Specific Features of Changes in the Properties of One- and Two-Alkali Borate Glasses Containing Water: I. Viscosity, Thermal Expansion, and Kinetics of Structural Relaxation in Binary Alkali Borate Glasses

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Abstract—Alkali borate glasses with different contents of residual water are prepared by varying the synthesis conditions. The temperature dependences of the viscosity and thermal expansion of glasses are obtained. The structural relaxation parameters are calculated from the hysteresis dilatometric curves measured. The water content is determined using the IR absorption spectra in the range of stretching vibrations of hydroxyl groups at room temperature. It is found that an increase in the water concentration in alkali borate glasses leads to a decrease in the viscosity. The character of variations in the viscosity logarithm with a change in the water content depends on the alkali cation concentration. The glass transition temperatures determined from the dilatometric curves for all the studied glasses decrease with an increase in the water content. As the water concentration increases, the thermal expansion coefficient (above and below the glass transition range) and the degree of fragility decrease for glasses containing 25 mol % Na_2O, increase for glasses with an alkali oxide content of 15 mol %, and remain virtually unchanged for glasses involving 5.5 mol % Na_2O. A change in the water content in the concentration range under investigation does not affect the structural relaxation parameters.

INTRODUCTION

Batch materials usually contain water—a component of the atmosphere. As a consequence, any glass synthesized in air involves water in one or other form.

The amount of water formed in the glass in the course of synthesis can vary from hundredths of a percent to few percent. The kinetics of interaction between a glass melt and water, the water content in glasses, and the influence of water on the glass properties have been studied by many authors. Reasoning from the results of these investigations, Shelby [1, p. 183] made the inference that, depending on the water content, glasses can be divided into three categories: "conventional" glasses containing no more than 0.5–1.0 wt % of water predominantly in the form of hydroxyl groups, "intermediate" glasses involving up to few weight percent of water in the form of hydroxyl groups and molecules, and "hydrosilicate" glasses [2], which contain water in the molecular form in amounts of more than few percent when it can be considered a main component of the material. The removal of water in any form from the glass is a rather complex problem.

The problem concerning the investigation into the structural features of glasses with residual water in different forms is especially topical for borate glasses, which are strongly hygroscopic and possess a rather high sensitivity of their properties to the water content in glass [3–6].

For glasses with a water content of less than 1 wt %, the interaction between water and the network of borate glasses can be represented by the scheme [7–9]

$$=B–O–B= + H_2O \Leftrightarrow 2HO–B=.$$
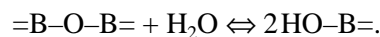
The hydroxyl groups incorporated in this way into the glass network have an effect on the structure-sensitive properties of glasses.

The aim of the present work was to investigate how water affects the viscosity and thermal expansion of binary alkali borate glasses and the structural relaxation parameters determined from the temperature dependences of the thermal expansion (dilatometric curves).

SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Glass synthesis. In this work, we studied glasses of compositions $15R_2O \cdot 85B_2O_3$ (where R = Li, Na, and K), $5.5Na_2O \cdot 94.5B_2O_3$, and $25Na_2O \cdot 75B_2O_3$ (Table 1).

Boric acid and carbonates of the corresponding alkali metals were used as initial components. The glasses were synthesized in a platinum crucible with a volume of 200 ml in a Globar-heater electric melting furnace. In order to prepare glasses of the same composition with different water contents, the time of glass melting at 1200°C was varied from 1 to 4 h. With the aim of producing the glasses with a minimum water

Table 1. Designations, compositions, synthesis conditions, spectral characteristics of the 2.8-μm band, and calculated water contents for the studied glasses

Glass designation	Glass composition (mol %) as-batched/as-analyzed				Synthesis time, h	ν_S, cm^{-1}	$\Delta\nu_H$, cm^{-1}	ΔI, l/(mol cm^{-2})	$[\varepsilon_{max} \cdot \Delta\nu_H]$, cm^{-2}	C_{OH}, mol/l	C_{H_2O}, mol %
	B$_2$O$_3$	Li$_2$O	Na$_2$O	K$_2$O							
5.5Na$_2$O	94.5/94.6	–	5.5/5.6	–	1	3485	100	29	15370	0.28	0.50
	94.5/94.7	–	5.5/5.3	–	2.5	3495	90	28	11590	0.22	0.38
	94.5/94.7	–	5.5/5.3	–	4	3485	100	29	9128	0.17	0.31
15Li$_2$O	85.0/84.7	15.0/15.3	–	–	1	3500	85	25	10570	0.20	0.28
	85.0/84.7	15.0/15.3	–	–	2.5	3500	85	25	7090	0.14	0.21
	85.0/84.9	15.0/15.1	–	–	4	3410	175	48	4905	0.06	0.11
15Na$_2$O	85.0/84.5	–	15.0/15.5	–	1	3460	125	36	14250	0.23	0.50
	85.0/84.8	–	15.0/15.2	–	2.5	3460	125	35	10050	0.16	0.38
	85.0/85.0	–	15.0/15.0	–	4	3470	115	33	6954	0.12	0.31
15K$_2$O	85.0/85.9	–	–	15.0/14.1	1	3470	115	33	13900	0.23	0.36
	85.0/85.9	–	–	15.0/14.1	2.5	3470	115	33	7191	0.12	0.20
	85.0/85.7	–	–	15.0/14.3	4	3445	140	40	5975	0.09	0.16
	85.0/85.9	–	–	15.0/14.1	1.5*	3480	105	31	4790	0.08	0.12
25Na$_2$O	75.0/75.9	–	25.0/24.1	–	1	3405	180	43	5495	0.08	0.11
	75.0/75.6	–	25.0/24.4	–	2.5	3400	180	43	4189	0.06	0.07
	75.0/75.8	–	25.0/24.2	–	4	3415	170	40	2395	0.04	0.03

* With subsequent heat treatment in a vacuum furnace at 1000°C for 1 h.

content, a number of glasses were melted in a vacuum furnace at 1000°C for 1 h.

For the purpose of preventing the absorption of atmospheric moisture, the studied glasses were stored in desiccators and the samples were ground and polished using anhydrous suspensions.

Determination of the water content by IR spectroscopy. The water content in the studied glasses was evaluated using the IR absorption spectra in the range of stretching vibrations of OH groups. The spectra were recorded at room temperature on an SF-2-LSS spectrophotometer whose optical scheme was designed at the Laboratory of Glass Properties, Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences [10]. This two-beam grating instrument operated in the spectral range 0.6–4 μm. A halogen quartz lamp served as a radiation source, and a FUO photosensitive element was used as a receiver. The absolute error in measurement of the optical density on this instrument was equal to ±0.005.

Samples in the form of plates ~0.5 mm thick were prepared for measuring the IR spectra.

