

Effect of structure parameters and composition of high-silica porous glasses on their thermal and radiation resistant properties

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The influence of a composition of initial phase-separated alkali borosilicate glass and its thermal treatment as well leaching conditions on the parameters of the porous glass structure are discussed. The results obtained by adsorption and conductivity methods, transmission electron microscopy and dilatometer technique were used to analyse the effect of structure parameters and composition of high-silica porous glasses on their thermal and radiation resistant properties.

Keywords: porous glass (structure, thermal and radiation resistant properties), electron microscopy, dilatometry.

1. Introduction

The information on structural transformations in porous glasses (PGs) during their heating and data on their thermal and radiation resistant properties are necessary for optimization of a procedure of manufacturing quartz-like glasses (QGs) and small size (so-called microoptical) elements (MOE) [1]. Unlike in the case of a sintering in the furnace, when the whole sample is heated up at regular intervals (a manufacture of QGs) [2], a sintering during local laser heating (a manufacture of MOE) [3] is approximately limited by section of a laser beam and begins at a surface, and then the border of sintering moves further in depth of a sample. This results in significant acceleration of the process of sintering PGs [4]. Due to extremely small area of influence of a laser beam, the data on structural transformations in PG are difficult to access in an experimental research. Indirectly, it is possible to judge from these

transformations about the change of the structure and change of the optical properties occurring in the entire volume of PG sample upon its heating in the electric furnace. This is possible owing to the fact that sintering of PGs by laser heating occurs at the same temperatures as sintering in the furnace, and properties of glass sintered by laser heating do not practically differ from properties of glass sintered in the furnace [4].

Taking into account a spongy-corpuscular structure of PGs formed by particles of fine-dispersed secondary silica, allocated in macropores in high-silica phase [5], one should expect the following processes to occur on PG heating: i) condensation of the hydroxyl groups on a surface of pore walls and particles of secondary silica with formation of siloxane bonds and isolation of water that results in gelation; ii) change of the parameters of PG's porous structure (size, volume and a specific surface of pores); iii) change of geometrical characteristics of PG samples (linear and volumetric shrinkage). The sintering of PG is caused by the processes of pore re-condensation and the viscous flow, the driving force of which is a change of superficial energy that aspirates to reduce a surface of each pore (see review in [3]).

In the present work, the results of experimental determination of structural parameters (average radius r , volume V and specific surface area S_{spes} of the pores, coefficient of structural resistance β), and also thermo-mechanical properties (linear shrinkage ΔL , viscosity η) of the initial and completely sintered PG samples as well as laser beam durability of PGs are discussed.

2. Technique

For research purposes, PG samples were used in the form of plates or disks of 1–3 mm thickness obtained as a result of through leaching of alkali borosilicate (ABS) glasses with a two-frame structure in HCl solutions (see Tab. 1 and Fig. 1).

In order to determine the parameters of PG pore structure the adsorption methods have been used. Investigation of electro-superficial properties of PGs was carried out by the known techniques used for studying membranes and disperse systems. Change of the linear sizes ΔL of the samples of two-phase glasses and porous glasses upon heating in the electric furnace with a fixed speed of 7 K/min at temperatures ranging from room temperature up to 850°C was registered by a quartz dilatometer. The relative error of ΔL definition including the error of measurement of the thickness of a sample did not exceed $\pm 10\%$.

For investigation of PG beam durability in view of the thermal mechanism of glass destruction, a continuous CO₂-laser radiation ($\lambda = 10.6 \mu\text{m}$) with power density $\leq 160 \text{ W}/\text{cm}^2$ has been chosen. In the experiments, continuous CO₂-laser radiation was focused by a lens to a spot approximately 500 μm in diameter on the sample surface.

3. Experimental results and discussion

During the PG heating at temperatures in the range of about 120–650°C the W values are practically not varied, S_{spes} values are decreased, and r values are increased

Table 1. Compositions and structure parameters of the porous glasses (sample thickness $L = 2$ mm).

