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Porous glass: inhomogeneities and light transmission

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Basic optical characteristics were studied to reveal the structure of porous glass samples. Acid leaching technology was used to manufacture porous glasses from the bulk of phase-separated alkali borosilicate glasses. The transmission electron microscopy, selected area diffraction and shadow graph techniques, optical microscope and spectrophotometry, reflective ellipsometry were used to obtain new information about some inhomogeneities such as strata and spindle-like silica precipitates as well as boron containing microcrystalline phases inside porous glasses.

1. Introduction

Much attention has been paid in the last years to the porous glasses (PGs) prepared through the leaching of two-phase alkali borosilicate (ABS) glasses because of their immense possibilities to meet demands of optics, including laser technology, quantum electronics, analytical instrument-making, *etc.* These films demonstrated high thermostability, chemicall durability, transparency within visible spectral range, durability, and so on. Actually, these properties of PGs allow one to employ them for producing, for example, the new heterogeneous laser media as well as the high efficient microoptical or gas sensitive elements [1].

One of the demands for PG to be applied in practice is bulk optical homogeneity. Unfortunately, most of the porous PG plates are heterogeneous along their thickness. At present, direct optical methods have revealed two main types of homogeneity in PGs: lamellar inhomogeneities (or strata) and spindle-like inhomogeneities oriented perpendicular to the strata. Prevalence of one inhomogeneity depends on the temperature and concentration of the leaching solution or glass composition, and sample thickness [2], [3]. Apart from the above-mentioned silica gel precipitates other inhomogeneities such as microcrystalline alkali borates and silica phases can be formed in PGs [4].

2. Experimental part

2.1. Objects

The disposition of initial ABS glasses, more often used in practice to produce the PGs, is shown in the immiscibility diagram of Na_2O–B_2O_3–SiO_2 system [1]. Besides this three-component system, the many-component systems with different additions

are also successfully used for preparation of the optical PGs. During the special thermal treatment of the initial glass samples the phase-separated glasses with two-network interconnected structure are obtained. One of the glass phases is enriched with oxides of boron and alkali metals and, hence, is chemically unstable. The other phase is a high-silica network. The interaction between a two-phase ABS glass and an acid solution is a complex multistep process [4], [5]. The physicochemical feature of this process, which manifests itself in the dissolution of components of the unstable phase and in the interdiffusion of the dissolved substances in the porous layer formed, is the possibility of formation of silica and boron containing inhomogeneities in this layer owing to pH gradient inside the porous layer.

2.2. Methods

The porous structure of the PGs is generally studied by such methods as adsorption technique, transmission electron microscopy (TEM), electric conductivity method (see reviews in [6]–[8]). The strata formation in PGs is sometimes studied using optical microscopy and shadow graph technique (SGT) (see review in [3]). The determination of the basic optical characteristics of PGs, such as spectral dependences of light transmission, depolarization of transmission and reflectance of samples, birefringence, index of refraction, is very useful to reveal inhomogeneities in PGs, especially the spindle-like ones. For this purpose, the different methods of optical spectroscopy, polarimetry, reflective ellipsometry, to name but a few, can be used (see revievs in [7], [9]). Since PGs are X-ray amorphous glasses the selected area electron diffraction (SAED) technique is employed in order to investigate the possible microcrystallization of the boron containing products inside the PGs [6], [10]. Compared to the well-known X-ray diffraction analysis, this technique is more suitable because the short wavelength and strong interaction between electrons and the substance make it possible to produce a well-defined reflection when the crystals are of smaller sizes and the substance is in smaller amounts.

3. Inhomogeneities inside porous glasses

3.1. Microcrystalline phases

According to the main statements of the physicochemical model of glass leaching [4] the pH of the solution in pores depends on the leaching acid concentration and affects the composition of the products of dissolution of unstable phase components. So, for the leaching in concentrated HCl solutions the fact that the pH of the solution in pores is low enough (below zero) favours the precipitation of boric acid as the most stable solid phase under these conditions. In the case of dilute acid solutions a significant increase of the pH in the reaction zone inside the porous layer due to the effect of the alkali borate buffer causes precipitation of the solid alkali borates as borax-type. During the glass leaching a high pressure created in PGs at the boundary of "silica skeleton–air in pores" can cause the microcrystallization of secondary silica [4].

