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Effect of the Ratio $R = [Na_2O]/[B_2O_3]$ on the Structure of Glass in the Na_2O-B_2O_3-SiO_2 System

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Abstract—Sodium borosilicate glass, with the ratio $R = [Na_2O]/[B_2O_3]$ varied from 0.31 to 1, were studied by IR spectroscopy and Raman scattering techniques. The dependence of the structure of borosilicate glasses on their composition was studied also for the section with a constant value $R = 1$. The main borate and silicate groups in the system, and especially changes in the structure of glasses depending on the ratio R were identified.

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Ternary silicate systems containing one additional glass forming oxide besides silica are of particular interest in chemistry, geochemistry, and material science. The borosilicate system is the most important among them, due to its specific properties. Its study is of great significance particularly for the development of glasses for different purposes and matrices for the disposal of radioactive waste. One feature of the structure of borosilicate glasses is the ability of boron to be in a different coordination states with respect to oxygen. The properties of these matrices are known [1] to be largely determined by the coordination and structural position of boron in the borosilicate glass. Boron oxide can form both its own and mixed borosilicate anionic groups. The laws of formation of borate and silicate component and their interaction determine the basic structural features and physico-chemical properties of borosilicate glasses and melts.

The main structural units of crystalline silicates, silicate melts, and glasses are SiO_4 tetrahedra, which consist of a central silicon atom and four oxygen atoms. Variety of structures of silicates in nature is due to the fact that connected SiO_4 tetrahedra can form a complex silicate anions. The union of the tetrahedra occurs through the formation of the bridging bonds Si–O–Si connecting their vertices, therewith the tetrahedra have no common edges or faces [2]. Among the SiO_4 tetrahedra five types can be distinguished differing by the ratio of the number of nonbriging and bridging oxygen atoms. These five types of tetrahedra are the basic structural units of silicates. They are denoted as Q^n, where n indicates the number of bridging oxygen atoms [3].

Crystalline silicates are composed of structural elements of the same type. Thus, orthosilicates are built from isolated Q^0 tetrahedra linked by cationic modifier. The sequential increase in the content of silicon oxide results in the polymerization of the tetrahedra to form initially the dimers consisting of Q^1 that is typical of pyrosilicates, then isolated silicon–oxygen chains characteristic of metasilicates (Q^2). The chain uniting leads to the formation of a layer consisting of Q^3 tetrahedra, as in the disilicate, and finally the union of the layers leads to the formation of three-dimensional framework consisting of Q^4 units, as in silica.

In this paper we apply the additional symbols of the structural units of silicate systems to account for the influence of the second coordination sphere of silicon atoms on the position of characteristic bands in the Raman spectra of the respective glasses. For this purpose we introduce additional structural units $Q^{nn'}$, characterized by their “neighbors.” Thus, Q^{33} tetrahedra are a component of the sheet structure, and Q^3 are their neighboring tetrahedra. The Q^{32} are also structural units with three bridging oxygen atoms, but these units are connected to Q^2 units and are located at the site of branching chain structures. The need for this notification becomes apparent at performing computer simulation of superposition of the lines in the Raman spectra of silicate and borosilicate glasses, corresponding to vibrations of a certain type.

Variations of the borate structural units are much broader, view of the fact that, unlike silicon, boron atom can have coordination either III or IV. It has been suggested in [4] that the framework of B_2O_3 glass includes the boroxol groups consisting of three BO_3 triangles connected by a common oxygen atom. This assumption was later supported in [5]. It is also assumed that in the alkali-borate glasses besides the boroxol rings, triangles, and tetrahedrons with different ratios of bridged and non-bridged oxygen atoms, the formation of diborate, triborate, and pentaborate groups is expected in which the boron atom can be surrounded by either three or four oxygen atoms [6].

The presence of more than one glass-forming oxide in the glass leads to the formation of a mixed network. In borosilicate glasses, both the glass-forming cations (Si and B) can form their own anionic groups. Features of the structure of these groups depend on the *competition* of the glass-forming cations trying to create the energetically most favorable environment of oxygen atoms around themselves. To describe their composition the ratio R = [Na_2O]/[B_2O_3] is commonly used which is one of the most important structural parameters of the models of borosilicate glasses [7].

