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The influence of thermal treatment of the porous glass plates on the character of their scattering in visible spectral region

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The pore structure and light transmission of the high-silica porous glasses in visible spectral region are investigated depending on a temperature of their thermal treatment and composition of the initial two-phase alkali borosilicate glasses. The character of light transmission in porous glasses is analyzed considering the features of their pore space structure and processes occurring in porous glass upon heating. It is shown that with an increase in temperature of thermal treatment of the porous glasses of different composition the pore size increases, and their specific surface decreases (at practically constant common porosity), which is due to the processes of pore overcondensation, that occur owing to the regrouping and change of packing density of the secondary silica particles. It is shown that introducting phosphate and fluoride ions in the basic alkali borosilicate glass results in an increase in the light attenuation factors of the porous glasses owing to an increase in the sizes of liquation areas of heterogeneity in initial two-phase glasses, formation of larger pores and presence of the nanostructured microcrystalline phases in the porous glasses.

Keywords: phase-separated alkali borosilicate glasses, porous glass, light transmission.

1. Introduction

Porous glasses (PGs) based on the phase-separated alkali borosilicate (ABS) glass-forming systems represent the chemically, biologically and thermally steady nanostructured porous materials with controllable parameters of the structure and properties [1]. PGs are the matrices for creation of the high silica materials with adjustable properties, such as the spectral-optical sensors of sorption type for optoelectronic analyzers of structure of the gas environment; the microoptical elements for creation of integrated microcircuits working in an optical range and used for transfer, storage and processing of information; the functional nanoporous elements for microfluidic devices, *etc*. [2, 3]. In connection with the availability of PG's application in optical technologies information on their optical properties, namely, light transmission τ in visible spectral area and τ change depending on various factors, is necessary.

Generally, a light transmission of the PG plates is defined by absorption and dispersion on inhomogeneities in PGs [4].

Spectral dependences of the light transmission allow us to obtain data on the scattering of a light flux from the boundary of the media, as well as from the structure inhomogeneities and surface. Depending on the size, form and distributions of the inhomogeneities the various variants of light scattering are possible. When the inhomogeneity sizes are smaller than the wavelengths λ, the Rayleigh scattering is observed [5, 6]. In this case, the light extinction factor $K_\lambda = A/\lambda^{-\beta}$ (A = const, β is a parameter, which is determined as a tangent of angle of inclination of dependence $-\log(-\log\tau) = f(\log\lambda)$ [7]) is proportional to the quantity $\lambda^{\beta=4}$ [8, 9]. The presence of large inhomogeneities results in diffraction scattering. The absence of a strict connection between PG's τ values (in a wavelengths range λ = 350−800 nm) and the pore sizes (at pore radius $r < \lambda$) testifies to the complex mechanism of light scattering in PG [10]. Besides the pores the sizes of which are less than a wavelength and the inhomogeneities of liquation type which are inherent to two-phase ABS glasses there are larger heterogeneities, namely silica gel precipitations and microcrystalline inclusions [4, 11]. These heterogeneities poorly absorb light, but bring about the essential contribution to the weakening of a light stream because of light scattering [6] and can influence the light transmission character [4, 5, 7, 10, 12, 13]. The observed dependences of τ values on the various factors which influence the glass leaching process and the structure of the PGs obtained are connected to these facts (see the review in [14]).

Earlier we investigated the τ values of the porous glasses depending on the ABS glass composition and its leaching conditions (*i.e.*, the concentration and temperature of an acid solution) [10], thickness of samples [10], an angle of the light stream falling on a glass plate surface [12], PG's thermal background [4]. In the present work, the light transmittance of the PG plates (thickness L = 3 mm) at λ = 400−800 nm is investigated depending on the composition of the initial two-phase ABS glasses and the values of temperature of subsequent thermal treatment (T_{tt}) of the PG samples obtained.

2. Technique

The composition and pore parameters of the PGs, obtained as a result of through acid leaching of two-phase ABS glasses that are a base glass (PG-1) and the glasses of modified composition (PG-2a, PG-2b, PG-3), and the following PG's thermal treatment at T_{tt} = 120−750 °C, are presented in Tabs. 1 and 2. Values of porosity W are determined by a weight method; sizes of a specific surface pore S (m^2/g) – by porosimetry BET method using a SORBTOMETER-M (Russia) analyzer. The values of average pore diameter D were calculated with the formula [15]:

$$D = \frac{4}{S}\left(\frac{1}{\rho_{\text{seeming}}} - \frac{1}{\rho_{\text{Si}}}\right)$$

where ρ_{Si} = 2.18 g/sm^3 is the density of silica skeleton; $\rho_{seeming} = P/V$ is a seeming density of PG, g/sm^3; P [g] – weight of the sample, g; V [sm^3] – volume of the sample.

