Thermodynamic properties of the Na_2O-BaO-B_2O_3 glasses and melts

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ABSTRACT

The glass formation region in the system Na_2O-BaO-B_2O_3 has been established. Thermodynamic properties for this system were derived. It is found that the lower border of glass formation region is limited to composition containing 10–30 mol.% Na_2O, 10–30 mol.% BaO and 60 mol.% B_2O_3. A region with partial crystallization has been found inside the glass formation region. This region is limited to compounds 5 Na_2O-20 BaO-75 B_2O_3 mol.% and 10 Na_2O-20 BaO-75 B_2O_3 mol.%. The vaporization processes and thermodynamic properties of the Na_2O-BaO-B_2O_3 melts were investigated by the Knudsen effusion mass spectrometry in the temperature range 1290–1750 K. The values of the component activities, Gibbs energies and excess Gibbs energies were derived from experimental data. It was shown that the studied system is characterized by a negative deviation from the ideal behavior.

1. Introduction

The systems containing boron oxide with addition of the alkali and alkali-earth metals oxides are the base of various refractories. The β-barium borate is using in production of the ceramic glazes, phosphors, oxide cathodes [1]. Also, β-barium borate received increased attention from researchers after the discovery of nonlinear optical properties of this modification [2]. Laser materials may be synthesized from melts at temperatures above 1000 K [1]. In aims of homogenization the melt is overheated. This may be led to lose of components with high volatility, changes of the composition of condensed phase and difficulties of the nanocrystals synthesis. The optical crystals on base of borates and in particular β-BaB_2O_4 are possess optical non-linearity [2]. The synthesis of this compound may be provided from the melt of Na_2O-BaO-B_2O_3 system with 22 – 30% mol. fr. of Na_2O in temperature range 1175–1204 K [2]. It is impossible to grow perfect β-BaB_2O_4 crystals from the melt which enriched (more than 60 mol percent) of boron oxide [3] because the crystallization is performed from binary melts with an absence of the components separation possibility.

The glass formation region in the Na_2O–BaO–B_2O_3 system wasn't studied extensively previously. As shown in refs. [4,5] that lower border of glass formation region passes near to the node with 0.6 B_2O_3 mole fraction. In refs [6–9] the properties of the glasses of the composition $Na_2O \cdot 2BaO \cdot 9B_2O_3$ were studied. The properties of the glasses with other compositions were not studied in these works. The glass transition

temperatures and thermal expansion coefficients were obtained in ref [10] for the $Na_2O \cdot 2B_2O_3$–$BaO \cdot 2B_2O_3$ pseudo binary system.

The components of ternary system Na_2O-BaO-B_2O_3 may interact to form sodium and barium borates. At high temperatures the processes of selective vaporization of the sodium borate which is more volatile than pure oxides of barium, sodium and boron may be observed. The sodium borate is most volatile compound in Na_2O-BaO-B_2O_3 system. Pure $NaBO_2$ evaporates at temperature above 1080 K [11–15]. According to the data systematized in ref. [16], B_2O_3 is evaporating congruently without decomposition at temperatures of the order of 1300–1450 K.

The component with lowest vapor pressure formed in the Na_2O-BaO-B_2O_3 system is barium borate. Vaporization of BaB_2O_4, as well as the BaO – B_2O_3 system with an initial component ratio of 67 mol.% BaO-33 mol.% B_2O_3 (2 $BaO \cdot B_2O_3$) was studied in ref. [17]. The analysis of the obtained data showed that in the temperature range 1500–1600 K, two parallel reactions, evaporation (1) and thermal dissociation (2), occur.

$$BaB_2O_4(l) = BaB_2O_4(gas) \tag{1}$$

$$BaB_2O_4(l) = BaO(s) + B_2O_3(gas) \tag{2}$$

As the condensed phase is enriched with barium oxide and as the temperature increases, the molecules of $BaBO_2$, BaO, and atomic barium begin to pass into the vapor. At temperatures above 2000 K, the vapor contains $BaBO_2$, BaO, BO, atomic barium and oxygen.

Phase equilibria in the Na_2O–BaO–B_2O_3 system were studied earlier

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in connection with the search for optimal conditions for growing high-quality single crystals of the well-known nonlinear-optical compound β-BaO·B$_2$O$_3$ from the melt [18]. The region of glass formation has not been studied before, only the study of the thermal expansion of glasses in the Na$_2$O·2B$_2$O$_3$–BaO·2B$_2$O$_3$ section is known [19].

Thermodynamic properties of the Na$_2$O-BaO-B$_2$O$_3$ system at high temperatures were not determined previously. So, the main objectives are clarification of the borders of glass formation region in the Na$_2$O-BaO-B$_2$O$_3$ system and determination thermodynamic properties of this system at the high temperature.

2. Experimental details

In present work thirty-eight samples of the ternary system Na$_2$O–BaO–B$_2$O$_3$ including sodium borate NaBO$_2$ were synthesized.

Barium carbonate, sodium carbonate and boric acid with purissimum grade (the content of main substance not less than 99%) were taken as reagents. The mixture of the initial substances in needed proportion was grinded in jasper mortar during two hours. The synthesis of the glasses was performed in platinum crucibles in silit furnace at temperatures 1000–1200 °C in the air atmosphere. The temperature of the synthesis was selected in the dependences of sample composition. The annealing of the glasses was made during three hours at the temperatures with was lower than T$_g$ (glass transition temperature) on 20–50 ^{0}C. The part of the samples was crystallized during the synthesis.

