

IR Spectroscopic Study of Water in the Structure of Binary Alkali Borate Glasses

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Abstract—The influence of the synthesis conditions and composition of binary sodium and potassium borate glasses on the spectral absorption in the wavelength range 2.5–4 μm due to the presence of structurally bound water is investigated. It is demonstrated that water in the structure of alkali borate glasses, as in the structure of alkali silicate glasses, can exist in the form of so-called free and bound hydroxyl groups that are incorporated into the glass network in different ways. The ratio between the numbers of these forms of structural water in borate glasses is determined by the synthesis conditions and composition of the glass. The synthesis under different conditions makes it possible to prepare glasses not only with different water contents but also with different ratios between the numbers of free and bound hydroxyl groups.

INTRODUCTION

As is known, water is one of the most widespread impurities that enters into the composition of glasses, affect a number of their structure-sensitive properties (see, for example, [1–5]), and are responsible for the substantial absorption in the near-IR spectral range [6–8]. The effect of structurally bound water on the glass properties is determined by the composition and structure of initial glasses. Since water in the glass structure can be in different forms, predominantly in the form of hydroxyl groups differently incorporated into the glass-forming network and also in the molecular form, it can be assumed that a change in the ratio between forms of structural water can also affect the glass properties.

In our earlier works [9–12], the influence of water in the structure of alkali borate glasses on their physico-chemical properties was studied using IR absorption spectroscopy in the range of stretching vibrations of hydroxyl groups. However, most attention in consideration of binary alkali borate glasses was concentrated on the problem associated with the quantitative determination of the water content in glasses. The effect of the glass composition and synthesis conditions on the forms of water in the structure of these glasses was not analyzed. On the other hand, investigations of two-alkali borate glasses [11, 12] revealed that there is a correlation between the content of water in the form of so-called bound hydroxyl groups with an absorption maximum at 3.5–3.7 μm and the manifestation of the mixed alkali effect in the properties of these glasses. This finding is important for understanding the mechanism of manifestation of the mixed alkali effect in the properties of borate glasses and illustrates the relation of the glass composition to the ratio between two forms of hydroxyl groups in the glass structure. The revealed

correlation is of special interest because a number of authors [13, 14] believe that the presence of bound hydroxyl groups is not characteristic of the structure of alkali borate glasses.

In the present work, we investigated how the synthesis conditions and the glass composition affect the spectral absorption in the range 2.5–4 μm due to the presence of structurally bound water in binary sodium and potassium borate glasses.

SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

In this work, we studied glasses of compositions $5.5R_2O-94.5B_2O_3$, $15R_2O-85B_2O_3$, and $25R_2O-75B_2O_3$, where $R = \text{Na}$ and K .¹ Boric acid and carbonates of the corresponding alkali metals (reagent grade) were used as initial components. The glasses were synthesized in a platinum crucible with a volume of 200 ml in a Global-heater electric furnace.

The glasses of each composition were prepared several times under different conditions by varying the temperature and duration of the synthesis. The synthesis conditions for the studied glasses are presented in Table 1. The glasses of different compositions were melted at temperatures of 950, 1200, and 1300°C for 1–4 h. For convenience of further discussion, identical synthesis conditions for glasses of different compositions in Table 1 are designated by identical letters (from A to F).

The chemical analysis of the glasses (performed at the Laboratory of Analytical Chemistry, Greben-

¹ The $5.5K_2O-94.5B_2O_3$ glass was not investigated because of its high hygroscopicity.