The most effective methods for studying the structure of oxide glasses are the methods of vibration spectroscopy. Raman spectroscopy data are sufficiently informative, but as an additional method it is desirable to use the method of infrared spectroscopy. This is due to the fact that differences in the physical nature of the light scattering and absorption are characterized by different selection rules. Thus, the same oscillations appear in either IR or Raman spectra, or they intensity is different. For example, vibrations of the molecules having a center of symmetry being active in the Raman spectra do not appear in the IR spectrum and vice versa (mutual exclusion rule in IR and Raman spectroscopy). Thus, the methods of infrared and Raman spectroscopy are complementary.

Figure 1a shows the Raman spectra of glasses with $R = 1$, obtained at room temperature. A Raman spectrum of borosilicate glass is divided conventionally into three areas: 300–800 cm^{-1} , 800–1250 cm^{-1} and 1250–1700 cm^{-1}. The range of 800–1250 cm^{-1} contains characteristic vibrations of the silicate groups Q^n (n is the number of bridging oxygen atoms). In the spectrum of the composition no. 1 there is a broad band around 1080 cm^{-1} due to the stretching vibrations of nonbridging bonds of the structural units Q^{33} associated with the same Q^3 tetrahedra.

A weakly expressed shoulder ~1180 cm^{-1} most likely corresponds to the vibrations of structural units Q^{34} connected with the Q^4 not having their own bands in the high-frequency region of the Raman spectrum. Upon increase in the boron oxide content the narrowing of this band is observed and the appearance of the band at 950 cm^{-1}, which is due to a decrease in the content of the tetrahedra with all the bridging bonds and the formation of structural groups of Q^2. In the low-frequency spectrum of the composition no. 1 there is a band at 530 cm^{-1} associated with the symmetric stretching and in part with the bending vibrations of the Si–O–Si bridges [3].

In the frequency range 610–630 cm^{-1} there is a band whose assignment is ambiguous. According to [6, 8–11], this band belongs to the ring type vibrations of the metaborate anion. However, in [12], the band at 630 cm^{-1} is associated presumably with variations of the danburite rings consisting of two SiO_4 and two BO_4 tetrahedra. A band near 770 cm^{-1} characteristic of glasses with a high content of B_2O_3 is due to the vibrations of the four-coordinated boron in the diborate and boroxol rings [6, 12]. In the region of vibrations of borate groups (1250–1700 cm^{-1}) there is a complex band with the maximum at 1490 cm^{-1}, which is related to the vibrations mainly in the BO_3 triangles with one nonbridging oxygen atom [12]. The intensity of this band increases with increasing content of B_2O_3 and Na_2O in the glass. The new band at 1266 cm^{-1} in the spectrum of the glass of the composition 40% Na_2O·40% B_2O_3·20% SiO_2 is associated with the stretching vibrations of BO bonds in the BO_3 triangles that form the boroxole ring, but are not a part of the ring [11, 13–14]. Thus, the appearance of the band 1266 cm^{-1} is characteristic of the Raman spectra of borosilicate glasses with a high content of boron oxide.

Figure 1b shows the results of Raman spectroscopy of the borosilicate glasses with the R ratio varied from 0.31 to 1. In the spectrum of the glass with the composition no. 9 a pronounced peak near 770 cm^{-1} is observed, corresponding to vibrations of the four-coordinated boron [6], and the bands at about 930 cm^{-1} and 1400 cm^{-1} attributed to the vibrations of boron in the ternary coordination. The increasing Na_2O/B_2O_3 ratio leads to clear changes in the spectra of borosilicate glasses in the frequency range 600–800 cm^{-1}.