For some glasses the chemical analysis was performed. The

deviations of the sample composition were not exceeded 1% from the declared composition.

X-ray diffraction experiment for the samples of the investigated system was performed in air at the temperature 25 °C using a DRON-3 diffractometer (Bourevestnik factory, Leningrad, USSR), Cu K$_\alpha$ radiation. The powder data were collected in the 2θ range of (10–70°) with scanning speed one grade per minute. The phase identification was carried out using the Powder Diffraction File database (PDF-2).

The study of vaporization of the Na$_2$O-BaO-B$_2$O$_3$ system and determination of its thermodynamic properties were performed by Knudsen effusion mass spectrometry (KEMS) method [20] on MS-1301 mass spectrometer. KEMS is unique direct method of determination of the qualitative and quantitative vapor composition above systems under study. The samples were evaporated from twin molybdenum Knudsen cell. The cell was heated by electron impact. The temperature was measured by optical pyrometer EOP-66 through the glass window in mass spectrometer vacuum system with accuracy ±10 K at temperature range 1250–1850 K. Correction on window absorption was made as usually fashion. The instrument was preliminary calibrated by the pressure of calcium fluoride [21]. The experimental technique in details was described elsewhere [22]. Determination of activities of condensed phase components was performed with using pure sodium borate and boron oxide as the activity standards.

Table 1
Composition of the samples in the Na$_2$O-BaO-B$_2$O$_3$ system.

Sample, N	The composition of the synthesis, mol.%			Estimated composition, mol.%			Phase composition
	Na$_2$O	BaO	B$_2$O$_3$	NaBO$_2$	B$_2$O$_3$	BaB$_2$O$_4$	
1	1.5	31.8	66.7	4.4	49.0	46.6	Glass
2	3.0	30.3	66.7	8.6	47.9	43.5	Glass
3	6.0	27.3	66.7	16.5	45.9	37.6	Glass
4	11.1	22.2	66.7	28.5	43.0	28.5	Glass
5	13.9	19.4	66.7	34.5	41.4	24.1	Glass
6	16.7	16.7	66.7	40.0	40.0	20.0	Glass
7	22.2	11.1	66.7	49.9	37.6	12.5	Glass
8	25.0	8.3	66.7	54.5	36.4	9.1	Glass
9	27.7	5.6	66.7	58.8	35.2	6.0	Glass
10	31.8	1.5	66.7	64.6	33.9	1.5	Glass
11	50.0	0	50.0	100	0	0	NaBO$_2$
12	10.0	40.0	50.0	33.0	0	66.7	β-BaB$_2$O$_4$ +NaBO$_2$
13	12.5	12.5	75.0	28.6	57.1	14.3	Glass
14	20.0	30.0	50.0	57.0	0	43.0	β-BaB$_2$O$_4$ + NaBO$_2$
15	25.0	25.0	50.0	66.7	0	33.3	β-BaB$_2$O$_4$ + NaBO$_2$
16	30.0	20.0	50.0	75.0	0	25.0	NaBO$_2$ + β-BaB$_2$O$_4$
17	40.0	10.0	50.0	88.9	0	11.1	NaBO$_2$ + β-BaB$_2$O$_4$
18	5.0	15.0	80.0	11. 8	70.6	17.6	Glass
19	10.0	10.0	80.0	22.2	66.7	11.1	Glass
20	15.0	5.0	80.0	31.6	63.1	5.3	Glass
21	3.3	36.7	60.0	10.4	31.6	58.0	β-BaB$_2$O$_4$ + Glass
22	6.7	33.3	60.0	20.0	30.0	50.0	β-BaB$_2$O$_4$ + Glass
23	10.0	30.0	60.0	28.6	28.6	42.6	Glass
24	15.0	25.0	60.0	40.0	26.7	33.3	Glass
25	25.0	15.0	60.0	58.8	23.6	17.6	Glass
26	30.0	10.0	60.0	66.7	22.2	11.1	Glass
27	35.0	5.0	60.0	73.7	21.0	5.3	NaBO$_2$ + Glass
28	8.33	24.97	66.7	22.2	44.5	33.3	Glass
29	2.5	17.5	80.0	6.1	72.7	21.2	Glass
30	20.0	20.0	60.0	50.0	25.0	25.0	Glass
31	5.0	20.0	75.0	12.5	62.5	25.0	Glass + NaBaB$_9$O$_{15}$
32	10.0	15.0	75.0	23.5	58.8	17.7	NaBaB$_9$O$_{15}$ + Glass
33	15.0	10.0	75.0	33.3	55.6	11.1	Glass
34	20.0	5.0	75.0	42.1	52.6	5.3	Glass
35	5.0	10.0	85.0	11.1	77.8	11.1	Glass
36	7.5	7.5	85.0	16.1	75.7	8.1	Glass
37	10.0	5.0	85.0	21.0	73.7	5.3	Glass
38	12.5	2.5	85.0	25.6	71.8	2.6	Glass

3. Results and discussion

In the samples under study next crystalline phases were identified: β-BaB_2O_4 - 80–1489, $NaBO_2$ - 76–0075, $NaBaB_9O_{15}$ ($Na_2O \cdot 2BaO \cdot 9B_2O_3$) – 01–070–7293.

In Table 1 data on the chemical and estimated phase composition are presented.

As the result of synthesis, the clear glasses were obtained for the secant with 66.7 mole fraction of boron oxide. For the secant with 50 mole fraction of boron oxide the crystallized glasses were obtained. This statement approved by the data of XRD analysis. As the result of synthesis were obtained transparent glasses for the secant containing 66.7 mol% B_2O_3 as well as for composition 12.5 $Na_2O \cdot 12.5$ $BaO \cdot 75$ B_2O_3 (samples 1–10 and 13). The samples 11, 12, 14–17 present themselves crystalline glasses.