Table 1. Compositions of glasses and conditions for their synthesis

Synthesis conditions	Glass composition (mol %) (as-batched/as-analyzed)			Synthesis temperature, °C	Synthesis time, h
	B ₂ O ₃	Na ₂ O	K ₂ O		
<i>C</i>	94.5/94.4	5.5/5.6	–	1200	1
<i>D</i>	94.5/94.7	5.5/5.3	–	1200	2.5
<i>E</i>	94.5/94.7	5.5/5.3	–	1200	4
<i>F</i>	94.5/94.9	5.5/5.1	–	1300	1*
<i>A</i>	85.0/85.7	15.0/14.3	–	950	2
<i>B</i>	85.0/86.1	15.0/13.9	–	950	3
<i>C</i>	85.0/84.5	15.0/15.5	–	1200	1
<i>D</i>	85.0/84.8	15.0/15.2	–	1200	2.5
<i>E</i>	85.0/85.0	15.0/15.0	–	1200	4
<i>F</i>	85.0/85.5	15.0/14.5	–	1300	1*
<i>C</i>	85.0/85.9	–	15.0/14.1	1200	1
<i>D</i>	85.0/85.9	–	15.0/14.1	1200	2.5
<i>E</i>	85.0/85.7	–	15.0/14.3	1200	4
<i>A</i>	75.0/76.0	25.0/24.0	–	950	2
<i>B</i>	75.0/76.0	25.0/24.0	–	950	3
<i>C</i>	75.0/75.9	25.0/24.1	–	1200	1
<i>D</i>	75.0/75.6	25.0/24.4	–	1200	2.5
<i>E</i>	75.0/75.8	25.0/24.2	–	1200	4
<i>F</i>	75.0/76.0	25.0/24.0	–	1300	1*
<i>A</i>	75.0/76.0	–	25.0/24.0	950	2
<i>B</i>	75.0/76.0	–	25.0/24.0	950	3
<i>C</i>	75.0/76.0	–	25.0/24.0	1200	1
<i>D</i>	75.0/76.1	–	25.0/23.9	1200	2.5
<i>E</i>	75.0/76.1	–	25.0/23.9	1200	4
<i>F</i>	75.0/76.0	–	25.0/24.0	1300	1*

* After heat treatment at a temperature of 950°C for 3 h.

shchikov Institute of Silicate Chemistry, Russian Academy of Sciences) demonstrated that variations in the composition of glasses synthesized under different conditions are insignificant and do not exceed 1% (Table 1).

The IR absorption spectra of the glasses were recorded at room temperature with the use of samples in the form of 0.1- to 0.2-mm-thick plates polished in kerosene. The experimental technique and preliminary data processing were described in more detail in [9].

RESULTS AND DISCUSSION

Figures 1–5 depict the absorption spectra $K(\lambda)$ of the studied glasses, where K is the absorption coefficient (cm^{-1}) and λ is the wavelength (μm). The absorption coefficients were calculated taking into account the losses by reflection from the sample surface [9].

The wavelength range under investigation contains two bands associated with the stretching vibrations of hydroxyl groups in the glass structure with absorption maxima at 2.8–2.9 and 3.5–3.7 μm . According to the experimental data for a number of oxide glasses, such as alkali silicate glasses and borate glasses containing alkaline-earth metal oxides, Scholze and Franz [6, 13, 15] attributed the absorption band at 2.8–2.9 μm to nonassociated, so-called free (not linked by hydrogen bonds), hydroxyl groups and assigned the band at 3.39–3.63 μm to so-called bound hydroxyl groups linked by hydrogen bonds to nonbridging oxygen atoms in the glass structure. The structures of pure silica glass and vitreous boron oxide involve only free OH groups. The addition of an alkali metal oxide to silicate or borate glasses leads to the appearance of nonbridging oxygen atoms. These atoms and hydroxyl groups can form hydrogen bridging bonds. As a result, the second absorption band at a larger wavelength arises in the IR spectra.

