

Application of high resolution microscopy and optical spectroscopy for study of phase separation in phosphorus- and fluorine-containing sodium borosilicate glasses

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The kinetics of phase separation in glass-forming $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2-\text{P}_2\text{O}_5-|\text{F}|$ system and structure parameters of the two-phase glasses have been investigated by transmission electron microscopy (TEM) and optical spectroscopy methods. The TEM images were analyzed with the help of specially designed software for the purpose of determination of the relative volume and size of the phases. An influence of duration of a glass heat treatment on the parameters of their structure was investigated at a temperature of 550 °C which is necessary for prompting a two-network structure and is most frequently used for manufacturing porous glasses. The time of glass heat treatment necessary for achieving phase equilibrium was established. A deviation of the phase inhomogeneity growth rate from theoretical one was determined. It was revealed that a certain third phase, the composition of which can include α -quartz, is formed in glass during the heat treatment. Fluorescence of the two-phase glass which has been subjected to heat treatment for a long time can be caused by the presence of this phase.

Keywords: alkali borosilicate glasses, phase separation, transmission electron microscopy, optical spectroscopy.

1. Introduction

Phosphorus- and fluorine-containing (PF) glasses are of interest for various technological applications due to a combination of the useful qualities inherent in fluorine and metaphosphate glasses [1–9]. In particular, the PF-glasses are characterized by unique optical and laser properties, that, alongside with high chemical stability and big opportunities on introduction of the alkaline-earth and rare-earth

elements into a glass matrix, makes them by perspective material for the decision of the applied tasks of optoelectronics. Successful application of PF-glasses is promoted by their technological properties (a good glass-forming ability, the high thermal expansion coefficients, a low viscosity) which have a positive effect in industrial production of the glass, shown in the lowering of a liquidus temperature and temperature of glass melting.

The important direction is practical use of PF-glasses for creation of the porous glasses (PGs). Even small additives of fluorine and phosphorus in the glasses of sodium borosilicate (SBS) system significantly influence the process of phase separation during their heat treatment [5, 6], which ultimately determines the course of acid leaching of two-phase glasses and structural parameters of PGs [10]. Using the two-phase fluorine- and phosphorus-containing SBS glasses in some cases helps to reduce cracking of the leached samples [6]. This accelerates the process of alkaline etching of the microporous [11] glasses during manufacture of the macroporous [11] glasses, and facilitates the process of obtaining PGs with bigger pore radiuses [7, 8]. The last circumstance is extremely important because the functional elements from macroporous glasses are promising for use as electroosmotic pumps in microfluidic analytical systems [12–14]. With proper conduct of alkaline etching of the microporous glass a silica skeleton structure of the macroporous glass obtained corresponds to the phase structure of the initial two-phase glass.

To optimize the structural parameters of PGs the directional choice of the initial glass composition and its heat treatment regime are necessary to regulate the structure of the coexisting phases in two-phase glass. The most important condition for solving this problem is the availability of information about the structure of two-phase glass and PGs.

A comparative study of the structure of the phase-separated SBS glasses with and without additives of fluorides and phosphorus oxide has been initiated by us through the use of electronic microscopy and X-ray phase analysis methods [15]. There were found out the distinctions of phase morphology of the two-phase glasses which either contain or not a fluorine and phosphorus additives. Since the purpose of the research was to identify the influence of the initial glass composition on the morphology of two-phase glasses, the experiments were conducted under condition of only one regime of the thermal treatment of glass. At the same time, the processes of phase separation in the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2-\text{P}_2\text{O}_5-|\text{F}|$ (NaBSiPF) system have been little studied, making it difficult to directionally select the regimes of heat treatment of the initial glasses for future manufacture of the macroporous glasses with the predicted structure of a pore space.

This governs the statement of this work, which is aimed at studying the effect of temperature and duration of heat treatment of the NaBSiPF-glasses (in comparison with the base SBS-glass [10, 15, 16]) on structure of coexisting phases in the phase-separated glasses with high resolution microscopy and optical spectroscopy methods.

2. Technique

The objects of investigation were the samples of NaBSiPF-glass (see the Table). The initial glasses were clarified at temperature $T = 810$ °C for 15 min, were roughly annealed to room temperature at a rate of 100 °C/min, and then heat treated at temperature $T_{\text{ht}} = 550$ °C during a time $t_{\text{ht}} = 0.5\text{--}500$ hrs, or at 700 °C during 1–6 hrs. The choice of such T_{ht} values is caused by the fact of using them in practice for production of the two-phase glasses suitable for manufacture of PGs.

