Specific Features of Changes in the Properties of One- and Two-Alkali Borate Glasses Containing Water: III. Thermal Expansion and the Structural and Mechanical Relaxation Parameters of Two-Alkali Borate Glasses

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Abstract—The thermal expansion and stress relaxation in mixed alkali borate glasses containing lithium, sodium, and potassium oxides with a total alkali oxide content of 15 mol % are measured on an inclined quartz dilatometer and a relaxometer. The experimental data obtained are used to determine the thermal expansion coefficients and the structural and mechanical relaxation parameters. No deviations from the additivity are found in the concentration dependences of the thermal expansion coefficient and the calculated parameters determining the width of the spectra of the structural and stress relaxation times. The IR absorption spectra of the studied glasses are recorded in the range of stretching vibrations of hydroxyl groups. Analysis of the IR spectra makes it possible to assume that the content of residual water in the structure of borate glasses affects the manifestation of the mixed alkali effect in the properties of these glasses.

INTRODUCTION

The relaxation dependences of the properties in the glass transition range can be quantitatively described in the case when the kinetic parameters of the structural and mechanical relaxation are determined for the glasses under investigation. However, no data on systematic investigations into the influence of composition on these parameters are available in the literature. It was of interest to elucidate how the replacement of one alkali oxide by another oxide in series of mixed alkali borate glasses affects the parameters of their structural and mechanical relaxation.

In our earlier work [1], we determined the temperature dependences of the viscosity in the range 10^{10}–10^{13} dPa s for three series of one- and two-alkali borate glasses. When one alkali oxide was replaced by another oxide, we observed negative deviations from an additive behavior, i.e., the mixed alkali effect, in the concentration dependences of the viscosity isotherms for the studied series of mixed alkali glasses.

The aim of the present work was to investigate the manifestation of the mixed alkali effect in the concentration dependences of the thermal expansion coefficient, the structural relaxation parameters determined from dilatometric curves, and the mechanical relaxation parameters for two-alkali borate glasses.

EXPERIMENTAL TECHNIQUE

Glass synthesis. In this work, we studied three series of mixed alkali borate glasses with the following pairs of alkali oxides: Li_2O–Na_2O, Na_2O–K_2O, and Li_2O–K_2O. The total alkali oxide content was equal to 15 mol %. The as-batched and as-analyzed compositions of the studied glasses and their designations were given in our previous work [2]. The glass designations indicate the type of alkali cations and their as-batched content (in mol %) in the glass composition. For example, the designation L3N12 corresponds to lithium sodium borate glass with the as-batched composition involving 3 mol % Li_2O and 12 mol % Na_2O.

Boric acid and carbonates of the corresponding alkali metals (chemically pure) were used as the initial components for the preparation of the batch. The glasses were synthesized in a platinum crucible with a volume of 200 ml in a Globar-heater electric furnace at temperatures of 1150–1200°C for 1.5–2 h.

The water content in the glasses under investigation was estimated by IR absorption spectroscopy. The technique was described in detail in [1]. The IR spectra were recorded on an SF-2-LSS spectrophotometer designed at the Laboratory of Glass Properties (Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences) and a commercial Shimadzu IR-470 (Japan) spectrophotometer.[1]

All the glasses studied were synthesized under identical conditions and likely involved approximately equal amounts of residual water. This assumption is confirmed by the estimates of water content in certain

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[1] We are grateful to V.Kh. Khalilov for performing the measurements on the IR-470 spectrophotometer.

Designations and some properties of the studied glasses: thermal expansion coefficients below (α_g) and above (α_l) the glass transition range, glass transition temperatures T_g, and parameters of structural (b_s and $\log K_s$) and mechanical (b_σ and $\log K_\sigma$) relaxation

