

# Sintering of optical porous glasses

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The changes in the visible light transmission of the optical porous glasses (PGs), arising from PGs thermal treatment, have been investigated by transmission electron microscopy and optical spectroscopy technique. Also the PGs thermal properties such as linear shrinkage and viscosity have been studied. These PGs are used in optics and laser technology as the base for the micro-optical elements produced by a local laser sintering of PGs.

Keywords: porous glass, sintering, light transmission, porosity, microstructures, shrinkage, viscosity.

## 1. Introduction

As it is known, the production technology of the porous glasses (PGs) of preassigned parameters of porous structure is based on the liquation regulation in the glasses of alkali borosilicate (ABS) systems [1].

A surface of the high-silica PGs which are obtained by phase-separated glass leaching in aqua solutions is hydrated and carries the silanol groups  $\text{Si}(\text{OH})_n$  [2]–[4]. In addition, there are some water adsorption acid centres due to a boron presence on the PGs surface [5]–[9].

Over the course of the last two decades PGs came into use as the materials to produce microoptical elements by the methods of local laser sintering of PG samples [10]. This new application of PGs results from such properties as their thermal stability, transparency in visible spectrum, ray strength, and the great volume of pores with the developed surface capable of the active chemisorption of a great number of different substances.

At heating of porous glasses in a certain temperature range and up to the temperature of the linkage their shrinkage is under way and they turn into a transparent high-silica glass (similar to the quartz glass in properties). The thus far gained information about structural transformations in the porous glass in a very small region of laser beam action is insufficient to conduct the experiment. At the same time the knowledge of such transformations is necessary for working out the controllable regimes of laser interaction. These transformations can be estimated indirectly from the structure change and from the optical properties of the whole volume of a microporous sample at its heating in a furnace.

In the course of PGs heating the processes of water desorption and destruction of the hydroxyl cover of the pore surface take place [9]. Also, the changes in the PG pore parameters (such as dimension, surface area and pore volume) as well as the geometric characteristics of the PG samples (shrinkage) result from sintering of the PGs [9], [11]–[13].

Near the temperature  $T \leq 200$  °C a removal of physically adsorbed water occurs. The adsorption centres of the water are H<sub>2</sub>O molecules which are coordinate-bonded with the pore surface. In the region of temperature  $T$  about 200–600 °C coordinate-bonded water molecules, the centres of which are the oxygen atoms of the silanol groups and the admixed boron atoms, are removed. At  $T$  about 600–800 °C dehydroxylation of the linked silanol groups takes place. Thermal treatment of PGs at the temperature  $T > 800$  °C is accompanied by both irreversible surface dehydroxylation and condensation of the adjacent silanol groups which are located on the pore walls. These processes lead to pore closure.

Sintering of the porous glass is caused by viscous flow that is characterised by viscosity coefficient  $\eta$  [14], [15]. Viscous flow is driven by surface energy reduction to decrease a pore surface area [14]–[17].

The values of temperature and the rate of PG sintering depend on its composition and pore dimensions [9], [11], [13], [15], [18]. During the PGs sintering, the process of the so-called over-condensation takes place, which consists in an increase in the dimension of big pores through decrease and then full disappearance of small pores [19]. A rise in pore size causes an increase in PG cloudiness that is a light attenuation factor. A tendency to porosity for zero results in a decrease in PG cloudiness. Superposition of these effects is the cause of an extremum in the dependences of PG cloudiness vs. heating temperature.

This work presents the investigation results concerning the influence of thermal treatment (sintering) regimes of porous glasses on their structural parameters, as well as thermal and optical properties.

## 2. Experimental

In this work the scientific enquiry has been concerned the PGs obtained by leaching of the samples of phase-separated ABS glasses in the R<sub>2</sub>O–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system (R = Na, K). The composition of initial ABS glasses, the regimes of their heat treatment and parameters of liquation (phase-separated) structure are given in Tab. 1.

The samples of two-phased ABS glasses in the form of plane-parallel polished plates of 20×20×2 mm<sup>2</sup> and 20×20×3 mm<sup>2</sup> were leached in the solution of 3 M HCl at 100 °C, then they were washed in distilled water and dried in a desiccator at 120 °C for 1 hour. The parameters of PG's structure and their compositions are shown in Tab. 2.