Initial glass	Glass thermal treatment T/t [°C/h]	Glass transition temperature T_g [°C]	Porous glass composition (as-analysed, wt%)							Porous structure parameters (adsorption methods)			
			Na ₂ O	K ₂ O	B ₂ O ₃	SiO ₂	PbO	Al ₂ O ₃	P ₂ O ₅	F	W [cm ³ /cm ³]	r [nm]	S_{spes} [m ² /g]
8B	550/144	501	0.25	—	4.25	95.53	—	≤ 0.1	—	—	0.26	1.7	260
NFF40	550/40	468	0.41	—	6.11	93.35	—	—	0.08	0.05	~0.2	~5	~40
NFF140	550/142	458	0.30	—	5.51	94.15	—	—	0.04	—	~0.2	~5	~40
NK-I	550/24	435	0.10	0.15	6.93	92.82	—	—	—	—	0.47	7.0	88
NK-3	500/30	436	0.10	0.13	6.31	93.46	—	—	—	—	0.37	5.1	95
NKS	500/24	432	0.37	0.30	3.87	95.14	0.07	0.25	—	—	0.43	2.9	329

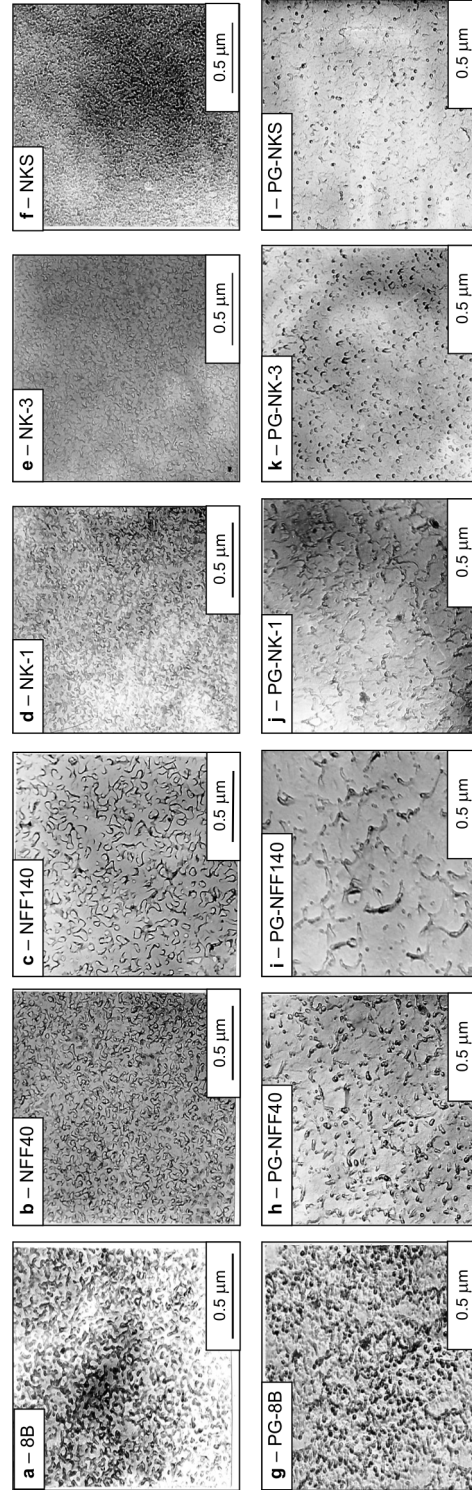
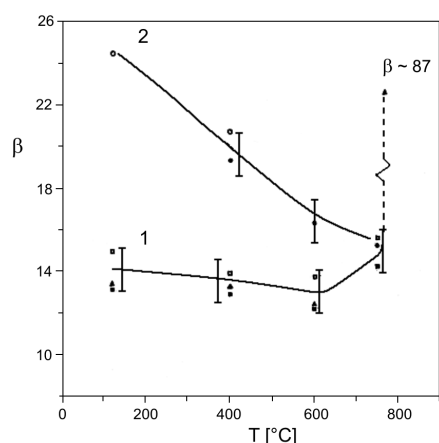


Fig. 1. Transmission electron micrographs of (a–f) initial phase-separated glasses and (g–l) electron micrographs of the porous glass samples produced upon leaching of the phase-separated glasses (consequently) at 100°C in 3 M HCl solution. Sample thickness $L = 2$ mm.

T a b l e 2. Structure parameters of the thermal treated PG-8B samples.

