Effect of P$_2$O$_5$ Impurities and Fluoride Ions on The Rheological Properties of Porous Glasses and Bismuth-Containing Composites Based on Them

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Abstract—The results of a study of the rheological properties (shrinkage on heating, viscosity) of porous glasses (PGs) obtained as a result of through acid leaching of two-phase sodium borosilicate glass doped with small additives of P$_2$O$_5$ and fluoride ions, as well as bismuth-containing PGs and quartzoid glasses based on them, depending on the temperature of the heat treatment of the PG and in comparison with the characteristics of the samples obtained from sodium borosilicate glass without additives, are presented. It is found that doping glass with the indicated impurities leads to a decrease in the thermal resistance of the obtained PGs and bismuth-containing PGs. The introduction of bismuth nitrate into PG in the case of the low-temperature treatment (at 120°C) lowers the temperature for the same viscosity values of quartzoid glasses by 15–20°C, in contrast to samples without additives, as well as from higher-temperature treatment (at 650°C) PGs with additives.

Keywords: porous glass, quartzoid glass, bismuth-containing glass, shrinkage, viscosity

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INTRODUCTION

One of the determining factors influencing the formation of bismuth active centers (BACs) in luminescent materials is the composition of the glassy matrix [1–6]. It is known that doping phosphate and phosphorosilicate glasses with bismuth is accompanied by a higher solubility of bismuth and lower temperatures for obtaining such glasses compared to silicate systems, which reduces the loss of bismuth during the synthesis of the glass (see review in [7]). In this case, the effect of the structure of the glassy matrix on the luminescent properties of bismuth-containing phosphate and phosphorosilicate glasses is noted [8–11]. The addition of P$_2$O$_5$ as a dopant effectively increases the light guide gain factor, but can lead to a decrease in the part of BACs responsible for IR luminescence.

To create bismuth-containing luminescent glass materials, the practical significance of which is due to the prospects of their use as preform materials for optical fibers with laser generation in the IR spectral region, high-silica porous glasses (PGs) can be successfully used [12–17]. PGs are obtained as a result of the through leaching of two-phase sodium borosilicate (SBS) glasses in aqueous solutions of mineral acids [18].

It is known that with the same composition of two-phase SBS glass, an increase in the heat treatment temperature ($T_{treat}$) of the received PG from 120 to 600–750°C leads to an increase in the pore size. All other things being equal, the pore size of PGs obtained by leaching two-phase glasses increases when the glass is alloyed with P$_2$O$_5$ and fluoride ions in comparison with PG made from the basic SBS glass [19, 20]. A larger pore size can contribute to an increase in the amount of incorporated bismuth salts in the PG and, thereby, to a decrease in the viscosity of bismuth-containing glass materials based on them [21]. When fluoride ions are introduced into two-phase SBS glass, the degree of connectivity of the silicon-boron-oxygen framework decreases due to the formation of oxyfluoride polar structural groups [BO$_3$/2F]$^-$, which leads to a decrease in its viscosity, that is, to a decrease in the viscosity of the resulting PG [22]. Reducing the viscosity of the glass makes it easier to pull the fiber from the preforms.

It is of interest to study the rheological properties of samples of bismuth-containing porous glasses (BPGs) and sintered quartz-like glass (BQGs) based on SBS glass doped with P$_2$O$_5$ and fluoride ions, in comparison with the samples obtained based on the basic SBS glass [23], to which this paper is devoted.
EXPERIMENTAL

The objects of study were samples of the PG and BPG based on them. The PG samples (in the form of polished sticks with a cross-sectional size of 3.5 × 3.5 mm² and 37 mm long) were made according to the previously developed technique by the through leaching of two-phase glass NFF-I (composition according to the analysis, mol %: 6.8Na₂O-22.1B₂O₃-70.4SiO₂-0.19P₂O₅-0.52F [20]) in an aqueous 4 M solution of HNO₃ during boiling followed by washing in distilled water and drying at 120°C for 1 hour. The mean diameter D and specific surface S_{sp} of the pores of the PG samples of a similar thickness (3 mm), obtained from two-phase glass NFF-I, are 10 nm and 65 m²/g, respectively.