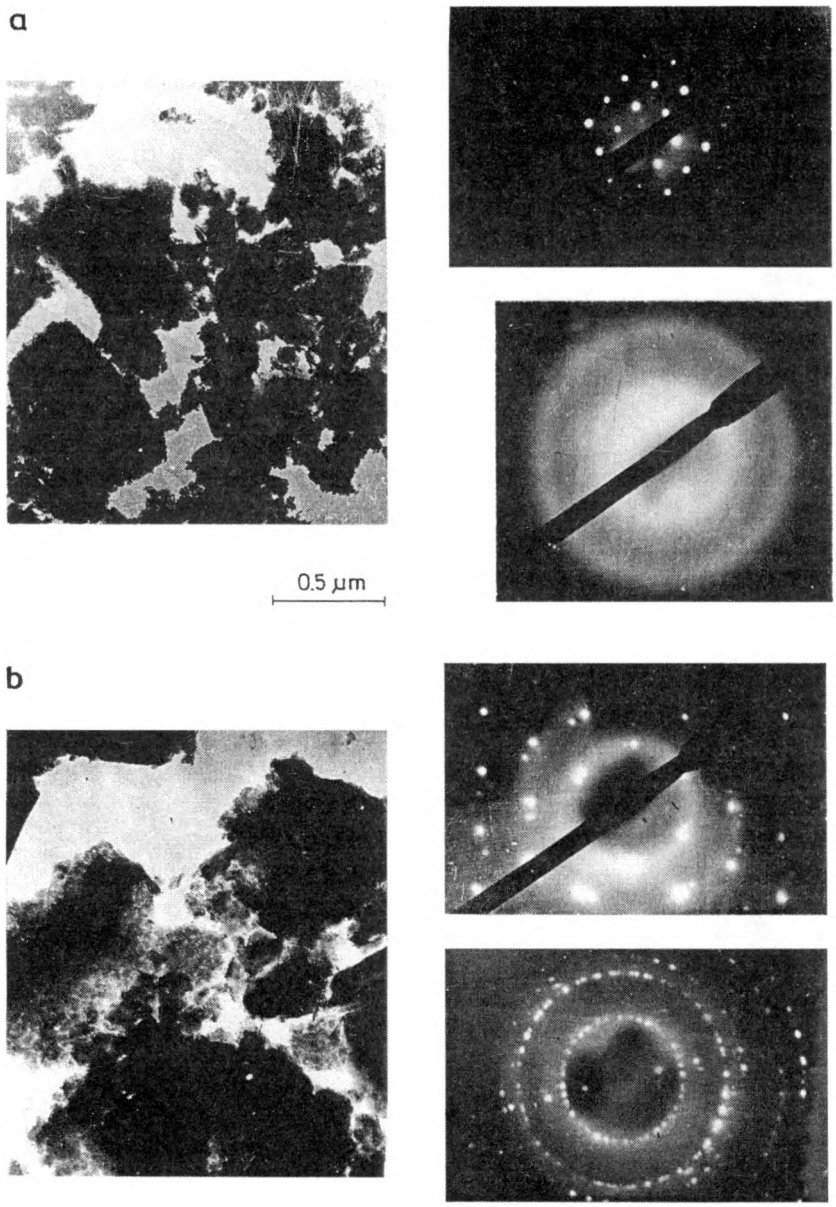

Fig. 1. Electron micrographs and electron diffraction patterns (shown in the insets) of the powder particles of the porous glasses (initial thickness $l = 2$ mm) PG1 (a) and PG2 (b).