Glass designation	Thermal expansion coefficient $\times 10^7$, K^{-1}		T_g, °C	Structural relaxation parameters		Mechanical relaxation parameters	
	α_g	α_l		b_s	$\log K_s$	b_σ	$\log K_\sigma$
L15B	81 ± 6	683 ± 14	414.3 ± 0.6	0.49 ± 0.03	10.23 ± 0.03	0.46 ± 0.05	11.39 ± 0.30
N15B	88 ± 5	788 ± 21	394.1 ± 2.2	0.57 ± 0.03	9.76 ± 0.10	$-$	$-$
K15B	117 ± 4	957 ± 28	371.9 ± 1.8	0.55 ± 0.02	10.04 ± 0.04	0.48 ± 0.06	11.35 ± 0.09
L12N3	106 ± 5	731 ± 18	388.5 ± 1.9	0.54 ± 0.03	10.45 ± 0.06	0.41 ± 0.02	10.96 ± 0.16
L9N6	87 ± 7	724 ± 26	388.2 ± 0.6	0.55 ± 0.03	9.96 ± 0.09	0.44 ± 0.02	11.15 ± 0.09
LN7.5	88 ± 5	706 ± 17	396.9 ± 1.3	0.58 ± 0.02	10.21 ± 0.02	0.47 ± 0.03	11.51 ± 0.12
L6N9	84 ± 3	743 ± 18	385.8 ± 1.9	0.58 ± 0.02	10.19 ± 0.02	0.49 ± 0.03	11.72 ± 0.11
L3N12	105 ± 2	767 ± 60	384.7 ± 4.7	0.53 ± 0.06	10.45 ± 0.02	0.49 ± 0.05	11.56 ± 0.11
N12K3	88 ± 4	839 ± 36	381.9 ± 1.6	0.54 ± 0.04	10.00 ± 0.09	0.47 ± 0.04	11.34 ± 0.08
N9K6	106 ± 5	805 ± 31	386.8 ± 1.1	0.55 ± 0.03	9.41 ± 0.08	0.48 ± 0.05	11.25 ± 0.08
NK7.5	114 ± 4	830 ± 26	376.1 ± 1.4	0.47 ± 0.01	9.73 ± 0.12	0.49 ± 0.02	11.55 ± 0.08
N6K9	109 ± 4	865 ± 54	371.9 ± 1.6	0.59 ± 0.04	9.82 ± 0.12	0.44 ± 0.02	11.25 ± 0.03
N3K12	116 ± 5	1017 ± 86	371.7 ± 1.1	0.55 ± 0.01	9.96 ± 0.03	0.51 ± 0.04	10.95 ± 0.16
L12K3	87 ± 7	763 ± 34	398.5 ± 0.5	0.50 ± 0.03	10.10 ± 0.02	0.47 ± 0.03	10.49 ± 0.15
L9K6	96 ± 8	835 ± 18	383.9 ± 0.5	0.50 ± 0.03	9.52 ± 0.07	0.46 ± 0.03	10.78 ± 0.13
LK7.5	98 ± 1	838 ± 18	383.4 ± 2.3	0.52 ± 0.01	10.25 ± 0.07	0.45 ± 0.03	11.46 ± 0.09
L6K9	103 ± 5	882 ± 24	376.9 ± 0.9	0.55 ± 0.03	9.51 ± 0.05	0.47 ± 0.15	10.76 ± 0.13
L3K12	113 ± 7	962 ± 15	365.4 ± 1.1	0.57 ± 0.05	9.54 ± 0.06	0.48 ± 0.15	10.76 ± 0.13

glasses from the IR spectroscopic data. Since the method of determining the water content in mixed alkali borate glasses has not been developed, the calculations were carried out using the technique proposed for one-alkali borate glasses [1]. The results of calculations showed that the water content in the glasses studied is equal to 0.30 ± 0.05 mol %.

Measurements of thermal expansion. The thermal expansion of the glasses was investigated on an inclined quartz dilatometer with a small measuring load [3] under thermocycling conditions. The rate of change in the temperature was equal to 3 K/min. The obtained dilatometric curves were used for determining the thermal expansion coefficients in ten-degree temperature ranges above the upper boundary of the glass transition range (α_l) and twenty-degree ranges below the lower boundary of the glass transition range (α_g) and also the glass transition temperatures T_g. The calculated data are listed in the table. The technique of measurements and data processing was described in more detail in [1].