On drying, the porous glasses were heat treated (for 1 hour) at the temperatures from 120 to 900 °C. The heat treatment of PG was carried out in the laboratory electric furnace with temperature accurate to  $\pm 1$  degree, and in the vacuum chamber of NVA-1 device (under vacuum not lower than 10<sup>-4</sup> mmHg).

Table 1. Compositions of the initial glasses, regime of their thermal treatment and the parameters of the phase-separated glass structure.

Initial glass	Composition [mol%]				Time of the thermal treatment at 550 °C [h]	Relative volume [%]	Chemical unstable phase parameters			
	Na <sub>2</sub> O	K <sub>2</sub> O	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>			Diameter of the liquation channels [nm]	Na <sub>2</sub> O	K <sub>2</sub> O	B <sub>2</sub> O <sub>3</sub>
8B	7.3	—	20.8	71.9	144	50–55	15.0	—	39.2	45.8
NK-1	4.0	3.6	32.4	60.0	24	~ 50	~ 15	~ 59	~ 20	~ 26

Table 2. Composition and pore structure characteristics of the porous glasses.

Initial glass	Composition [mol%]				Mean pore radius $r$ [nm]	Volume porosity $W$ [sm <sup>3</sup> /sm <sup>3</sup> ]	Specific surface area [m <sup>2</sup> /g]	Structural resistance coefficient $\beta$	Pore tortuosity factor $\chi$
	Na <sub>2</sub> O	K <sub>2</sub> O	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>					
8B	0.2	—	3.2	96.6	3.5	0.27	113	16.0	2.1
NK-1	<0.1	<0.1	6.1	94.0	7.0, 10.0	0.42	88	5.3	1.5

To study the two-phase structure of phase-separated glasses and also the porous structure of PG with the help of transmission electron microscopy (TEM), the cellulose coal replicas were used [20]. The values of radius  $r$  and specific surface area (SA) of PG pores were determined by the well-known BET methods. The values of volume porosity  $W$  were determined by the adsorption methods and the weight ones. The values of structural resistance coefficients  $\beta$  were determined by the electroconductivity method [21]. Light transmission  $\tau$  of glasses in the range of wavelength  $\lambda$  from 400 to 750 nm was measured with the spectrophotometer SF-26 at the normal light fall on the great sample surface [22].

The measurement of viscosity ( $\log\eta$ ) of the sintered PGs was carried out by the beam-bending method [23]. The relative errors of measured values at the confidence coefficient of 0.95 were the following: for  $r \pm 10\%$ ; for  $W \pm 2\%$ ; for  $\beta \pm 10\%$ ; for  $\tau \pm 7\%$  (at  $\lambda = 400\text{--}500$  nm) and  $\pm 5\%$  (at  $\lambda > 500$  nm); for  $\log\eta \pm 0.05 \log\eta$ .

### 3. Results and discussion

The information about the two-phase structure of initial phase-separated ABS glasses after the results of TEM is given in Tab. 1.

Figures 1 and 2 show the TEM photographs illustrating the structure of initial phase-separated ABS glasses and the samples of PG with different heating history. The two-phased glasses under study have the liquation structure with the interpenetrating phases (Fig. 1a, b). The macropore radius  $R$  values of freshly prepared PG samples ( $R < 40$  nm, Fig. 1c, d) are close to the ones of liquation channels in the corresponding two-phased glasses (Fig. 1a, b).

