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Features of the structure of phase-separated and porous borosilicate glasses with/without an impurity of fluorid-ions according to electron microscopy

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The comparative research of the structure of the phase-separated glasses of sodium borosilicate system with/without the additives of fluorides and phosphorus oxide, as well as of the porous glasses received from the two-phase glasses were carried out with the help of the methods of electronic microscopy and X-ray phase analysis. It was founded out the distinctions of phase morphology of the two-phase glasses which contain or not a fluorine and phosphorus. Inside the phase-separated glasses with the additives, the microcrystalline formations which are kept inside the porous glasses were detected. An assumption was made that the revealed structure features of the porous glasses can be the reasons for observable differences of their optical properties, namely a light transmittance in the visible region.

Keywords: phase-separated glass, porous borosilicate glass, structure, electron microscopy, micro crystallization, light transmittance.

1. Introduction

Products of leaching of the phase-separated alkali borosilicate glasses – so-called porous glasses (PGs) – with certain parameters of the pore structure and properties are the perspective basic matrixes for the creation of the microoptical devices (MOD) [1], and also the functional elements in the microanalytical devices [2].

Among the glass forming systems suitable for manufacturing of such PGs, by sodium borosilicate (SBS) system with additives of fluorine and phosphorus oxide awakes some interest. Their introduction into the initial SBS glass lowers the activation energy of volumetric diffusion in a course of spinodal decomposition, thus strengthens the process of phase separation, and it also promotes a shift of its borders in the low-silica region [3, 4]. Thus, practically all the amount of fluorine passes in boron rich chemically unstable phase due to the formation of the oxy-fluoride structural

$Na^+[F^- BO_{3/2}]$ groupings [5], and the silica content in this phase essentially goes down in comparison with the basic SBS glass. The presence of fluorides in the two-phase SBS glass suppresses the sedimentation of the secondary silica inside the porous space during the glass leaching [6]. It allows to receive the PGs with bigger radius values and smaller sizes of a specific surface area of the pores. In some cases it promotes a decrease of a bursting of the leached samples and it also accelerates an extraction of secondary silica in the course of alkaline treatment of PG for creation the so-called macroporous glasses [7]. Thus, a viscosity of PG's silica skeleton is significantly reduced [8], which promotes an optimization of the modes of MOD controlled synthesis [9]. Application of PGs in the creation of sensitive elements of the bio/chemo-sensors assumes a use of the spectral methods of detecting. A study of the PGs received from the two-phase SBS glasses with/without the above-mentioned additives, has shown the essential distinctions of their optical properties [10] which cannot be explained taking into account only the parameters of the pores.

Present work is devoted to the electron microscopic study of the structure features of the SBS phase-separated and porous glasses which contain small amounts of fluorine and phosphorus oxide for the purpose of bringing to light a possible reason for the difference in transmittance between these glasses and PGs without such additives.

2. Technique

We investigated the plates of two-phase SBS glasses 8B and NFF and the porous glasses received by leaching them in 4M HCl solutions (PG-8B and PG-NFF correspondingly) by electron microscopy (EM). The glasses contain approximately 70 mol% SiO_2 and molar ratio $B_2O_3/Na_2O \approx 3$. In the NFF glass the additives of P_2O_5 and $|F|$ average 0.2 and 0.5 mol% correspondingly. The information about the as-analyzed compositions of the porous glasses and the parameters of their porous structure obtained by the porosimetry methods are presented/discussed in [11].

The transmission electron microscopy (TEM) study of the glasses was realized via electronic microscope EM-125 at an accelerating voltage 75 kV with the resolution in 5 Å. To study the two-phase glasses, a method of platinum-carbon replica [12], which had been prepared from freshly cleaved surface etched in 2% solution HF or in 2% solution HCl at room temperature during 5–7 seconds, was used. For studying the PGs we used the well-known method of cellulose-carbon replica from a fresh chip surface in the plane perpendicular to the larger faces of the PG samples [8, 11]. Since the replicas brought out the relief of the PG fracture surfaces quite distinctly, no additional surface treatment was needed.

The micro crystalline formations inside the roentgenoamorphous PG samples were investigated by the method of selected area electron diffraction (SAED) [13]. The object of the SAED study was one drop of the ethanol suspension of glass powder which was put on a collodion support. An X-ray analysis of all glasses was previously executed on DRON-3 device with monochromatic Cu Kα-radiation.

The light transmittance coefficient τ values of the PG plates were measured with SF-26 and Specord UV VIS spectrophotometers. Measurements were carried out concerning a corresponding two-phase glass, which allowed to eliminate the influence of scattering on the liquation channels.