Structural relaxation. The dilatometer design made it possible to perform measurements over a wide range of temperatures, including the glass transition range. By using this dilatometer, we measured the dilatometric hysteresis loops whose processing pro-

vided a way of calculating the relaxation parameters [1] of the Tool–Narayanaswamy model according to the ISC algorithm [4]. The constant b_s and the modulus K_s characterizing the structural relaxation process were determined with 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 calculated parameters b_s and K_s are presented in the table.

Mechanical relaxation. The mechanical relaxation was investigated on a relaxometer [5] whose operation is based on measuring the time dependence of the force under a constant deformation produced by a modified McLoughlin dynamometer [6]. Samples were prepared in the form of cylindrical springs coiled from fibers drawn from melts of the studied glasses directly in the course of glass making. The prepared glass springs [7] were not subjected to any additional treatment, which ruled out the possibility of reacting the samples with water vapors contained, for example, in the flame of a gas burner.

Numerous experiments (see, for example, [7–9]) demonstrated that mechanical relaxation processes in

glasses can be successfully described by the fractional exponential equation

$$\frac{\sigma(t)}{\sigma_0} = \exp\left[-\left(\frac{t}{\tau_\sigma}\right)^{b_\sigma}\right], \qquad (1)$$

where $\sigma(t)$ and σ_0 are the stresses in the sample at the instants of time t and $t = 0$, respectively; τ_σ is the most probable stress relaxation (Kohlrausch) time; and the constant b_σ $(0 < b_\sigma \leq 1)$ determines the width of the spectrum of the stress relaxation times τ_σ. The smaller the constant b_σ, the longer the time it takes for the relaxation process to be completed. At $b_\sigma = 1$, Eq. (1) transforms into a simple exponential equation. At present, in the literature on relaxation phenomena, Eq. (1) proposed by Kohlrausch [10] for representing the stress relaxation in quartz fibers of electrometers is referred to as the Kohlrausch–Williams–Watts equation (see, for example, [11]). This equation is very convenient from the viewpoint of experimenters (because it includes only two parameters!), even though it has defied theoretical treatment by virtue of an infinite discontinuity at the time $t = 0$. However, this equation is used to advantage not only for the description of the mechanical relaxation and not only in inorganic glasses.

De Bast and Gilard [12] showed that the ratio between the relaxation time τ_σ entering into Eq. (1) and the viscosity of the studied glass is constant and independent of temperature (because the temperature dependences of the relaxation time and the viscosity are very similar to each other), that is,

$$\frac{\eta}{\tau_\sigma} = K_\sigma, \qquad (2)$$

where K_σ is the constant numerically equal to such a viscosity of the glass at which the time τ_σ is equal to 1 s. The smaller the constant K_σ at a certain fixed viscosity, the lower the relaxation process rate. This circumstance permits one to represent the data obtained on the stress relaxation at different temperatures in the same plot in the coordinates $\sigma(t)/\sigma_0 - \log t$, which is termed the muster curve in the English-language literature [9].

Therefore, the investigation into the kinetics of stress relaxation amounts to determining the parameters K_σ and b_σ.

In our relaxometer, the system of experimental data collection consists of the following components: an IBM PC AT 286 computer, a CAMAC or unibus data converter, a small-displacement transducer on the basis of a mechanotron (a vacuum-tube twin diode with an elastic diaphragm) or an inductive transducer, a measuring instrument [a V7-28 digital voltmeter (for CAMAC) or a V7-34 digital voltmeter (for unibus)], thermoelectric transducers (reference and controlling thermocouples), a temperature controller of the PTR-105 type (AO Thermex), and a resistance furnace.

Analogous signals from the reference thermocouple and the small-displacement transducer arrive at the voltmeter and are digitized. The converter samples the corresponding channel through a multiplexer, converts the analogous signal into a binary decimal code, and transmits it to computer memory for primary processing.

The thermocouple thermopower and the signal from the displacement transducer are the recorded quantities. The temperature with due regard for the applied corrections and the displacement in terms of length are the output quantities.