Spectral dependences of the values τ have been measured on a SF-26 spectrophotometer relative to air (PG/air) or a sample of corresponding two-phase

T a b l e 1. Composition of the porous glasses under study.

	Composition as-analyzed [wt%]			
Glass	Na_2O	B_2O_3	SiO_2	$R_x(O_y)^*$
PG-1	0.22	4.25	95.53	–
PG-2a	0.17	5.96	93.75	0.07 P_2O_5 0.05 |F|
PG-2b	0.30	5.48	94.08	0.08 P_2O_5 0.06 |F|
PG-3	0.09	6.29	93.49	0.13 K_2O

T a b l e 2. The pore structure parameters of the porous glasses under study.

Glass	Thermal treatment temperature T_{tt} [°C]	Parameter of pore structure [15] Porosity W [sm^3/sm^3]	Diameter D [nm]	Specific surface area S [m^2/g]
PG-1	120	0.28	3.9	160
	400	0.28	4.9	135
	600	0.29	5.0	137
	650	0.29	5.9	117
	700	0.31	7.3	95
	750	0.27	8.4	83
PG-2a	120	0.27	9.9	65
	400	0.27	17.6	35
	600	0.28	17.9	37
	650	0.27	20.0	31
	700	0.28	24.9	27
PG-2b	120	0.28	14.3	45
	400	0.28	18.7	36
	600	0.27	18.2	38
	650	0.29	25.3	28
	700	0.27	27.4	26
	750	0.27	27.5	25
PG-3	120	0.43	9.3	149
	400	0.43	10.4	136
	600	0.44	12.4	115
	650	0.45	14.3	102
	700	0.44	17.3	83
	750	0.44	26.6	54

glass (PG/two-phase glass). Transmittance spectra of the PG samples, which were thermally treated at $T_{tt} \geq 400$ °C (PG_T), have been measured relative to PG samples with $T_{tt} = 120$ °C (PG_{120}).

The obtained spectra have been used to reveal the scattering type by parameter β.

3. Experimental results and discussion

The pore parameters of the PGs investigated depend on the initial two-phase glass composition and their thermal background (Tab. 2). Upon heating of PG samples in interval $T_{tt} \leq 750$ °C the pore size increases, and their specific surface decreases (at practically constant common porosity) as a result of processes of the pore over-condensation, caused by the regrouping and change of packing density of the secondary silica particles [16].

Some results of the measurement of the spectral dependences of porous glasses under study are given in Fig. 1. The PG plates having larger pores are characterized by smaller τ values (Fig. 1, Tab. 2). This result is adjusted with data [10] about an increase of turbidity of the PGs at increase in the sizes of scatterers, which is caused by the pore over-condensation processes at T_{tt} increase. At the same time, for similar D values the various values τ of the PG plates from modified glasses are

