Structure of Ca–Sr–Ba Sodium–Borosilicate Glasses according to ^{11}B and ^{29}Si NMR Spectroscopy

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Abstract—The structure of borosilicate glasses is studied with ^{11}B and ^{29}Si NMR spectroscopy in order to investigate the influence of replacement of Na_2O by oxides of alkali earth metals on their local structure. The quantitative data are analyzed with respect to their correspondence to the criterion of the average charge of the structural unit. The reasons for the deviation between the experimental results and this criterion are considered. It is shown that, in the case of glass devoid of borate structural units with nonbridging oxygen atoms, the corrected contents of these units are consistent with the predictions of thermodynamic modeling of the structure and properties of oxide glasses.

INTRODUCTION

The glasses of the $Na_2O–B_2O_3–SiO_2$ system are studied the most among diverse alkali-borosilicate glasses. Indeed, a model of their structure was proposed as early as 1978 [1] and further repeatedly specified [2–5]. Progress in understanding their structure and properties was made after the thermodynamic modeling of oxide glasses [6–9]. The current knowledge on structure of the $Na_2O–B_2O_3–SiO_2$ glasses (e.g., the principles of the change in the structure of glass in the short- and intermediate-order ranges depending on its composition) allow considering them as a specific standard or a starting point for studying the influence of the cation-modifier type on the glass structure at the complete or partial replacement of Na_2O by other typical oxides-modifiers. In this case, the compositions of the glasses should exhibit unchanged contents of network-forming oxides and the total content of the modifying oxides. This approach was implemented in [10], where we considered the vibrational spectra of Ca- and Ba-bearing glasses with constant parameters $K = 2$ ($K = [SiO_2]/[B_2O_3]$) and $R = 1$ ($R = [MO]/[B_2O_3]$, M = Ca, Ba) and the Na_2O content varying from 25 to 6.2 mol % (the BaO and CaO content varied from 0 to 18.8 mol %, respectively). It was shown that the Q^4, Q^3, and Q^2 tetrahedra (Q^n is a silicate tetrahedron with n bridging oxygen atoms) are silicate structural units of

these glasses and the borate units include $[B\emptyset_{4/2}]^-$ tetrahedra and symmetric completely polymerized $B\emptyset_{3/2}$ and asymmetric metaborate $B\emptyset_{2/2}O^-$ triangles and the concentration of the $B\emptyset_{2/2}O^-$ units in primary sodium-borosilicate glass is close to 0 and, in both cases, increases as Na_2O oxides are replaced by the oxides of alkali earth metals. This study logically continues the work [10].

The aim of the work is a detailed study of the local structure of sodium-borosilicate glasses with dopes of oxides of alkali earth metals and the influence of the cation-modifier type on their structure in a short-range order.

EXPERIMENTAL

The symbols and nominal content of the components (oxides) of the synthesized glasses are shown in Table 1. The initial reagents (SiO_2, B_2O_3, and Na_2CO_3 of especially high purity and highly pure CaO, SrO, and BaO) were preliminarily dried in a muffle at 120°C, weighted, and thoroughly mixed. A 10-g charge was placed in a Pt crucible and melted in an electric oven for four hours at 1200–1250°C under normal atmosphere and pressure; further the melt was quenched in air up to room temperature.

The nuclear magnetic resonance (NMR) spectra were registered on a CMX-300 Infinity Plus (Agilent)

Table 1. Symbols and composition (mol %) of synthesized glasses

Sample	Na_2O	CaO	SrO	BaO	B_2O_3	SiO_2
BSN	25	0	0	0	25	50
BSNC	12.5	12.5	0	0	25	50
BSNS	12.5	0	12.5	0	25	50
BSNB	12.5	0	0	12.5	25	50

spectrometer with induction of an outer constant magnetic field of 7 Tl at the University of Regensburg (Germany). The rotation frequency of the samples under magic angle spinning (MAS) was 6 kHz. The chemical shift was calculated as a part per million (ppm) relative to the resonance frequency of the reagents $NaBH_4$ ([11]B) and $C_4H_{12}Si$ ([29]Si) taken as the standards. All the spectra were measured at room temperature.