The data obtained are corrected for systematic errors in measurements by a primary processing program. When operating with the relaxometer, one of these errors is the error of the thermopower measurement for a particular thermocouple. In order to allow for this error, the thermocouple in the operating position directly in the relaxometer furnace was preliminarily calibrated against the melting temperatures of pure metals followed by applying the corresponding correction to all the temperatures measured. As a consequence, the error of the temperature measurement was reduced to ± 0.5 K, variations in the temperature during isothermal treatments for one day did not exceed ± 0.5 K, and the error of the stress measurement at a small-displacement transducer sensitivity of 0.02 μm was as small as $\pm 0.5\%$. As a result of these errors, the errors of calculating $\log \tau_\sigma$ and b_σ are equal to ± 0.1 and ± 0.05, respectively.

The investigation of the stress relaxation can be essentially simplified using a preliminary stabilization of the samples, i.e., such heat treatment which results in almost completion of the structural relaxation. Indeed, the study of the mechanical relaxation against the background of the structural relaxation involves additional problems [13]. With the aim of overcoming these problems, experimenters should preliminarily determine the parameters characterizing the kinetics of the structural relaxation in the studied glass.

The mechanical relaxation in the stabilized samples can be studied by performing the following three additional operations: (1) the preliminary measurement of the temperature dependence of the viscosity, (2) the determination of the structural stabilization time at a chosen experimental temperature (for example, according to the procedure recommended in [14]), and (3) the stabilization of the sample at the chosen temperature.

In a number of works (see, for example, [5, 13]), analysis of the experimental data with the use of Eq. (1) was reduced to the linearization of this equation by taking the double logarithm and the determination of the sought parameters τ_σ and b_σ by the least-squares technique.

It follows from Eq. (1) and the results obtained by Kurkjian [8] that, when processing the experimental data on stress relaxation, the stress σ_0 should be deter-
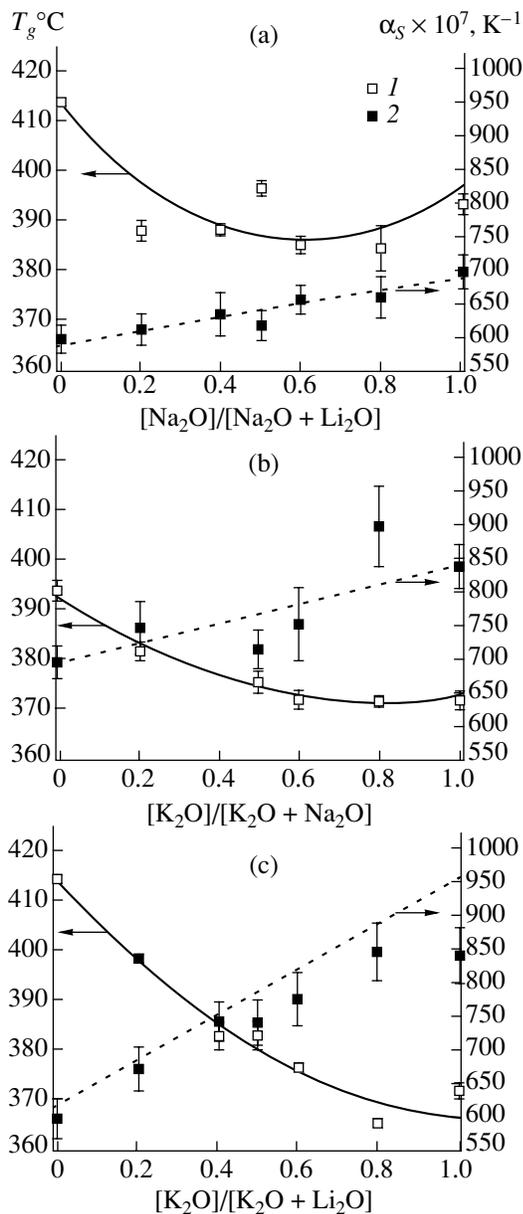
Fig. 1. Concentration dependences of (*1*) the glass transition temperature T_g and (*2*) the structural thermal expansion coefficient α_s for (a) lithium sodium, (b) sodium potassium, and (c) lithium potassium glasses.