Additional processing of PG was carried out in air in a laboratory electric SNOL 6/10 (Russia) furnace at T_{treat}. of 600, 650 or 700°C for 1 hour, which leads to an increase in D and, accordingly, to a decrease in S_{sp} of the PG pores based on NFF-I glass by a factor of approximately 1.8, 2, or 2.5, respectively. The temperature deviation T_{treat.} from the average value, due to the inertia of the furnace, did not exceed ±10°C. To obtain BPGs, the PG samples were used after isothermal treatment at 120 or 650°C. The samples were impregnated in three stages (for a total of 72 h) in accordance with [14] in a 0.5 M solution of bismuth nitrate prepared based on an aqueous 2 M solution of HNO₃ and Bi(NO₃)₃·5 H₂O, with intermediate drying between impregnations at ~50°C and final drying at 120°C in an air thermostat. To obtain monolithic quartzoid glasses (QGs and BQGs), the PG and BPG samples were heated in an air atmosphere in an SNOL 6/10 furnace from room temperature to 850°C with isothermal treatment at this temperature for 15 min until the pores collapsed. During the heat treatment of the BPGs, a microcrystalline phase of Bi₂O₃ oxide was formed in the pores as a result of Bi(NO₃)₃ thermolysis [14]. Taking into account the data we received earlier, according to which the bismuth content in the BPG (BQG) samples made of NFF-I glass after one-stage (for 24 h) impregnation is ~2 wt % (in terms of Bi₂O₃), and taking into account that with a threefold increase in the duration of impregnation, the content of bismuth in BPG increases by ~1.4 times [16], it was concluded that the content of bismuth in the studied samples of BPG (BQG) made of NFF-I glass is no less than ~2.8 wt % Bi₂O₃.

The study of the shrinkage (relative change in linear dimensions ΔL/L₀) of the samples and viscosity η during heating was carried out in accordance with the procedure [23] using a KB-1665 vertical quartz viscometer-dilatometer (Russia) with a low measuring force (0.05 N) of the design [24] with automatic recording of the experimental curves at a sample heating rate of 3 K/min from room temperature to ~850°C (sample load 5 g). The regulation and measurement of temperature T were carried out with an accuracy of ±1°C. The viscosity was measured by the rod bending method in the interval 10¹³–10¹⁵ P at T in the range 650–850°C. The error in determining the viscosity did not exceed ±0.05 log (η, P). The linear dependences of the logarithm of viscosity on the reciprocal temperature were constructed using the least squares method and approximation by the Frenkel equation similar to the procedure [23].

RESULTS AND DISCUSSION

When studying shrinkage upon heating of the PG samples made of NFF-I glass, heat-treated at T_{treat.} = 120, 600, 650, or 700°C, the same tendency which is characteristic for the shrinkage of PG specimens from basic SBS glass [22, 23] was observed. The increase in T_{treat.} ≥ 600°C, which is accompanied by an increase in the size and a decrease in the specific surface area of the PG pores, leads to the fact that the shrinkage of the samples, caused by the onset of the viscous flow process in the silica frame of the PG, begins at higher temperatures (Fig. 1a). This indicates an increase in the viscosity of the framework and is consistent with the main provisions of the theory of sintering glasses with low density, including PGs, based on the Frenkel concept and developed in Scherer’s works (see [25–29] and reviews there), according to which an increase in viscosity, in addition to the indicated change in pore parameters, also causes a decrease in the amount of surface hydroxyl ions, which occurs, as is known, during the high-temperature treatment of PGs [30–32].

Comparison with the previously obtained data [23] showed that the shrinkage of PG made of NFF-I glass (Fig. 1a) begins at a temperature ~100°C lower than the shrinkage of PG made of 8B-NT glass (D = 4 nm) [20]. This may be due to the increase in the D pores and loosening of the silicon-boron-oxygen framework due to the formation of groups [BO₃/₂F]⁻.

The introduction of bismuth compounds into PG barely changes the temperature of the onset of changes in the linear dimensions of the samples upon heating, but slightly decreases the value of ΔL/L₀ (Fig. 1b), which, according to [26], may indicate a lower viscosity of the BPG samples than the PG samples.