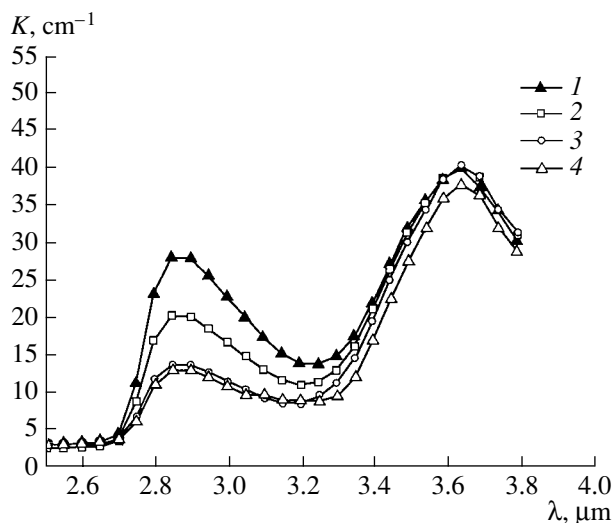


Fig. 1. IR absorption spectra of the alkali borate glasses containing 5.5 mol % Na₂O. Synthesis conditions (see Table 1): (1) C, (2) D, (3) E, and (4) F.

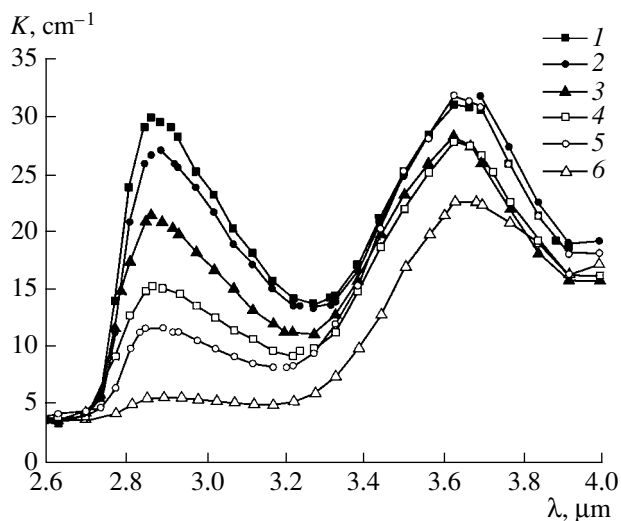


Fig. 2. IR absorption spectra of the alkali borate glasses containing 15 mol % Na₂O. Synthesis conditions (see Table 1): (1) A, (2) B, (3) C, (4) D, (5) E, and (6) F.

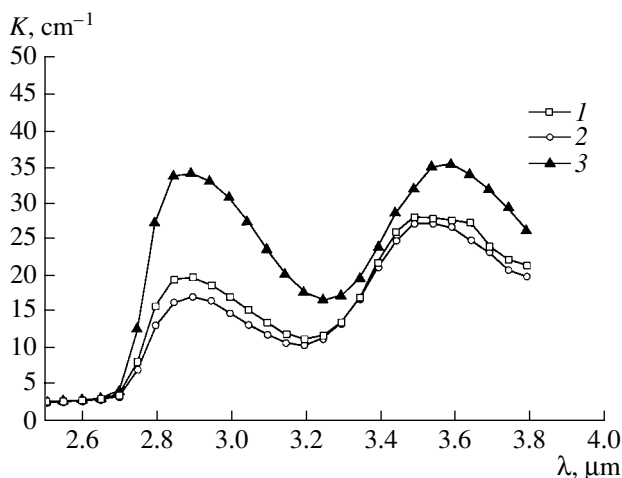


Fig. 3. IR absorption spectra of the alkali borate glasses containing 15 mol % K₂O. Synthesis conditions (see Table 1): (1) C, (2) D, and (3) D.