In order to determine the reliable mean absorption coefficients and to exclude the errors associated with optical inhomogeneity of the measured samples, each sample was measured several times at different points on the surface. The absorption coefficients were calculated with inclusion of the losses by reflection from the glass–air interface [10]. In this case, the refractive index was taken equal to 1.5 (which corresponds to the mean refractive index of the studied glasses in the visible spectral range [11]), because data on the refractive index in the IR range were unavailable.

The absorption spectra $K(\lambda)$ (where λ is the wavelength in μm) were recorded in the range 2.5–4.0 μm. In this range, two bands at 2.8 and 3.5 μm are associated with hydroxyl groups in the glass structure [8]. The IR spectra of the 5.5Na$_2$O glasses synthesized under different conditions are displayed in Fig. 1.

The use of the IR data for quantitative analysis is based on the Bouguer–Lambert–Beer law (see, for example, [12, pp. 160–162]), according to which the concentration of hydroxyl groups in the glass can be represented in the following form:

$$C_{OH} = K_{max}(\lambda)/\varepsilon_{max}. \tag{1a}$$

Here, C_{OH} is the concentration of hydroxyl groups (mol l^{-1}), $K_{max}(\lambda)$ is the absorption coefficient of the studied sample at a maximum of the band at the wavelength λ, and ε_{max} is the molar spectral absorption coef-

ficient ($l \, mol^{-1} \, cm^{-1}$) at the wavelength corresponding to the maximum of the used band. The $K_{max}(\lambda)$ coefficient is defined by the relationship

$$K_{max}(\lambda) = (1/d)\log(1/T_{max}(\lambda)), \quad (2)$$

where d is the sample thickness (cm) and $T_{max}(\lambda)$ is the peak value of the transmission coefficient of the sample. The ε_{max} coefficient is preliminarily determined for a reference sample with a known concentration of hydroxyl groups as the ratio between the absorption coefficient of this sample at a given wavelength and this concentration.

Since the band contour can change with a variation in the matrix composition, instead of relationship (1a), an expression including integral characteristics rather than spectral parameters is often used. In this case, it is common practice to use the molar integral absorption coefficient ε_{int} ($l \, mol^{-1} \, cm^{-2}$) and the integral absorption coefficient determined by the area under the band in the absorption coefficient spectrum $[\int K_{max}(\lambda)d\lambda]$ of the studied sample; the concentration of the groups under consideration is found as the ratio of these coefficients,

$$C_{OH} = \frac{\int K_{max}(\lambda)d\lambda}{\varepsilon_{int}}. \quad (1b)$$

Note that the value of ε_{int} is determined as the ratio between the integral absorption coefficient of the band in the spectrum of the reference sample and a known concentration of hydroxyl groups in the reference.

The calculation carried out by Eagan and Bergeron [13] included only the absorption band of OH groups at a wavelength of 2.8–2.9 μm and ignored the second band at about 3.5 μm observed in our spectra. It is known (see, for example, [12]) that the absorption spectra of glasses contain a considerably larger number of bands assigned to water in one form or another. However, in [13], the water concentration was estimated using only the data for one band. These estimates can be sufficiently reliable in the cases when the intensity ratio of the bands attributed to different structural states of water remains approximately constant from sample to sample and when glasses are synthesized under similar conditions (the data on the influence of the synthesis temperature on the absorption spectra of phosphate glasses were obtained, for example, by Efimov *et al.* [14]). Reasoning from the foregoing, we can infer that the method proposed in [13] for determining the water content gives only rough estimates.

Eagan and Bergeron [13] noted that the integrated intensity I of the absorption associated with hydroxyl groups introduced into the composition of alkali borate glass is changed by the value of ΔI proportional to the frequency shift Δv_S of the absorption maximum with respect to its location in the spectrum of vitreous boron oxide. Figure 2 shows the plot of this dependence taken
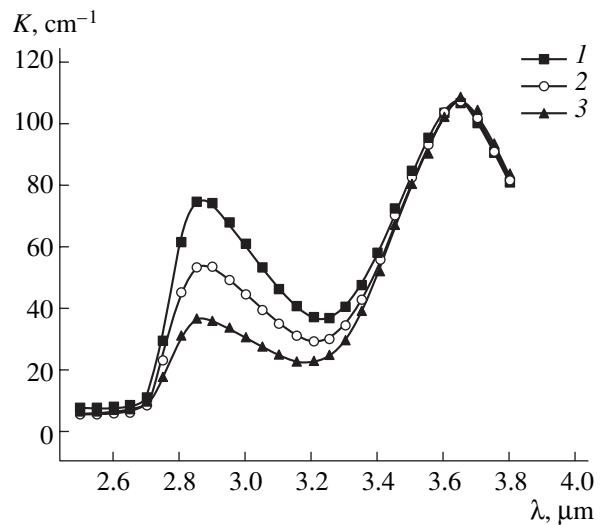

Fig. 1. IR absorption spectra of the 5.5Na$_2$O glasses synthesized at 1200°C for (*1*) 1, (*2*) 2.5, and (*3*) 4 h.
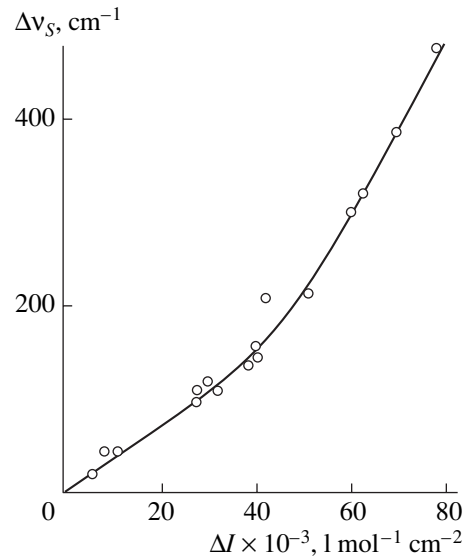

Fig. 2. Dependence of the change in the integrated intensity ΔI of the absorption caused by OH groups on the shift Δv_S in the frequency at a maximum of the absorption band [13].

from [13]. An increase in the integrated intensity is caused by the formation of hydrogen bonds in the glass structure. Nagel [15] assumed that this technique can also be used for any binary alkali borate glass.

In [13], the authors proposed to calculate the water concentration in lead borate glasses in the following way. The integrated index of the absorption caused by OH groups in vitreous boron oxide was defined as the product of the molar spectral absorption coefficient at the wavelength of the band maximum into the half-width of this band Δv_H (cm^{-1}). This product, which is

designated by $[\varepsilon_{max}\Delta\nu_H]_{B_2O_3}$, appeared to be equal to 25.6×10^3 l/(mol cm^2). The calculation of this product in [13] was performed using the coefficient $\varepsilon_{max} = 141$ l/(mol cm) determined by Franz [3] for vitreous boron oxide.

