

Leaching of phase-separated glasses in the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2-\text{Fe}_2\text{O}_3$ system

M. Konon, T. Antropova, T. Kostyreva, I. Drozdova, I. Polyakova

Institute of Silicate Chemistry, Russian Academy of Sciences (ISC RAS)

Makarova emb. 2, Saint-Petersburg, 199034 Russia

E-mail: marina-konon@mail.ru

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The leaching behavior of heat-treated phase-separated iron-containing sodium borosilicate glasses within the range of compositions of $8\text{Na}_2\text{O} \cdot (22-x)\text{B}_2\text{O}_3 \cdot 70\text{SiO}_2 \cdot x\text{Fe}_2\text{O}_3$, where x varies from 0.3 to 10 mol.%, and $(8-x)\text{Na}_2\text{O} \cdot 22\text{B}_2\text{O}_3 \cdot 70\text{SiO}_2 \cdot x\text{Fe}_2\text{O}_3$, where x varies from 2 to 6 mol.%, in the 3M aqueous HCl solution at boiling, was studied. It has been shown that the introduction of Fe_2O_3 in these phase-separated glasses increases their chemical durability, the values of porosity and the average pore diameter, but reduces the specific surface area in the porous glasses based on them, compared with glass without Fe_2O_3 . The compositions suitable for producing porous glasses were determined.

Key words: $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2-\text{Fe}_2\text{O}_3$ system, phase-separated glasses, chemical durability, magnetite.

Introduction

It is well known that porous glasses (PGs) derived from glass forming sodium borosilicate (SBS) system are widely used as materials for various purposes [1–3]. Filling the pore space of the PG with different dopants allows one to create composites with new useful properties. Imparting new unique properties to the composites is possible not only by impregnating the PG but also by modifying the matrix itself.

For example, to produce new composite materials with multiferroic properties (combining both the electric and the magnetic components [4, 5]) it is required that the matrix itself would already possess magnetic properties before the introduction of a ferroelectric dopant into it. Such materials can be used as a nonvolatile memory elements and/or durable recording media with a high stability and reliability of the operation (FeRAM, FLESH-memory). To create these matrices, phase-separated glasses of the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2-\text{Fe}_2\text{O}_3$ system can be used, in which ferric oxide was introduced into the charge at the initial stage of glass melting [6]. The following leaching allows to extract components of the chemically unstable phase [7]. At the same time, the presence of iron in the form of magnetite (Fe_3O_4) gives magnetic properties to the resulting porous matrix [8, 9].

The successful obtaining of a surviving porous matrix directly depends on the structure and chemical stability of the initial phase-separated glass. In this connection, it is necessary to systematically study the effect of Fe_2O_3 on phase separation and leaching behavior in the four-component $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2-\text{Fe}_2\text{O}_3$ system depending on the content of Fe_2O_3 and Na_2O , which is addressed in this work.

Materials and methods

In this work, two series of iron-containing SBS glasses were studied: 1) $8\text{Na}_2\text{O} \cdot (22-x)\text{B}_2\text{O}_3 \cdot 70\text{SiO}_2 \cdot x\text{Fe}_2\text{O}_3$, where x varies from 0.3 to 10 mol.% and 2) $(8-x)\text{Na}_2\text{O} \cdot 22\text{B}_2\text{O}_3 \cdot 70\text{SiO}_2 \cdot x\text{Fe}_2\text{O}_3$, where x varies from 2 to 6 mol.%, synthesized using the conventional glass-melting method [10]. The initial components of the charge were Na_2CO_3 of ultra high purity grade, H_3BO_3 and Fe_2O_3 of reagent grade, and SiO_2 in the form of ground quartz glass. The samples were synthesized in platinum crucible with a volume of 300 ml in a silit (silicon carbide) furnace with forced stirring of the melt at 1500–1540 °C in air for 2–4 h depending on the composition. After pouring the glass melt onto a metal plate, the obtained glass was annealed in a muffle furnace at 520–550 °C for several minutes and then cooled to room temperature (20 °C) in the furnace during 6–7 hours.

To obtain the phase-separated structure, the initial (after the synthesis) glasses were heat-treated at 550 °C for 144 hours.

The compositions of glasses, density, and volumetric concentration of the components are shown in Table 1. The density (ρ) of phase-separated glasses was determined by hydrostatic weighing in water, the measurement error $\pm 0.005 \text{ g/cm}^3$.