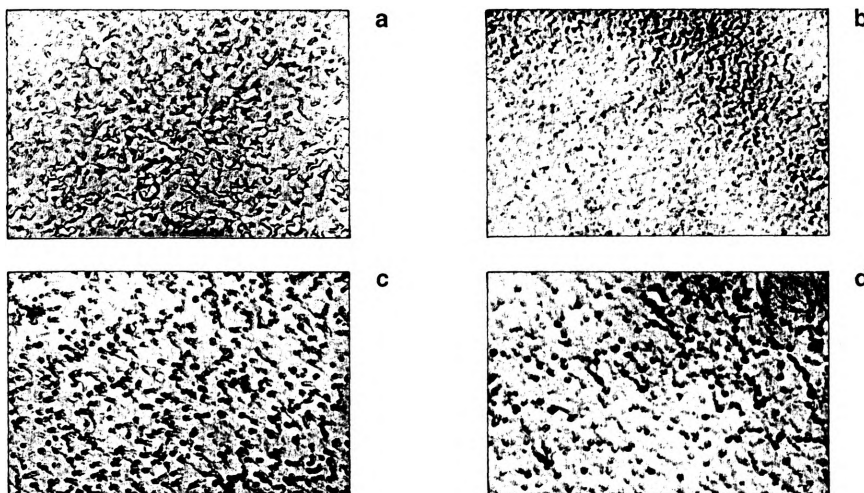


Fig. 1. Transmission electron micrographs of the initial phase-separated glasses: 8B (a), NK-1 (b) and electron micrographs of the porous glass samples (c, d) produced upon leaching of both phase-separated glasses (respectively) at 100 °C in 3 M HCl solution. Magnification 60000 $\times$  (a, b) and 45000 $\times$  (c, d).

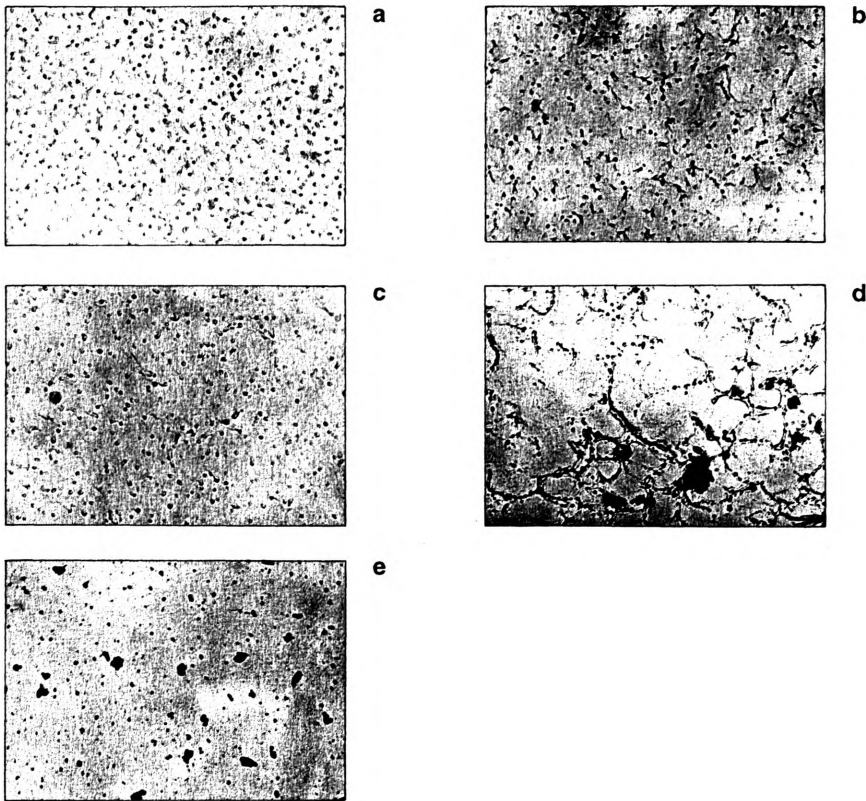


Fig. 2. Transmission electron micrographs of the porous glass samples produced upon leaching of phase-separated glass 8B in 3 M HCl at 100 °C and heat treated additionally in vacuum at 500 °C (a), 700 °C (b), 750 °C (c), 780 °C (d) or in an electric furnace at 890 °C (e). Magnification 60000× (a–d) and 45000× (e).

The parameters of porous structure of initial PG (the initial PG is that which after the obligatory drying at 120 °C was not heat treated additionally) determined with the help of adsorption methods are given in Tab. 2. One can see that the PGs obtained at acid leaching of two-phased ABS glass 8B with high silica contents have lower total porosity, their pores are smaller and they have higher specific surface of pores. It is evident from Tab. 2 that the lower the values of PG pore radius  $r$ , the higher the values of coefficient  $\beta$ . It corresponds to the increase in the share of nonconducting framework in these kinds of PG.