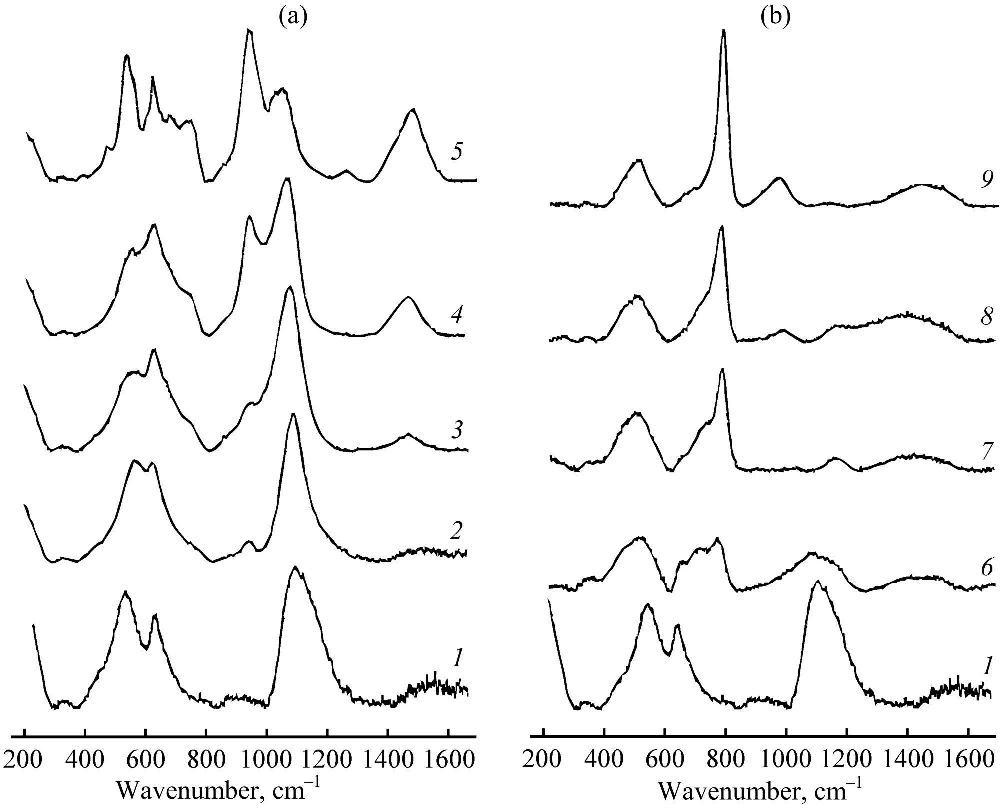

Fig. 1. Raman spectra of glass. (a) Composition: xNa$_2$O + xB$_2$O$_3$ + (100 – 2x)SiO$_2$, where x (%): (*1*) 20, (*2*) 25, (*3*) 30, (*4*) 35, and (*5*) 40; (b) Compositions nos. 1, 6–9 of the table.

The intensity of the peak at 770 cm^{-1} decreases to the value observed for the composition no. 6 with R = 0.62. At further increase in the Na$_2$O/B$_2$O$_3$ ratio bands appear in the region of 1070 cm^{-1} (composition no. 7) and 1140 cm^{-1} (composition no. 6) corresponding to vibrations of the terminal silicon–oxygen bonds in the Q^3 tetrahedra differing by the second coordination sphere of silicon atoms. In addition, at increasing in R from 0.31 to 0.62 a peak appears near 630 cm^{-1}. In the Raman spectrum of a borosilicate glass of the composition no. 1 with R = 1 the band at 770 cm^{-1} is almost not expressed, and the band at 630 cm^{-1} is characterized by the maximum intensity value in the considered cross-section of the compositions. The spectra of glasses with compositions nos. 6 and 1 (R = 0.62 and 1, respectively) contain the bands in the region of 1100 cm^{-1} characteristic of the vibrations of nonbridging oxygen atoms in the Q^n tetrahedra.

Compositions of the studied glasses (mol %)

Sample	Na$_2$O	B$_2$O$_3$	SiO$_2$	R = [Na$_2$O]/[B$_2$O$_3$]
1	20	20	60	1
2	25	25	50	1
3	30	30	40	1
4	35	35	30	1
5	40	40	20	1
6	23	37	40	0.62
7	22	52	26	0.42
8	25	62	13	0.41
9	24	76	0	0.31

Figure 2 shows infrared absorption spectra of the studied glasses, obtained at room temperature. In the spectrum of sodium borosilicate with low boron content (composition no. 1) there are two main bands, about 465 and 1005 cm^{-1}. The first one is due to the Si–O–Si bending vibrations [3]. At the increase in the boron oxide content no obvious changes are observed in the low-frequency region of the spectra. The second band is characteristic of asymmetric Si–O–Si stretching vibrations. In the frequency range of 850–1100 cm^{-1} the changes can be traced in the spectral patterns depending on the composition. These changes are associated with the appearance of vibration bands of nonbridging Si–O$^-$ bonds in the region of 950 cm^{-1}.