mined as precisely as possible; i.e., it is necessary to account for the noninstantaneous character of deformation. The influence of this factor resides in the fact that the first reliable measurement of relaxing stresses can be carried out only beginning with a certain instant of time when the relaxation can proceed in part, and, hence, processes described by shorter relaxation times will be completed. For this reason, the zeroth instant of time should be chosen between the last measurement before the starting of deformation and the first measurement after its completion. The algorithm used in our work for determining the parameters τ_σ and b_σ

included the possibility of choosing the initial instant of time and the stress at this instant by a researcher.[2]

RESULTS

The concentration dependences of the glass transition temperature calculated from the dilatometric curves obtained upon cooling of the glasses studied are plotted in Fig. 1. This figure also shows the concentration dependences of the structural thermal expansion coefficient α_s, which is equal to the difference between the thermal expansion coefficients determined at temperatures above and below the glass transition range ($\alpha_s = \alpha_l - \alpha_g$). The lines in Fig. 1 are represented by the polynomials of best approximation to the experimental data.

The glass transition temperatures of glasses in all three series are characterized by the negative deviation from the additivity. This agrees with the behavior observed for the concentration dependences of the viscosity.

The replacement of smaller sized cations by larger sized cations leads to an increase in the structural thermal expansion coefficient. Note that this increase is largest for lithium potassium series and reflects the tendency to a change in the amount of fourfold-coordinated boron in the glass structure [15]. No deviations from the additivity are found in the concentration dependences of the structural thermal expansion coefficient.

Figure 2 displays the concentration dependences of the kinetic parameters of the structural (b_s) and mechanical (b_σ) relaxations and the dependences of the Kohlrausch relaxation times τ_s and τ_σ. These times were calculated by the relationship $K_j = \eta / \tau_j$, where K_j are the moduli derived by processing the data on the structural ($j \equiv s$) and mechanical ($j \equiv \sigma$) relaxations. The relaxation times for lithium sodium, sodium potassium, and lithium potassium glasses are given at 420, 400, and 410°C, respectively. The solid lines in Fig. 2 are represented by the polynomials of best approximation to the experimental data on the parameters τ_j and b_j.

As can be seen from Fig. 2, the behavior of the concentration dependences of the relaxation times for glasses in all series reflects the behavior of the concentration dependences of the viscosity. It should be noted that the structural relaxation times are somewhat longer than the mechanical relaxation times. This is in agreement with a similar difference previously found for commercial multicomponent silicate glasses [5, 7, 9, 11].

As one alkali oxide is replaced by another alkali oxide, the parameters b_s and b_σ have a certain tendency to increase; however, this increase is within the limits of