XRD patterns of samples with 10, 20, 25, 30 and 40 mol.% Na_2O content are presented at the Figs. 1 and 2. Sample 11 (Fig. 1) corresponds to pure sodium borate and only one phase of $NaBO_2$ was found in it. Apparently sample 11 contains some amount of glass. This statement is approved by broad regions of amorphous scattering on corresponding XRD pattern. In the samples 12, 14–17 amorphous scattering is absent and samples are fully crystalized. According to the phase diagram of this section [19] in this region the mixtures of β-BaB_2O_4 and $NaBO_2$ are formed. Reference Intensity Ratio (RIR) of β-Barium borate is equal 5.55 (80–1489) whereas RIR for $NaBO_2$ is equal 0.64 (76–0075). Hence XRD pattern for β-BaB_2O_4 is 8.5 times more intense than for $NaBO_2$. So, the seeming dominance of the β-BaB_2O_4 in the samples with high content of sodium oxide is explained by this phenomenon.

It should be noted that after hardening from the melt in the secant with 50 mol% B_2O_3 samples were full crystalize. On other hand in the secant with 60 mol% B_2O_3 partially crystalize only samples near to ends of the row (21, 22, 27) whereas secants with 66.7, 80 and 85 mol% B_2O_3 contain only glasses.

In the region with high content of boron oxide the tendency to glass-forming is predominant. The exception is the secant with 70 mol% B_2O_3 where glasses near to the composition of the ternary compound $Na_2O \cdot 2BaO \cdot 9B_2O_3$ are crystalized.

On the results of XRD analysis of the samples (see Table 1) the glass formation region of the Na_2O-BaO-B_2O_3 system were schematically shown at Fig. 3. As one can see from Fig. 3 the low border of the glass formation region is restricted by approximately 0.1–0.3 mole fraction of $Na2O$ and BaO and 0.6 mole fraction of boron oxide. Inside the glass
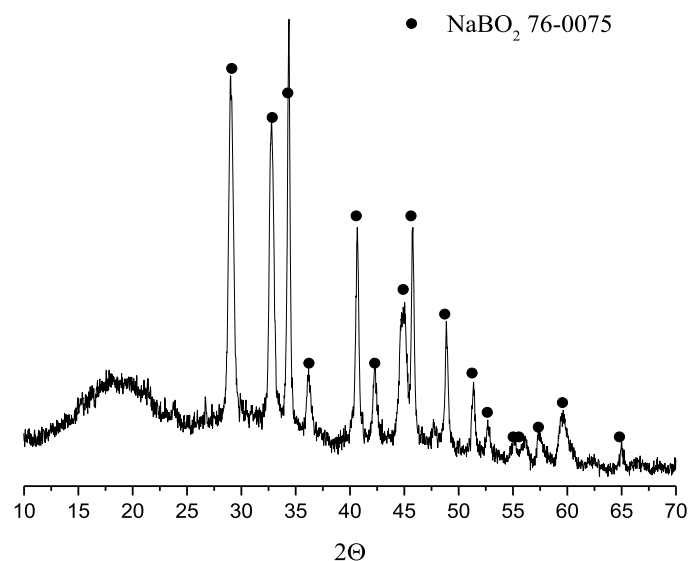
formation region, the region of the partial crystallization was found with presents of the $NaBaB_9O_{15}$ ($Na_2O \cdot 2BaO \cdot 9B_2O_3$) phase. This region is bordered by samples 31 and 32. The literature [4,5] and experimental data about position of the glass formation region are in good agreement. Nevertheless, there are some differences between the results of the present work and ref. [5]. In particular, we haven't found region of liquid-liquid immiscibility but found the region of partial crystallization which is absent in the refs [4,5].

In the mass spectra of vapor above samples of Na_2O-BaO-B_2O_3 at temperature range 1290–1320 K the Na^+ and $NaBO_2^+$ ions were detected in the ratio 23 : 100. When temperature increased up to 1330–1350 the $B_2O_3^+$ ion was also detected. At the isothermal holding the intensities of Na^+ and $NaBO_2^+$ gradually decreased to background and intensity of $B_2O_3^+$ increased simultaneously. At temperature range 1600–1650 K in mass spectra the Ba^+ and $BaBO_2^+$ ions were detected in the ratio 20 : 100. In temperature range 1600–1750 K the intensity of the $B_2O_3^+$ ion decreased and intensities of Ba^+ and $BaBO_2^+$ increased.

In order to determine the origin of mass spectra ions their appearance energies were measured by the method of vanishing ion current [20]. The obtained appearance energies (AE) are as follows (eV±0.3): 9.6 (Na^+), 9.2 ($NaBO_2^+$), 13.6 ($B_2O_3^+$), 11.7 (Ba^+), 10.7 ($BaBO_2^+$). The AEs of sodium and barium ion is higher than ionization energy of atomic sodium and barium (5.14 and 5.21 eV respectively) hence these are fragment ions and they are formed in processes of the dissociative ionization of sodium and barium borates molecules.