The chemical analysis of initial glasses (Table 1) was performed according to the standard techniques [11]. The crystalline phases in the glasses were identified by X-ray powder diffractometry (XRPD) on the DRON-2.0 unit, $\text{CuK}\alpha$ – radiation. Electron microscopic studies in the transmission mode (TEM) were carried out on the EM-125 (JSC SELMI) device at an accelerating voltage of 75 kV (resolution $\sim 10 \text{ nm}$).

In this paper, the kinetics of leaching of phase-separated glasses in a 3 M HCl solution at boiling was studied. The growth rate of the leached layer thickness (h) was measured on polished plate-shaped glass samples with the dimensions

of 10×10×3 mm, using an optical microscope MIN-8. The kinetics of extraction of the Na₂O, B₂O₃, SiO₂, Fe₂O₃ components from glasses was examined using polished plates with the size of 10×10×1 mm.

The concentration of glass components in the leaching solution was determined by standard procedures [7]. The leaching rate was estimated by the experimental value of components (Q_{exp}) passed from the glass surface unit (S_0) into the solution in a definite time. The (Q_{exp}/S_0) values were compared with the theoretically possible ones (Q_{calc}/S_0) which were calculated on the basis of the glass composition (in wt.%, not presented in the paper) and the value of ρ [9].

As a result of a straight-through leaching of the investigated phase-separated glasses, PGs were obtained. The structure parameters of the PGs were examined by the

BET method from nitrogen equilibrium adsorption and desorption isotherms at 77 K (specific surface area SA), and by the gravimetric method (porosity W). The average pore diameters D were calculated from the equation:

$$D = (4/SA) \cdot (1/\rho_{app} - 1/\rho_s),$$

here $\rho_s = 2.18 \text{ g/cm}^3$ 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) [12].

The obtained results were compared with the leaching kinetics of iron-free glass with the composition (as synthesized, mol.%) 8 Na₂O, 22 B₂O₃, 70 SiO₂ according to [13] (hereinafter we are going to use the designation 8/70).

Table 1. Composition, density and volumetric concentration of glasses under study (double column)

Designation of glass*	Glass composition as-analyzed, mol.%				Volumetric concentration C_0 , g/cm ³				Density ρ , g/cm ³
	SiO ₂	B ₂ O ₃	Na ₂ O	Fe ₂ O ₃ total	SiO ₂	B ₂ O ₃	Na ₂ O	Fe ₂ O ₃ total	
Series 1									
8/70-0.3	71.86	20.59	7.17	0.38	1.558	0.518	0.160	0.021	2.258
8/70-2	71.69	19.33	7.08	1.90	1.543	0.482	0.157	0.109	2.291
8/70-3	71.29	18.44	7.11	3.16	1.539	0.461	0.158	0.181	2.340
8/70-4	71.63	17.25	7.35	3.77	1.557	0.435	0.165	0.218	2.375
8/70-6	70.91	15.89	7.22	5.98	1.547	0.402	0.162	0.347	2.458
8/70-8	70.80	14.11	7.38	7.71	1.545	0.357	0.166	0.447	2.516
8/70-10	70.59	12.15	7.24	10.02	1.538	0.307	0.165	0.580	2.588
Series 2									
22/70-2	72.22	20.59	5.26	1.93	1.527	0.505	0.115	0.108	2.246
22/70-4	71.83	20.51	3.72	3.94	1.531	0.329	0.080	0.219	2.288
22/70-6	70.51	21.72	1.86	5.91	1.444	0.515	0.039	0.321	2.320

*The numbers in the designation correspond first: in Series 1 – to the content of sodium oxide, in Series 2 – to boron oxide, the second through the fraction – to silicon oxide, and the last through the hyphen to the content of Fe₂O₃ according to the synthesis (mol.%).

Results and discussion

The results of dilatometric measurements along with the XRD and TEM data for the 1st series of glasses are described in [10]. It was shown that over the entire range of selected compositions the interconnected phase-separated structure with crystalline inclusions of Fe₃O₄ is formed during heat treatment at 550 °C for 144 h. Magnetite starts to form in the glass containing 3 mol.% of Fe₂O₃. The content of magnetite increases with the further increasing of the amount of iron (III) oxide added to the initial charge. Because of the interconnected structure, all glasses of this series have been subjected to leaching. The previously unpublished electron-microscopic photographs of the 1st series of glasses and the glass 22/70-2 from the 2nd series are shown in Fig. 1.