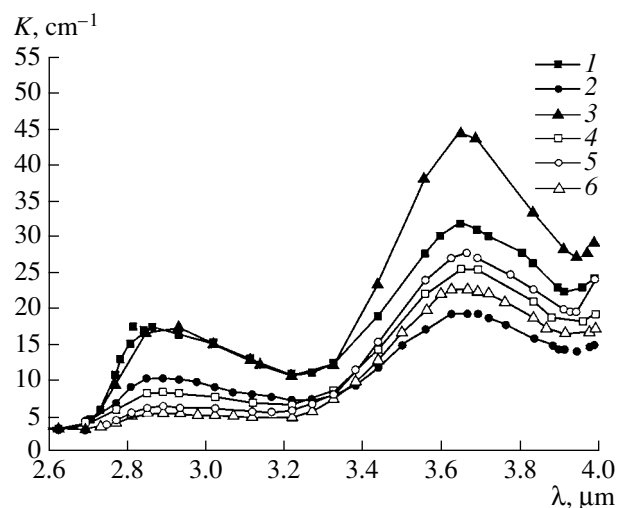


Fig. 4. IR absorption spectra of the alkali borate glasses containing 25 mol % Na₂O. Synthesis conditions (see Table 1): (1) A, (2) B, (3) C, (4) D, (5) E, and (6) F.

It should be noted that different researchers revealed other absorption bands associated with water. In particular, the authors of [6, 13, 15] assigned the absorption at 4.25 μm to vibrations of hydroxyl groups linked by very strong hydrogen bonds. Adams [8] rather convincingly justified the assumption that the absorption in this spectral range is attributed to CO₂ molecules of atmospheric air rather than to water in the glass structure.

Ernsberger [16] found a band at a wavelength of 6.1 μm in the spectra of glasses with a very high water content. At present, this band is attributed to dissolved molecular water.

Furthermore, there are alternative interpretations of the absorption spectra of glasses due to the presence of water. According to Efimov [17], the IR absorption spectra of inorganic glasses contain a considerably larger number of absorption bands associated with water in the glass structure. The total number of these bands in the wavelength range from 2.7 to 6.5 μm can be as large as 15. Among these bands, at least four bands correspond to water in the molecular form.

Tomozawa [18] showed that, at a water content up to 1 wt % in silicate glasses, water is predominantly represented by hydroxyl groups in the glass structure. As

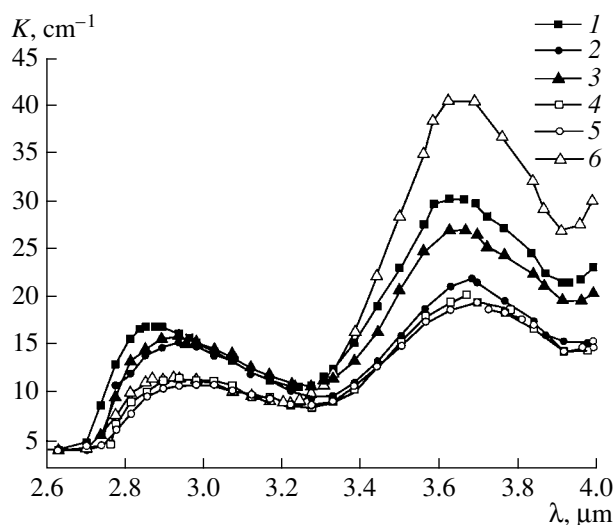


Fig. 5. IR absorption spectra of the alkali borate glasses containing 25 mol % K_2O . Synthesis conditions (see Table 1): (1) A, (2) B, (3) C, (4) D, (5) E, and (6) F.

the water content in the glass increases, the molecular form becomes dominant.

The water contents in the glasses studied in the present work were estimated from the IR spectroscopic data with the use of the techniques proposed by Franz [13] and Eagan and Bergeron [19]. The results of the calculations for a number of glasses were presented in [9]. The calculated data demonstrate that the water content in the glasses prepared without using special procedures for saturating the glasses with water does not exceed 1 wt %. Therefore, we can believe with a high probability that water in the studied glasses is predominantly in the form of hydroxyl groups and that the IR spectra in the range under consideration well characterize water in the glass structure. Hereafter, for convenience, the absorption bands at 2.8–2.9 and 3.5 μm will be referred to as the first and second bands, respectively.