DISCUSSION

The ^{11}B MAS NMR spectra are shown in Fig. 1. It is seen that replacement of Na_2O by oxides of alkali earth metals (up to 50%) does not yield a significant change in the spectra. All the spectra exhibit a narrow intense peak with the maximum near -1 ppm, which corresponds to BO_4 tetrahedra, and a weak signal without a clear maximum in the range of 15 to -15 ppm, which indicates the presence of some trigonal borate units [11–14]. The similarity of the spectra indicates

that the partial replacement of Na_2O by oxides of alkali earth metals weakly changes the local structure of the glasses at the concentration level of three- and four-fold coordinated boron atoms.

To determine the concentrations of the boron atoms in a different coordination environment (N_4 and N_3), these spectra were modeled as a superposition of two components, the relative integral intensities of which reflect the portion of BO_4 and BO_3 units in the synthesized glasses. (An example of modeling of the ^{11}B MAS NMR spectrum of the sodium-borosilicate glass is shown in the inset of Fig. 1). The modeled values are given in Table 2. A comparison of the N_4 value (0.64) for the BSN glass with the experimental data of other authors ($N_4 = 0.58$ [1], $0.70–0.73$ [15], 0.61 ($K = 2.12$, $R = 1.06$) [16], 0.60 [17], 0.60 [18]), as well as the results of the theoretical calculations of the concentration of BO_4 tetrahedra in the borosilicate glasses of identical composition ($N_4 = 0.63$ [7], 0.625 [3]), showed their agreement.

As follows from Table 2, the concentrations of borate tetrahedra within the experimental error are independent of the composition of the glasses and are caused by the bulk content of the oxides-modifiers. It is known that, in Ca borosilicate glass with $R = 1$ and $K = 2$, the portion of borate tetrahedra occur in the range of $0.36–0.38$ [19], which is significantly lower than our value of 0.61 for the BSNC glass. Thus, it can be expected that the BO_4 concentration of the $Na_2O–CaO–B_2O_3–SiO_2$ glasses in the section considered
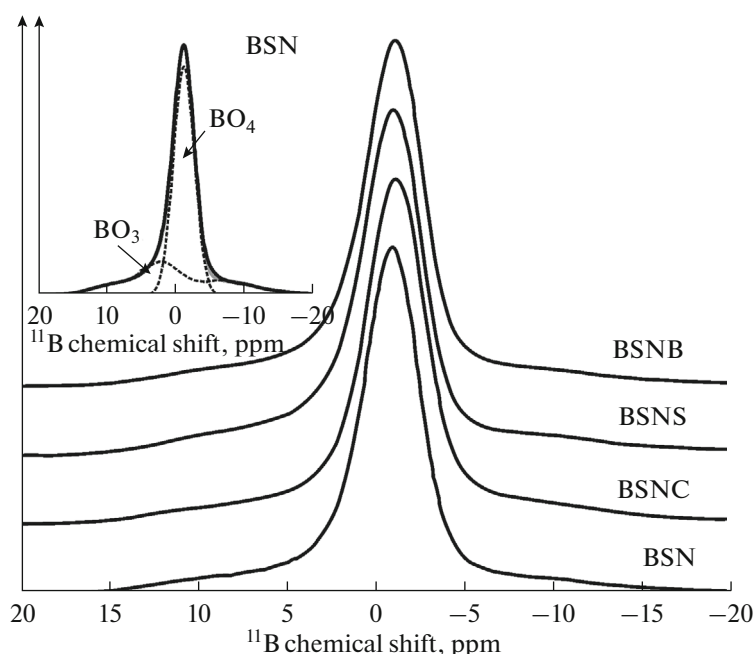

Fig. 1. ^{11}B MAS NMR spectra of studied borosilicate glasses (inset demonstrates example of modeling spectrum of BSN glass).