In the 2nd series of glasses, according to TEM, glass 22/70-2 with 6 mol.% of Na₂O (Fig. 1, *b*) has an

interconnected phase-separated structure with the diameter of liquation channels 45–65 nm. However, with decreasing the Na₂O content and with increasing the Fe₂O₃ content, respectively, the structure tends to change from interconnected to a droplet-matrix one (glass 22/70-6). Glass 22/70-4 is intermediate as the droplets of the boron-rich phase in it are somewhat connected. According to XRD, even at a low content of Fe₂O₃ (2 mol.%) a small amount of magnetite starts to form during the heat treatment at 550 °C for 144 hours. With an equal content of Na₂O and Fe₂O₃ of 4 mol.% in addition to magnetite, the crystalline compounds of β -Fe₂O₃ and FeSiO₃ (iron metasilicate) are formed. In the glass 22/70-6, magnetite and FeSiO₃ are the only iron-containing crystalline phases [14]. Due to the structural features of these glasses, we chose two compositions with 2 and 4 mol.% of Fe₂O₃ for the subsequent leaching.

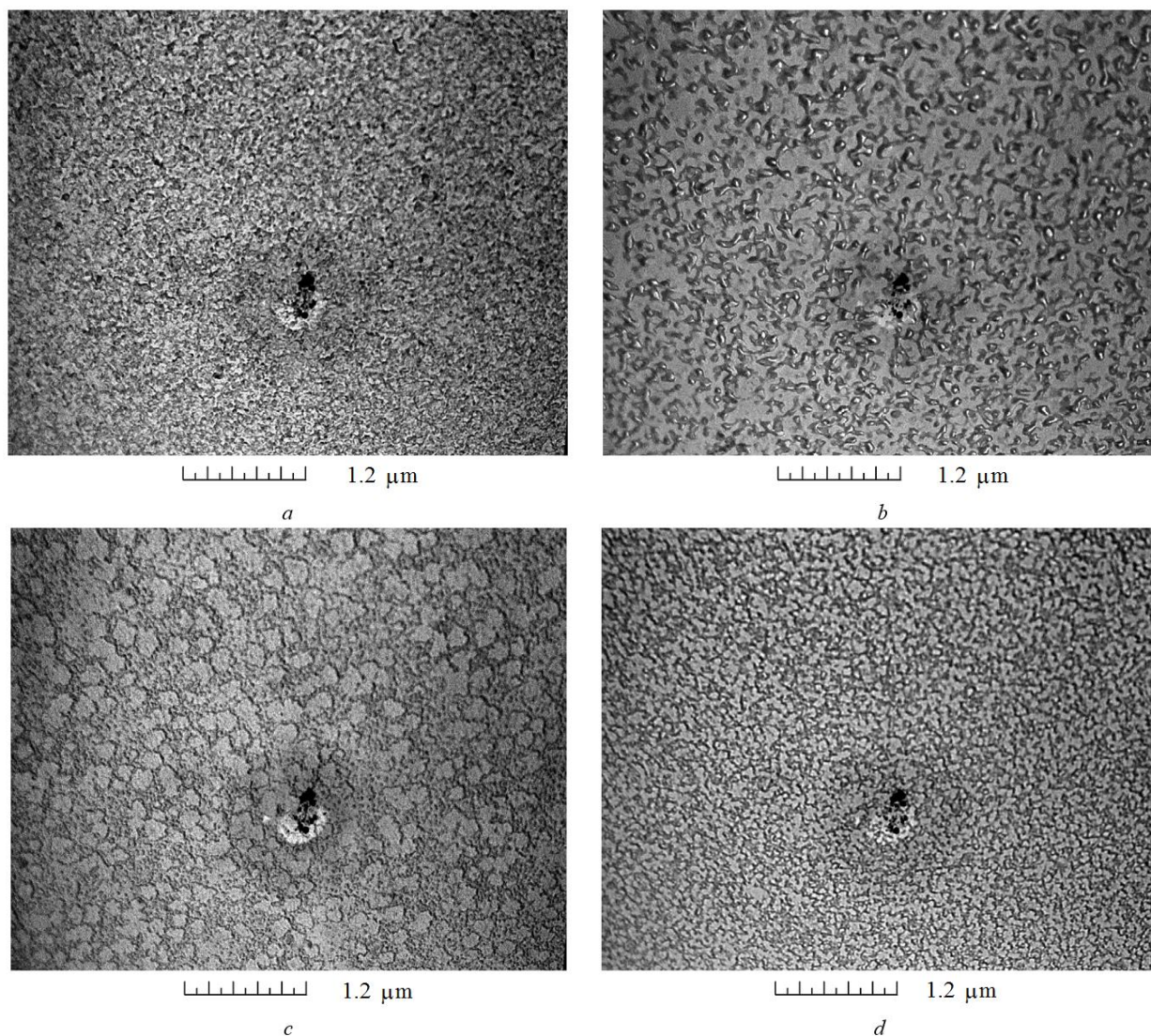


Fig. 1. TEM photographs for phase-separated glasses after heat treatment: a) 8/70-2, b) 22/70-2, c) 8/70-6, d) 8/70-10.

As one can see from Fig. 2, the addition of Fe_2O_3 to SBS glasses does not change the general nature of the diffusion-leaching process as evidenced by the linear character of the dependences. In some cases, the curves do not pass through the origin but cross the abscissa axis. This kind of dependences is characteristic of the interdiffusion process enhanced by the glass network hydrolysis [11]. The visual determination of h in the glasses 8/70-8 and 8/70-10 has been hampered by an intense coloration caused by the high iron content. For the glass 22/70-4, the visual determination of h (not shown in Fig. 2) was difficult due to chips and fractions appearing in the sample during leaching. After 4 hours of subjecting the sample to the acid solution, the inner tensions caused the glass sample destruction.