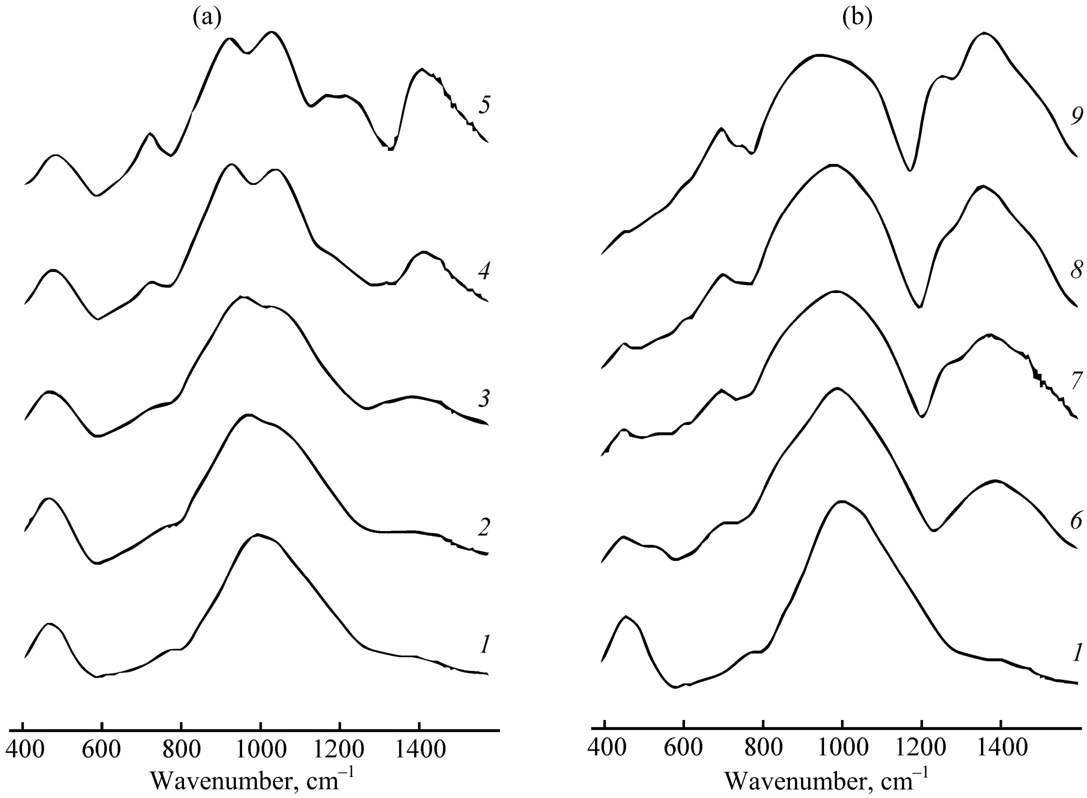

Fig. 2. Infrared absorption spectra of glasses with the following compositions: (a) xNa$_2$O·xB$_2$O$_3$·(100–2x)SiO$_2$, where x (%): (*1*) 20, (*2*) 25, (*3*) 30, (*4*) 35, and (*5*) 40; (b) compositions nos. 1, 6–9 (see the table).

In the spectra of glass a band is observed near 730 cm^{-1} attributable to the symmetric vibrations of the bridging bonds in the silicate and borate frameworks. With increasing content of B_2O_3 a band appears in the region of 1230–1250 cm^{-1} due to vibrations localized on the fragments of the structural units BO_3, and the band with maximum near 1410 cm^{-1}, which is attributed to the vibrations of the BO_3 groups [8, 15].

