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The phase separation phenomenon in the $Na_2O–B_2O_3–SiO_2–Fe_2O_3$ glass-forming system and its application for producing porous glasses

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Glasses in the $Na_2O–B_2O_3–SiO_2–Fe_2O_3$ system with a constant SiO_2 content 70 mol% were synthesized using conventional melting in platinum crucibles in SiC-furnace in air. After synthesis and annealing, glasses were heat treated at 550°C for 96–144 hrs to promote phase separation. A tentative region of phase separation for this temperature was outlined. X-ray powder diffractometry results showed three iron-containing phases (Fe_3O_4, $FeSiO_3$ and β-Fe_2O_3) forming in the investigated glasses with magnetite being the main phase as it is observed in most of the glasses. Chemical durability studies showed that compositions of phase-separated glasses suitable for synthesis of porous glasses, both iron-free and iron-containing lie in between 4 and 8 mol% of Na_2O. Bulk samples of porous glasses were obtained within the chosen region having the following parameters: specific surface area 40–185 m^2/g, porosity 30%–45%, pore diameter 3–14 nm. The parameters of porous structure of iron-containing porous glasses are of the same order of magnitude as the porous glass used for the multiferroic nanocomposite synthesis.

Keywords: $Na_2O–B_2O_3–SiO_2–Fe_2O_3$ glass-forming system, phase separation, crystallization, phase separation diagram, chemical durability, magnetite, leaching, porous glass.

1. Introduction

The phase separation phenomenon in sodium borosilicate (SBS) glass forming system has been known for a long time and is of interest both from a scientific and a practical point of view [1]. The most prominent practical application of SBS glasses is porous glasses (PGs) which are employed as catalyst supports, membranes, adsorbents, Vycor® glass, host matrices for composite materials, *etc*. [1–4]. In the recent years, the main focus of research on SBS glasses was aimed at studying their properties when the SBS system was modified with various additives which provided new useful properties as for phase-separated and for resulting PGs, for instance, electrical properties by introduc-

ing In_2O_3 [5], increased alkali resistance by doping with ZrO_2 [6], the radiation shielding properties by adding BaO [7], magnetic properties by including Fe_2O_3 [8], *etc*. In the latter case, it is possible to obtain magnetite-containing PG by acid leaching the phase-separated glass. Doping this porous magnetic glass with a ferroelectric phase (such as KNO_3 or $NaNO_2$) enables one to create a multiferroic nanocomposite material with simultaneous ferroelectric and ferromagnetic orderings [8–11]. Such multiferroic composites are promising materials for a wide range of applications, such as different kinds of sensors, transducers, actuators or magnetoelectric memory cells. In order to optimize the technique and successfully synthesize PGs with required properties, it is necessary to know the boundaries of immiscibility and formation regions of magnetic phases in the glasses of the Na_2O–B_2O_3–SiO_2–Fe_2O_3 system and also how Fe_2O_3 affects the parameters of the porous structure, which is addressed in this work.

2. Experimental procedure

2.1. Sample preparation and chemical analysis

To synthesize glasses in the Na_2O–B_2O_3–SiO_2–Fe_2O_3 system, the following raw materials were used: Na_2CO_3 of ultra high purity grade (ECROS, Russia), H_3BO_3 (Vekton, Russia) and Fe_2O_3 (LenReactiv, Russia) of reagent grade, and SiO_2 in a form of ground quartz glass (KV-glass, Russian state standard 15130-86, metal impurities $\leq 1 \times 10^{-2}$ wt%, OH groups – from 1.5×10^{-2} to 6×10^{-2} wt%). The silica content in all glasses was fixed at 70 mol%. This SiO_2 content was chosen because it is often used to obtain PGs in the ternary SBS system and also one iron-containing glass in this section was previously used [8, 9] for the successful synthesis of a porous magnetic glass matrix for multiferroic composite material. The Na_2O content was varied from 2 to 14 mol%, B_2O_3 content was varied between 12 and 23 mol%. Ferric oxide in an amount of 0.3 to 10 mol% was introduced either instead of boron or sodium oxide. Glasses were synthesized in platinum crucibles in SiC-furnace using conventional melting at 1500°C for 2–4 h in air with forced stirring of the melt. After synthesis all glasses were annealed in a muffle furnace at 510–560°C for 10 min. After annealing, the glasses were additionally heat treated to initiate phase separation at 550°C for 96–144 hrs in a muffle furnace in air. All glasses were analyzed using analytical chemistry techniques. The SiO_2 content was determined applying the gravimetric method using quinoline–silicon–molybdenum complex (accuracy ±0.08 rel%) [12]. B_2O_3 amount was estimated by means of potentiometry (accuracy ±0.4 rel%) [13]. Sodium and iron content was analyzed by standard techniques (accuracy: Na_2O ±2 rel%, total iron content ± 1 rel%, FeO ±4 rel%) [14–16].