The analysis of mass spectra above the system under study, the dependencies of ion currents intensities on time and temperature and also value of appearance energies allow to conclude that in temperature range 1290–1320 K the vapor consist of $NaBO_2$ molecules only. The AE of $NaBO_2^+$ ion correspond to ionization energy of $NaBO_2$ molecule and AE of Na^+ correspond to dissociative ionization of $NaBO_2$ according to the next scheme (3) [11–13,23,24]

$$NaBO_2 + e^- = Na^+ + BO_2 + 2e^- \tag{3}$$
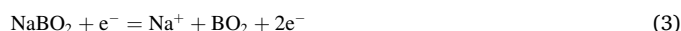
When temperature increased up to 1330–1350 K in the vapor mass spectra above the samples 1–10, 13 and 18–38 additionally $B_2O_3^+$ ion is occurred. This ion corresponds to direct ionization of B_2O_3 molecule because its AE within experimental error is equal to ionization energy of B_2O_3 [23,24]. The nature of Ba^+ and $BaBO_2^+$ was discussed in details in ref. [17]. Both of these ions in temperature range 1600–1750 K are the products of the dissociative ionization of BaB_2O_4 molecule according to the schemes (4) and (5) respectively:

$$BaB_2O_4 + e^- = Ba^+ + 2BO_2 + 2e^- \tag{4}$$

$$BaB_2O_4 + e^- = BaBO_2^+ + BO_2 + 2e^- \tag{5}$$

At the end of experiment when the sample was removed from the cell by increasing temperature up to 1870–1900 K in mass spectra of vapor BaO^+ and BO^+ ions were appearance additionally. The AEs of these ions are equal 7.0 and 13.1 eV. These values within experimental error are equal to ionization energies of BaO and BO molecules [23,24]. Besides the values of AEs of Ba^+ and $BaBO_2^+$ ions decrease down to 5.2 and 5.4 eV respectively. This fact is explained by the appearance of Ba, BO and $BaBO_2$ species in the vapor phase [17].

As it is known [16] sodium oxide is vaporizes with dissociation in form of atomic sodium and molecular oxygen and barium oxide is vaporizes congruently without dissociation. Considering the fact that vapor above the system Na_2O-BaO-B_2O_3 in temperature range 1290–1350 K according to the experimental data described above contains $NaBO_2$, B_2O_3 and BaB_2O_4 molecules only may be concluded that the barium, sodium and boron oxides interact with each other. As the result of this interaction between the base oxides (Na_2O and BaO) and acid oxide (B_2O_3) the ternary system Na_2O-BaO-B_2O_3 transform into the system $NaBO_2$-BaB_2O_4-B_2O_3. The ratio of initial oxides and the compounds which was obtained as the synthesis result is presented in Table 1 and Fig. 4.
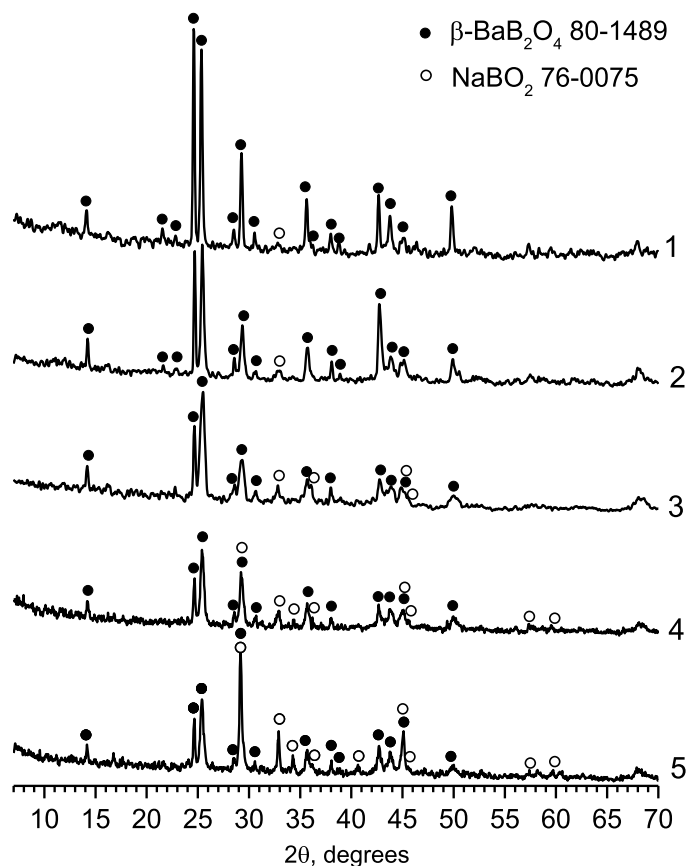

Fig. 1. XRD pattern of the crystallized sample 11 of composition 50Na_2O-50B_2O_3, mol. fr.

Fig. 2. XRD patterns of crystallized samples:
1 - Sample 12 (10Na$_2$O-40BaO-50B$_2$O$_3$), *2* - Sample 14 (20Na$_2$O-30BaO-50B$_2$O$_3$), *3* - Sample 15 (25Na$_2$O-25BaO-50B$_2$O$_3$), *4* - Sample 16 (30Na$_2$O-10BaO-50B$_2$O$_3$), 5 - Sample 17 (40Na$_2$O-10BaO-50B$_2$O$_3$), mol. fr.%.
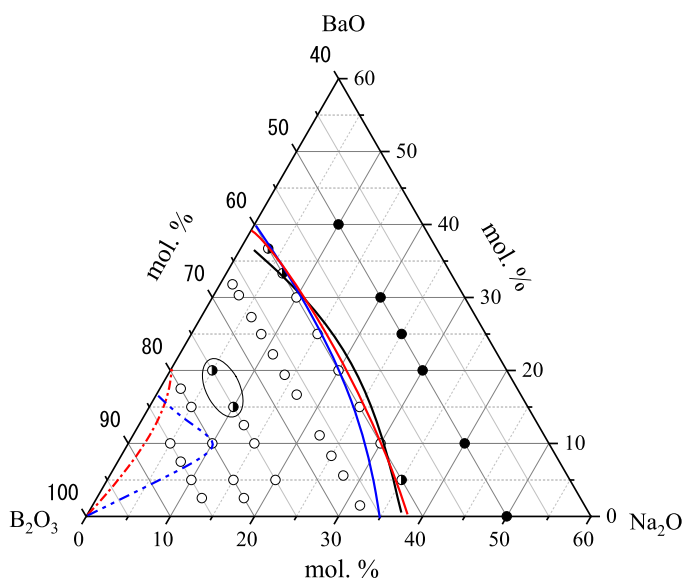