Hence, the calculated integrated absorption index is equal to $[\varepsilon_{max}\Delta\nu_H]_{B_2O_3} + \Delta I$, where ΔI is the increase in the integrated intensity due to the formation of hydrogen bonds.

Therefore, by determining the shift $\Delta\nu_S$ in the location of the absorption band attributed to OH groups, the increase ΔI in the integrated intensity can be determined from the graph depicted in Fig. 2 (taken from [13]).

Now, the concentration of hydroxyl groups in binary borate glass can be calculated by the formula

$$C_{OH} = (K_{max}(\lambda)\Delta\nu_H)/([\varepsilon_{max}\Delta\nu_H]_{B_2O_3} + \Delta I). \quad (3)$$

The experimental values of the absorption band location ν_S (on the wave number scale, cm^{-1}), $\Delta\nu_H$, ΔI, and $[\varepsilon_{max}\Delta\nu_H]$ and also the concentrations C_{OH} and the water contents C_{H_2O} (calculated from the experimental data) in the studied glasses are listed in Table 1.

Determination of the temperature dependences of the viscosity. The viscosity of the studied glass samples was measured on a viscometer by the central rod bending method in the temperature range corresponding to a change in the viscosity from 10^{10} to 10^{13} dPa s. Essentially, the method consists in determining the bending rate of a rod horizontally mounted on two supports under a load applied to the center of the sample. The method and the setup were described in detail in [16]. The root-mean-square error of measurements using this method was equal to $\pm 0.04 \log\eta$.

The sample temperature was measured with a chromel–alumel thermocouple graduated against the melting temperatures of pure metals and was maintained constant accurate to within ± 0.2 K for several hours. The viscometer was checked against a reference SRM 710A glass [17]. Polished rectangular samples $32 \times 4 \times 2$ mm in size were used for measurements.

The experimental viscosities obtained were approximated by the Vogel–Fulcher–Tammann equation

$$\log\eta = A + \frac{B}{T - T_0}, \quad (4)$$

where A, B, and T_0 are the parameters of the equation and T is the absolute temperature (K).

The parameters of the equation were calculated using the special program developed at the Laboratory of Glass Properties, Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences. The calculated parameters of the Vogel–Fulcher–Tammann equation for the studied glasses are presented in Table 2.

Dilatometric measurements. The thermal expansion of the glasses was studied on an inclined dilatometer with a small measuring load [18]. The dilatometer design made it possible to perform measurements over a wide range of temperatures (including the glass transition range) at a constant rate of change in the temperature. In turn, this made it possible to measure the dilatometric hysteresis loops, whose processing provided a way of determining the structural relaxation parameters.

In the course of experiments, the sample temperature was measured with the use of the chromel–alumel thermocouple graduated against the melting temperatures of pure metals (zinc, lead, and aluminum). The dilatometer was checked against a reference corundum sample in the temperature range 150–500°C, which covered the temperature range of measurements for the studied glasses. The error in measurement of the thermal expansion coefficient was no larger than ±5%, although the instrumental error determined for the dilatometer from the thermal expansion of corundum was equal to $\pm 1 \times 10^{-7}$ K^{-1}.

The dilatometric measurements were performed using polished rectangular samples $20 \times 6 \times 4$ mm in size.

The measurements were carried out under thermocycling conditions at a constant rate of change in the temperature. During the measurements, the rate of cooling and subsequent heating was equal to 2 K/min for the glasses with alkali oxide contents of 5.5 and 15 mol % and 3 K/min for the glasses with an alkali oxide content of 25 mol %.

The use of a rate of 2 K/min was caused by the low melting temperatures of borate glasses with a relatively small content of alkali oxides. In order to determine closed hysteresis loops, the thermal expansion of these glasses should be measured from 150–180°C. However, the design of the dilatometer furnace did not make it possible to cool the furnace to these temperatures at a regulated rate of 3 K/min. Higher melting temperatures of glasses with a larger content of alkali oxide and their crystallization ability allowed us to use a rate of 3 K/min.

The effect associated with the lag of the sample temperature from the temperature recorded by the thermocouple due to a larger thermal inertia of the sample as compared to that of the thermocouple was compensated for by shifting the cooling and heating curves toward each other until they coincided in the portions above and below the glass transition range. The obtained closed dilatometric curves were used for determining the thermal expansion coefficients at temperatures above (α_l) and below (α_g) the glass transition range and also the glass transition temperatures T_g. The T_g temperature was determined from the cooling curves as the intersection point of the straight lines that describe the dependences of the specific elongation $\delta L/L_0$ at temperatures above and below the glass transition range and

Table 2. Parameters of the Vogel–Fulcher–Tammann equation, fragility parameters S [see Eq. (7)], thermal expansion coefficients below (α_g) and above (α_l) the glass transition range, glass transition temperatures T_g, and structural relaxation parameters for the studied glasses

Glass	C_{H_2O}, mol %	Parameters of the Vogel–Fulcher–Tammann equation			S	Thermal expansion coefficient $\times 10^7$, K^{-1}			Structural relaxation parameters	
		A	B	T_0		α_g	α_l	T_g, °C	b_S	$\log K_S$
5.5Na$_2$O · 94.5B$_2$O$_3$	0.50	−0.43	2730.2	373.2	37.6 ± 3.4	110 ± 4	1250 ± 28	300 ± 2	0.61 ± 0.03	10.08 ± 0.04
	0.37	1.64	1899.0	416.4	38.9 ± 3.5	108 ± 4	1236 ± 17	306 ± 1	0.58 ± 0.03	10.23 ± 0.03
	0.31	−5.47	5288.0	301.5	37.7 ± 3.4	105 ± 4	1261 ± 8	313 ± 1	0.62 ± 0.02	10.02 ± 0.06
15Li$_2$O · 85B$_2$O$_3$	0.28	0.32	2409.5	494.8	44.9 ± 4.0	76 ± 4	695 ± 22	407 ± 2	0.62 ± 0.03	9.82 ± 0.05
	0.21	−6.98	5900.5	395.2	46.6 ± 4.2	76 ± 1	706 ± 21	412 ± 2	0.59 ± 0.05	9.87 ± 0.07
	0.11	−4.26	4190.3	452.6	49.0 ± 4.4	67 ± 3	674 ± 12	418 ± 1	0.58 ± 0.03	10.05 ± 0.07
15Na$_2$O · 85B$_2$O$_3$	0.34	−2.52	3528.2	437.5	44.9 ± 4.0	110 ± 4	844 ± 20	395 ± 2	0.52 ± 0.03	9.86 ± 0.01
	0.23	−1.74	3262.8	453.8	44.5 ± 4.0	98 ± 3	806 ± 8	398 ± 1	0.54 ± 0.03	10.15 ± 0.06
	0.19	−2.52	3295.0	466.3	49.2 ± 4.4	98 ± 2	800 ± 14	400 ± 1	0.51 ± 0.04	10.19 ± 0.12
15K$_2$O · 85B$_2$O$_3$	0.36	−14.4	11381.0	215.9	41.4 ± 3.7	116 ± 3	1007 ± 1	354 ± 1	0.52 ± 0.04	10.20 ± 0.03
	0.20	−3.0	3424.0	425.4	41.1 ± 3.7	117 ± 4	1014 ± 24	364 ± 2	0.54 ± 0.02	10.05 ± 0.04
	0.16	−12.2	9007.0	290.0	45.6 ± 4.1	108 ± 3	940 ± 4	371 ± 2	0.57 ± 0.02	10.13 ± 0.09
	0.12	−8.78	6663.2	342.1	45.9 ± 4.1	112 ± 5	779 ± 34	370 ± 1	0.65 ± 0.02	10.22 ± 0.10
25Na$_2$O · 75B$_2$O$_3$	0.11	−1.59	2158.9	588.0	57.1 ± 5.1	102 ± 1	657 ± 36	461 ± 1	0.45 ± 0.02	9.94 ± 0.04
	0.07	−2.45	2500.8	577.4	53.5 ± 4.8	113 ± 1	684 ± 18	464 ± 2	0.48 ± 0.02	10.13 ± 0.14
	0.03	−1.27	2144.5	592.9	59.3 ± 5.3	109 ± 2	708 ± 42	471 ± 1	0.54 ± 0.04	10.09 ± 0.09