3. Experimental results and discussion

Our previous research showed that the samples of two-phase glass 8B and PG-8B are roentgenoamorphous [14, 15]. Yet, it was established by SAED method that alongside with an amorphous phase there are the traces of the micro crystalline phase identified as *i*) α-quartz that is connected to the partial crystallization of secondary silica (in PGs with abnormal light scattering) and *ii*) boron acid (in PGs with Rayleigh scattering). In contrast to this, results of the X-ray analysis of two-phase glass NFF evidence for the presence of crystalline α-quartz (ICPDS, no. 33-116) (Fig. 1**a**). But the PG-NFF samples are roentgenoamorphous (Fig. 1**b**) just as the glass PG-8B.

Figure 2 presents TEM photographs of the two-phase glasses 8B (**a**) and NFF (**b** and **c**). Because of a sufficiently large magnification one can observe the features of the phase structure. It can be seen that both glasses under study possess a liquation structure with the interpenetrating phases (Figs. 2**a** and 2**b**). Their parameters are given in the Table. However, on the micrographs of NFF glass we can see one more phase, whose relative volume is approximately 7–10%. The more contrasted image of chemical unstable boron-rich phase with the surviving silica skeleton which was

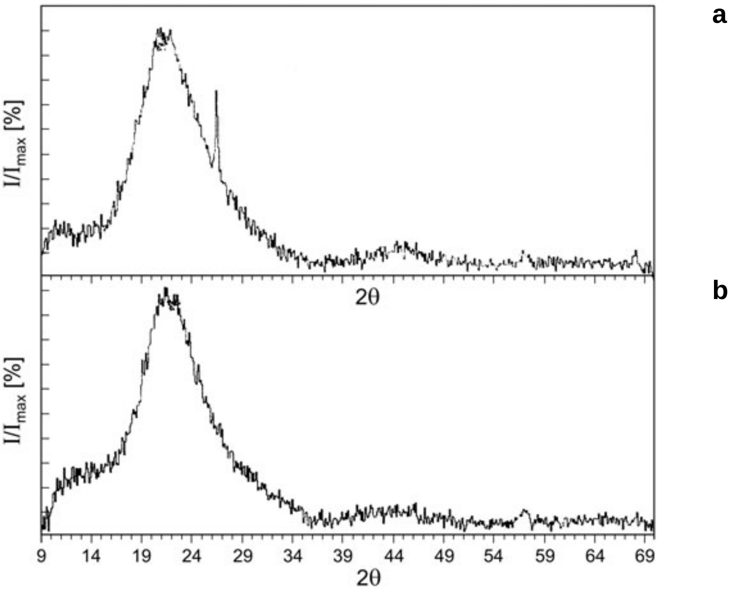

Fig. 1. Difractograms of the initial two-phase glass NFF (**a**) and porous glass PG-NFF (**b**); I/I_{max} – relative intensity, 2θ – Bragg's angle (grad).

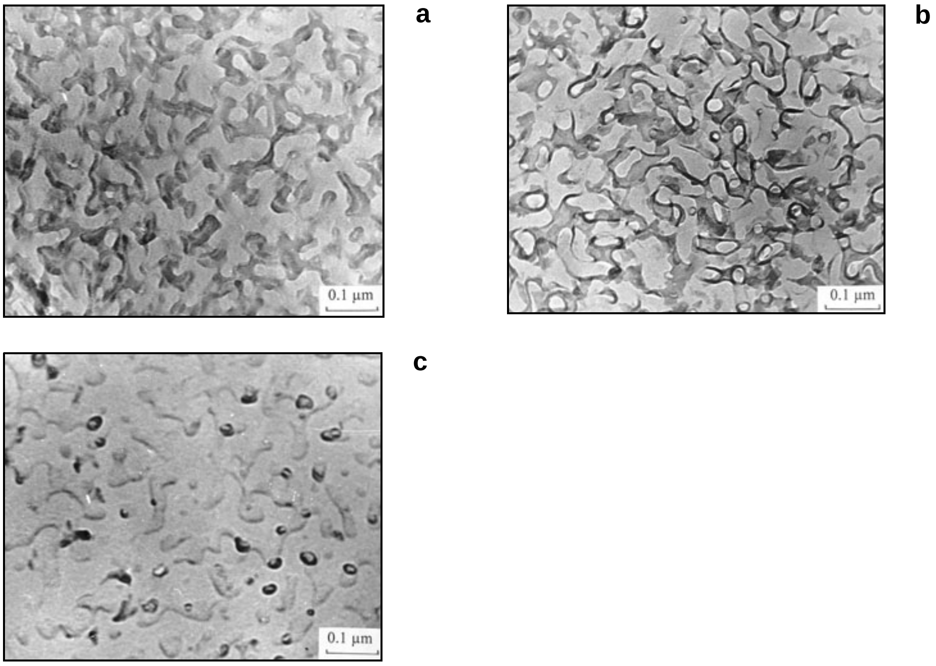

Fig. 2. Transmission electron micrographs of the initial two-phase 8B (**a**) and NFF (**b**, **c**) glasses. Etching solution: HF (**a**, **b**), HCl (**c**).