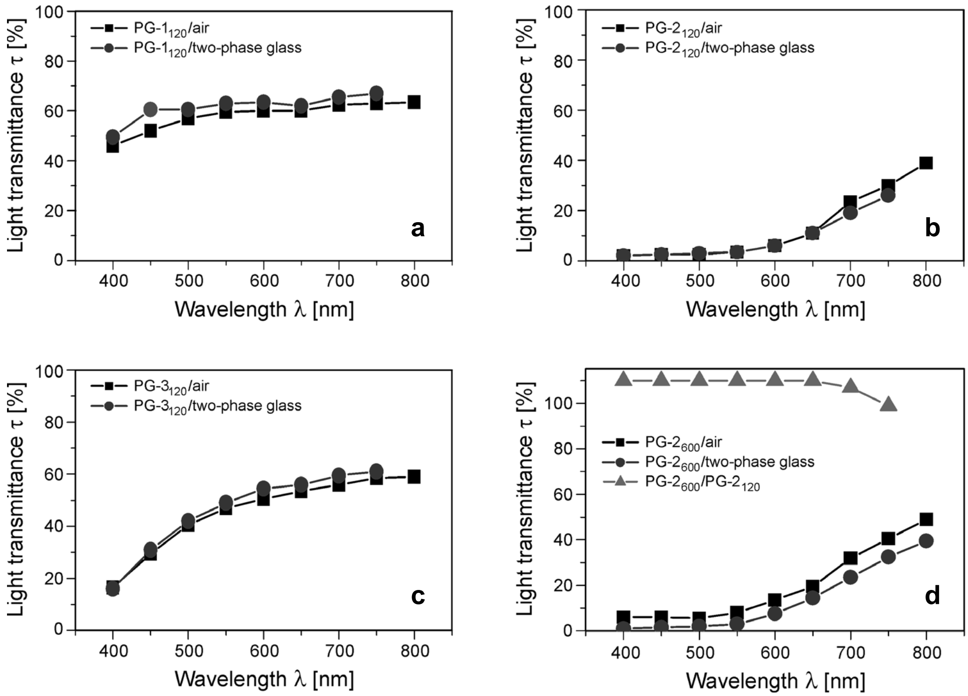

Fig. 1. Spectral dependences of light transmission of the porous glasses after drying at 120 °C (**a**–**c**) and after thermal treatment at 600 °C (**d**).

observed. The PG-2 samples made from two-phase ABS glass with P_2O_5 and fluoride ion additives possess a practically zero light transmission in the wavelength area $\lambda \leq 550$ nm (Fig. 1**b**).

The low light transmission of PGs from the two-phase glasses with additives is most likely caused (besides both an increase in the sizes of the liquation areas of heterogeneity in initial two-phase glasses [5, 7] and a presence of larger pores) by the presence of the nanostructured microcrystalline phases [13]. In certain λ intervals for PGs from two-phase glasses with additives the value τ (PG_T/PG_{120}) is greater than τ (PG_T/air) and τ (PG_T/two-phase glass) values (Fig. 1**d**). This fact can also serve as a proof of the presence of such phases in PG and gives grounds for judging their sizes and temperatures of their fusion (decomposition).

According to Fig. 1, light transmittance of the PG samples, measured relative to air is a little bit less than that measured relative to two-phase glass, and to PG_{120} in long-wave region ($\lambda > 600$ nm). It was shown that the presence of fluoride-ions in initial two-phase glass results in an increase in K_λ (at the same T_{tt}) [15]. For these PGs an increase of T_{tt} up to 600 °C is accompanied by reduction of K_λ, contrary to PGs from the glass without fluoride-ions. At $T_{tt} > 600$ °C the light attenuation of PGs decreases. In the long-wave spectral region ($\lambda \approx 700-800$ nm) the character of T_{tt} influence on K_λ is maintained, but absolute sizes of K_λ values decrease by 1.5–2.5 times (at the same λ). Under such conditions, for PGs from the glasses with the additives of fluoride-ions a Rayleigh scattering is inherent ($\beta \approx 4$) (Tab. 3). In other cases, a more complicated character of scattering ($\beta \approx 0.3-1.9$), which is caused by the features of PG's porous space structure [17] is observed. An increase of T_{tt} value from 120 °C up to 600 °C–750 °C is accompanied by a small increase in β values (Tab. 4).

T a b l e 3. The values of factor β of the porous glasses (T_{tt} = 120 °C) in different spectral regions.

	Factor β	
Glass	λ = 400–550 nm	λ = 550–750 nm
PG-1	1.4	0.4
PG-2a	3.7	4.0
PG-2b	0.3	3.7
PG-3	3.3	1.3

T a b l e 4. The values of factor β of the porous glasses treated thermally at different temperatures.

		Factor β		
Glass	λ [nm]	T_{tt} = 120 °C	T_{tt} = 600 °C	T_{tt} = 750 °C
PG-1	400–550	1.4	1.9	1.7
	550–750	0.4	0.6	0.9
PG-2b	400–550	0.3	0.4	0.8
	550–750	3.7	3.8	4.1

4. Conclusions

A study of an influence of the composition and temperature of thermal treatment of the porous glass plates on their light transmission in visible spectral area has been carried out.

Temperature ranges have been determined of the thermal treatment of the porous glass plates in which a change of light attenuation, a character of which is defined by the pore over-condensation processes and depend on an initial glass composition, is observed. A complex character of the light scattering caused by the structural features of a pore space has been shown.

The results obtained can be used for optimization of the technological modes of creating the high-silica porous functional elements of the devices with optical detection.

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