Fig. 3. Glass formation region of the Na$_2$O-BaO-B$_2$O$_3$ system according to the present work (open circles – glass samples, filled circles – crystalline samples, half-filled circle – crystalline samples) and literature data [4,5]. Solid lines are borders of glass formation region. Doted lines are region of liquid-liquid immiscibility. Red and blue color present data of works [4] and [5] respectively.
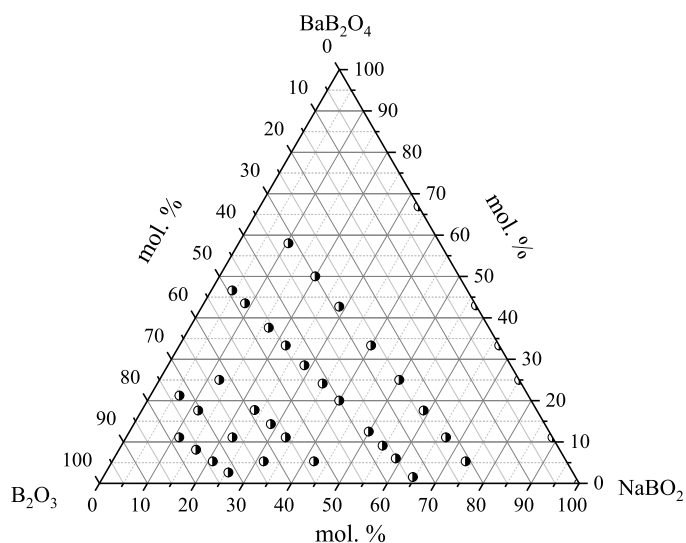
Fig. 4. A graphical plot of the chemical composition of the samples in the ternary NaBO$_2$-BaB$_2$O$_4$-B$_2$O$_3$ system.

The simultaneous presences of the NaBO$_2$ and B$_2$O$_3$ in the vapor phase at the temperature range 1330–1350 K allows to obtain the values of activities of sodium borate and boron oxide in the condensed phase. The activities of NaBO$_2$ and B$_2$O$_3$ were derived according to Eqs. (6) and (7). In one cell of twin Knudsen effusion cell [20] the samples under study was placed. In another cell pure sodium borate or boron oxide was placed alternately.

$$a(NaBO_2) = \frac{p(NaBO_2)}{p^0(NaBO_2)} = \frac{I(NaBO_2^+)}{I^0(NaBO_2^+)} \tag{6}$$

$$a(B_2O_3) = \frac{p(B_2O_3)}{p^0(B_2O_3)} = \frac{I(B_2O_3^+)}{I^0(B_2O_3^+)} \tag{7}$$

$$p = kI^+T \tag{8}$$

Here a is activity of the component in the condensed phase, p and p^0 – partial pressures of vapor species above the sample and the standard respectively, I and I^0 – ion currents intensities in mass spectra of vapor above the sample and the standard respectively.

According to the Eq. (8) [20] the ratio of partial pressures may be substituted by the ratio of corresponding ion currents. The values of the BaB_2O_4 activities cannot be determined by the same way because of low partial pressure of BaB_2O_4 in temperature range 1330–1350 K . These values were calculated by the method of graphical integration of Gibbs-Duhem, Eq. (9). This equation may be written in the next form (10).

$$x(NaBO_2)dln\ a(NaBO_2) + x(B_2O_3)dln\ a(B_2O_3) + x(BaB_2O_4)dln\ a(BaB_2O_4)$$
$$= 0 \tag{9}$$

$$lna(BaB_2O_4) = - \int_{lna^0(BaB_2O_4)}^{lna(BaB_2O_4)} \frac{x(NaBO_2)}{x(BaB_2O_4)}dln\ a(NaBO_2)$$
$$- \int_{lna^0(BaB_2O_4)}^{lna(BaB_2O_4)} \frac{x(B_2O_3)}{x(BaB_2O_4)}dln\ a(B_2O_3) \tag{10}$$

The values of the activities of the components of melt allow to calculate the values of Gibbs energy (ΔG) and excess Gibbs energy (ΔG^E) for $NaBO_2$ – BaB_2O_4 - B_2O_3 system at the temperature 1330 K. All calculations were performed by Eqs. (11) and (12). The obtained data were presented in Table 2.

$$\Delta G = \sum_i x_i RTln\ a_i \tag{11}$$

$$\Delta G^E = \sum_i x_i RTln\frac{a_i}{x_i} \tag{12}$$

The values of the Gibbs energy in the $NaBO_2$-BaB_2O_4-B_2O_3 system at the temperature 1330 K are given in Fig. 5.