are extrapolated to their intersection within this range. The dilatometric curve for the 15Li$_2$O glass and the scheme of determining the values of α_l, α_g, and T_g are depicted in Fig. 3.

Determination of the structural relaxation parameters. The relaxation parameters (the constant b_s and the modulus K_s) of the Tool–Narayanaswamy model were determined from the dilatometric hysteresis according to the ISC algorithm [19]. The constant b_s characterizes the width of the spectrum of the structural relaxation times τ_s and describes the kinetics of change in the structural relaxation time by the equation

$$M = \exp\left[-\left(\frac{t}{\tau_s}\right)^{b_s}\right]. \tag{5}$$

The modulus K_s is equal to the ratio of the viscosity η to the structural relaxation time. These constants were calculated using both the algorithm proposed in [20] and a special optimizing program that minimizes the square of the difference between the computed and experimental values of the thermal expansion in the dilatometric loops obtained upon cooling and subsequent heating at the same rate. The above algorithm and the program were based on the Tool–Narayanaswamy structural relaxation model [19]. The algorithm of the optimizing program was described in [21]. Discussion of this algorithm is beyond the scope of the present work.

RESULTS AND DISCUSSION

The isothermal dependences of the viscosity logarithm on the water content for the studied glasses are plotted in Fig. 4. As can be seen from this figure, an increase in the water concentration leads to a decrease
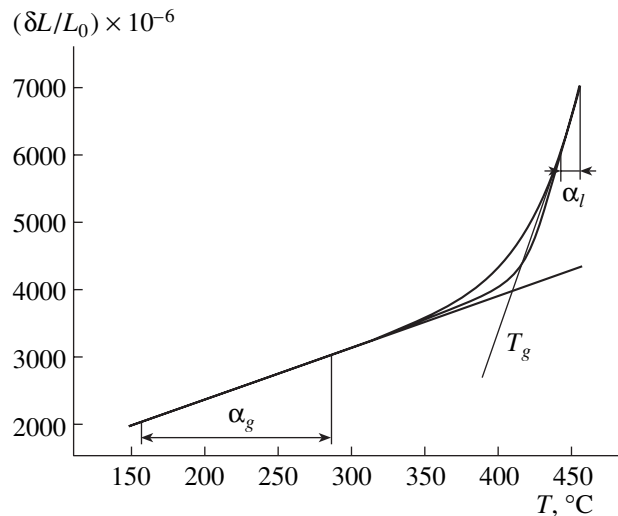

Fig. 3. Scheme of determining the thermal expansion coefficients below (α_g) and above (α_l) the glass transition range and the glass transition temperature T_g from the dilatometric curves.
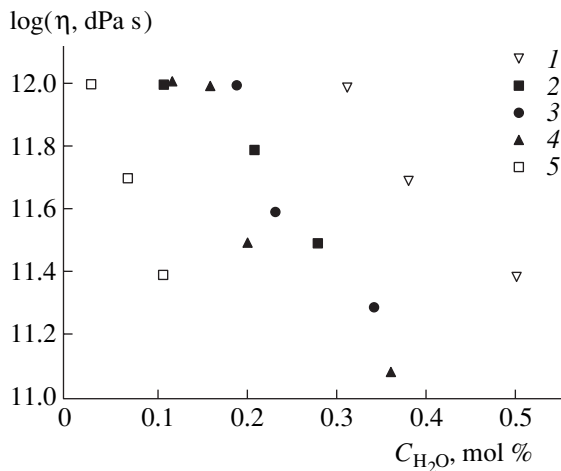
log(η, dPa s)

Fig. 4. Isothermal dependences of the viscosity logarithm on the water content for the studied glasses with different alkali oxides (according to the designations given in Table 1): (*1*) $5.5Na_2O$ at 331°C, (*2*) $15Li_2O$ at 437°C, (*3*) $15Na_2O$ at 420°C, (*4*) $15K_2O$ at 389°C, and (*5*) $25Na_2O$ at 481.5°C.

In recent years, comparison of the temperature dependences of the viscosities for compounds of different structures in the $\log\eta - T_{13}/T$ coordinates [where T_{13} is the temperature corresponding to the logarithm $\log(\eta, dPa\ s) = 13$] has been widely used in world literature [22–27]. According to the behavior of the dependences constructed in these coordinates, materials are divided into two groups: strong compounds with an Arrhenius dependence over a wide range of temperatures and fragile compounds characterized by a pronounced deviation from linearity (Fig. 5). The degree of deviation from linearity or the degree of fragility of glasses is an important parameter, because it characterizes the rate of structural transformations observed in the liquid upon glass transition.