It can be seen from Figs. 1–5 that an increase in the temperature and time of synthesis leads to a decrease in the intensity of the first band for all the glasses. Such a change in the intensity is quite reasonable, because an increase in the synthesis time favors a more complete removal of water formed in the melt due to the decomposition of the batch materials. This result is in agreement with the data obtained by Stolyar *et al.* [4], who investigated the influence of the synthesis time on the viscosity of binary sodium borate glasses, all other factors being the same. In [4], it was revealed that an increase in the synthesis time to 3 h at 1200°C results in an increase in the viscosity and, hence, in a decrease in the water content in glasses. Similar data on the effect of the synthesis conditions and residual water on the viscosity of alkali borate glasses were obtained in [9].

Therefore, a decrease in the intensity of the first absorption band for the glasses of one series with an increase in the time and temperature of synthesis indicates a decrease in the content of water in the form of free hydroxyl groups in the glass structure. A variation in the synthesis conditions of the glasses also leads to a change in the intensity of the second band. However, this change does not necessarily correlate with the change in the intensity of the first absorption band. Actually, in some cases, an increase in the intensity of the first band is accompanied by a decrease in the intensity of the second band. The above tendency is clearly seen in Figs. 2 (synthesis conditions D, F) and 4 (synthesis conditions B, F). This tendency is especially pronounced in Fig. 5, which shows the IR absorption spectra of the glasses containing 25 mol % K_2O . The spectrum of this glass prepared at 1300°C (synthesis conditions F) is characterized by the lowest intensity of the first band (as is the case with the glasses synthesized under conditions D and E) among the spectra of other glasses that have the same composition but are synthesized under different conditions. This fact seems to suggest a minimum water content in the sample under consideration. However, the intensity of the second band for this sample is highest compared to those for the other glasses of the series. Therefore, the inference that the water content in this sample is lowest cannot be made unambiguously.

The calculated intensity ratios $K_{2.9}/K_{3.7}$ of the absorption bands for the studied alkali borate glasses are listed in Table 2.

As can be seen from Table 2, there is a systematic dependence of the intensity ratios $K_{2.9}/K_{3.7}$ of the absorption bands on the composition and the synthesis conditions.

An increase in the temperature or the time of synthesis (compare synthesis conditions A and B at a temperature of 950° or conditions C, D, and F at a temperature of 1200° in Table 1) leads to a decrease in the intensity of the first band and an increase in the intensity of the second band. The same tendency is observed with an increase in the alkali metal oxide content in the glass composition: the intensity of the first band in the spectra decreases and the intensity of the second band increases for the glasses synthesized under identical conditions. This behavior agrees with the results obtained by Scholze [6] and Leko *et al.* [7], who investigated the effect of composition on the intensity of the absorption band associated with water in the IR spectra of alkali silicate glasses in which the existence of bound hydroxyl groups is undeniable.

The probability of forming hydrogen bonds in the structure increases with an increase in the number of nonbridging oxygen atoms. The number of nonbridging oxygen atoms increases with an increase in the content of modifier ions in the glass structure, i.e., the content of alkali metal cations. This fact explains the increase in the intensity of the 3.7- μm absorption band

Table 2. Ratios $K_{2.9}/K_{3.7}$ for alkali borate glasses

Synthesis designation (according to Table 1)	$K_{2.9}/K_{3.7}$				
	5.5 mol % Na ₂ O	15 mol % Na ₂ O	15 mol % K ₂ O	25 mol % Na ₂ O	25 mol % K ₂ O
A	–	0.9	–	0.6	0.6
B	–	0.8	–	0.6	0.7
C	0.7	0.8	0.9	0.4	0.6
D	0.5	0.6	0.7	0.3	0.6
E	0.4	0.4	0.6	0.2	0.5
F	0.3	0.2	–	0.2	0.3