will be a nonlinear function of the [CaO]/([CaO] + [Na$_2$O]) value and a significant decrease in the N_4 value will be observed in the area, where the [CaO]/([CaO] + [Na$_2$O]) ratio is >0.5, i.e., when [CaO] > [Na$_2$O]. Judging from the data of [12], a similar situation for the BaO–B$_2$O$_3$–SiO$_2$ system arises in the Na$_2$O–BaO–B$_2$O$_3$–SiO$_2$ glasses that are similar in composition. The data of vibrational spectroscopy [10] showed that most trigonal borate units of the 25Na$_2$O–25B$_2$O$_3$–50SiO$_2$ glass (the composition is given in mol %) include symmetric BØ$_{3/2}$ triangles and, as Na$_2$O is replaced by Ca or Ba oxides, the concentration of metaborate BØ$_{2/2}$O$^-$ units increases. At a constant N_4 value, the increases in the portion of metaborate BØ$_{2/2}$O$^-$ triangles in the structure requires an increase in the concentration of highly polymerized silicate structural units, because the average charge of the structural unit cannot change under constant K and R values, i.e., when the glass composition varies in a manner that the mean number of oxygen atoms of the cation–network former is constant. Thus, a slightly higher concentration of Q^4 units is expected in Ba- and Ca-bearing glasses in comparison with the initial BSN glass.

The ^{29}Si NMR spectra of the synthesized borosilicate glasses are shown in Fig. 2. Even a simple visual comparison showed that the form of the spectral contour of the BSN glass is evidently distinct from that of the spectra of the other three glasses with oxides of alkali earth metals. The intensity of the resonance signal of ~100 ppm of the BSNC, BSNS, and BSNB spectra is higher than in the spectrum of the sodium-borosilicate glass and the intensity of the component with the maximum of about −90 ppm is lower. Only the third component (about −75 ppm) is weakly correlated with the glass composition. Judging from the intensity of some lines in the ^{29}Si NMR spectra, the silicate structural units of these glasses mostly include two types of SiO$_4$ tetrahedra (Q^4 (−100 ppm) and Q^3 (−90 ppm) units), whereas the concentration of the Q^2 units (−75 ppm) is insignificant. It follows from Fig. 2 that the portion of the Q^4 units is really higher in the Ca-, Sr-, and Ba-bearing glasses in comparison with sodium-borosilicate glass. The fact of dominating silicate tetrahedra of Q^4 and Q^3 types in the structure of silicate tetrahedra is consistent with the data on Raman spectroscopy [20], according to which a line in the range of 1075−1085 cm^{-1} with an intense shoulder from the high frequencies (1150 cm^{-1}) is observed in the high-frequency range of the spectrum of the 25Na$_2$O–25B$_2$O$_3$–50SiO$_2$ glass. The origin of these lines was discussed by different authors [21−26] and is

Table 2. Concentrations of borate and silicate structural units in studied glasses

Sample	N_4	N_3	N_{Q^4}	N_{Q^3}	N_{Q^2}	N_4'	N_3'	N_{Q^4}'	N_{Q^3}'	N_{Q^2}'
BSN	0.64	0.36	0.37	0.55	0.08	0.32	0.18	0.19	0.28	0.04
BSNC	0.61	0.39	0.58	0.36	0.05	0.31	0.20	0.29	0.18	0.03
BSNS	0.62	0.38	0.57	0.39	0.04	0.31	0.19	0.29	0.20	0.02
BSNB	0.63	0.37	0.53	0.41	0.06	0.32	0.19	0.27	0.21	0.03

Concentrations are given locally (N_i) separately for borate and silicate structural units and generally (N_i') relative to all (borate and silicate) structural units of glass ($i = 3, 4, Q^2, Q^3$, and Q^4). Determination error of concentrations of structural units is ± 0.03.

considered to be related to the presence of the Q^3 and Q^4 units in the structure of silicate and borosilicate glasses.