Figure 2 shows the temperature dependences of the viscosity (in the heating mode) of the quartzoid glasses QG and BQG from SBS glass NFF-I doped with P₂O₅ and fluoride ions, depending on the T_{treat.} of the initial PG and in comparison with the data [23] for the samples obtained from the basic SBS glass 8B-NT without the indicated additives.

When introducing small additions of phosphorus and fluorine into SBS glass, the viscosity of the obtained quartzoid glasses decreases (Fig. 2a, dependences I and J), which is consistent with the data presented in Fig. 1a, and the results obtained earlier in the study of samples with a smaller cross-sectional area of
2 × 2 mm² [22]. In Fig. 2a it can be seen that the temperature values at the same viscosity values \( \eta = 10^{13} \) P \( (T_{13}) \) for a QG sample based on 8B-NT glass without additives (dependence I) are ~70–80°C higher compared to NFF-I glass (dependence 3).

With the same composition of two-phase SBS glass, the increase in \( T_{\text{treat.}} \) of the PG samples (obtained, respectively, from the SBS glasses of basic or doped compositions) in the studied intervals 120–750°C and 120–650°C barely affects the viscosity of the monolithic QG, i.e., PG sintered until the pores collapse. It can be seen that with increasing \( T_{\text{treat.}} \) values \( T_{13} \) vary in the intervals 763–759°C and 680–677°C, respectively (Figs. 2a, 2b, dependences I, 3).

The effect of impregnating the PG in a solution of bismuth nitrate on the viscosity of quartzoid glasses is uncertain and depends on both the glass composition and the temperature of the preliminary heat treatment of the PG (Figs. 2a, 2b, dependences 2 and 4). At a lower \( T_{\text{treat.}} = 120°C \) (Fig. 2a), the introduction of bismuth into PG lowers the viscosity of BQG based on doped SBS glass \( (T_{13} \text{ decreases by } 15–20°C) \), in contrast to glass without additives. At a higher \( T_{\text{treat.}} \) of PG (Fig. 2b), the opposite result is observed: the decrease in the viscosity of the BQG made of doped SBS glass is insignificant \( ( \text{the change in } T_{13} \text{ does not exceed } 5°C) \), while in the case of 8B-NT glass, the decrease in the value of \( T_{13} \) of the BQG samples is 10–15°C.

In order to interpret the results obtained, additional studies are required, during which it is necessary to take into account the provisions of the current models of sintering (viscous flow) materials with low density, open porosity, and rigid (not sintered during heating) inclusions (see [25–29] and the reviews in them).

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**Fig. 1.** Temperature dependences of the relative change in linear dimensions \( \Delta L/L_0 \) of PG NPF-I samples heat-treated at different temperatures (a, b) \( T_{\text{treat.}}, °C: 120 \) (a, curve 1; b), 600 (a, curve 2), 650 (a, curve 3) and 700 (a, curve 4) before impregnation (a; b, curve 1) and after impregnation (b, curve 2) in Bi (NO₃)₃ solution.

**Fig. 2.** Temperature dependences of the logarithm of viscosity \( \log (\eta, P) \) (in heating mode) of quartzoid glasses based on PG 8V-NT (dependences I, 2) [23] and PG NFF-I (dependences 3, 4) before impregnation (dependences I, 3) and after impregnation (dependences 2, 4) in Bi (NO₃)₃ solution. Heat treatment temperature of PG \( T_{\text{treat.}}, °C: 120 \) (a), 650 (b, dependences 3, 4), 750 (b, dependences I, 2).
CONCLUSIONS

The rheological properties of PG obtained as a result of leaching two-phase SBS glass doped with small additions of phosphorus oxide and fluoride ions (~0.2 and ~0.5 mol %, respectively), as well as bismuth-containing quartzoid glasses based on it, are studied. The experimental temperature dependences of the shrinkage and viscosity of the PG samples during heating from room temperature to ~850°C, depending on their thermal history and impregnation in a solution of bismuth nitrate, were obtained.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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