosity and thermal expansion of binary borate glasses containing lithium, sodium and potassium oxides obtained by different glass melting conditions were studied. Several glasses of the same composition with different water contents were obtained. Water content in studied glasses was estimated by absorption spectroscopy in the near infrared region. The results of this study can be summarised as follows.

1. At the same glass melting conditions, glasses with lower content of alkali oxide kept higher water concentrations.
2. On increasing time of glass melting from 1 up to 4 h water content in glasses containing 5.5 and 15 mol% R_2O decreased approximately by half, water content in glasses containing 25% R_2O decrease to the less extent.
3. Viscosity values of all studied glasses show the tendency to decrease as the water content increases in glass structure.
4. The studied glasses have approximately the same sensitivities of viscosity to the changes in water content independently of kind and concentration of alkali oxide. On the average additions of ~ 0.1 mol% water corresponds to 0.3 order of magnitude reduction on logarithm of viscosity.
5. Glass transition temperatures of studied glasses determined by the dilatometer curve decreases on increasing water content.

6. Thermal expansion coefficients determined in the range of temperatures below and above glass transition interval increases on increasing water content in glasses containing alkali oxide up to 15 mol%. Glasses containing 25 mol% Na_2O show the reverse tendency.

References

1. Merker, L. & Scholze, H. Der Einfluß des Wassergehaltes von Silikatgläsern auf Transformations- und Erweichungsverhalten. *Glastech. Ber.*, 1962, **35**, 1, 37-43.
2. Sakka, S. Effects of small amounts of water on the viscosity, glass transformation temperature and Vickers hardness of silicate glasses. *J. Ceram. Soc. Japan*, 1981, **89**, 10, 577-84.
3. Poch, W. Vollständige Entwässerung einer B_2O_3 -Schmelzer und einige Eigenschaftswerte des daraus erhaltenen Glases. *Glastech. Ber.*, 1964, **37** (12), 533-5.
4. Franz, H. Effect of water content on density, refractive index and transformation temperature of alkali borate glasses. In *Borate glass: structure, properties and applications*. Volume 12. 1978. Edited by L. D. Pye, V. D. Frechette & N. J. Kreidl. Plenum, New York. Pp 567-75.
5. Boov, J. The viscosity of fused boric oxide. *Phys. Chem. Glasses*, 1967, **8** (2), 45-55.
6. Visser, Th.J. Rheological properties of alkali borate glasses. *PhD. Thesis*. Eindhoven, Netherlands. 1971.
7. Franz H. Solubility of water in alkali borate glasses. *J. Am. Ceram. Soc.*, 1966, **49** (9), 473-7.
8. Griscom, D. L. Borate glass structure. In *Borate glass: structure, properties and applications*. Volume 12. 1978. Edited by L. D. Pye, V. D. Frechette & N. J. Kreidl. Plenum, New York. Pp 11-149.
9. Bray, P. J. NMR and NQR studies of borates and borides. In *Proc. Second. Int. Conf. on Borate glasses, crystals and melts*. 1997. Edited by A. C. Wright, S. A. Feller & A. C. Hannon. Oxford, UK. Pp 1-20.
10. Prokhorenko, O. A., Mazurin, O. V., Chistokolova, M. V., Tarakanov, S. V., Reznik, Yu. E. & Anfimova, I. N. Problems of spectrophotometry of glass-forming melts. II. A technique for measuring the absorption spectra of the glasses and melts in the red and near infrared ranges at temperatures from 20 to 1500°C. *Glass Phys. Chem.*, 2000, **26** (2), 187-98.
11. Mazurin, O.V., Streltsina, M. V. & Shvaiko-Shvaikovskaya, T. P. *Handbook of glass data. Part B. Single-component and binary non-silicate oxide glasses*. 1983. Elsevier, Amsterdam, Oxford, New York.
12. Klyuev, V.P. & Totesh, A.S. Technique and devices for the glass viscosity measurements, Moscow. 1975. (In Russian.)
13. *Certificate on standard reference material 710a. Soda-lime-silica glass*. 1962. National Inst. Stand. Technol, Washington.
14. Klyuev, V. P. *Abstracts of the 1st All-Union Conference on the devices for the precise dilatometer measurements*. Leningrad, 1975. (In Russian.)
15. Scholze, H. Der Einbau des Wassersin Gläsern. *Glastech. Ber.*, 1959, **32**, 81-8, 278-81, 314-20, 381-6.
16. Adams, R. V. Infrared absorption due to water in glasses. *Phys. Chem. Glasses*, 1961, **2** (2), 39-49.
17. Sholze, H. *Glass. Nature, structure and properties*. 1991. New York.
18. Eagan, R. V. & Bergeron, C. G. Determination of water in lead borate glasses. *J. Am. Ceram. Soc.*, 1972, **55** (1), 53-4.
19. Nagel, S. Crystallization kinetics in binary borate glass melts. *PhD Thesis*. Urbana, Illinois, USA. 1973.
20. Chryssikos, G. D., Kamitsos, G. D. & Karakassides, M. A. Structure of borate glasses. Part 2. Alkali induced network modifications in terms of structure and properties. *Phys. Chem. Glasses*, 1990, **31** (3), 109-16.
21. Shelby, J. E. Thermal expansion of alkali borate glasses. *J. Am. Ceram. Soc.* 1983, **66** (3), 225-8.