Within the glasses with the same Fe_2O_3 content of 2 mol.%, the glass 22/70-2 with a lower content of Na_2O is characterized by a higher leaching rate (Fig. 2). It can be calculated from Fig. 2 that for a straight-through leaching of the glass layer of 0.5 mm it takes 1.8 h for the glass 22/70-2, while for the composition 8/70-2 the time of 2 h is required. It is known that the rate of the interaction process of glass with acid is determined not by the size of the phase formations but by the composition of the unstable phase.

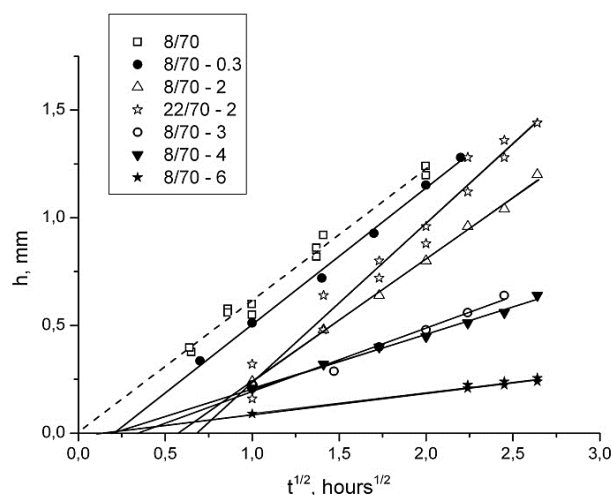


Fig. 2. Kinetic dependences of porous layer thickness in the phase-separated glasses leached in 3M HCl solution at boiling. The values for the glass 8/70 are given according to [15].

Thus, even though the size of liquation channels for the glass 22/70-2 is twice as great as for the glass 8/70-2 (20–

33 nm) (Fig. 1), the amount of Na₂O introduced in the initial charge of the glass 22/70–2 was less than in the glass 8/70–2, which means that the compositions of the unstable boron-rich phases in these glasses would be different even with the same amount of Fe₂O₃. Also, one should take into account that the pore diameter in the glass 22/70–2 (Table 2) is 3 times larger than in the PGs obtained from the glass 8/70–2, which possibly could simplify the leaching process [15].

Considering the fact that the sodium ion exchange process occurs to be the fastest during leaching, the leaching rate of the porous glass can be characterized through the sodium extraction kinetics [15]. The dependencies of boron and iron (III) oxides extraction of these glasses are similar to the sodium extraction kinetic curves (Fig. 3).