With the increase in the ratio R from 0.31 to 0.62 (Fig. 2b), in the high-frequency region of the spectrum the intensities of the borate bands associated with vibrations of BO_3 groups smoothly decrease. In the region of medium frequencies the band at 700 cm^{-1} disappears, which is assigned, in particular, to the bending vibrations of the bridges B(III)–O–B(IV) [16].

The data obtained by vibration spectroscopy indicate that the degree of polymerization of silicate network depends on the composition of the borosilicate glass. Reducing intensity of the band at 530 cm^{-1} with a change in the content of silica from 60 to 20 mol. %, but with a constant $R = 1$ in the glass of the composition xNa$_2$O·xB$_2$O$_3$·(100–2x)SiO$_2$ (Fig. 1a), is a result of depolymerization of the silicate network, which is consistent with the NMR data [17, 18]. For more information on Q^n-distribution of silicate structural units in glasses intensities are used of the characteristic bands in the high-frequency region of the Raman spectra. The method of simulating this region of the spectra was described in detail [19, 20]. Figure 3 shows an example of simulating the Raman spectrum of glass of the composition 40% Na_2O·40% B_2O_3·20% SiO_2.

The isolated bands are characteristic of the structural units Q^1, Q^2 and Q^3. Accounting for the middle-order structure (the second coordination sphere of silicon atoms) makes it possible to simulate most clearly the high-frequency part of the Raman spectra. For the Raman spectra of glasses of the first series the region of 800–1250 cm^{-1} is presented through the superposition of five lines of Gaussian shape, which made it possible to determine the integral intensities of the characteristic bands of groups Q^n. Their dependence on the composition is shown in Fig. 4a. It is seen that the silicate component of the glass containing the minimum amount of boron and sodium contains mainly the Q^{33} tetrahedra with three bridging bonds,

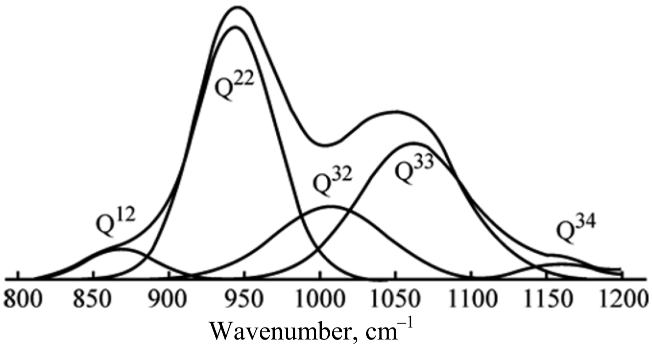

Fig. 3. Simulation of high-frequency Raman spectrum of the glass with the composition 40% Na_2O·40% B_2O_3·20% SiO_2.

which are associated with the same structural units Q^3. At increase in the borate component, the degree of polymerization of silicate network is reduced: the tetrahedra Q^2, appear, the Q^4 tetrahedra disappear, as evidences a decrease in the content of the structural units Q^{34} associated with them, and the appearance of the structural units Q^{32} associated with Q^2. Figure 4b shows the total integral intensity of the characteristic bands of Q^3 on the composition without accounting for the second coordination sphere of silicon atoms.

The most interesting for the discussion are the results of the spectroscopy of the second series of samples. Interpreting the appearance of a peak near 630 cm^{-1} in the Raman spectra by the formation of metaborate rings according to [6, 8–11], we can assume that the increase in the ratio R from 0.31 to 1 will be accompanied by a decrease in the content of triborate groups with the simultaneous formation of metaborate rings. In this case the transformation is expected of four-coordinated boron into three-coordinated one. If we accept the second point of view in the interpretation of the band at 630 cm^{-1}, then the content of four-coordinated boron in the glasses practically does not change with an increase in the ratio R from 0.31 to 1, but there is only a change in the type of existing suprastructural groups in the glass. Comparing our data with the results of [21, 22], which showed the presence of four-coordinated boron in almost all parts of this section, we can conclude that the band 630 cm^{-1} is probably due to the vibrations of borate groups containing four-coordinated boron. In addition, for the second series of glasses with $R > 0.62$ the appearance of the bands is observed in the region of vibrations of nonbridging oxygen atoms of the structural units of Q^3 and the increase in their intensities, which corresponds to the decrease in the degree of polymerization of silicate subnetwork.