attributed to bound hydroxyl groups in alkali silicate glasses [7] and the alkali borate glasses studied in the present work. For the sodium borate glasses, the ratio $K_{2.9}/K_{3.7}$ either passes through a weak maximum at 15 mol % with an increase in the alkali oxide content from 5.5 to 25 mol % (Table 2, synthesis conditions C, E) or insignificantly varies with an increase in the Na₂O content from 5.5 to 15 mol %. According to [7], the ratio $K_{2.9}/K_{3.7}$ for alkali silicate glasses rather considerably varies as a result of an increase in the contribution of the band at 3.7 μm with an increase in the alkali oxide content in the glass. In particular, as the alkali oxide content increases from 4 to 25 mol %, the ratio $K_{2.9}/K_{3.7}$ decreases from 9.1 to 1.2 for lithium silicate glasses, from 1.9 to 0.3 for sodium silicate glasses, and from 0.4 to 0.1 for potassium silicate glasses. A somewhat different behavior of this ratio for alkali borate glasses can be explained by their specific structural features. In borate glasses, unlike silicate glasses, the introduction of alkali oxides into the network does not result in a drastic increase in the number of nonbridging oxygen atoms in the glass structure, because part of the boron atoms transform from the threefold-coordinated state to the fourfold-coordinated state [20–23]. Oxygen introduced into the glass with the alkali metal oxide is used for the transformation of a number of boron–oxygen triangles into boron–oxygen tetrahedra. This leads to a increase in the network connectivity and is not attended by the appearance of nonbridging oxygen atoms. According to data of different authors (see, for example, [20–23]), this process only partially occurs beginning with a content of 25–30 mol % R₂O. Some of the oxygen atoms introduced with the alkali metal oxide transform bridging oxygen atoms into nonbridging oxygen atoms. In this case, boron atoms remain in the threefold coordination with respect to oxygen. However, at lower oxide contents, a number of alkali metal atoms most likely also fulfill a destructive function, i.e., lead to the breaking of the network and the appearance of nonbridging oxygen atoms [24]. These structural features of alkali borate glasses are responsible for the observed dependence of the ratio $K_{2.9}/K_{3.7}$ on the alkali oxide content. As the Na₂O content increases in the range from 5.5 to 15 mol % in which the number

of nonbridging oxygen atoms is small, the contribution from the intensity of the band at 2.9 μm to the ratio $K_{2.9}/K_{3.7}$ somewhat increases as compared to the intensity of the absorption band with a maximum at 3.7 μm. The content of water in the form of free hydroxyl groups increases in the glass structure. A further increase in the sodium oxide content to 25 mol % and an increase in the number of nonbridging oxygen atoms in the structure of borate glasses are accompanied by an increase in the intensity of the second band.

The probability of forming hydrogen bonds should also increase with an increase in the negative charge at nonbridging oxygen atoms due to the change in the field strength of alkali cations. The replacement of sodium oxide in the glass by potassium oxide leads to an increase in the negative charge at nonbridging oxygen atoms and, hence, to an increase in the fraction of hydroxyl groups linked by hydrogen bonds. Such a tendency is observed for the sodium and potassium glasses under investigation (Figs. 2–5, Table 2), even though it is not so pronounced as for alkali silicate glasses [7]. This can also be associated with the aforementioned structural features of borate glasses, namely, with the smaller number of nonbridging oxygen atoms in the structure of borate glasses as compared to that in the structure of silicate glasses at identical alkali oxide contents.

Therefore, the results obtained demonstrate that water in the structure of alkali borate glasses, as in the structure of alkali silicate glasses, can be in the form of free and bound hydroxyl groups.