Figure 2 demonstrates the results of TEM investigation of PG samples subjected to the additional heat treatment in vacuum (Fig. 2a–d) and in an open furnace (Fig. 2e). It is necessary to mention that at the same temperature the processes of structural transmission in the PG samples heat-treated in vacuum proceed more quickly than in those treated in the open furnace. Such kind of acceleration corresponds to the transformations in PG samples heat-treated in the open furnace at the temperature some

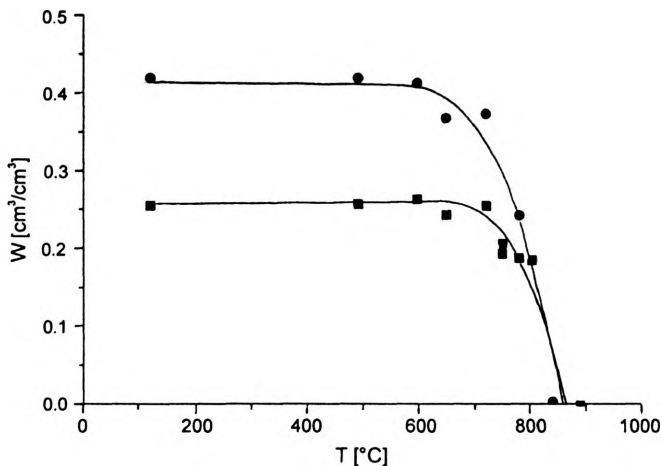


Fig. 3. Dependences of the total porosity  $W$  of PG samples produced upon leaching of phase-separated glass 8B (■) and NK-1 (●) at  $100^\circ\text{C}$  in 3 M HCl solution on the heat treatment temperature.

ten degrees higher than the temperature in the vacuum chamber. According to the obtained data, the PG heat treatment in vacuum at the temperature  $T \leq 500^\circ\text{C}$  and in the open furnace at the temperature up to  $750^\circ\text{C}$  does not influence the parameters of macroporous structure of PG (see Figs. 1c and 2a). At PG heating in the electric furnace at the temperature up to  $600^\circ\text{C}$  no perceptible changes in the total porosity of PG determined by the weight method take place (Fig. 3). At higher temperature a sharp decrease in porosity of the PG heat-treated happens, especially over the interval of  $800\text{--}900^\circ\text{C}$  when the closure of pores is in progress and the sintered glass similar to the quartz glass forms. In the TEM photographs of PG samples treated at the temperature higher than  $700^\circ\text{C}$  the tendency of macropores to create closed-type aggregations is observed (Fig. 2b–d). Such movement of macropores is connected with the change in material viscosity [9]. These results correlate qualitatively with the existing notions about the structure transformations mentioned above in PG at sintering.

The spectral dependences of light transmission  $\tau$  of the PG samples obtained by leaching of the two-phased glasses, 8B and NK-1, in visible spectrum are typical of PGs.

Figure 4 gives the light transmission dependences of PGs for different wavelengths on the temperature  $T$  of their heat treatment. As evident from the figure, the transmission of both initial porous glasses does not change within the temperature range from  $120^\circ\text{C}$  to about  $600^\circ\text{C}$ . At  $600\text{--}650^\circ\text{C}$  a sharp decrease in light transmission takes place. The fall in light transmission for the PG obtained from the NK-1 glass is less great than for the other, for the 8B glass. At  $800\text{--}900^\circ\text{C}$  the transmission of heat-treated PG increases up to 90–95% for the totally sintered glass. Such shape of light transmission dependences on the temperature of PG heat treatment  $\tau(T)$  within the temperature range under study is qualitatively similar to the