All components of the unstable boron-rich phase (Na₂O and B₂O₃) in the glasses of the 1st series containing up to 4 mol.% of Fe₂O₃ are fully extracted into the leaching solution along with Fe₂O₃, which means that in these compositions all iron, including the crystalline formations, exists in an unstable phase. Fe₂O₃ is present in the obtained PGs only in the form of impurities (hundredths of a percent, Table 2). Figure 3 shows that for the glass 8/70–6 the curves of Na₂O extraction have not reached the plateau for the selected time of leaching. The samples retain their geometric shape without destruction. Perhaps the taken time of leaching is not enough to obtain a porous glass with through porosity. The value of SA (60.1 m²/g) (Table 2) apparently corresponds to the SA of the pores in the surface layer of a glass sample since the through porosity has not been reached. The further increase of the iron (III) oxide content in the glasses leads to a decrease of components extraction which completely stops at the Fe₂O₃ content of 10 mol.% (Fig. 3); thus, glasses 8/70–8 and 8/70–10 are not suitable for producing PGs, at least at the selected acid concentration.

The silica, which is the basis of chemically resistant glass framework, hardly transfers from the glass sample to the leaching solution: the amount of SiO₂ in it is less than 10 %.

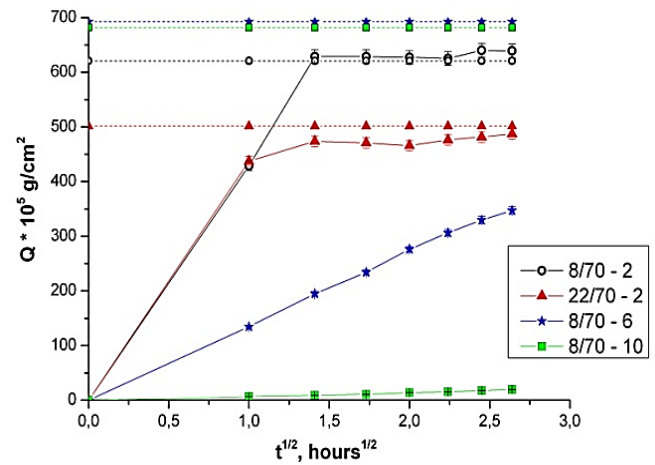


Fig. 3. The kinetics of Na₂O extraction from glass samples. Q_{exp}/S_0 values – solid lines, Q_{calc}/S_0 values – dashed lines.

In general, the presented data show the following regularity: with increasing the Fe₂O₃ content in glasses, the extraction of alkali borate components and Fe₂O₃ decreases.

Table 2 shows that, compared with the glass 8/70, the introduction of even a small addition of Fe₂O₃ (0.3 mol.%) results in the increase of porosity nearly 1.5 times and of the pore diameter approximately 2–3 times, but leads to a reduction of the specific surface area around 2 times. Among PGs derived from iron-containing glasses, the composition 8/70–3 has the highest proportion of Fe₂O₃ remaining in the pores, the most developed SA and the maximum porosity. For the glasses containing 6–10 mol.% of Fe₂O₃, the values of SA and W can be attributed to the surface porous layer as no PGs with through porosity could be obtained.

In the glasses containing the same amount of Fe₂O₃ (2 mol.%) (8/70–2 and 22/70–2) in the initial phase-separated glass, the composition with a lower Na₂O content forms the PG with a 3 times smaller SA and a 3 times greater pore diameter, maintaining the same value of porosity.

Table 2. The parameters of the obtained porous glasses

Designation of initial phase-separated glass	Porous glass composition as-analyzed, mol.%				ρ_{app} , g/cm ³	Parameters of porous structure		
	SiO ₂	B ₂ O ₃	Na ₂ O	Fe ₂ O ₃ total		SA, m ² /g	W, cm ³ /cm ³	D, nm
8/70*	95.53	4.22	0.25	-	-	260.0	0.26	1.7
8/70–0.3	96.61	3.18	0.21	-	1.5469	124.5	0.35	6.1
8/70–2	96.57	3.18	0.24	0.01	1.4865	174.5	0.36	4.5
8/70–3	91.96	7.68	0.30	0.05	1.5398	201.8	0.39	4.3
8/70–4	96.91	2.84	0.24	0.01	1.4735	183.7	0.35	4.6
8/70–6	77.49	10.09	8.49	3.93	1.9849	60.1	0.29	3.0
8/70–8	73.00	12.99	6.40	7.60	2.4214	4.9	0.19	-
8/70–10	70.32	12.28	7.54	9.86	2.5067	-	0.18	-
22/70–2	93.15	6.52	0.32	0.01	1.5517	51.9	0.39	14

*Data according to [12].