According to the Angell concepts [22–24], the fragility of glass only not is a characteristic that reflects a different type of the temperature dependence of the viscosity but is also a characteristic that reflects the stability of short-range and long-range orders in glasses, i.e., the stability of the structure to the breaking of particular bonds with a variation in the temperature and to the formation of new configurations caused by these breakings.
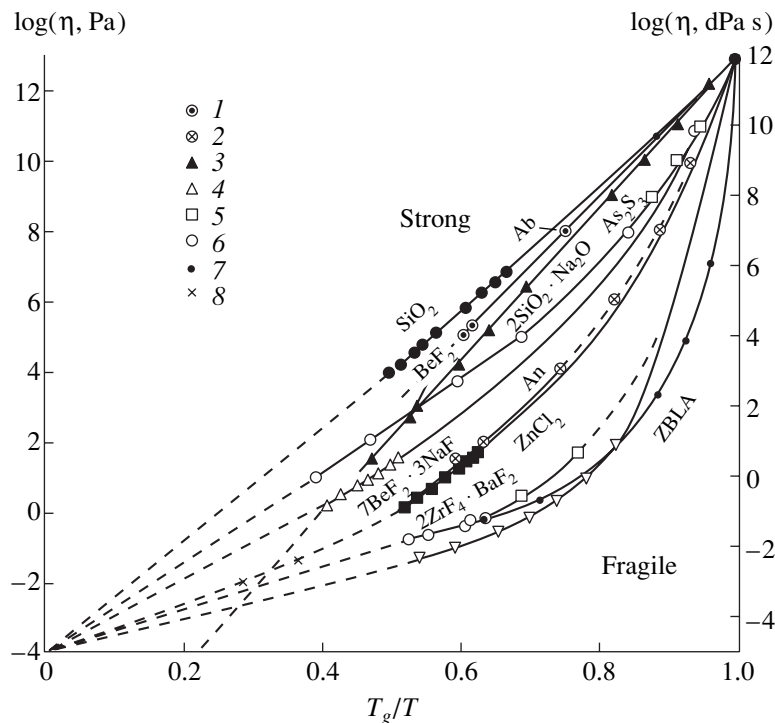
in the viscosity of all the glasses. Note that the sensitivity of the viscosity logarithm to a change in the water content in the glass somewhat increases with an increase in the alkali oxide concentration.

Fig. 5. Temperature dependences of the viscosity for compounds with different structures in the coordinates $\log\eta - T_g/T$, where the glass transition temperature T_g corresponds to the temperature at which $\log(\eta, dPa\ s) = 13$ (according to the Angell classification of compounds into strong and fragile [24]). Compounds: (*1*) albite (Ab) $NaAlSi_3O_8$ (1038), (*2*) anorthite (An) $CaAl_2Si_2O_8$ (1112), (*3*) BeF_2 (590), (*4*) $7BeF_2–3NaF$ (383), (*5*) As_2S_3 (454), (*6*) $2ZrF_4–BaF_2$ (550), (*7*) ZBLA (552), and (*8*) propanol (85.2). The T_g temperatures are given in °C in parentheses.

Strong liquids (such as SiO_2, GeO_2, and B_2O_3) have a three-dimensionally linked network structure composed of polyhedra shared by vertices. This structure is stable and only slightly changes with a variation in the temperature, which results in straight-line dependences in the $\log\eta - T_{13}/T$ coordinates. On the other hand, fragile compounds have no three-dimensional structure and the loss in the directional character of bonds leads to a fast change in the medium-range order with an increase in the temperature and, hence, to a nonlinear dependence in the $\log\eta - T_{13}/T$ coordinates.

In silicate glasses of nearly all known compositions, the coordination number of silicon is equal to four. The coordination number of boron is equal to three in boron oxide belonging to strong liquids and can be equal to either three or four in alkali-containing borate glasses. It seems likely that this is why the fragility of alkali borate glasses is considerably higher than that of alkali silicate glasses and boron oxide [22]. Moreover, the degree of fragility of alkali borate glasses passes through a maximum in the range of compositions containing about 30% alkali oxide, which corresponds to the maximum content of fourfold-coordinated boron in the glass structure.

The temperature dependences of the viscosity in the $\log\eta - T_{13}/T$ coordinates for the studied sodium borate glasses are compared in Fig. 6. The dashed line shows the dependence corresponding to the strongest liquids, such as SiO_2 and GeO_2 [22–24]. It is seen from Fig. 6 that an increase in the alkali oxide content results in an increase in the fragility. This is in agreement with the data available in the literature [25, 27]. The influence of the water content on the deviation from a linear dependence in these coordinates depends on the alkali oxide content.

Jewell *et al.* [26] studied the influence of water on the viscosity of a number of aluminosilicate glasses and drew the inference that the effect of water is associated with the degree of fragility of their melts.

According to [26], the structure of strong liquids is more sensitive to the bond breakings caused by an increase in the content of hydroxyl groups in the glass structure. By contrast, compared to the structure of strong liquids, the melt structure of fragile compounds (characterized by instability of the medium-range order with a variation in the temperature), to a considerably smaller extent, is affected by a small number of additional broken bonds arising from an increase in the content of hydroxyl groups in the glass. As a consequence, the viscosity of fragile compounds changes to a lesser degree with an increase in the water content. These inferences are at variance with our results obtained for alkali borate glasses, according to which the glasses with a larger content of alkali oxide have a higher fragility and a higher sensitivity of the viscosity to the water content.
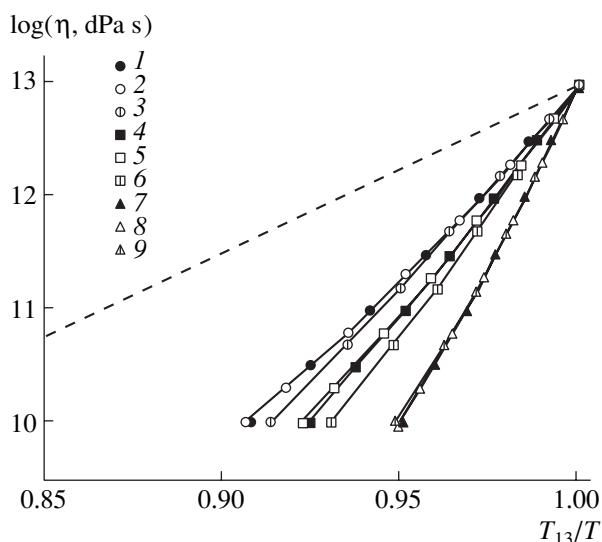

Fig. 6. Dependences of the viscosity on the normalized temperature T_{13}/T (where T_{13} is the temperature corresponding to $\log\eta = 13$) for the studied sodium borate glasses: (*1*, *2*, *3*) $5.5Na_2O$ with water contents of 0.5, 0.37, and 0.31 mol %; (*4*, *5*, *6*) $15Na_2O$ with water contents of 0.34, 0.23, and 0.14 mol %; and (*7*, *8*, *9*) $25Na_2O$ with water contents of 0.11, 0.07, and 0.03 mol %. The dashed line represents the dependence corresponding to the strongest liquids [24].

Quantitatively, the degree of fragility can be evaluated in different ways. In particular, Nemilov [27, 28] considered the strong and fragile glasses in terms of "long" and "short" glasses and used the activation entropy of viscous flow (entropy unit $\equiv 1$ kcal mol^{-1} K^{-1}) as a measure of the glass length; that is,

$$\Delta S^* = \frac{R}{T_{13}}\frac{\partial\log\eta}{\partial(1/T)} - 75.24, \qquad (6)$$

where R is the gas constant. In this case, long (or strong) melts correspond to small values of ΔS^* and short (or fragile) melts correspond to large values of ΔS^*.