obtained at etching of glass surface chip in HCl solution (Fig. 2**c**), allows to specify the presence and the kind of the additional phase. This is a micro crystalline phase with the dimensions of crystals approximately 12–25 nm. For its identification additional research, in particular with the help of the small angle X-ray scattering method, is required. Nevertheless, it is possible to assume that the complex composition of this microcrystalline phase includes the diverse products of crystallization of both silica (silicate melt) and the phosphate- and fluoride-containing compounds. The yielding of crystal is typical for fluorine and phosphate glasses [16, 17]. In particular, the fluorides-ions are characterized by small solubility in the silicate melts and they considerably lower the superficial tension of SBS glass that causes allocation of the fluorine-containing compounds as crystals.

Figure 3 demonstrates the TEM photographs of the porous glasses PG-8B and PG-NFF. It should be noted that in both cases the matrix of high silica phase is porous one with the dimension of the closed pores ~(5–8) nm. But relative part of this matrix in PG-NFF glass is larger than in PG-8B glass.

The feebly marked orientation of the through macro pores which are densely packed by the secondary silica globules by diameter of 5–8 nm is observed in PG-8B (Fig. 3**a**). These globules are built in linear chains. The central chained structure is denser and is better defined in comparison with the lateral ones which are formed by the globules of the smaller size [18]. The same globules of secondary silica are also

T a b l e. The structure parameters of the two-phase glasses and porous glasses on the data of transmission electron microscopy study.

Two-phase glass	Glass thermal treatment T/t [°C/hrs]	Parameters of the boron-rich phase		Porous glass	Diameter of the macropores [nm]
		Relatively volume [%]	Diameter of the liquation channels [nm]		
8B	550/144	45–50	25–40	PG-8B	30–35
NFF	550/142	40–45	20–25	PG-NFF	25–30

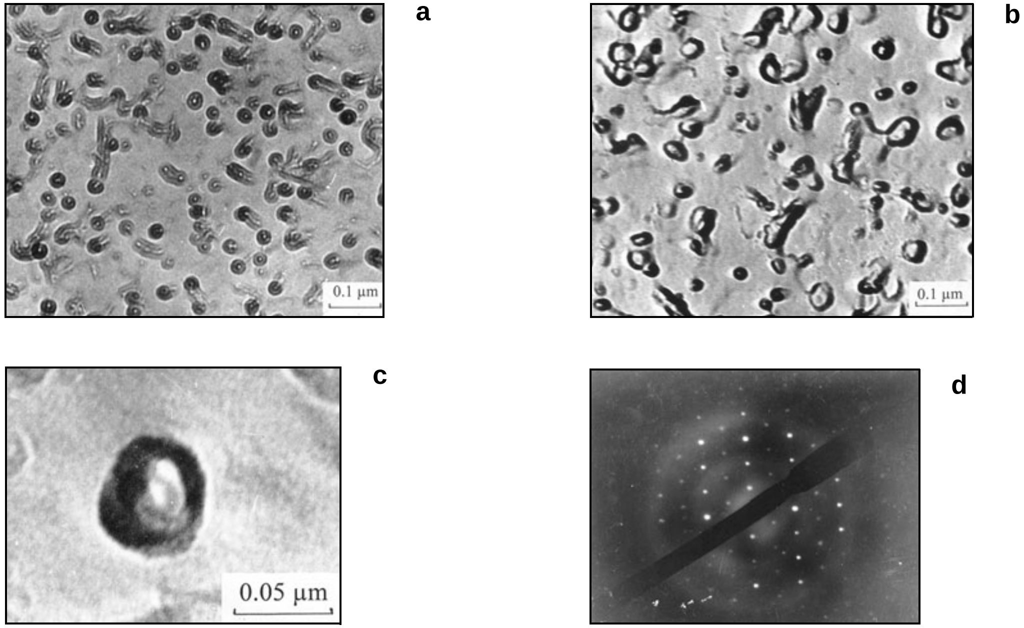

Fig. 3. Transmission electron micrographs of the porous PG-8B (**a**) and PG-NFF (**b**, **c**) glasses; fragment of porous structure with micro crystalline phase (**c**); electron diffraction pattern of PG-NFF glass powder (**d**).