Table. The compositions, density $\rho_{\text{H}_2\text{O}}^{20}$ and glass transition temperature T_g values of the glasses under investigation.

Glass	Initial glass composition as-analyzed [mol%]						$\rho_{\text{H}_2\text{O}}^{20}$ [g/sm ³]	t_{ht} at 550 °C [hrs]	T_g [°C]*
	Na ₂ O	B ₂ O ₃	SiO ₂	Al ₂ O ₃	P ₂ O ₅	F			
NaBSi	7.6	20.4	71.9	0.1	–	–	2.262 [17]	140	495 [17]
NaBSiPF	6.8	22.1	70.4	–	0.2	0.5	2.200 [17]		468 [19]
									454 [18]
								140	458 [19]
									449 [18]
							500	450 [18]	

*Dilatometer measurements in a mode of heating a sample at a speed of 3 °C/min [17, 18], or 7 °C/min [19].

The transmission electron microscopy (TEM) study of the two-phase glasses was performed via electronic microscope EM-125 at an accelerating voltage 75 kV with the resolution at 5 Å. A well-known method of platinum–carbon replica [15] prepared from freshly cleaved surface etched in 5% solution HF at room temperature during 5–7 seconds has been used.

An analysis of TEM images including calculation of relative volume and the sizes of co-existing phases in a glass was carried out with the help of special software [20, 21], which had been developed in MatLab system. In these programs the histograms of analyzed grey images are used [5]. To estimate a relative volume of boron-rich phase (V) the cross-section of areas selected on the appropriate image of glass structure is made. An approach for the choice of rules for a section (in the center span of the histogram, the peak of the histogram, the half-width at half-height, *etc.*) depends on the morphology of the phases. To smooth the origin image the filtering operation was carried out.

X-ray analysis of all glasses was previously executed on DRON-3 device with monochromatic CuK α -radiation.

The transmission spectra of the two-phase glass samples were measured on Hitachi U-3410 spectrophotometer in the wavelength range of 250–850 nm with a step of

10 nm. Fluorescence spectra of the samples were measured on Hitachi F4010 spectrofluorimeter, within the spectral range from 220 to 800 nm, with the speed of scanning of the spectrum of 120 nm/min and spectral width of the slit of 2 nm.