In recent years, the parameter S, which is defined as the temperature coefficient of the viscosity in the vicinity of the temperature corresponding to the viscosity $\eta = 10^{13}$ dPa s, that is,

$$S = \lim_{\frac{T_{13}}{T} \to 1} \frac{d\log\eta}{d(T_{13}/T)}, \qquad (7)$$

has been extensively used for evaluating the degree of fragility of glasses (see, for example, [25, 29, 30]). By this definition of the fragility, the parameter S coincides with the activation entropy calculated according to relationship (6) to within a constant factor, even though its sense changes essentially. Since the fragility defined by expression (7) is preferred by the authors in the litera-

ture, hereafter, we will use this definition of the parameter S.

Chryssikos *et al.* [25] showed that the parameter S for binary lithium and sodium borate glasses increases with an increase in the alkali oxide content in the composition of borate glass.

The parameters S for the glasses under investigation as a function of the water content are presented in Fig. 7 and Table 2. Although the error in determination of the
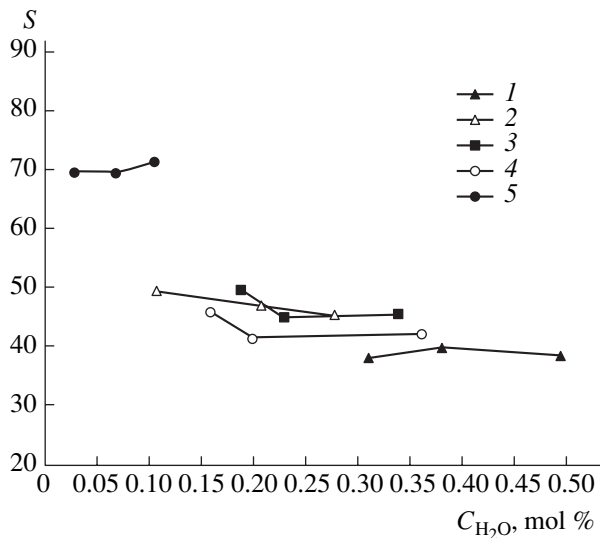
parameter S is equal to about 10%, the data given in Table 2 enable us to draw an inference as to the tendency in change in the degree of fragility, as was done in [25]. For the glasses containing 15 mol % of any oxide, an increase in the water content leads to a decrease in the degree of fragility. The opposite tendency is observed for the glasses involving 25 mol % Na_2O: an increase in the water content results in a small increase in the degree of fragility. The fragility of the glasses with 5.5 mol % Na_2O remains constant and is independent of the water content.

Figures 8 and 9 depict the dependences of the glass transition temperature and the thermal expansion coefficients determined above and below the glass transition range on the water content in the studied glasses. As the water content increases, the glass transition temperatures of all the glasses decrease irrespective of the sort and the concentration of alkali cations in the glass composition.

The character of the change in the thermal expansion coefficient depends on the alkali oxide concentra-

Fig. 7. Dependences of the fragility parameter S on the water content for the studied glasses: (*1*) 5.5 Na_2O, (*2*) 15 Li_2O, (*3*) 15 Na_2O, (*4*) 15 K_2O, and (*5*) 25 Na_2O.
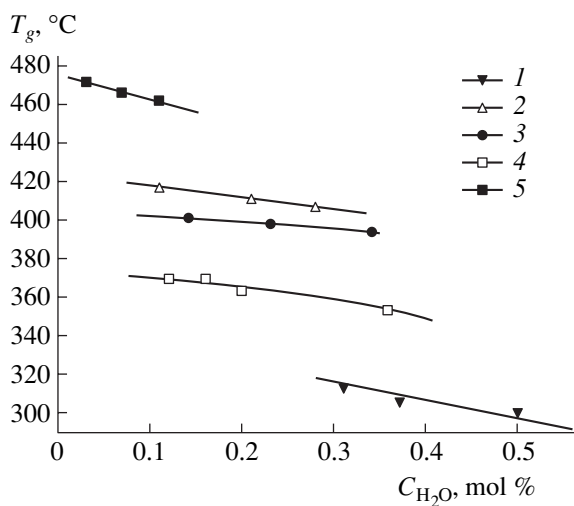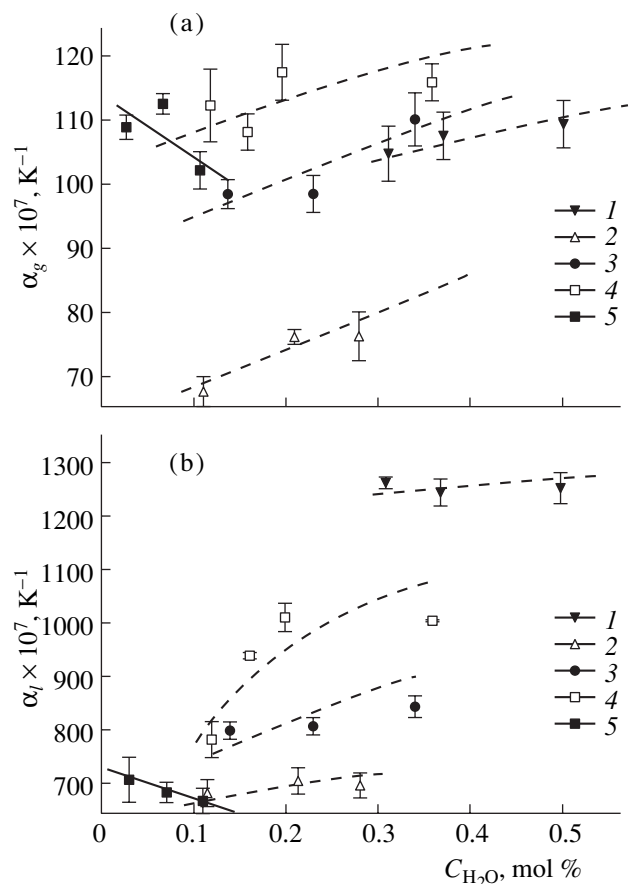

Fig. 8. Dependences of the glass transition temperature on the water content for the studied glasses: (*1*) 5.5 Na_2O, (*2*) 15 Li_2O, (*3*) 15 Na_2O, (*4*) 15 K_2O, and (*5*) 25 Na_2O.

Fig. 9. Dependences of the thermal expansion coefficient (a) below and (b) above the glass transition range for the studied glasses: (*1*) 5.5 Na_2O, (*2*) 15 Li_2O, (*3*) 15 Na_2O, (*4*) 15 K_2O, and (*5*) 25 Na_2O.

tion. Actually, the thermal expansion coefficients of the glasses with 5.5 mol % Na_2O are virtually independent of the water content. At the same time, both thermal expansion coefficients of the glasses with an alkali oxide content of 15 mol % increase with an increase in the water content. As for the fragility, the dependences of the thermal expansion coefficients on the water content for the glasses containing 25 mol % Na_2O exhibit an opposite tendency (Figs. 8 and 9).