As was noted above, Franz [13] and Shelby [14] believed that, unlike silicate glasses, bound hydroxyl groups are not characteristic of alkali borate glasses. This conclusion was based on the fact that no changes in the intensity of the band with a maximum at 3.5 μm were observed in the IR spectra of the borate glasses studied in [13, 14] with different water contents, whereas the intensity of the band with a maximum at 2.9 μm depended on the water content. According to [14], the band at 3.5 μm in the IR spectrum of alkali borate glasses is attributed to the boric acid on the glass surface, i.e., to water sorbed on the glass surface. However, in this case, the intensity of the band at 3.5 μm

should be maximum for glasses with the lowest alkali oxide content because of their lowest chemical durability [25]. We did not measure the IR spectra of the glasses containing 5.5 mol % K_2O due to their very high hygroscopicity. Water was sorbed on the surface of these glasses when they were held in air even for a short time. According to [25] and our observations, glasses with higher alkali oxide contents have a higher chemical durability. It can be seen from Figs. 1–5 that an increase in the alkali oxide content in the glass composition and, correspondingly, an increase in the chemical durability of the glasses do not result in a decrease in the intensity of the second absorption band in the IR range under consideration, as should be expected from the assumption made in [14]. Moreover, Adams [8] showed that water sorbed on the surface of borate glasses is characterized by the absorption band with a maximum at 3.09 μm rather than at 3.7 μm .

The discrepancy between our results and the data obtained by Franz [13], who assumed that the structure of alkali borate glasses does not contain bound hydroxyl groups, can be explained by the differences between the synthesis conditions of glasses. Franz [13] investigated the water solubility in borate glasses. For this purpose, melts of glasses synthesized under identical conditions were saturated with water vapor. The IR spectra of the prepared glasses are characterized by a change in the intensity of the absorption band with a maximum at 2.9 μm , i.e., by a change in the number of free hydroxyl groups, whereas the intensity of the band with a maximum at 3.5 μm remains unchanged.

In the present work, we studied the glasses prepared at different temperatures and times of synthesis. Note that the largest changes in the intensity of the second band for series of glasses with the same chemical composition are observed for the largest differences between the synthesis temperatures (Figs. 1–5). For the glasses prepared at identical temperatures (1200, 950°C) but for different times (synthesis conditions *C*, *D*, *E* and *A*, *B*), the intensities of the second band in the IR spectra are relatively close to each other. For example, it can be seen from Fig. 1 that, for the glasses (containing 5.5 mol % Na_2O) prepared at a temperature of 1200°C for 1, 2.5, and 4 h, the absorption bands characterizing bound hydroxyl groups almost coincide with each other, whereas the intensity of the band assigned to free hydroxyl groups decreases in the IR spectra. However, an increase in the alkali oxide content in the glasses leads to an increase in the difference between the intensities of the second band in the spectral range under consideration (Figs. 2–5).

Therefore, the ratio between the numbers of free and bound hydroxyl groups in the structure of alkali borate glasses is determined by the synthesis conditions and composition of glasses. A change in this ratio can affect the structure-sensitive properties of alkali borate glasses. Specifically, a correlation between the content of bound hydroxyl groups in the structure of glasses

and their viscosity has already been revealed for two-alkali borate glasses [12].

CONCLUSIONS

Thus, the results of the investigation into the influence of synthesis conditions and composition of binary alkali borate glasses on the spectral absorption in the range 2.5–4 μm allowed us to make the inference that water in the structure of these glasses occurs in the form of free and bound hydroxyl groups. The ratio between the numbers of these hydroxyl groups depends on the composition and synthesis conditions of glasses. Glasses not only with different water contents but also with different ratios between the numbers of free and bound hydroxyl groups can be prepared under different synthesis conditions. Consequently, the quantitative water content in the structure of borate glasses cannot be uniquely judged only from the absorption band with the maximum at a wavelength of 2.9 μm , which is attributed to free hydroxyl groups. The results of the investigation into the properties of water-containing mixed alkali borate glasses have made it possible to assume that a change in the ratio between two types of hydroxyl groups in the structure of glasses can affect the structure-sensitive properties of the binary alkali borate glasses under consideration.

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