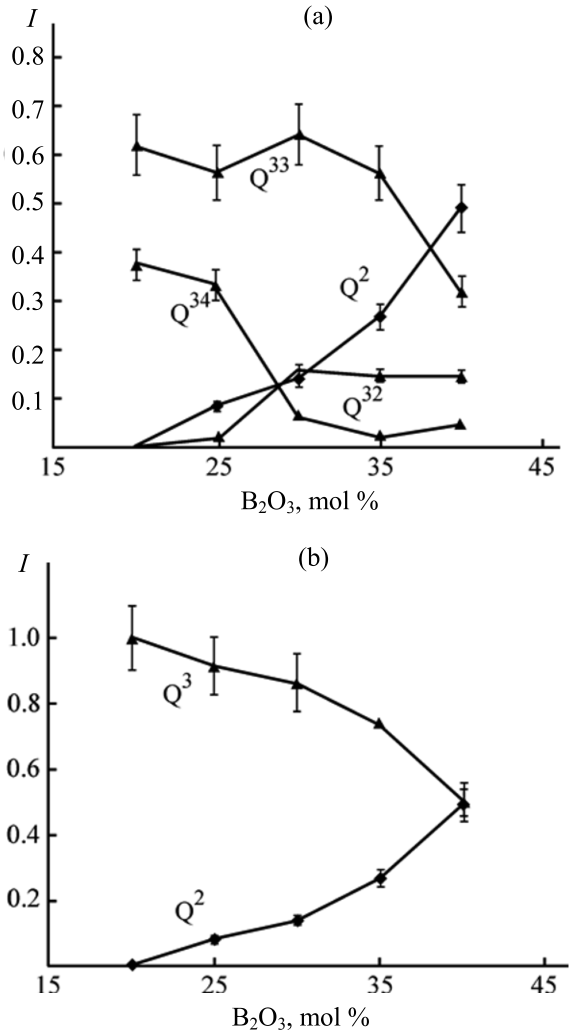

Fig. 4. Dependence of the integral intensities of the characteristic bands of silicate Q^n groups on the composition of the glasses of series no. 1, taking into account (a) and without accounting for (b) the second coordination sphere of silicon atoms.

The results of IR spectroscopy of glasses of the series no. 2 showed that with increasing R ratio a decrease occurs in the intensity of bending vibrations of the bridges B(III)–OB(IV). This is well consistent with the results of Raman spectroscopy and the corresponding decrease in the content of six-membered borate rings containing four-coordinated boron.

In addition, it is possible hypothetically to complete the series no. 2 with another compound, sodium tetrasilicate. Its structure can be investigated by thermodynamic simulation [23–25]. Based on the principles of the model of ideal solutions and using the method of [24–25], the distribution of silicon oxide tetrahedra with different ratios of bridging and nonbridging oxygen atoms (Q^n distribution) was determined. From the calculations it follows that the glass of the composition of 20% $Na_2O \cdot 80\%\ SiO_2$ consists of the basic structural units of Q^4 and Q^3, their mole fractions are equal within the error of the method (5%). The calculated data are in good agreement with the results based on of NMR spectroscopy [26]. Thus, after complete substitution of boron atoms by the silicon atoms the lattice of the silicate glass consisting of 20% $Na_2O{\cdot}80\%\ SiO_2$ is represented by the structural units of Q^4 and Q^3 as the fragments of a three-dimensional lattice and layers, respectively.

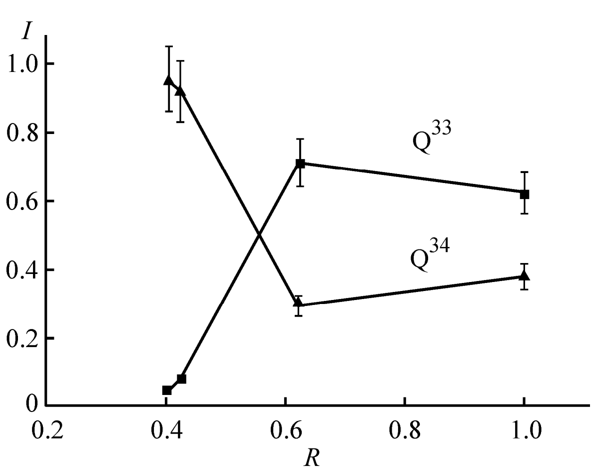

Fig. 5. The dependence of the integral intensities of the characteristic bands of silicate groups Q^n on the glass composition of the series no. 2 taking into account the second coordination sphere of silicon atoms.