2.2. Experimental techniques

X-ray powder diffractometry (XRD). The crystalline phases in the glasses were identified by XRD on the DRON-3 unit (Scientific Production Association "Burevestnik", Russia), CuKα radiation. Crystalline compounds were identified by the powder diffraction files using the PDF-2 database.

Chemical durability. The chemical durability was studied by leaching polished glass plates with the size of 10 × 10 × 1 mm^3 in aqueous 3 M HCl solution at boiling (overall volume of the solution – 500 ml). To evaluate the leaching rate and the kinetics of components extraction (Na_2O, B_2O_3, SiO_2, Fe_2O_3) from the glass during the acid treatment (for 7 h), the aliquots (15 ml) were taken every hour to measure the concentrations of the components in the leaching solution. The leaching rate was estimated by the experimental value of components quantity Q_{exp}, passed from the glass surface unit S_0 into solution in a definite time. Values of Q_{exp}/S_0 were compared with the theoretically possible ones Q_{calc}/S_0. Parameter Q_{calc} was calculated by multiplying volumetric concentration C_0 (g/cm^3) by the sample volume (cm^3). Concentration C_0 was calculated using the glass composition (in wt%) and the value of density [17] (Table 1). The density was determined by hydrostatic weighing in water at 20°C (±0.005 g/cm^3).

Determination of the glass components concentration in the leaching solution was carried out by the analytical chemistry methods. The content of boron was determined using potentiometry (accuracy ±0.4 rel%) [13], sodium and iron content – using flame atomic absorption spectrometry (accuracy ±2 rel%) [14], and the silicon concentration was evaluated by spectrophotometric measurement (accuracy ±10 rel%) [18]. As a result of a straight – through leaching of investigated phase-separated glasses PGs were obtained. Structure parameters of PGs were examined by BET method (specific surface area SA, m^2/g) and gravimetric method (porosity W, %, pore volume V, cm^3/g). To detect the values of SA of mesopores in the porous glasses, the equilibrium adsorption

T a b l e 1. Composition, density and volumetric concentration of glasses in the 5 and 6 mol% of Na_2O sections.

Glass designation[1)]	Glass composition as-analyzed [wt%][2)]				Volumetric concentration C_0 [g/cm^3]				Density ρ [g/cm^3]
	SiO_2	B_2O_3	Na_2O	Fe_2O_3[3)]	SiO_2	B_2O_3	Na_2O	Fe_2O_3	
	5 mol% of Na_2O section								
5/70-2	67.11	23.53	4.76	4.60	1.50	0.52	0.11	0.10	2.233
5/70-4	64.55	21.31	4.89	9.25	1.48	0.49	0.11	0.21	2.299
5/70-6	62.80	18.95	4.81	13.44	1.49	0.45	0.11	0.32	2.375
	6 mol% of Na_2O section								
6/70-2	67.71	22.38	5.09	4.81	1.53	0.50	0.11	0.11	2.246
6/70-4	64.53	20.40	5.70	9.37	1.51	0.48	0.13	0.22	2.336
6/70-6	65.75	16.45	5.34	12.46	1.57	0.39	0.13	0.30	2.394
6/70-8	61.34	15.61	5.59	17.47	1.51	0.38	0.14	0.43	2.465
6/70-10	59.79	13.33	5.05	21.82	1.52	0.34	0.13	0.55	2.543

[1)] The numbers in the designation correspond first – to the content of sodium oxide, second – through the fraction to silicon oxide, and last – through the hyphen to the content of Fe_2O_3 according to the synthesis, in mol%.
[2)] Unlike glass designation, glass compositions as-analyzed are given in wt% because wt% are required for C_0 calculation.
[3)] In terms of Fe_2O_3.

and desorption isotherms of nitrogen at 77 K [19] were recorded using Sorbtometr-M instrument (KATAKON, Russia) in the range of mesopore filling at capillary condensation. The average pore diameter D was calculated as follows:

$$D = \frac{4}{\mathrm{SA}}\left(\frac{1}{\rho_{\mathrm{app}}} - \frac{1}{\rho_{\mathrm{s}}}\right) \tag{1}$$

where $\rho_s = 2.18$ g/cm^3 is the density of the silica skeleton, $\rho_{app} = P/V$ is the apparent density of the porous glass (g/cm^3), P is the sample weight (g) and V is the sample volume (cm^3) [20]. The calculated results are in a good agreement with the ones obtained from N_2 adsorption.