The studied glasses of Na_2O-BaO-B_2O_3 system may be divided in two groups by their evaporation character. To the first group the samples 1–10 and 18–38 belong. The samples of this group may be presented as another ternary system $NaBO_2$ – BaB_2O_4 - B_2O_3. The partial pressures of sodium borate and boron oxide do not differ much at the same temperature. This fact allows to obtain the values of activities of $NaBO_2$ and B_2O_3 by experimental method of differential KEMS by Eqs. (6) and (7)

Table 2
Activity values and activity coefficients of components in the $NaBO_2$ – BaB_2O_4 - B_2O_3 system at a temperature of 1330 K, Gibbs mixing energies and excess Gibbs mixing energies depending on the melt composition.

Sample, N	Activity, a_i			Activity coefficient, γ_i			-ΔG, kJ/mol	-ΔG^E, kJ/mol
	$NaBO_2$	B_2O_3	BaB_2O_4	$NaBO_2$	B_2O_3	BaB_2O_4		
1	8.0×10^{-3}	0.42	0.48	0.18	0.85	1.0	10.87	1.55
2	0.02	0.39	0.45	0.23	0.82	1.0	12.51	2.28
3	0.05	0.35	0.39	0.30	0.76	1.0	14.72	3.42
4	0.11	0.31	0.27	0.38	0.72	0.95	16.70	4.77
5	0.15	0.29	0.21	0.42	0.7	0.87	17.17	5.28
6	0.20	0.27	0.14	0.50	0.67	0.70	17.25	5.59
7	0.27	0.25	0.07	0.55	0.66	0.56	16.60	5.82
8	0.33	0.24	0.03	0.60	0.65	0.33	15.91	5.78
9	0.38	0.22	0.01	0.65	0.64	0.17	14.92	5.54
10	0.45	0.21	7.7×10^{-4}	0.70	0.63	0.05	12.76	4.85
11	1.0	0	0	1.0	0	0	–	–
12	1.0	0	1.0	1.0	0	1.0	–	–
13	0.10	0.24	–	0.35	0.42	–	–	–
14	1.0	0	1.0	1.0	0	1.0	–	–
15	1.0	0	1.0	1.0	0	1.0	–	–
16	1.0	0	1.0	1.0	0	1.0	–	–
17	1.0	0	1.0	1.0	0	1.0	–	–
18	0.04	0.60	0.17	0.34	0.85	0.96	11.64	2.76
19	0.12	0.55	0.09	0.54	0.82	0.81	12.57	3.23
20	0.19	0.53	0.02	0.60	0.84	0.37	12.52	3.58
21	0.09	0.15	0.80	0.86	0.47	1.39	11.08	0.67
22	0.16	6.0×10^{-2}	0.45	0.82	0.20	0.90	18.63	6.36
23	0.26	4.5×10^{-2}	0.31	0.91	0.16	0.74	20.61	7.58
24	0.35	3.3×10^{-2}	0.21	0.88	0.12	0.62	21.69	8.52
25	0.47	2.6×10^{-2}	0.10	0.80	0.11	0.54	19.92	8.40
26	0.67	2.1×10^{-2}	1.7×10^{-2}	1.00	0.09	0.16	18.37	8.00
27	0.79	1.7×10^{-2}	2.7×10^{-3}	1.00	0.08	0.05	15.55	7.02
28	0.18	0.28	–	0.81	0.63	–	–	–
29	0.05	0.49	0.17	0.82	0.67	0.80	11.91	3.88
30	0.46	0.22	–	0.92	0.88	–	–	–
31	0.05	0.39	0.23	0.38	0.63	0.91	14.71	4.79
32	0.10	0.36	0.4	0.42	0.61	0.78	14.42	5.95
33	0.16	0.32	5.5×10^{-2}	0.48	0.58	0.50	17.31	6.90
34	0.24	0.26	2.9×10^{-3}	0.57	0.49	6.0×10^{-2}	17.90	8.41
35	0.06	0.55	6.6×10^{-2}	0.54	0.71	0.60	11.93	4.33
36	0.08	0.56	2.9×10^{-2}	0.49	0.74	0.36	12.52	4.70
37	0.09	0.56	9.1×10^{-3}	0.43	0.76	0.17	13.07	5.23
38	0.07	0.57	3.6×10^{-4}	0.27	0.79	1.3×10^{-2}	14.27	6.83
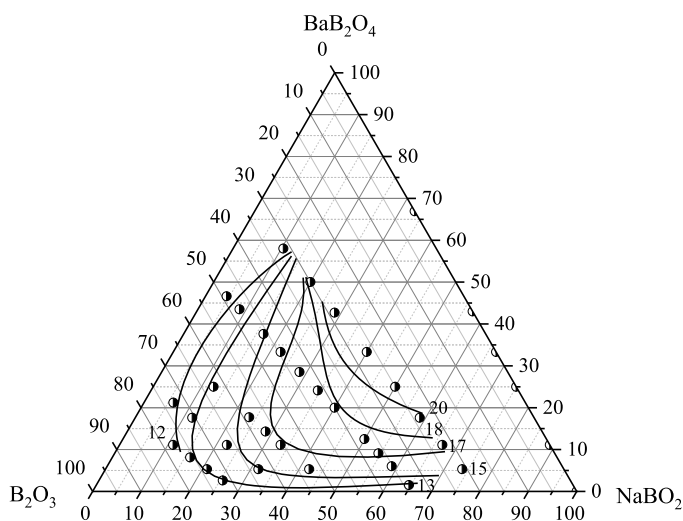
Fig. 5. The absolute values of Gibbs energies (kJ/mol) in the $NaBO_2$-BaB_2O_4-B_2O_3 system at the temperature 1330 K. The lines are drawn through points of equal values of the Gibbs energies.

respectively. According to the phase diagram [19] all samples 1–10 and 18–38 are in homogeneous melt at temperature 1330 K. Hence the activity of barium borate may be calculated by Eq. (10).