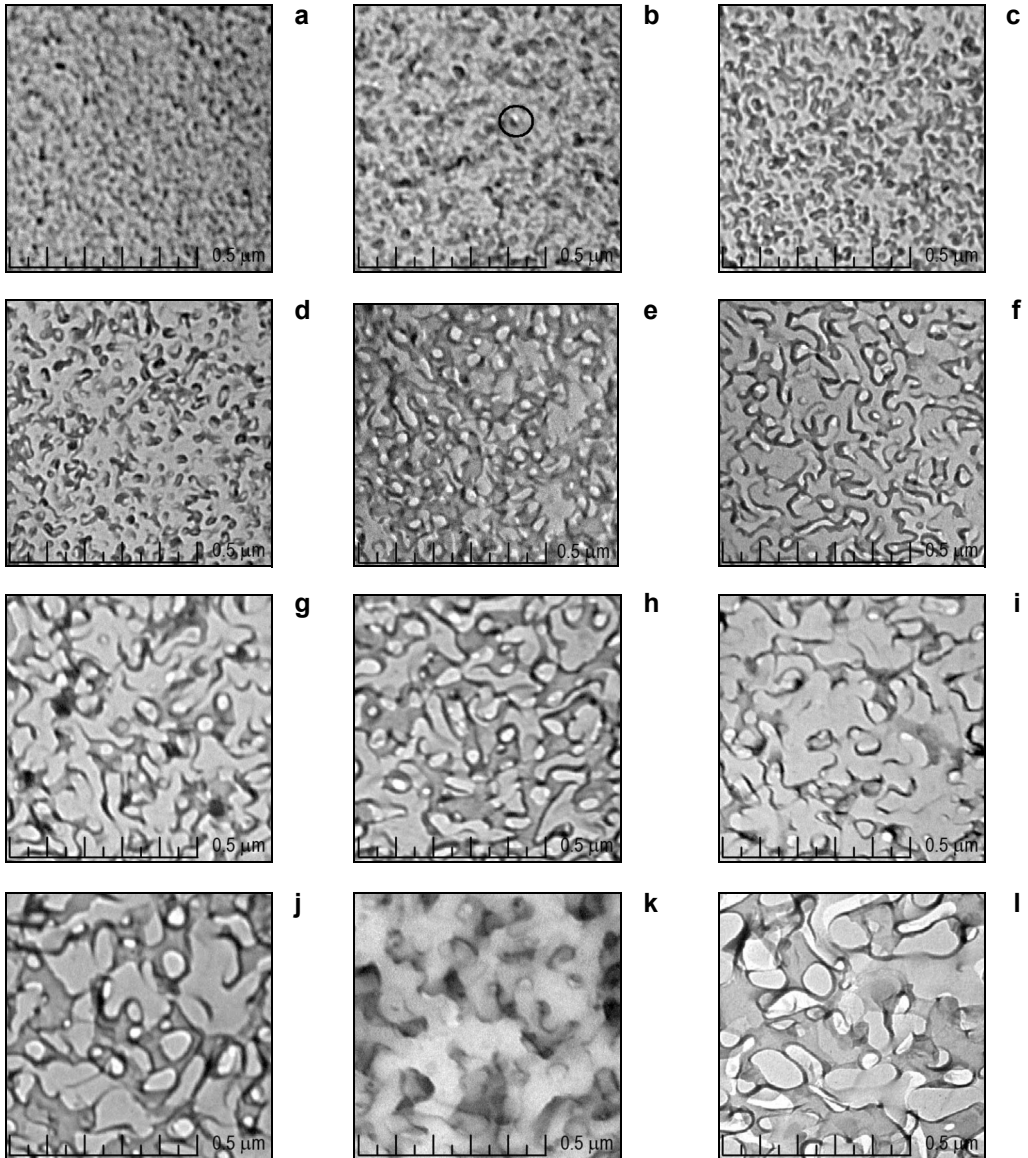


Fig. 1. TEM images of the NaBSiPF-glass: after annealing (a) as well after heat treatment at 550 °C (b–k) and 700 °C (l). Heat treatment time t_{ht} : 1 hrs – b, 6 hrs – l, 10 hrs – c, 40 hrs – d, 65 hrs – e, 90 hrs – f, 198 hrs – g, 240 hrs – h, 344 hrs – i, 500 hrs – j, k.

3. Experimental results and discussion

It is possible to obtain some notions about the course of the glass phase separation process on TEM images on which there are precise phase borders between the sites of the various structures [22, chapter 5]. This can be readily done under the circumstances where a nucleation mechanism takes place and there is a distribution of one phase drops inside a matrix of another phase. In the case of a drop-matrix structure it is possible to estimate the relative volume V values and the size (average radius R) of co-existing phases on TEM images. The TEM data can be used for the description of glass phase separation kinetics [22, pp. 29–34]. According to the Lifshitz–Slyozov theory (see review in [22], Chapter 2), the growth of the radius of the germs formed of the second phase is proportional to a root square of time of heat treatment, and to a root cubic of time for the over-condensation stage. The parameter α , determined on a tangent of an angle of inclination of dependences $R = f(t_{\text{ht}})$ in logarithmical coordinates, is accordingly equal to 1/2 and 1/3. In the first case the size α is characteristic of diffusion on an inter-phase surface, in the second case, it is characteristic of the growth controllable by volumetric diffusion; for diffusion through an interface $\alpha = 1/4$ [23]. However, in our case, as is apparent from Fig. 1, on which TEM images of the glasses investigated are submitted, the structure variant described is not characteristic even at small values t_{ht} . At the same time, it is known that the laws described according to the Lifshitz–Slyozov theory are carried out for qualitatively similar structures in base SBS system [24, 25]. Results of our estimation of the phase parameters in the two-phase glasses on their TEM images are presented in Figs. 2–4.