3. Results and discussion

Studying the phase-separated glasses of this system by transmission electron microscopy (TEM) [21–23] allowed outlining the tentative immiscibility region (within the studied range of compositions) for 70 mol% of SiO_2 section for 550°C (Fig. 1). According to XRD results, there are several iron-containing crystalline phases forming in these glasses during heat treatment. After identifying Fe_3O_4 (39-1346) and β-Fe_2O_3

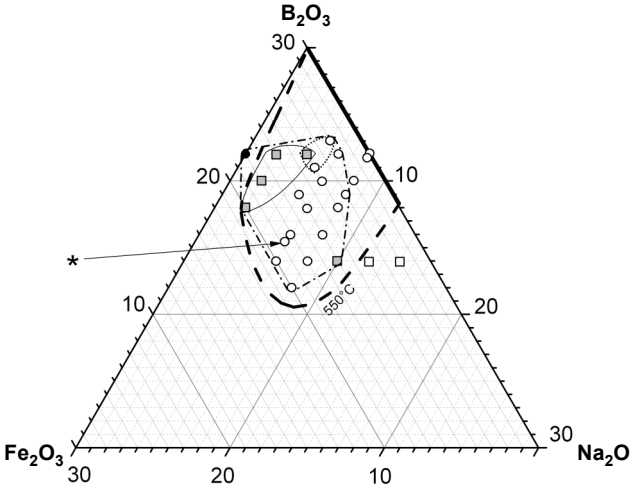

Fig. 1. Region of immiscibility and crystalline phases' formation in the Na_2O–B_2O_3–SiO_2–Fe_2O_3 system for 70 mol% of SiO_2 section for 550°C. The asterix corresponds to the glass composition from [9, 10] which was successfully used for obtaining a porous magnetic glass matrix for multiferroic composite material. Dashed line marks tentative immiscibility region in this system; bold line marks the immiscibility region in the SBS system; dash-dot line indicates the area of magnetite formation; thin solid line marks the area of $FeSiO_3$ formation; short-dot line shows the area of β-Fe_2O_3 formation; white circles mark the glass compositions with the inter-connected phase-separated structure; grey squares correspond to glasses with droplet-matrix type of phase-separated structure; white squares mark the singe phase glasses and black circle marks the glass composition where the fusion of charge components was not complete at given temperature.

(39-238) there was still a group of peaks which corresponded well with the data in the card No. 76-1638 which was attributed to $FeSiO_3$. Ferrosilite ($FeSiO_3$) is the end member of the pyroxene series and known as a high-pressure phase [24]. However, $FeSiO_3$ which was found in the investigated glasses was a silicate with anorthite (triclinic) structural type (unlike ferrosilite), and it was not attributed to the minerals in the file, so the identification of this phase is to be debated and further investigated, which is beyond the scope of this work. The regions of the existence of these crystalline phases on the diagram are adjacent to the iron–boron silica side of the tetrahedron (Fig. 1). Glass compositions with low Fe_2O_3 content adjacent to the sodium–boron silica side of the tetrahedron are amorphous. The glass compositions with inter-connected structure required for obtaining PGs lie between 4 and 10 mol% of Na_2O. Hence these glasses were chosen for further chemical durability investigation (Table 1).

The results of chemical durability studies of the glasses in 8 mol% of Na_2O section were previously published elsewhere [17]. It was determined that introducing Fe_2O_3 does not change the general nature of the diffusion controlled leaching process, as evidenced by the linear character of the dependences ($h = f(t^{1/2})$, where h is the leached layer thickness and t is time), but reduces the leaching rate of these glasses in 3 M HCl solution. The only compositions suitable for obtaining PGs contain up to 4 mol% of Fe_2O_3. Na_2O, B_2O_3 and Fe_2O_3 in those glasses are fully extracted into the leaching solution. Fe_2O_3 is present in the obtained PGs only in hundredths of a percent. Those PGs have the following parameters: SA = 125–202 m^2/g, W = 0.35–0.39 cm^3/cm^3, D = 4–6 nm. As the concentration of Fe_2O_3 increases, the Na_2O and B_2O_3 extraction slows down and fully stops at the maximum content of iron used in the study (10 mol%), which makes those compositions unsuitable for producing PGs.