The results obtained can be explained by the structural transformations that occur in boron oxide upon addition of alkali oxides. According to the NMR data obtained by Bray [31] for alkali borate glasses, the maximum amount of fourfold-coordinated boron in their structure is observed approximately at an alkali oxide content of 30 mol %. However, the concentration dependences of the properties exhibit extrema at somewhat different alkali oxide concentrations. For example, as follows from the data obtained by Shelby [32], the concentration dependence of the thermal expansion for alkali borate glasses has a minimum at about 20 mol % R_2O. In [33, 34], the location of this minimum was attributed to the fact that the number of tetraborate groups becomes maximum, boroxol groups disappear, and diborate groups appear at this glass composition (see, for example, Fig. 10). This assumption is confirmed by the dependences of the degree of fragility and the thermal expansion coefficients on the water content for the glasses investigated in the present work.

The structural relaxation parameters calculated from the dilatometric curves for the studied glasses are listed in Table 2. The parameters of the Vogel–Fulcher–Tammann equation, thermal expansion coefficients below (α_g) and above (α_l) the glass transition range, and the glass transition temperatures T_g are also given in this table. As can be seen from Table 2, the structural relaxation parameters for the studied glasses do not depend on the water content. Note that the b_s parameter for the glasses with a large alkali oxide content (25 mol %) is smaller than those for the glasses with alkali oxide contents of 5.5 and 15 mol %. As was noted above, the b_s constant characterizes the width of the spectrum of the structural relaxation times. A decrease in this parameter indicates that the distribution of structural relaxation times becomes broader. In [35], the b_s parameter in the Kohlrausch fractional exponential equation was treated as the degree of structural inhomogeneity in the glass. Therefore, within the limits of the error in determination of the b_s parameters presented in Table 2, the width of the spectrum of the structural relaxation times and, hence, the degree of inhomogeneity in the studied glasses remain constant with a change in the water content in the concentration range under consideration. An increase in the alkali oxide content leads to an increase in the degree of inhomogeneity in the glass. This is associated both with an
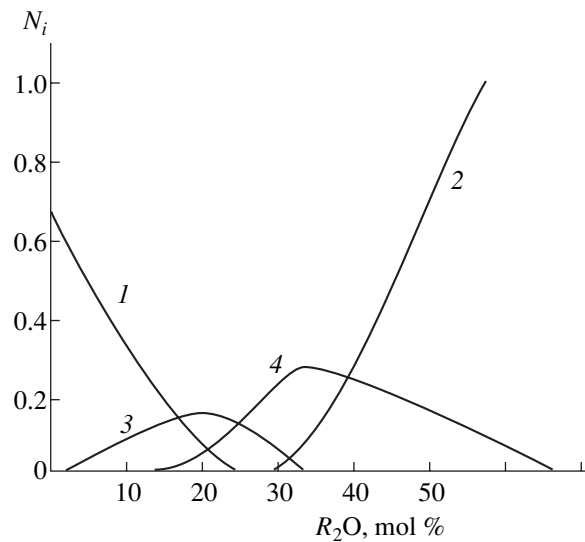

Fig. 10. Fractions of the groups occurring in the model structure of alkali borate glasses [33] constructed on the basis of the Krogh-Moe model [34] and NMR data: (*1*) boroxol rings, (*2*) nonbridging oxygen atoms, (*3*) tetraborate groups, and (*4*) diborate groups.

increase in the number of fourfold-coordinated boron atoms and with the occurrence of other structural groupings (see Fig. 10).

CONCLUSIONS

The results of the above investigation into the influence of residual structural water (whose content depends on the time of glass synthesis) on the viscosity and thermal expansion of binary alkali borate glasses can be summarized as follows.

(1) The presence of residual water in alkali borate glasses leads to a decrease in the viscosity. In this case, the character of the change in the viscosity logarithm with a variation in the water content is determined by the alkali cation concentration and the fragility of the glass under consideration.

(2) The glass transition temperatures determined from the dilatometric curves decrease with an increase in the water content for all the studied glasses.

(3) With an increase in the water concentration, the thermal expansion coefficient (above and below the glass transition range) and the degree of fragility decrease for the glasses containing 25 mol % Na_2O, increase for the glasses with an alkali oxide content of 15 mol %, and remain virtually constant for the glasses involving 5.5 mol % Na_2O.

(4) A change in the water content in the studied concentration range has no effect on the fragility and structural relaxation parameters (calculated from the dilatometric curves).

REFERENCES

1. Shelby, J.E., Handbook of Gas Diffusion in Solids and Melts, *ASM Int.*, 1992.

2. Bartolomew, R.F., Water in Glass, in *Treatise on Materials Science and Technology*, Doremus, R.H. and Tomozawa, M., Eds., New York: Academic, 1982, vol. 22, pp. 75–127.

3. Franz, H., Effect of Water Content on Density, Refractive Index, and Transformation Temperature of Alkali Borate Glasses, *Mater. Sci. Res.*, 1978, vol. 12, pp. 567–575.

4. Boow, J., The Viscosity of Fused Boric Oxide, *Phys. Chem. Glasses*, 1967, vol. 8, no. 2, pp. 45–55.

5. Visser, Th.J., Rheological Properties of Alkali Borate Glasses, *Thesis*, Eindhoven, 1971.

6. Stolyar, S.V., Klyuev, V.P., and Bulaeva, A.V., Viscosity and Thermal Expansion of Sodium Borate Glasses in the Glass Transition Range, *Fiz. Khim. Stekla*, 1984, vol. 10, no. 7, pp. 447–454.

7. Adams, R.V., Some Experiments on the Removal of Water from Glasses, *Phys. Chem. Glasses*, 1961, vol. 2, no. 2, pp. 52–54.

8. Scholze, H., Der Einbau des Wassers in Glässern, *Glastech. Ber.*, 1959, vol. 32, no. 3, pp. 81–88; no. 4, pp. 142–152; no. 7, pp. 278–281; no. 8, pp. 314-320; no. 9, pp. 381–386.

9. Adams, R.V., Infrared Absorption Due to Water in Glasses, *Phys. Chem. Glasses,* 1961, vol. 2, no. 2, pp. 39–49.

10. Prokhorenko, O.A., Mazurin, O.V., Chistokolova, M.V., Tarakanov, S.V., Reznik, Yu.E., and Anfimova, I.N., Problems of Spectrophotometry of Glass-forming Melts: II. A Technique for Measuring the Absorption Spectra of Glasses and Melts in the Red and Near-Infrared Ranges at Temperatures from 20 to 1500°C, *Fiz. Khim. Stekla*, 2000, vol. 26, no. 2, pp. 447–454 [*Glass Phys. Chem.* (Engl. transl.), 2000, vol. 26, no. 2. pp. 187–198].