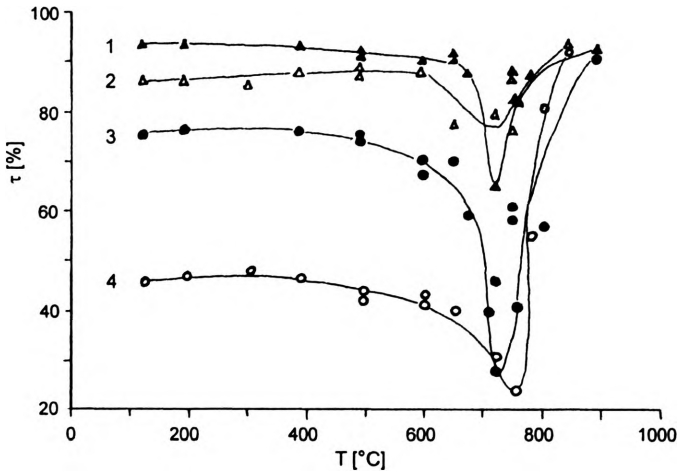


Fig. 4. Light transmission dependences  $\tau$  of PG samples produced upon leaching of phase-separated glass for various wavelengths vs. the temperature of their heat treatment  $T$  for 1 hour at each temperature. The initial phase-separated glass: 8B (curves 1, 3); NK-1 (curves 2, 4). The leaching conditions: 3 M HCl solution at 100 °C. The sample thickness is 3 mm. Wavelength  $\lambda$  [nm]: 400 (curves 3, 4); 630 (curves 1, 2).

dependences observed for the PG samples with smaller thickness and with the other way of obtaining (Fig. 5). The obtained results are the consequence of structure change in PGs, on the other hand, stemming from the over-condensation processes, *i.e.*, from the increase in the dimension of great pores at the expense of smaller ones; and from the decrease in the total porosity at temperatures higher than 600 °C [19]. The existence of minimum in the dependences of  $\tau(T)$  is likely to be caused by the superposition of

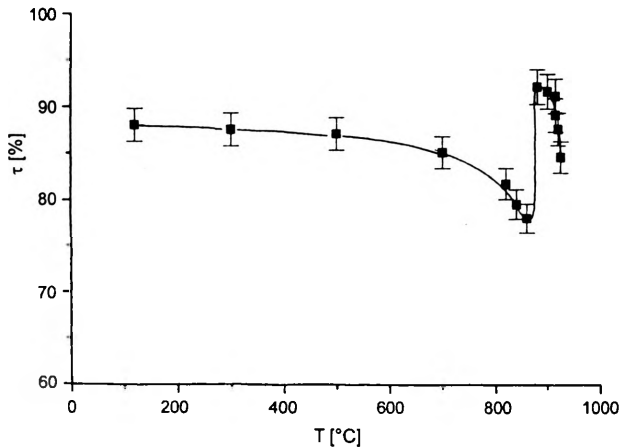


Fig. 5. Light transmission dependences  $\tau$  of PG samples produced upon leaching of phase-separated glass 8B vs. the temperature of their heat treatment  $T$  for 0.5 hour at each temperature ( $\lambda = 630$  nm). The leaching conditions: 0.1 M HCl solution at 100 °C. The sample thickness is 1.8 mm. The data were obtained by ROSKOVA, SMIRNOVA [24].

both processes. The increase in  $\tau$  at the temperature range from 750 to 900 °C (Figs. 4 and 5) is accompanied by a sharp decrease in porosity (Fig. 3). It is felt that the decrease in the value of  $\tau$  for full sintered glasses at their further heating at temperatures higher than 900 °C (Fig. 5) results from the crystallisation [18].

Thermal properties of phase-separated and porous glasses were studied in the temperature range from 20 °C to 850 °C with the help of a quartz dilatometer-viscosimeter [23]. The linear size change of sample  $L$  was measured at heating (cooling) with the fixed rate of 7 °C/min.

It has been found that the thermal behaviour of the phase-separated glasses under study is typical of the vitreous state. Namely, first at heating the glass samples their linear expansion begins, next, all the dependences have a quite sharp break (at the glass transition temperature  $T_g$ ), and then further linear expansion of glass takes place and the viscous flow begins.

Figure 6 shows the temperature dependences of the size change of PG samples. Unlike the two-phased glasses that expand at heating, the shrinkage of porous glasses is observed beginning with 90–100 °C. At the temperatures higher than 650 °C the shrinkage of PG increases sharply. Such behaviour of PGs at their heating is due to the processes of porous structure rebuilding mentioned above. The shrinkage of glasses under study is influenced by their composition in accordance with the viscosity of a silica skeleton.