Kinetics behavior in the Na_2O sections of 5 and 6 mol% is similar to the 8 mol% one in terms of linear character of the dependences, but different in terms of the amount of component extraction. Sodium ion exchange process in SBS glasses occurs to be the fastest during leaching. Thus the leaching rate of the PG can be characterized through the sodium extraction kinetics [25]. It is shown (Table 2) that the Na_2O extraction reaches more than 90% for most of the glasses in these sections, which means the leaching process is complete and PGs are obtained. The dependence of B_2O_3 extraction is similar to the sodium extraction but experimental values are lower, due to the fact that boron

T a b l e 2. Glass components extraction (in percentage) for the Na_2O sections 5, 6 and 8 mol% depending on the Fe_2O_3 concentration (mol% as synthesized).

	Na_2O			B_2O_3			SiO_2			Fe_2O_3		
Fe_2O_3	Na_2O											
	5	6	8	5	6	8	5	6	8	5	6	8
2	96	97	100	81	87	90	6	3	9	95	99	98
4	97	93	57	83	91	86	4	6	5	96	99	86
6	90	98	50	80	98	52	4	6	4	54	98	38
8	–	90	17	–	85	5	–	6	0.7	–	44	11
10	–	71	3	–	69	6	–	7	0.9	–	64	2

T a b l e 3. Porous glasses structural parameters.

Fe_2O_3	V [cm^3/g]			W [%]			SA [m^2/g]			D [nm]		
	Na_2O											
	5	6	8	5	6	8	5	6	8	5	6	8
2	0.30	0.31	0.26	39	40	36	43	52	179	11	14	4
4	0.27	0.36	0.25	37	44	35	82	101	184	8	8	5
6	0.27	0.31	0.20	37	40	30	65	134	60	7	5	3
8	–	0.26	0.11	–	36	19	–	125	5	–	4	–
10	–	0.33	–	–	43	–	–	106	–	–	4	–

can be partially located in silica-rich phase or due to its reprecipitation in the pores. Component release rate dependences ($Q = f(t^{1/2})$) for Na_2O, B_2O_3 and Fe_2O_3 were linear up until the values of Q_{exp}/S_0 reached the plateau close to Q_{calc}/S_0. As expected, silicon practically does not get extracted from the glass while leaching in acid because it forms a silica framework. At low Fe_2O_3 concentration iron's yield into the leaching solution is more than 95%, but after reaching 8 and 6 mol% (for 6 and 5 mol% sections of Na_2O, respectively) the extraction of Fe_2O_3 is reduced by half. According to chemical analysis these PGs have the following compositions: 5/70-6 glass ($0.52Na_2O$ $–5.77B_2O_3–89.86SiO_2–3.01Fe_2O_3–0.84FeO$) and 6/70-8 glass ($0.47Na_2O–3.74B_2O_3$ $–89.46SiO_2–5.13Fe_2O_3–1.20FeO$). Considering the fact that the components of the soluble phase (Na and B) are fully retrieved from PGs and through-leaching process is complete, it can be assumed these iron oxides remaining in the glass are located in the silica phase. The presence of both Fe_2O_3 and FeO in PGs enables the crystallization of magnetite. So the glasses in the Na_2O sections of 5 and 6 mol% with high Fe_2O_3 content compared to 8 mol% of Na_2O section are prone to leaching with the iron-containing PG as a result, while the 8 mol% section glasses are not.

The values of porosity and pore volume (Table 3) differ only within the experimental error for all the obtained PGs. The SA values increase as the sodium oxide content in the phase-separated glass increases within the same Fe_2O_3 content. The porous structure parameters of glasses containing iron oxides after leaching are of the same order of magnitude as the glass which was used in [9, 10] for obtaining a porous magnetic glass matrix for multiferroic composite material.

4. Conclusions

Phase separation and chemical durability of glasses in the $Na_2O–B_2O_3–SiO_2–Fe_2O_3$ system with a constant SiO_2 content 70 mol% were studied. A tentative region of phase separation and areas of crystallization of iron-containing phases (Fe_3O_4, $FeSiO_3$ and β-Fe_2O_3) for 550°C were outlined. Magnetite is the main crystalline phase forming in these glasses. Chemical durability investigation showed which glass compositions are suitable for synthesis of porous glasses, both iron-free and iron-containing. Bulk samples of porous glasses were obtained within the chosen region having the following parameters: SA = 40–185 m^2/g, W = 30%–45%, D = 3–14 nm. The parameters of po-

rous structure of iron-containing porous glasses are of the same order of magnitude as the porous glass used for the multiferroic nanocomposite synthesis.

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