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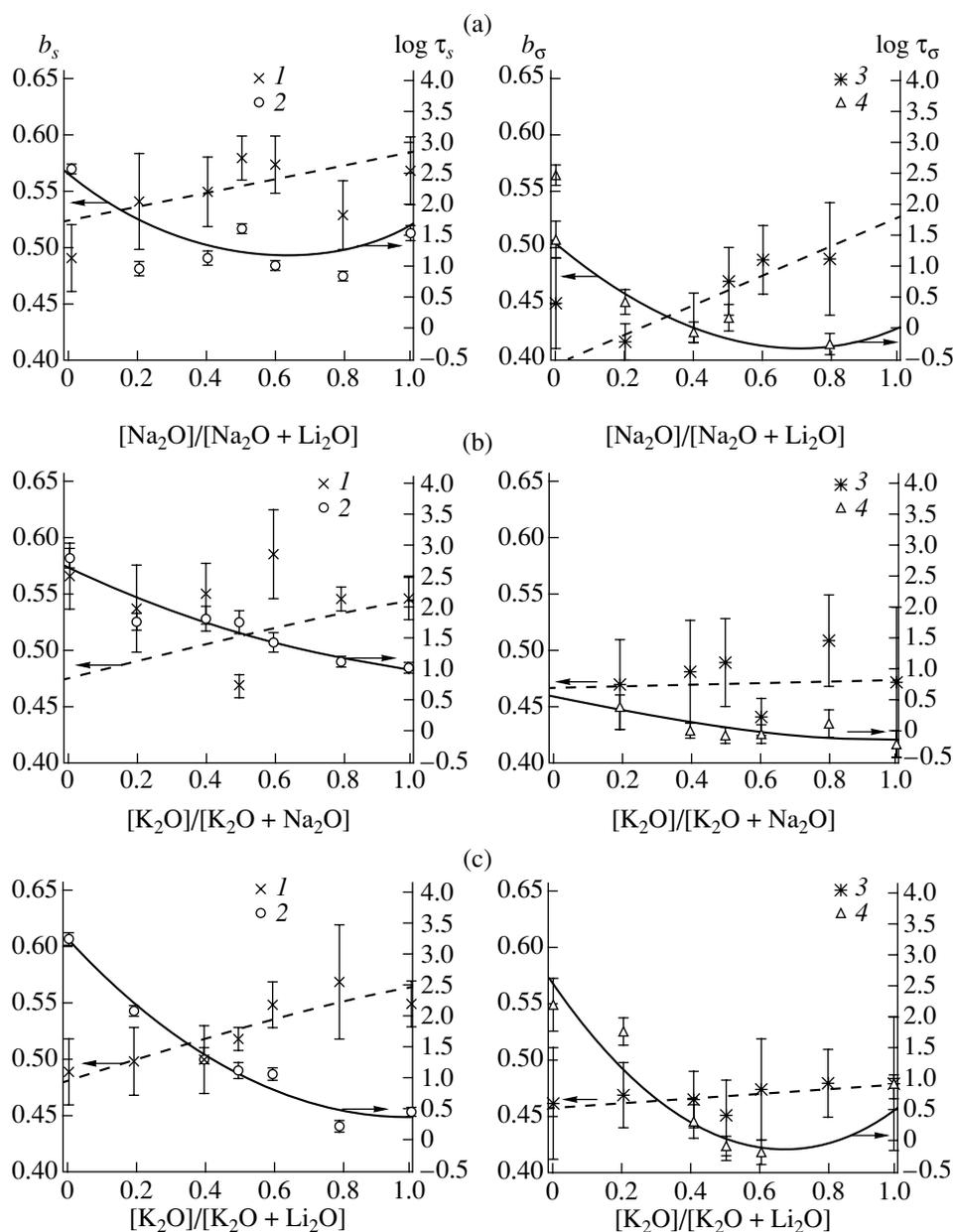[2] The computer code for this algorithm was developed by A.I. Priven (AO Thermex, St. Petersburg).

Fig. 2. Concentration dependences of the kinetic parameters of the structural (b_s and τ_s) and mechanical (b_σ and τ_σ) relaxations for (a) lithium sodium, (b) sodium potassium, and (c) lithium potassium glasses: (1) b_s, (2) τ_s, (3) b_σ, and (4) τ_σ.

their computational error. The dependences of the parameters b_s and b_σ do not deviate from the additive behavior.

DISCUSSION

Zhong and Bray [16] studied mixed alkali borate glasses at a total alkali oxide content of 40 mol % and drew the inference that the manifestation of the mixed alkali effect in the properties of these glasses is associated with a decrease in the number of boron atoms in the fourfold-coordinated state as compared

to their number calculated from the additivity principle (see [2]).