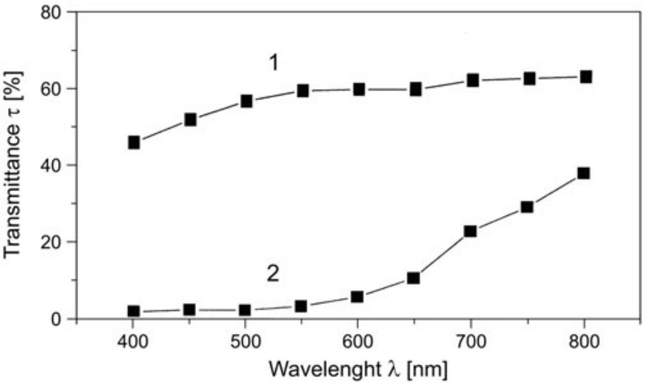

Fig. 4. Transmission spectrum of 3 mm polished porous glass plates PG-8B (1) and PG-NFF (2). The size of points corresponds to an absolute error of a measurement.

present inside the macro pore space of PG-NFF glass (Fig. 3**b**). But they are absent on the pore walls. In this case, besides the macro pores which are formed by the liquation channels of boron-rich phase exempted at two-glass leaching, one more kind of pores is observed. These are the pores of 35–65 nm in diameter with some micro crystals of 25–50 nm in diameter inside them. A fragment of such structure is given in Fig. 3**c**. It is possible to notice the faceting of these crystals and the presence of silica particles on their surface.

The electron-diffraction pattern of the powder particles of the roentgenoamorphous PG-NFF glass (Fig. 3**d**) confirms the presence of the same crystalline phase α-quartz (ICPDS, no. 33-116) as in the two-phase glass NFF. However, this method did not allow to identify correctly the micro crystals in glass (an example of which is given in Fig. 3**c**) because of smallness of their sizes, the sparseness and small amount of them, as well as because of multicomponent composition of the researched glass. On the basis of the literary data [16, 17, 19] it is possible to assume that such compounds as, for example, sodium ortho-fluoride and Na_2SiF_6 can be present at the revealed microcrystalline phase.

Comparison of the data submitted in Figs. 2**b**, 2**c** and Fig. 3**b** shows that the dimensions of these pores and the micro crystals conformably inside the PG-NFF samples exceed the same in the two-phase NFF glass. We suppose that these facts can result from the hypothetical possibility that fluorine-containing microcrystalline compounds are formed mainly inside the boron-rich phase. At the contact of the two-phase SBS glass with the leaching solution the alkali borate components are eliminated from the liquation channels. If on the way of leaching front, there is a microcrystalline inclusion, which is hard soluble in leaching solution, the arising diffusion difficulties most likely cause an accumulation of dissolved alkali borate components in this place, which results in a local increase of the solution pH [20]. At that moment/stage the processes of supersaturation of the solution and precipitation of hard soluble products, including crystal ones, occur. Apparently, due to that the size of present microcrystalline formation can increase. In turn, an alkalization of solution can cause a partial dissolution of the walls of high silica matrix that is an observable widening of the macro pores.

So, accordingly to EM study the plates of porous glass PG-NFF contain the microcrystalline inhomogeneities which have not been revealed in PG-8B glass. It is quite probable that exactly their presence causes other character of light transmittance of the PG-NFF plates in comparison with PG-8B samples (see, for example, Fig. 4 and [10]) as the parameters of such scatterers what are the pores and the secondary silica particles not strongly differ in both PGs. The observable changes of the spectral dependences of transmission coefficient can be caused by a formation of not only scattering but also the absorbing structures in PG-NFF [10]. It is possible to assume that, taking into account both their small sizes and little amount in glass, the above mentioned microcrystalline formations can act in the role of those.

4. Summary

The features of the structure of the phase-separated SBS glasses and the products of their acid leaching (the porous glasses) with/without the small additives of fluorides and phosphorus oxide were investigated by electron microscopy methods and X-ray analysis.

It was discovered that the presence of these additives is accompanied by a formation of crystalline α-quartz (ICPDS, no. 33-116) in the two-phase glass and causes a formation of an additional microcrystalline phase, in composition of which such compounds as sodium ortho-fluoride and Na_2SiF_6 can be included.

The assumption is stated that these microcrystalline inclusions can cause a light absorption that results in small values of transmission coefficient of the porous glass.

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