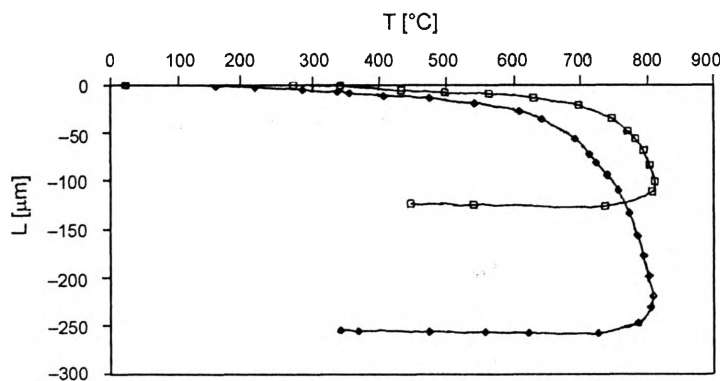


Fig. 6. Dependences of changes in the linear sizes  $L$  of PG samples produced upon leaching of phase-separated glass 8B (curve 1) and NK-1 (curve 2) at 100 °C in 3 M HCl solution vs. the temperature of their heat treatment  $T$  in the course of their heating and cooling. The initial linear size of sample is 5 mm.

Figure 7 shows the experimental data on the temperature dependences of the viscosity of the quartz-like glasses obtained by sintering of the PGs under study at the temperatures which results in the closure of pores. As may be seen from the Fig. 7, the sintered glass from the PG synthesised by leaching of the phase-separated NK-1 glass is characterised by a smaller value of viscosity in comparison with the sintered glass produced from the PG on the basis of 8B glass. This result correlates with the data on compositions of the two-phased glasses and the PG samples (Tabs. 1 and 2). The PG



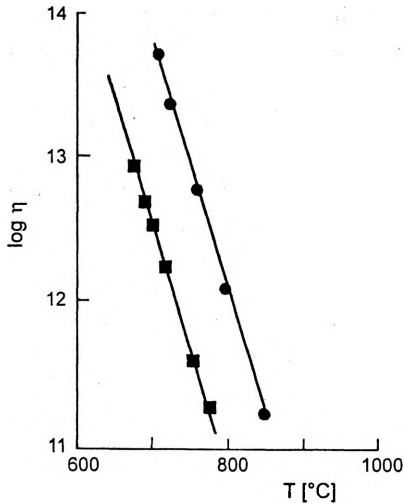


Fig. 7. Temperature dependences of viscosity ( $\log \eta$ ) of the sintered PG samples produced upon leaching of phase-separated glass 8B (●) and NK-1 (■) at 100 °C in 3 M HCl solution.

obtained from the phase-separated NK-1 glass enriched with boron contains less silica and much more boron in comparison with the PG made of more siliceous 8B glass. The enrichment of PG sample with boron gives rise to the decrease in viscosity [9], [15]. Because the silica skeleton of PG produced from the NK-1 glass has lower viscosity, the closure of pores begins in this glass at the temperature lower than that in the PG from the 8B glass (Fig. 6). In consequence of the viscous flow at the temperatures higher than 600 °C in the PG from the NK-1 glass a sharp decrease in porosity takes place, as Fig. 3 shows. It gives rise to the closure of pores, while for the PG from the 8B glass the decrease in porosity takes place at the temperature higher than 700 °C.

#### 4. Conclusions

The analysis of the investigation of structural, optical and thermal properties of the PG samples obtained from the phase-separated ABS glasses different in composition testifies to the great influence of the initial glass composition on them. It is the initial composition that determines the composition of unstable boron-rich phase of the phase-separated glass, the parameters of porous structure, the PG composition all other things being kept equal.

It has been demonstrated that the PG on the basis of silica-rich phase-separated ABS glass containing more silica has smaller porosity and is more transparent in visible spectrum. At the thermal treatment of PG in the range from 120 to 900 °C the temperature dependences of volume porosity and those of optical transmission have extreme character. The sharpest changes in these values take place at the temperatures over two intervals: about 650–750 °C and about 800–900 °C. These changes are due

to the structural transformations taking place in PG in the result of the processes of overcondensation in the course of its sintering and further crystallisation of sintered glass.