Our investigation of the thermal expansion and the structural and mechanical relaxations in alkali borate glasses with a total alkali oxide content of 15 mol % revealed that the mixed alkali effect manifesting itself in the deviation from the additivity is not observed in the concentration dependences of these properties. The found linear dependences of the properties allow us to assume that the content of fourfold-coordinated boron obeys the additivity principle upon replacement of one
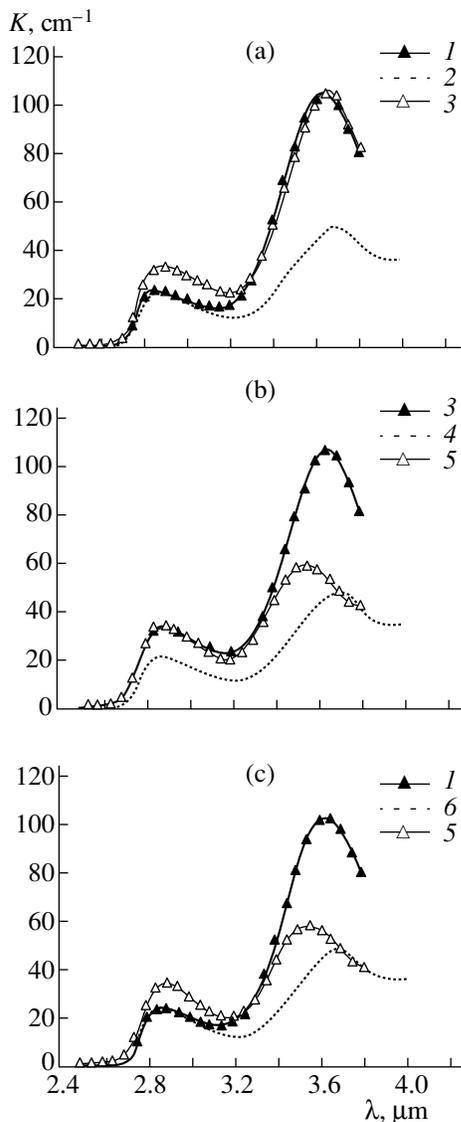
Fig. 3. Comparison of the IR absorption spectra of (a) lithium sodium, (b) sodium potassium, and (c) lithium potassium glasses: (*1*) L15B, (*2*) LN7.5, (*3*) N15B, (*4*) NK7.5, (*5*) K15B, and (*6*) LK7.5 (see table).

alkali oxide by another alkali oxide in the glasses of the studied series.

On the other hand, in our earlier work [2], we showed that the concentration dependences of the viscosity for the same glasses are characterized by the mixed alkali affect manifesting itself in negative deviations from the additivity.

The IR absorption spectra $K(\lambda)$ (where K is the absorption coefficient in terms of cm^{-1} and λ is the wavelength in terms of μm) of mixed alkali borate glasses with the same contents of alkali oxides for three studied series and the spectra of the corresponding binary alkali borate glasses are compared in Fig. 3. It is seen from this figure that, for binary and mixed alkali

glasses, the intensities of the absorption bands with a maximum at 2.8–2.9 μm attributed to free hydroxyl groups are close to each other, whereas the absorption bands with a maximum at 3.5 μm have different intensities. According to the data obtained in different works [17, 18], the latter absorption band is assigned to the so-called bound hydroxyl groups linked by hydrogen bonds to the nonbridging oxygen atoms that are formed upon introduction of alkali oxides into the glass structure. As can be seen from Fig. 3, the intensity of the absorption band associated with the bound hydroxyl groups for mixed alkali glasses of all the series studied is lower than that for the corresponding binary glasses. This can indicate that a smaller number of hydrogen bonds are formed in the structure of alkali borate glasses containing two alkali oxides.

The replacement of smaller sized alkali cations by larger sized cations results in a decrease in the number of hydrogen bonds and a linear decrease in the number of fourfold-coordinated boron atoms in mixed alkali glasses. This favors the viscous flow and leads to a negative deviation from the additivity in the concentration dependences of the viscosity without deviations from the additivity in the concentration dependences of the thermal expansion coefficient and the relaxation parameters.

Moreover, in our previous work [2], we noted that no mixed alkali effect is observed for anhydrous glasses. This fact can also be explained by the possible influence of two alkali oxides in the glass composition on the number of hydrogen bonds.

CONCLUSIONS

The results of the above investigation into the concentration dependences of the thermal expansion coefficient and the structural and mechanical relaxation parameters for mixed alkali borate glasses with a total alkali oxide content of 15 mol % can be summarized as follows.

(1) No deviation from the additivity is found for the structural thermal expansion coefficient and the structural and mechanical relaxation parameters upon replacement of one alkali oxide by another alkali oxide in the glass composition.

(2) The mixed alkali effect in the concentration dependences of the glass transition temperature and the structural and mechanical relaxation times manifests itself in negative deviations from the additivity. This agrees with the behavior observed for the concentration dependences of the viscosity.

(3) The replacement of one alkali oxide by another oxide leads to a change in the parameter b_s characterizing the structural relaxation and does not noticeably affect the parameter b_σ characterizing the stress relaxation.

(4) The content of residual structural water in mixed alkali borate glasses likely affects the manifestation of the mixed alkali effect in the properties of these glasses.

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