The values of activities of all three components in the $NaBO_2$–BaB_2O_4-B_2O_3 ternary system are characterized by the negative deviation from ideal case. The deviation extent increases with decreasing concentration of the respective component in the glass.

To the second group the samples 12, 14–17 belong. In this group the mole fraction of boron oxide is equal 50%. These samples may be presented as the binary system $NaBO_2$ – BaB_2O_4. Partial pressures of the sodium and barium borates differ much at the same temperature. The sodium borate $NaBO_2$ selectively evaporates at temperature range 1250–1400 K and barium borate accumulates in the condensed phase. BaB_2O_4 begin to evaporate from the temperature 1600 K. The big difference in partial pressures of sodium and barium borates gives possibility to obtain pure barium borate by selective evaporation of sodium borate from the binary system $NaBO_2$ – BaB_2O_4. The activity of $NaBO_2$ in samples 12–17 is equal unity, which indicates the presence of individual sodium borate in the glass.

The composition of sample 13 corresponds to ternary compound on phase diagram of the Na_2O-BaO-B_2O_3 system [19]. For this sample the values of activities of sodium borate and boron oxide was determined only. All these values have negative deviation from ideal case.

The views that borate glasses consist of the same base structure groups that crystals were determined on the base of the data obtained by NMR, EPR, X-rays scattering and optical vibration spectroscopy methods [25,26]. The results of the investigation of various borate glasses and crystals showed that interatomic distances in first and second coordination spheres, coordination numbers, the character of chemical bond in glasses and crystals are the same. The data from IR and Raman spectroscopy also show many similarities in specters for crystals and corresponding glasses [27]. This allows to apply conclusions from ref. [28] to other borate glasses. Hence, the structures of borate glasses may be considered as superposition of the various chemical groups similar with ones that exist in the crystal compounds [29]. The results obtained in present work showed that there are no differences in the qualitative and quantitative composition of vapor over crystallized samples or glasses. This agrees with the ideas presented in [25–29].

Obtained data on $NaBO_2$ and B_2O_3 activities may be compared with analogous values, which was determined for Na_2O-B_2O_3 [30], Na_2O-B_2O_3-GeO_2 [31–34] and Na_2O-B_2O_3-SiO_2 [15,35–37] systems. The main difference of these systems from the system under study is that all the systems consists of one base oxide Na_2O and one or two acid oxides. The

Na_2O-BaO-B_2O_3 system consist of two base oxides (Na_2O and BaO) and one acid oxide B_2O_3. When sodium oxide interacts with B_2O_3, GeO_2 or SiO_2 the thermally stable borates, germanates or silicates may be formed. In the Na_2O-BaO-B_2O_3 system thermally stable compounds $NaBO_2$ и BaB_2O_4 [15,17] are formed. All of the aforementioned compounds are formed as the result of interaction of oxides which are different in their acid-base properties.

The thermal stability of the ceramic system in great extent depends on the difference of acid-base properties and volatilities of the constituent oxides [38]. In ref. [39] as quantitative measure of acid-base properties, the value of the average electronegativity of the molecule was proposed. This value is calculated by additivity rule. The electronegativity of atom is electronegativity by Mulliken scale [40] and was taken as half sum of the first ionization energy and electron affinity of the neutral atom. According to this conception the base properties decreases and acid properties increases in the Na_2O (4.3) – BaO (4.80) - B_2O_3 (6.18) - SiO_2 (6.61) - GeO_2(6.63) row. The thermal stability in condensed phase of the sodium borate have to slightly lower than sodium silicate or germanate. Nevertheless, authors of the work [42] state that boron oxide possesses more acid properties than silicon dioxide.

As the prof of this statement may be considered the fact that atomic sodium was not found in the vapor above samples of the Na_2O-B_2O_3-GeO_2 and Na_2O-B_2O_3-SiO_2 systems in which mole fraction of Na_2O is less or equal than mole fraction of B_2O_3. Hence, sodium oxide reacts only with boron oxide to form sodium borate.

Atomic sodium was found in the vapor above Na_2O-B_2O_3-GeO_2 [31–34] and Na_2O-B_2O_3-SiO_2 [15,35–37]. This specie is formed as the result of the sodium silicate or sodium germanate thermal dissociation. Sodium silicate or germanate are present in the condensed phase in the case that $x(Na_2O) > x(B_2O_3)$ in the $NaBO_2$-B_2O_3-GeO_2 or Na_2O-B_2O_3-SiO_2 systems. It was stated that B_2O_3 – GeO_2 [41–43] and B_2O_3 – SiO_2 [42,44–46] binary systems have positive deviation from ideal case. At the same time Na_2O-GeO_2 [47,48] and Na_2O-SiO_2 [49–52] systems are characterized by the negative deviation.

Figs. 6 and 7 shows dependencies of the $NaBO_2$ or B_2O_3 activities vs mole fraction of $NaBO_2$ or B_2O_3 for the Na_2O-B_2O_3, Na_2O-B_2O_3-GeO_2, Na_2O-B_2O_3-SiO_2, Na_2O-BaO-B_2O_3, B_2O_3-GeO_2 and B_2O_3-SiO_2 systems. Ideal case is shown by dotted lines.