Using the relative integral intensities of some lines, we calculated the concentrations of silicate tetrahedra (N_{Q^n}), which are distinct in the amount of bridging oxygen atoms per silicon atom. The calculation results are shown in Table 2. The analysis of the published data showed that, in contrast to the N_4 value, which is reasonably consistent between different authors, no common opinion exists on the Q^n distribution in the 25Na$_2$O–25B$_2$O$_3$–50SiO$_2$ glass (or glasses close in composition). For example, according to [27], $N_{Q^4} = 0, N_{Q^3} = 0.93$, and $N_{Q^2} = 0.07$, whereas the work [28] provides three sets of concentrations of the Q^n units, which were calculated by different methods: $N_{Q^4} = 0.55, 0.767$, and 0.61; $N_{Q^3} = 0.45, 0.201$, and 0.39; and $N_{Q^3} = 0, 0.03$, and 0; and the thermodynamic calculations yield 0.674, 0.316, and 0.01 for the concentrations of the Q^4, Q^3, and Q^2 units, respectively [7]. In this case, the correctness of the calculations can conveniently be estimated by the average charge of the structural unit. This value can be calculated either from the nominal composition of the glass (or the real composition if it is known):

$$\langle q \rangle = \frac{2x_{Na_2O}}{x_{SiO_2} + 2x_{B_2O_3}}, \qquad (1)$$

(where x_i is the mole portion of the ith oxide), or via the concentrations of various types of borate and silicate triangles and tetrahedra, which were calculated by the ratio to the total amount of structural units in the system:

$$\langle q \rangle = N_4' + N_m' + 2N_p' + 3N_o' \\ + N_{Q^3}' + 2N_{Q^2}' + 3N_{Q^1}' + 4N_{Q^0}'. \qquad (2)$$
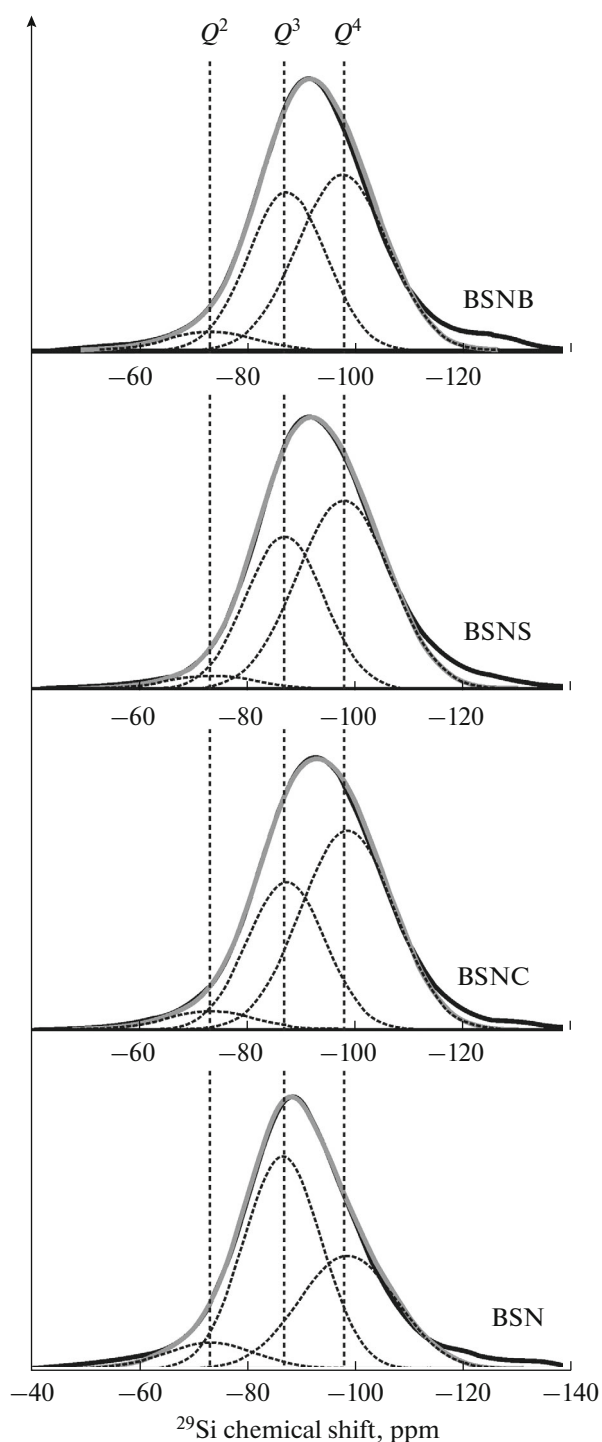
Fig. 2. ^{29}Si NMR spectra of studied borosilicate glasses.