11. Mazurin, O.V., Streltsina, M.V., and Shvaiko-Shvaikovskaya, T.P., *Svoistva stekol i stekloobrazuyushchikh rasplavov. Spravochnik. Odnokomponentnye i dvukhkomponentnye oksidnye nesilikatnye sistemy*, Leningrad: Nauka, 1975, vol. 2. Translated under the title *Handbook of Glass Data: Part B. Single-Component and Binary Non-Silicate Oxide Glasses: Physical Science Data 15*, Amsterdam: Elsevier, 1985.

12. Fanderlick, I., Optical Properties of Glass, in *Glass Science and Technology*, Elsevier, 1983, vol. 5.

13. Eagan, R.V. and Bergeron, C.G., Determination of Water in Lead Borate Glasses, *J. Am. Ceram. Soc.*, 1972, vol. 55, no. 1, pp. 53–54.

14. Efimov, A.M., Kostyreva, T.G., and Sycheva, G.A., Water-Related IR Absorption Spectra for Alkali Zinc Pyrophospate Glasses, *J. Non-Cryst. Solids*, 1998, vol. 238, pp. 124–142.

15. Nagel, S., Crystallization Kinetics in Binary Borate Glass Melts, *Thesis*, Urbana, 1973.

16. Klyuev, V.P. and Totesh, A.S., *Metody i apparatura dlya kontrolya vyazkosti stekla* (Methods and Instruments for Testing the Viscosity of Glasses), Moscow: VNIIESM, 1975.

17. *Certificate on Standard Reference Material 710 A: Soda–Lime–Silica Glass*, Washington: Nat. Inst. Stand. Technol., 1962.

18. Klyuev, V.P. and Chernousov, M.A., A Vibration-Proof Quartz Dilatometer, *Tezisy dokladov IV Vsesoyuznogo soveshchaniya "Metody i pribory dlya tochnykh dilatometricheskikh issledovanii materialov v shirokom diapazone temperatur"* (Abstracts of Papers, IV All-Union Conference "Methods and Instruments for Precision Dilatometric Investigations of Materials over a Wide Range of Temperatures), Leningrad: VNIIM, 1987, pp. 31–32.

19. Mazurin, O.V., *Steklovanie* (Glass Transition), Leningrad: Nauka, 1986.

20. Priven', A.I. and Startsev, Yu.K., Calculation of Constants for the Relaxation Model of Glass Transition, *Fiz. Khim. Stekla*, 1993, vol. 19, no. 2, pp. 316–328 [*Glass Phys. Chem.* (Engl. transl.), 1993, vol. 19, no. 2, pp. 157–163].

21. Startsev, Yu.K., Safutina, T.V., and Tarakanov, S.V., Structural Relaxation of Density (as Length) and Electrical Conductivity of Some Silicate Glasses within of Their Glass Transition Regions: I. Alkali Silicate Glasses, in *Fundamentals of Glass Science and Technology*, Vaxjo, 1997, pp. 691–697.

22. Angell, C.A., Scamehorn, S.A., List, D.J., and Kieffer, J., Glassforming Liquid Oxide at the Fragile Limit of the Viscosity–Temperature Relationship, *Proceedings of the XV International Congress on Glass*, Leningrad, 1989, vol. 1a, pp. 204–209.

23. Wong, J. and Angell, C.A., The Viscous Liquid and Glassy State: General Aspects, in *Glass Structure by Spectroscopy*, New York: Marcel Dekker, 1976, pp. 1–52.

24. Angell, C.A., Relaxation in Liquids, Polymers, and Plastic Crystals—Strong/Fragile Patterns and Problems, *J. Non-Cryst. Solids*, 1991, vols. 131–133, pp. 13–31.

25. Chryssikos, G.D., Duffy, J.M., Huthinson, J.M., Ingram, M.D., Kamitsos, E.I., and Pappin, A.J., Lithium Borate Glasses: A Quantitative Study of Strength and Fragility, *J. Non-Cryst. Solids*, 1994, vols. 172–174, pp. 378–383.

26. Jewell, J.M., Shaw, C.M., and Shelby, J.E., Effects of Water Content on Aluminosilicate Glasses and the Relation to Strong/Fragile Liquid Theory, *J. Non-Cryst. Solids*, 1993, vol. 152, no. 1, pp. 32–41.

27. Nemilov, S.V., Viscosity of Borate Glass-Forming Melts: Specific Features of the BO_4 Tetrahedron as a Kinetic Unit, *Fiz. Khim. Stekla*, 1997, vol. 23, no. 1, pp. 3–42 [*Glass Phys. Chem.* (Engl. transl.), 1997, vol. 23, no. 1, pp. 1–26].

28. Nemilov, S.V., The Viscosity and Structure of Glass, *Trudy IV Vsesoyuznogo soveshchaniya po stekloobraznomu sostoyaniyu* (Proceedings of the IV All-Union Conference on the Vitreous State), Moscow: Akad. Nauk SSSR, 1965, pp. 64–68.

29. Tatsumisago, M., Halfpap, B.L., Green, J.L., Lindsey, S.M., and Angell, C.A., Fragility of Ge–As–Se Glass Forming Liquids in Relation to Rigidity, Percolation, and the Kauzmann Paradox, *Phys. Rev. Lett.*, 1990, vol. 64, no. 13, pp. 1549–1552.

30. Bohmer, R. and Angell, C.A., Correlations of the Non-exponentiality and State Dependence of the Mechanical Relaxations with Bond Connectivity in Ge–As–Se Supercooled Liquids, *Phys. Rev. B: Condens. Matter*, 1992, vol. 45, no. 17, pp. 10091–10094.

31. Bray, P.J., NMR and NQR Studies of Borates and Borides, *Proceedings of the 2nd International Conference on Borate Glasses, Crystals and Melts*, Oxford (UK), 1997, pp. 1–20.

32. Shelby, J.E., Thermal Expansion of Alkali Borate Glasses, *J. Am. Ceram. Soc.*, 1983, vol. 66, no. 3, pp. 225–228.

33. Griscom, D.L., Borate Glass Structure, in *Borate Glass: Structure, Properties and Application*, Pye, L.D., Frechette, V.D., and Kreidl, N.J., Eds., New York: Plenum, 1978, pp. 11–149.

34. Krogh-Moe, J., Structural Interpretation of Melting Point Depression in the Sodium Borate System, *Phys. Chem. Glasses*, 1962, vol. 3, no. 4, pp. 101–110.

35. Lomovskoi, V.A. and Bartenev, G.M., High-Temperature Relaxation Spectra of Borate Glasses, *Fiz. Khim. Stekla*, 1993, vol. 19, no. 4, pp. 601–610 [*Glass Phys. Chem.* (Engl. transl.), 1993, vol. 19, no. 4, pp. 312–316].