In the Na_2O-BaO-B_2O_3 system at any of the Na_2O and BaO concentration ratios sodium and barium borates are formed. The competition of the two base oxides leads to increasing of the $NaBO_2$ activities at the same mole fraction in comparison of the Na_2O-B_2O_3, Na_2O-B_2O_3-GeO_2
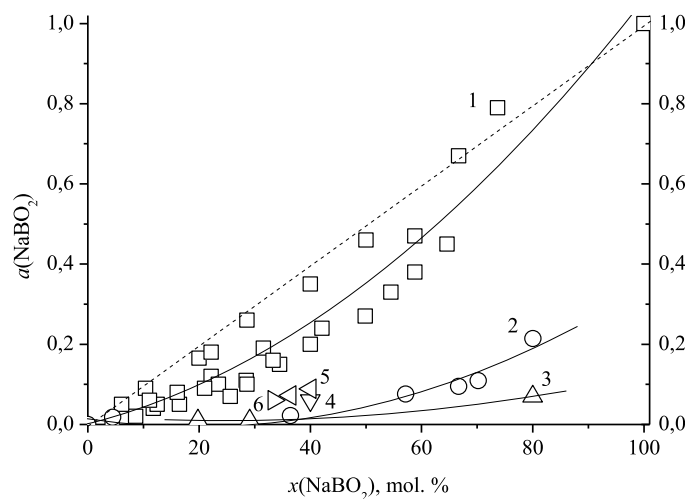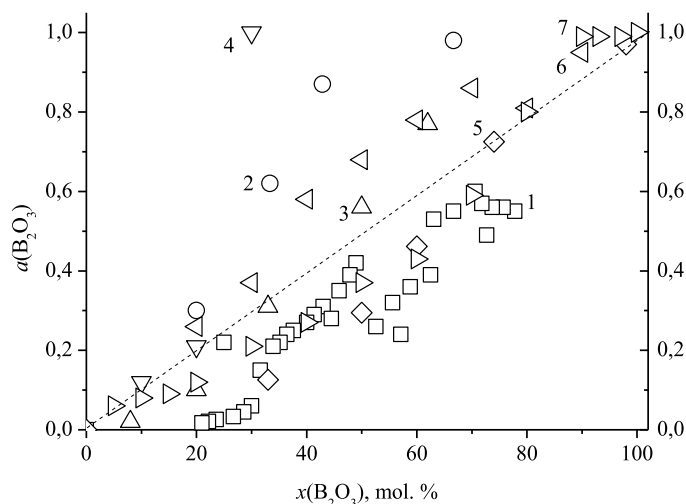

Fig. 6. The dependence of $NaBO_2$ activities vs mole fraction in various systems. 1 - Na_2O-BaO-B_2O_3 (this work), 2 - Na_2O-B_2O_3 [20], 3 - Na_2O-B_2O_3-GeO_2 [31–34], 4 - Na_2O-B_2O_3-SiO_2 [15], 5 - Na_2O-B_2O_3-SiO_2 [35], 6 - Na_2O-B_2O_3-SiO_2 [36].

Fig. 7. The dependence of B_2O_3 activities vs mole fraction in various systems. 1 - Na_2O-BaO-B_2O_3 (this work), 2 - Na_2O-B_2O_3 [20], 3 - Na_2O-B_2O_3-GeO_2 [31–34], 4 - Na_2O-B_2O_3-SiO_2 [15], 5 - Na_2O-B_2O_3 [33], 6 - B_2O_3-GeO_2 [41–43], 7 - B_2O_3-SiO_2 [42,44–46].

and Na_2O-B_2O_3-SiO_2 systems. In turn the substitution of an acid oxide to a base oxide leads to decreasing of the B_2O_3 activity value. So such regularities will be useful in prediction of thermodynamic properties of glass systems with similar nature.

Conclusions

The glass formation region in the system Na_2O-BaO-B_2O_3 has been established. The region of liquid-liquid immiscibility was not found. Inside the glass formation region, the region of the partial crystallization was found with presents of the $NaBaB_9O_{15}$ ($Na_2O \cdot 2BaO \cdot 9B_2O_3$) phase.

The thermodynamic study of Na_2O–BaO–B_2O_3 ternary system was carried out by KEMS method. It was shown that as a result of the interaction of oxides in the condensed phase, sodium and barium borates are formed. It is established that the studied system is characterized by complete selective evaporation of $NaBO_2$ in the temperature range of 1290–1350 K. The activities of $NaBO_2$ and B_2O_3 were determined by differential mass spectrometry at a temperature of 1330 K. Activities of BaB_2O_4 was obtained by the Gibbs-Duhem equation. The values of the activities and activity coefficients of the melt components are determined as well as the calculated values of the Gibbs energies and the excess Gibbs energies indicate significant deviations of the Na_2O–BaO–B_2O_3 system from the ideal behavior. We firstly found that formation of the β-BaB_2O_4 from melts of the Na_2O-BaO-B_2O_3 system going on because of $NaBO_2$ evaporation and not evaporation of Na_2O or other sodium-containing components from the melt. It is confirmed that when heating the samples of the studied system corresponding to the secant 50 mol.%, B_2O_3 the formation of β-BaB_2O_4 is possible.

CRediT authorship contribution statement

S.I. Lopatin: Conceptualization, Methodology, Investigation, Writing – review & editing. **S.M. Shugurov:** Conceptualization, Methodology, Investigation, Writing – review & editing. **Z.G. Tyurnina:** Investigation, Writing – original draft. **N.G. Tyurnina:** Conceptualization, Formal analysis, Writing – review & editing. **I.G. Polyakova:** Investigation, Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

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