Temperature T of porous glass heat treatment during 1 h [°C]	Porous structure parameters (adsorption methods)		
	W [cm ³ /cm ³]	r [nm]	S_{spes} [m ² /g]
120	0.26	1.7	260
385	0.26	2.5	280
596	0.26	3.0	210
648	0.25	3.0	115
720	0.25	3.5	110
750	0.24	2.0	250

Fig. 2. Values of the structural resistance coefficient β of PG membranes vs. the temperature of their heat treatment. Initial glass: NFF (1) and 8B (2).

(Tab. 2). Values of β coefficient of the PGs manufactured from basic 8B glass and from NFF glass are different (Fig. 2). Introduction of small additives of fluorides and phosphorus oxide into basic glass results in the following. At constant concentration of background electrolyte, the β values of PGs from NFF glass are practically not dependent on the thermal treatment temperature in an interval 120–600°C, but are increased at $T > 600^\circ\text{C}$, sharply growing towards pore closing. A comparison of $(\beta - T)$ dependences of the PGs under investigation shows that at the same temperature the β values of PG manufactured from NFF glass are less than for PGs from 8B glass. This gives the basis to assume that secondary silica leaves to a greater degree the pore space of PG from NFF glass in comparison with PG from 8B glass on their maceration.

Observable laws are connected with the various contents of secondary silica inside pore space of PGs, which were obtained from two-phase ABS glasses with different phase structure parameters. The process of pore recondensation, caused by regrouping of the secondary silica particles and by changing their packing density, results in an increase in the amount of large pores due to the sintering of fine pores [6]. This causes a reduction of β values. At $T > 750^\circ\text{C}$ there is, most likely, pore closing caused by the process of viscous flow, and, naturally, a sharp increase of β values. A sharp reduction of the porosity of PGs, under heat treatment over this temperature interval,

and aspiration of pores, formed by exempted liquation channels, up to creation of the closed congestions testifies to the change of viscosity and the softening of PG silica skeleton (*i.e.*, PG sintering).

Results of studying the thermo-mechanical properties of PGs by dilatometry methods depending on their composition and porous structure, as well as on temperature of PG heat treatment are presented in Figs. 3 and 4.

Appreciable changes of ΔL values of PG plates are observed upon their heating over temperature intervals $\sim(20-250)$, $\sim(300-550)$ and $\sim(600-800)^\circ\text{C}$. It is possible that small expansion of PGs in an interval $\sim(20-250)^\circ\text{C}$ is caused by removal from pores of moisture which was adsorbed during storage of the samples in air before measurements [7].

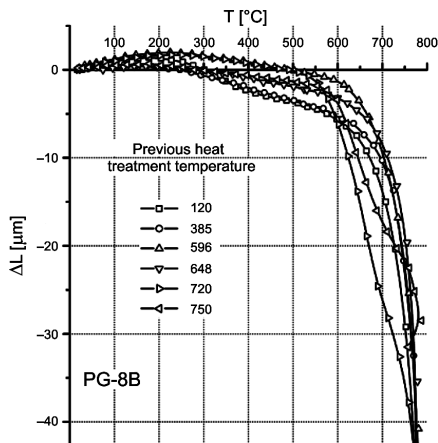


Fig. 3. Linear dimension change ΔL of PG-8B samples with different thermal history vs. temperature T upon heating at the rate 7 K/min. Sample thickness $L = 3$ mm.