According to the results obtained, formation of a micro-heterogeneous structure in the glass-forming NaBSiPF system occurs already during the cooling of glass melt (Fig. 1a). It is probable that at this stage a heterogeneity of glass structure is caused mainly by the occurrence of composition fluctuations, namely by formation of the high-polymerized silica-oxygen anionic groupings constructed from structural units Q_3 and Q_4 [26], the depolymerized ortho-phosphate PO_4^{3-} structural groupings [9] and oxyfluoride polar $[BO_{3/2}F]^-$ ones [27, 28], and also the germs of a new phase (for example, $[BO_{4/2}Me]$ structural complexes, compatible with $SiO_{4/2}$ [22, pp. 24–28]). These fluctuations result in formation of the areas strongly distinguished on composition from an initial melt at the following heat treatment of glass [22, pp. 28–45].

It is visible from Fig. 1 that at early stages of phase separation up to $t_{\text{ht}} < 10$ hrs the areas of heterogeneity have a drop-channel form with the least average diameter of the liquation channels $D_{\text{channel}} \sim 15$ nm (Fig. 2a, dependence 1). Already at $t_{\text{ht}} = 1–2$ hrs an origin of the third phase* (Fig. 1b) is observed. At $t_{\text{ht}} = 10–40$ hrs there

*The formations which have the expressed boundaries with the neighboring areas and an occurrence of which is not connected with three-phase immiscibility in glass forming systems [20, pp. 20–24, 158–161] are had in mind.

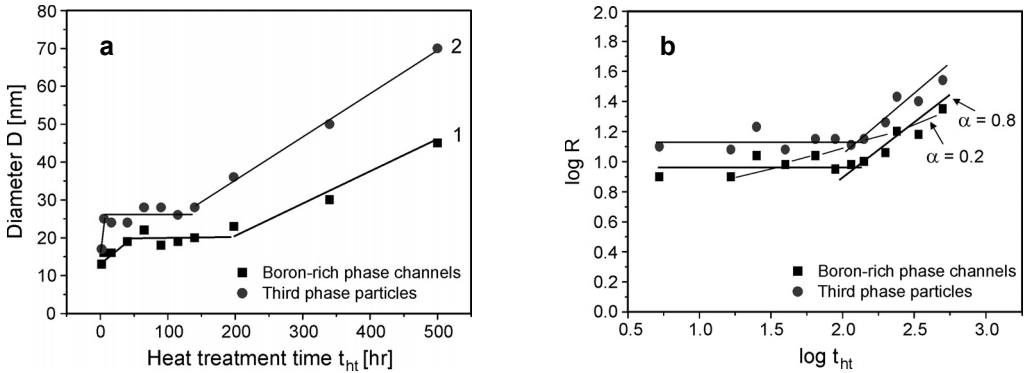


Fig. 2. Dependences of the phase inhomogeneity diameters D (a) or radius R (b) versus heat treatment time t_{ht} in the common coordinates (a) or in logarithmical coordinates (b).

is a formation of a structure with interpenetrating silica and alkali-borate phases, the channel diameters of which are $D_{\text{channel}} = 15\text{--}20$ nm (Figs. 1c and 1d; Fig. 2a, dependence 1). At the beginning of the t_{ht} interval mentioned the sizes of the third phase particles D_{particle} are commensurable with the sizes of the liquation channels (Fig. 2a, dependence 2).

As the t_{ht} value increases it is possible to observe some increase of the D_{channel} values as well as structure condensation due to the increase of the third phase amount. The occurrence of the third phase particles the sizes of which surpass the sizes of the channels occupied with a boron-rich phase is marked.

At $t_{ht} = 65$ hrs the sharp changes of a two-phase glass structure are observed (Fig. 1e) which undergo further development with an increase of t_{ht} (Figs. 1f–1j). The sizes of the silica phase areas are essentially increased. Along with occurrence of new fine particles of the third phase its larger part is presented by particles, for which $D_{\text{particle}} > D_{\text{channel}}$.

The fact of so-called “crushing” of the silica phase (an occurrence of the “cracks” in the areas contacting the particles of the third phase which considerably increases in size) at $t_{ht} \geq 198$ hrs has engaged our attention. In the long heat treatment of a glass ($t_{ht} = 500$ hrs) a faceting of the third phase particles (Fig. 1j) and their substantial growth (Fig. 2a, dependence 2) are observed.

The TEM image of glass structure, generated at elevated temperature $T_{ht} = 700$ °C, at which the phase separation processes occur much faster [24, 25], demonstrates the growth in the size of areas of silica phase and the faceted crystalline particles of the third phase (Fig. 1l). It should be noted that at longer etching of the cleaved surface of glass in 5% HF solution before a replica manufacturing these particles are dissolved as evidenced by the image of a spongy structure with a rounded through pores, corresponding to the size of liquation channels (Fig. 1k).