The first four addends correspond to the concentrations (in the share) of the borate $[B\varnothing_{4/2}]^-$, $B\varnothing_{2/2}O^-$ (*m*), $B\varnothing_{1/2}O_2^{2-}$ (*p*), and BO_3^{3-} (*o*) units. The remaining four addends are the concentrations of the silicate tetrahedra with one, two, three, and four nonbridging oxygen atoms, and the multiplier before every addend

corresponds to the charge of the structural unit. It is evident that, under the correct determination of the fraction of the structural units, the calculation results of the $\langle q \rangle$ value following Eqs. (1) and (2) should yield equal (ideally) or close (in reality) values (the experimental error, rounding of concentration values).

To verify our data by the criterion of the valid charge balance, the local distributions of borate and silicate structural units were recalculated in relation to the total distribution according to the following system of equations:

$$
\begin{cases}
N_4' + N_3' + N_{Q^4}' + N_{Q^3}' + N_{Q^2}' = 1, \\[2mm]
\dfrac{N_4'}{N_3'} = \dfrac{N_4}{1 - N_4}, \\[2mm]
\dfrac{N_{Q^3}'}{N_{Q^4}'} = \dfrac{N_{Q^3}}{N_{Q^4}}, \\[2mm]
\dfrac{N_{Q^2}'}{N_{Q^3}'} = \dfrac{N_{Q^2}}{N_{Q^3}}, \\[2mm]
\dfrac{N_4' + N_3'}{N_{Q^4}' + N_{Q^3}' + N_{Q^2}'} = \dfrac{2[B_2O_3]}{[SiO_2]}.
\end{cases}
\tag{3}
$$

The searching concentrations are given in Table 2. It is evident that the correct calculation of the average charge of the structural unit by formula (2) for all the synthesized glasses is possible only for the BSN glass, for which the proposed concentrations, equal to zero, of the borate triangles with nonbridging oxygen atoms are a sufficiently good approximation. As was noted above, the data on vibrational spectroscopy [10] ambiguously indicate the presence of borate triangles with nonbridging oxygen atoms in the structure of Ca- and Ba-bearing sodium-borosilicate glasses. Thus, in the absence of data on the distribution of borate structural units, Eq. (2) cannot be used to calculate the $\langle q \rangle$ value for the BSNC and BSNB glasses. We can surely state that the latter is true for the BSNS glass.

Using the necessary concentrations from Table 2 in Eq. (2) yields $\langle q \rangle$ of 0.68, whereas the calculation of the average charge of the structural unit by composition (Eq. (1)) provides a significantly lower value ($\langle q \rangle = 0.5$). Thus, it can be concluded that, for the BSN glass, we calculated a significantly higher portion of the Q^3 units and, correspondingly, a lower concentration of silicate tetrahedra with the four bridging oxygen atoms (Q^4 units). The most probable reason for this result is the rather strong correlation of the position of the maximum of the resonance line in the NMR spectra of the Q^4 units from their nearest environment (from

Table 3. Corrected concentrations of borate and silicate structural units calculated relative to all (borate and silicate) structural units (upper line) in comparison with thermodynamic results (lower line) for BSN glass [7]

N_4'	N_3'	N_{Q^4}'	N_{Q^3}'	N_{Q^2}'
0.32	0.18 ($N_m' = 0$)	0.36	0.10	0.04
0.31	0.17 ($N_m' = 0.02$)	0.33	0.16	0.01

the presence of bridging oxygen correlations between silicate Q^4 and borate units and the Si–O–B angle between them) [29]. As a result, the intensity of the line near −90 ppm can be supported both by the Q^3 units and the completely polymerized silicate tetrahedra with the borate tetrahedral units in their nearest environment [13]. This results in the higher content of the Q^3 units in the BSN glass.