Redistribution of structural groups in the network of silicon oxide glass with the composition 20% $Na_2O{\cdot}80\%\ SiO_2$ at the stepwise substitution of silicon atoms by the boron is reflected by the Raman spectra of the series no. 2 of the samples. We considered the high-frequency region of Raman spectra as a superposition of Gaussian lines and determined the integral intensities of the characteristic bands of the groups Q^n. The dependence of the integral intensities of the bands at 1070 and 1140 cm^{-1}, corresponding to vibrations of the structural groups Q^{33} and Q^{34}, on the composition is shown in Fig. 5.

It is seen that in the glass containing the highest amount of boron the silicate component consists mainly of tetrahedra with three bridging bonds connecting them with the structural units Q^4. With a decrease in the content of the borate component the contribution of these groups is reduced, and only the Q^{33} remain connected `with the structural units Q^3, indicating a decrease in the degree of polymerization of silicate subnetwork at a relatively constant content of the modifier cation. Although the high-frequency region of Raman spectra does not include the characteristic bands corresponding to vibrations of Q^4 units contained in the glass [3], the presence of the latter follows from the equilibrium between the structural units in glasses and melts with a high content of silica:

$$2Q^3 \leftrightarrow Q^4 + Q^2.$$

The revealed tendency of decrease in the degree of polymerization of silicate subnetwork with a decrease in the content of the borate component is well consistent with the results of calculation of distribution of the structural units in sodium tetrasilicate.

Thus, with the increase in the content of borate component in the sodium borosilicate system at a constant ratio $R = 1$ the silicate network undergoes a depolymerization, as evidence the changes in relative intensities of characteristic bands of silicon oxide tetrahedra in the Raman spectra. In the borate part, the interaction with sodium oxide leads both to the formation of a non-symmetric triangles BO_3 with a nonbridging oxygen atoms, and tetrahedra BO_4.

The obtained data on the distribution of borate suprastructural groups in dependence on the composition of the glass suggest that the band 630 cm^{-1} in the Raman spectrum of borosilicate glass is associated with the vibrations of B–O bond in the BO_4 tetrahedra. At a gradual substitution of boron by silicon (R varies from 0.31 to 1) in the sodium borosilicate glass with the same content of cation–modifier a redistribution occurs of structural units in borate subnetwork. Reduction in the degree of polymerization of silicate subnetwork becomes evident from spectroscopic data only when $R > 0.62$ (± 5%).

EXPERIMENTAL

The three-component glasses of the system Na_2O–B_2O_3–SiO_2 were synthesized from the amorphous SiO_2 of analytical grade, boron trioxide B_2O_3 of highly pure grade and sodium carbonate of reagent grade. The charge was thoroughly mixed in a mortar with alcohol, dried and melted in a platinum crucible in a silite furnace at a temperature up to 1373 K until complete homogenization of the melt, followed by air-hardening. The compositions of the studied glasses are shown in the table. We studied two series of samples of sodium borosilicate glasses with different ratios $R = Na_2O / B_2O_3$. In a series no. 1 the ratio R maintained constant and equal to unity (samples 1–5), in the series no. 2 the value of R decreased from 1 to 0.31 (samples 1, 6–9).

The study of the dependence of structure of borosilicate glasses on the composition was performed using Raman and infrared spectroscopy. Infrared spectra were obtained on a Fourier spectrometer Nexus-870 Thermo Nicolet. The glass samples were ground into powder with KBr in an agate mortar, the mixture was compressed into tablets in a vacuum. All registered transmission spectra were converted into absorption spectra (optical density) and normalized to unity. Registration of Raman spectra was performed on an iHR 320 Labram spectrometer with a microscope Olimpus BX41. For all registered spectra baseline correction was performed. The spectra processing was carried out using the OMNIC Thermo Nicolet software package.

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