An example of construction of the histograms accordingly to [20] is shown in Fig. 3a. The histograms, constructed for TEM images of the two-phase glasses with different time of heat treatment which are combined so that all maxima are at zero, are

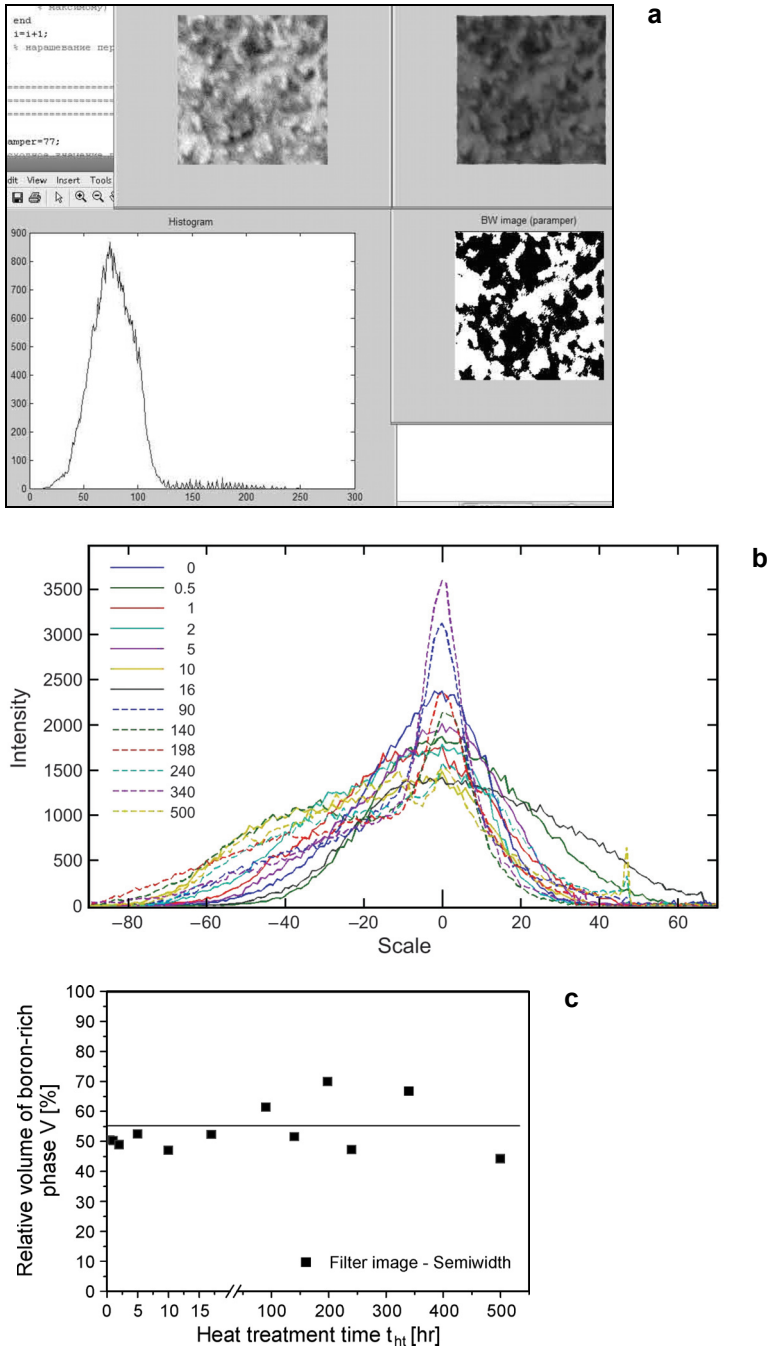


Fig. 3. An illustration of histogram designed by software (a). Overlapping of the histograms of the two-phase NaBSiPF-glass samples after heat treatment at 550 °C during different times t_{ht} (b). Dependence of a relative volume of boron-rich phase in the two-phase NaBSiPF-glasses versus the time t_{ht} of glass heat treatment at 550 °C (c).

presented in Fig. 3b. It is seen that the form of histograms depends on the time of glass heat treatment: the tendency towards reduction of a maximum height at essential increase of t_{ht} value is marked.