Assuming that the unresolved signals of the Q^3 and $Q^4(BO_4)$ units is the main reason for the higher content of the Q^3 units in the BSN glass and also that the concentration of borate triangles with nonbridging oxygen atoms in this glass is close to zero, the N_{Q^4}' and N_{Q^3}' values can be corrected so that the mean charge of the structural unit, which is calculated using formula (2), satisfies Eq. (1) (= 0.5). The corrected values of the concentrations of the structural units in the sodium-borosilicate glass with $R = 1$ and $K = 2$ are shown in Table 3. For comparison, we provide the thermodynamic data on the local structure of the BSN glass [7]. As seen from the table, using the criterion of the average charge of the structural unit to assess the correct concentrations of the structural units and their correction yields results that are in agreement with the theoretical calculations.

As was noted above, Eq. (2) cannot be used directly to calculate the average charge of the structural unit in the BSNC, BSNS, and BSNB glasses (here, $N_m' \neq 0$ [13]). Nonetheless, it is expected that estimating the concentrations of the silicate structural units according to the ^{29}Si NMR spectroscopy provided higher/lower values of the N_{Q^3}'/N_{Q^4}' values for the same reason as for the BSN glass. Thus, the argument that replacing Na_2O by the oxides of alkali earth metals results in the increased content of the polymerized SiO_4 tetrahedra in synthesized glasses remains correct, in spite of the fact that the corrected value of $N_{Q^4}' = 0.36$ (BSN glass) exceeds the noncorrected concentra-

tions of the Q^4 units for the BSNC, BSNS, and BSNB glasses. Moreover, taking into account the data on vibrational spectroscopy [10], it can be stated that the increase in the concentrations of the alkali earth oxides of the glasses through Na_2O leads to a redistribution of the oxygen atoms in the system that, in turn, results in an increased fraction of the Q^4 unit and metaborate $BØ_{2/2}O^-$ triangles in four-component glasses. The fraction of these structural units increases against a background of a decrease in the concentration of the symmetric $BØ_{3/2}$ triangles and silicate tetrahedra with one nonbridging oxygen atom. Formally, these changes in the local structure can be written as a reaction of the disproportionation between the silicate and borate units

$$Q^3 + BØ_{3/2} \Leftrightarrow Q^4 + BØ_{2/2}O^-. \qquad (4)$$

The equilibrium of this reaction is shifted to the right as Na_2O is replaced by the oxides of alkali earth metals and this shift does not affect the mean coordination number of the boron atoms; i.e., it does not change the concentrations of the tetrahedral and trigonal borate units.

CONCLUSIONS

The study of the coordination state of the boron atoms in the synthesized borosilicate glasses with ^{11}B NMR spectroscopy showed that the 50% replacement of Na_2O by the oxides of alkali earth metals does not affect the proportion between the boron atoms in the three- and four-fold coordination by oxygen. In all glasses, more than 60% of the boron atoms (local distribution) occur in a tetrahedral coordination. At the same time, the ^{29}Si NMR spectra showed a significant influence of the additions of the alkali earth oxides on the distribution of the silicate structural units. Despite the fact that, according to the data on the ^{29}Si NMR spectroscopy, the estimation of the concentration of silicate tetrahedra of various types in the local distribution, shows that the content of the Q^3 units increases and, correspondingly, the fraction of the Q^4 units decreases, all glasses with CaO, SrO, and BaO exhibited an increase in the concentration of the Q^4 units and a decrease in the concentration of the Q^3 units in comparison with sodium-borosilicate glass. The change in distribution of silicate Q^n tetrahedra at a constant correlation of the concentrations of the boron atoms in various coordination states can be described by the shift in the equilibrium of the reaction of disproportionation (4) to the right at the replacement of alkali oxide by oxides of alkali earth metals. The similarity of the local structure of the Ca-, Sr, and Ba-bearing glasses indicates the absence of the influ-

ence of the type of the bivalent alkali earth cation on the structure of the BSNC, BSNS, and BSNB glasses, at least, at the level of the concentration of the basic structural units. Correcting the concentrations of silicate structural units using criterion of the average charge of the structural unit yielded values close to those predicted by the thermodynamic modeling of the structure and properties of oxide melts.

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