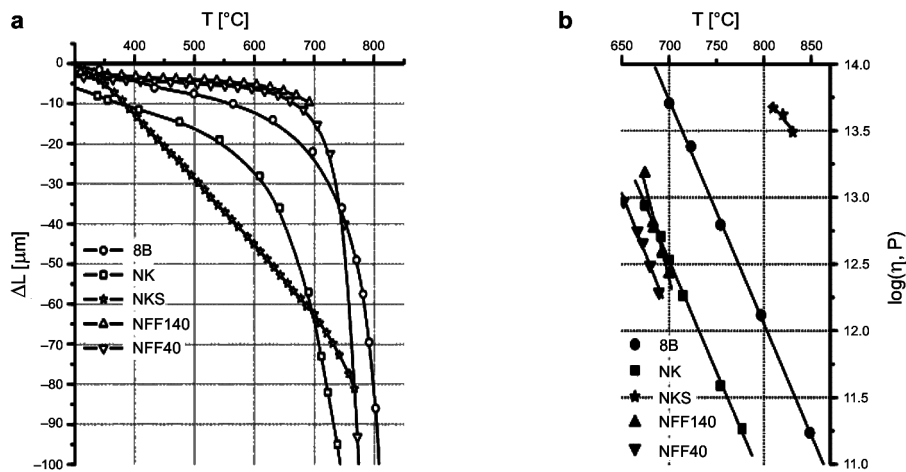


Fig. 4. Linear dimension change ΔL of PG samples (a) and viscosity $\log \eta$ of quartz-like glass ones (b) vs. temperature T for different compositions of initial phase-separated glasses. Sample thickness $L = 3$ mm.

Table 3. Experimental data for 2 mm thick porous glass plates exposed to CO₂ – laser radiation at an exposure time of 3 s.

Initial glass	Concentration of HCl solution (at 100°C) [mol/l]	Porous glass		Threshold power density q_0 [W/cm ²]	
		Weight relation B ₂ O ₃ /SiO ₂	r [nm]	Sintering	Formation of foamed white mass
8B	1.0	2.6/97.2	2.5	100	110
	3.0	4.3/95.5	1.7	80	140
NFF140	4.0	6.0/93.8	6.5	70	*

* No foamed white mass in the region exposed to laser radiation is observed at power densities in the range $q_0 \leq 160$ W/cm².

When heating PG samples at temperatures prior to the beginning of viscous flow in a skeleton their linear shrinkage is greater in cases where Na₂O/B₂O₃ molar ratio is larger and B₂O₃/SiO₂ is less. At identical values of these ratios (accordingly, for pairs of the base and modified glass) PG shrinkage is greater, than value r is less. The increase of B₂O₃/SiO₂ molar ratio in initial two-phase glass results in less viscous skeleton of PGs. At the same B₂O₃/SiO₂ ratio the presence of fluoride ions considerably lowers the viscosity of PGs. The presence of even a small amount of Al₂O₃ in PG from NKS-1 glass essentially raises its viscosity in comparison with PG from the basic NK-1 glass.

The smaller the viscosity of PG silica skeleton, the lower the temperature of PG sintering [2]. For example, the pore closing of PG samples obtained from NK-1 glass begins at a temperature that is lower in comparison with PGs from 8B glass.

Localization of thermal influence upon laser irradiation results in localization of the processes of pore sintering and shrinkage, and by that – to formation of microlens, *i.e.*, an area of transparent QG with a gradient of refractive index (*i.e.*, MOE) [4]. The depth of sintering of the PG plates can be controlled by varying the irradiation time τ at a constant laser power density q [8]. An increase in the q values leads to an increase in the temperature gradient during heating and cooling. Owing to that the probability of the sample cracking, due to the thermo-mechanical stresses, reaches threshold values. In this case, the micro-cracks of the dislocation type are formed at the center of the laser spot. Depending on PG manufacture conditions the experimentally determined threshold power density is from 70 to 100 W/sm² (see Tab. 3). An overheating of PGs accompanies the formation of foamed mass containing the microcrystalline silica phases [9].

4. Summary

The structural and thermo-mechanical properties of the PGs change with temperature of the glass thermal treatment. The sharpest changes were observed at temperature ranges of about: 20–250°C, 300–550°C, and 600–800°C. They are due to the structural transformations, which take place in PGs as a result of dehydration, surface

dehydroxylation and condensation of pores, as well as the thermal expansion and viscous flow processes.

The composition of the initial phase-separated glass influences both the structure parameters and properties of the PGs and QGs produced by sintering the PG samples at high temperatures up to pore closing as well as on their laser beam radiation resistant properties.

The investigation carried out showed the possibility of controlling the structure parameters as well as the optical and thermo-mechanical properties of PGs by means of heat treatment.

Acknowledgments – The work was supported by Russian Foundation for Basic Research (project no. 04-03-32165 and no. 05-03-32603) and by Saint-Petersburg Scientific Center.

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Received October 3, 2005