The PG enriched with boron results from leaching of less siliceous phase-separated ABS glasses. It gives rise to the decrease in their viscosity.

The investigation carried out showed a possibility to regulate the optical properties of PGs by their heat treatment (sintering) within the temperature range of about 500–900 °C.

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## References

- [1] MAZURIN O.V., ROSKOVA G.P., AVER'YANOV V.I., ANTROPOVA T.V., *Two-Phase Glasses: Structure, Properties, Application* (in Russian), [Ed.] Nauka, Leningrad 1991, pp. 222–230.
- [2] BOLF F., BEYER H. Z., *Anorg. Allg. Chem.* **300** (1959), 33.
- [3] ELMER T.H., CHAPMAN I.D., NORDBERG M.E., *J. Appl. Chem.* **66** (1962), 1517.
- [4] BRESLER S.E., KOLIKOV V.M., KATUSCHKINA N.V., ZHDANOV S.P., *Kolloid. Zh.* **36** (1974), 638.
- [5] HAIR M., CHAPMAN S.D., *J. Am. Ceram. Soc.* **49** (1966), 651.
- [6] LOW M.J.D., *J. Phys. Chem.* **70** (1966), 2740.
- [7] ALTUG S., HAIR M., *J. Phys. Chem.* **71** (1967), 4260.
- [8] LOW M.J.D., *J. Phys. Chem.* **71** (1967), 3077.
- [9] ELMER T.H., *Amer. Ceram. Soc. Bull.* **62** (1983), 513.
- [10] VEIKO V.P., KOSTUK G.K., ROSKOVA G.P., TSEKHOMSKAYA T.S., CHUIKO V.A., YAKOVLEV E.B., *Laser Formation of the Optical Elements* (in Russian), Leningrad 1988.
- [11] HAMMEL J.J., [In] *Proc. III Intern. Congr. Glass* **9** (1974), 117.
- [12] KIRUTENKO V.M., KISELEV A.V., LYGIN V.I., SCTCHEPALIN K.L., *Kinetika i Kataliz* **15** (1974), 1584 (in Russian).
- [13] DAWIDOWICZ A.L., CHOMA I., *Mater. Chem. Phys.* **8** (1983), 323.
- [14] FILIPOVICH V.N., *Fiz. i Khim. Stekla* **16** (1990), 81 (in Russian).
- [15] TAKAMORI T., IRIYAMA K., *Amer. Ceram. Soc. Bull.* **46** (1967), 1169.
- [16] SCHERER G.W., *J. Amer. Ceram. Soc.* **60** (1977), 236.
- [17] *Ibidem* p. 243.
- [18] ELMER T.H., *Amer. Ceram. Soc. Bull.* **61** (1982), 1215.
- [19] ANDREEV N.S., ERSCHOVA T.I., *Neorgan. Mater.* **3** (1967), 1898.
- [20] ANTROPOVA T.V., DROZDOVA I.A., *Glass Phys. Chem.* **21** (1995), 131.
- [21] ANTROPOVA T.V., TSYGANOVA T.A., KRYLOVA N.L., *Fiz. i Khim. Stekla* **16** (1990), 732 (in Russian).
- [22] ANTROPOVA T.V., DROZDOVA I.A., KRYLOVA N.L., *Glass Phys. Chem.* **18** (1992), 80.
- [23] ANTROPOVA T.V., STOLYAR S.V., STOLYAROVA V.K., SHANDYIBINA G.D., TSAPKO K.A., *Opt. Z.* **69** (2002), 89 (in Russian).
- [24] ANTROPOVA T.V., DROZDOVA I.A., KLOCHENKOVA U.A., KOSTUK G.K., ROSKOVA G.P., TSYGANOVA T.A., SHANDYIBINA G.D., YAKOVLEV E.B., *Optics and Scientific Instrument Making* (in Russian), [Ed.] GITMO(TU), Sankt Petersburg 2001, pp. 156–172.