Despite the fact that the results of leaching kinetics indicate that iron in the glass 22/70–2 fully transfers into the HCl solution and according to chemical analysis Fe₂O₃

exists in PGs in the form of impurities, the appearance of the PG sample shows that Fe₂O₃ remains in the glass, giving it an even color (Fig. 4). The rest of the leached glasses were

either transparent or opaque without brown coloring. It could be presumed that the iron ions are present either in the glass matrix or in secondary silica formations [16].

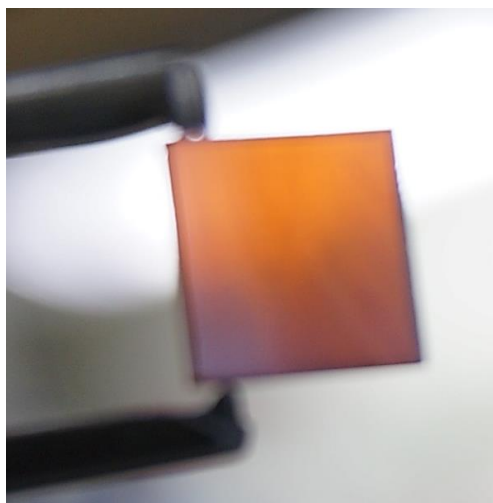


Fig. 4. Sample of a PG obtained from the glass 22/70–2 via leaching in 3M aqueous HCl solution for 7 hours.

Conclusions

The results of this study have shown that the introduction of Fe_2O_3 in the initial phase-separated glasses in the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2-\text{Fe}_2\text{O}_3$ system increases their chemical resistance, the values of porosity and the average pore diameter, but reduces the specific surface area in the porous glasses based on them, compared with the glass without Fe_2O_3 (8/70). The following compositions are amenable to the through-leaching, resulting in PGs formation: the glasses in the section of 8 mol.% of Na_2O containing 0.3 to 4 mol.% of Fe_2O_3 according to synthesis and Fe_2O_3 stays in PGs as an impurity. Also, the glass containing 6 mol.% of Na_2O and 2 mol.% of Fe_2O_3 is suitable for producing PG. The sample has an even brown color after leaching, indicating the existence of iron ions in the glass.

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I. Polyakova

NEVIENALYČIO STIKLO ĖSDINIMAS $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-$
 $\text{SiO}_2-\text{Fe}_2\text{O}_3$ SISTEMOJE

S a n t r a u k a

Tirta, kaip vyksta nevienalyčio ir termiškai apdoroto natrio boro silikatinio stiklo, į kurio sudėtį įeina geležis, ėsdinimas rūgštimi. Stiklo bandiniai, kurių sudėtis $8\text{Na}_2\text{O} \cdot (22 - x)\text{B}_2\text{O}_3 \cdot 70\text{SiO}_2 \cdot x\text{Fe}_2\text{O}_3$ ir x svyruoja nuo 0,3 iki 10 mol %, $(8 - x)\text{Na}_2\text{O} \cdot 22\text{B}_2\text{O}_3 \cdot 70\text{SiO}_2 \cdot x\text{Fe}_2\text{O}_3$ ir x svyruoja nuo 2 iki 6 mol %, buvo verdami 3M HCl koncentracijos vandeniniame tirpale. Nustatyta, kad Fe_2O_3 priedas padidina šio nevienalyčio stiklo cheminį stabilumą, poringumą ir vidutinį akučių skersmenį, tačiau sumažina savitąjį porėto stiklo paviršiaus plotą, palyginti su stiklu, kuriame nėra Fe_2O_3 priedo. Buvo ištirtos stiklo kompozicijos, kurios gali būti naudojamos norint pagaminti akytąjį stiklą.

Reikšminiai žodžiai: $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2-\text{Fe}_2\text{O}_3$ sistema, atskirų fazių stiklas, cheminis stabilumas, magnetitas.