For small t_{ht} values the histograms look like an asymmetrical parabola. With increasing t_{ht} , the narrowing of the peak with maximum and the appearance of strong skewness (a two-peak distribution) are observed. For $t_{ht} \geq 198$ hrs there appear reflexes (the small peaks) at the end of distributions. These reflexes correspond to the lightest gradations that are adequate to the lightest areas on TEM images, which can be correlated to areas of the third phase.

Figure 3c shows a dependence $V = f(t_{ht})$, obtained under the condition of choosing the histogram section as a half-width on half-height after filtering. It is seen that when $t_{ht} \geq 25-40$ hrs an equilibrium value $V \sim 55\%$ is achieved. The fluctuations of V around this value are caused by a process of formation and reorganization of the particles of third phase, which is denser in comparison with a boron-rich phase, which is manifested in the analysis of grey images.

It is worthwhile to note that, that judging by glass transition temperature T_g , a glass heat treatment during $t_{ht} = 40$ hrs is enough to achieve equilibrium composition of boron-rich phase in the NaBSiPF-glass investigated (the Table), whereas in the case of base NaBSi-glass not less than 100 hrs are required for this purpose [24]. From the Table, it is seen that the density and T_g value (for the same t_{ht} value) of the modified glass is much less than for base glass [17–19]. Most probably, this reflects the influence of fluoride ions, which are mainly in the boron-rich phase and reduce the degree of connectivity of a skeleton of the second glass-former B_2O_3 due to the formation of the oxyfluoride polar structural groupings $[BO_{3/2}F]^-$ [10, 27, 28].

On the curves representing the dependences of the sizes of phase inhomogeneities in two-phase glass versus t_{ht} value (taking into account the error caused by a sufficiently high degree of coherence of heterogeneity regions) in log–log coordinates there are points of inflection separating the initial and later stages of growth (Fig. 2b). The results of determining the α values indicate that the growth of the sizes of the heterogeneity areas in SBS glass with phosphorus and fluoride additives (under conditions of phase equilibrium) cannot be unambiguously explained within the framework of the mechanisms mentioned previously, because the α values do not correspond to any of the above.

Qualitatively similar results were obtained in research of phase separation kinetics in SBS glasses with ZrO_2 , CaO and Sb_2O_5 additives [23, 29]. According to the author of [23, 29] we can assume that in this case, it is not the over-condensation which is the late stage of phase separation, but the transitive stage of formation of the disperse system state called a metastable colloidal equilibrium [30] that takes place. At this stage, the growth of particles can be either slowed down or stopped for some time, as exemplified by our results (Fig. 2a). The occurrence of such a state in the phase decomposition of the metastable systems may be due to the simultaneous processes of nucleation, dissolution and growth of the particles that complicates the kinetics of a process [23].

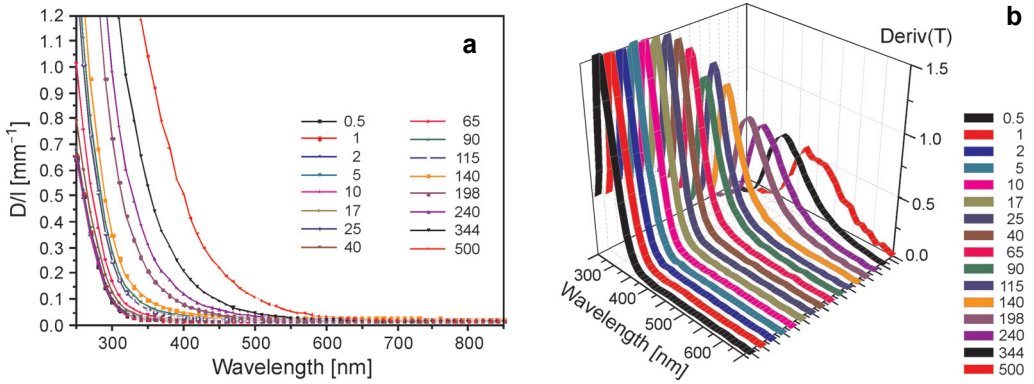


Fig. 4. Optical density spectra of the two-phase NaBSiPF-glass samples after heat treatment at 550 °C during different time t_{ht} , hrs (a). Dependences of the first derivative of transmission spectra of the two-phase NaBSiPF-glass samples after heat treatment at 550 °C during different time t_{ht} , hrs (b).

The results of research of the two-phase glasses with the help of optical spectroscopy (Fig. 4) reflect the structural transformations in glass with an increase in duration of its heat treatment (Fig. 1).

From the dependences of the first derivative of the transmission spectra of the samples it is seen that at $t_{ht} = 25\text{--}90$ hrs the maximum of the first derivative of transmission decreases smoothly and gradually shifts to longer wavelengths. This may indicate the appearance and enlargement of the scattering particles in the samples. With an increase in duration of the heat treatment of samples ($t_{ht} \geq 140$ hrs) there is a significant decrease in the peak of the derivative and its shift to longer

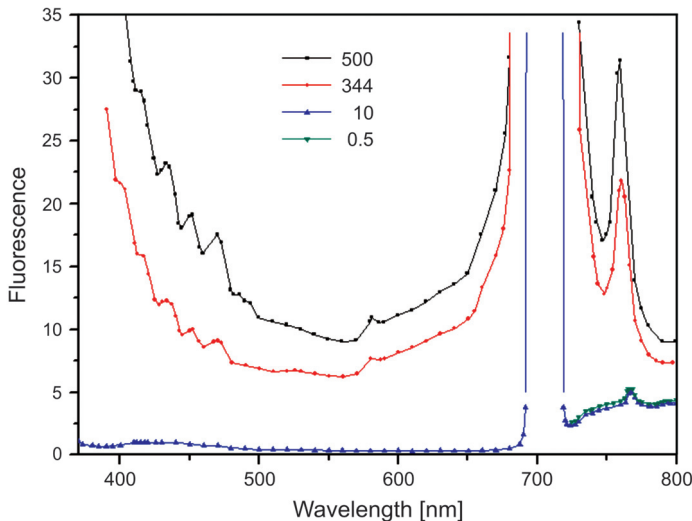


Fig. 5. Fluorescence spectra of the two-phase NaBSiPF-glass samples after heat treatment at 550 °C during different time t_{ht} (hrs).

wavelengths, which may be due to a significant enlargement of the structure. Thus observed broadening of a peak, in all probability, is caused by transition from a system with prevalence of disseminating and absorbing particles of equal size in a system with diffusers of different sizes.

The important question is identification of the third phase. Such compounds as, for example, sodium fluoride and Na_2SiF_6 [15], can be present at the microcrystalline phase revealed. Allocation of the fluorides in a separate phase can be caused by the known fact of their small solubility in silicate glass and propensity to crystallization [2, 3]. In the case of the introduction of P_2O_5 in SBS glass, formation of phosphates in the form of the teardrop-shaped particles the crystallization of which is improbable because of propensity to glass formation [3] is quite possible. Apparently, this explains the fact that accordingly to X-ray analysis data there is only a crystalline modification of silica, namely α -quartz (ICPDS, no. 33-116) in the samples of the two-phase glasses under investigation.

The intensity of crystallization increases at great t_{ht} values. This fact can be evidenced by the spectra of fluorescence which can be caused by presence of α -quartz in the two-phase glass: the expressed peaks of fluorescence are observed at $t_{\text{ht}} = 344\text{--}500$ hrs (Fig. 5).

4. Conclusions

The structure of the phase-separated glasses of $\text{Na}_2\text{O}\text{--}\text{B}_2\text{O}_3\text{--}\text{SiO}_2\text{--}\text{P}_2\text{O}_5\text{--}|\text{F}|$ system subjected to heat treatment at 550°C during $0.5\text{--}500$ hrs is investigated using electronic microscopy and optical spectroscopy techniques. The programs developed in MatLab environment in which the histograms of analyzed grey images are used have been applied for the processing of TEM images, which enabled us to analyze the kinetics of phase separation in system under study. The deviation of growth rate of the liquation heterogeneity areas from theoretical dependence is established.

Propensity to formation of micro-heterogeneous structure in the glass-forming system during the cooling of glass melt is revealed.

There was found the generation of the particles of a third phase in the glasses with a two-frame structure which is formed by coexisting silica and alkali borate phases. The growth of the third phase particles with an increase in duration of the heat treatment of a glass is shown. The presence of crystal modification of silica (α -quartz; ICPDS, no. 33-116) in this phase is established.

It is shown that the light transmission spectra and fluorescence spectra of the two-phase glasses under study are influenced by the structural transformations in glass with an increase in duration of its heat treatment.

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