These model predictions are supported by results of the PG investigations by SAED technique [6], [10], [11]. Figure 1 shows the electron micrographs and electron diffraction patterns (in the insets) taken from the powder particles of porous glasses that exhibit different optical properties, namely abnormal (PG1) and ordinary (PG2) light transmission. In addition to an amorphous phase that is identified

by the presence of the diffuse halo in a photo plate, miroctystalline particles are also observed in both cases. Their diffraction patterns are characterized by the electron diffraction spots. Calculating the patterns of electron diffraction spots makes it possible to identify the following microcrystalline phases. The hexagonal low-temperature tridimite (the unit cell parameters: $a_0 = 5.03$ Å, $c_0 = 8.22$ Å, and the [001] zone axis, an analog, ASTM-18-1169) is observed in the case of PG1 sample. The traces of α-quartz and sassolite are found in the PG2 sample.

3.2. Strata formation

Using the SGT, we proved that the deposition of silica in PGs changes periodically, and studied how selected praparation conditions influence the strata distribution [3]. By way of illustration the micrographs of scattering patterns of a He-Ne laser beam ($\lambda = 632$ nm) propagating perpendicular to the outer face in PGs including PG1 (photo 3) and PG2 (photo 6) are presented in Fig. 2. Examination of shadow graph for different PG strips showed that at the same acid concentration leaching at 20 °C produces widely separated irregular strata, whereas at 100 °C, strata are regular and closely packed, indicating higher homogeneity of the samples. When the temperature of the leaching solution is 50 °C, the shadow graphs of PGs are virtually free of strata. The fact that, of all glasses, PG obtained at 50 °C is the most homogeneous is apparently related to the following event. Over the temperature range studied it is only at this temperature that boron containing microcrystals,

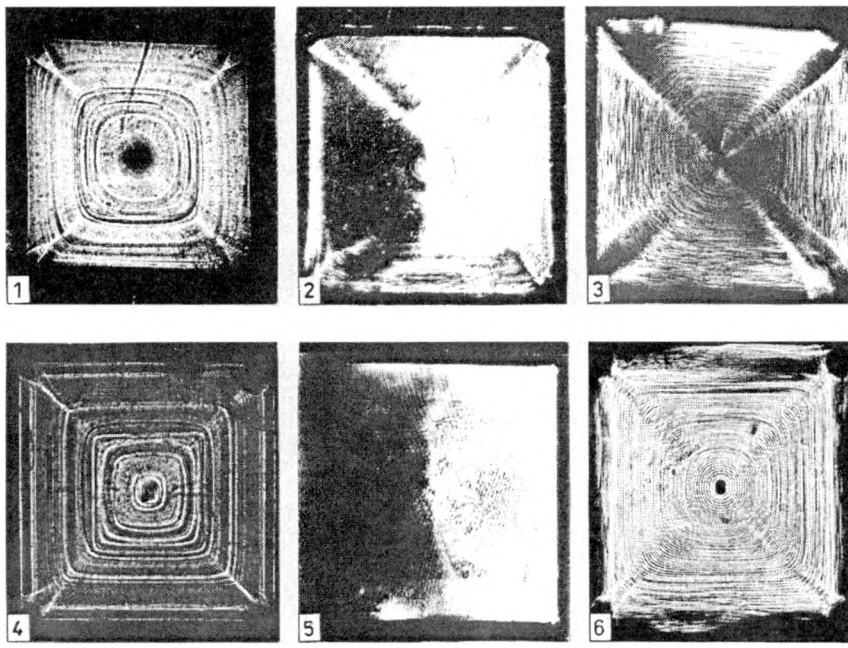

Fig. 2. Shadow graphs of scattering patterns of a He-Ne laser beam ($\lambda = 632$ nm) propagating perpendicular to the outer face (5×5 mm^2) in microporous glasses obtained by completely leaching the two-phase glass with (1–3) 1, and (4–6) 3 M HCl at (1, 4) 20, (2, 5) 50, and (3, 6) 100 °C [3].

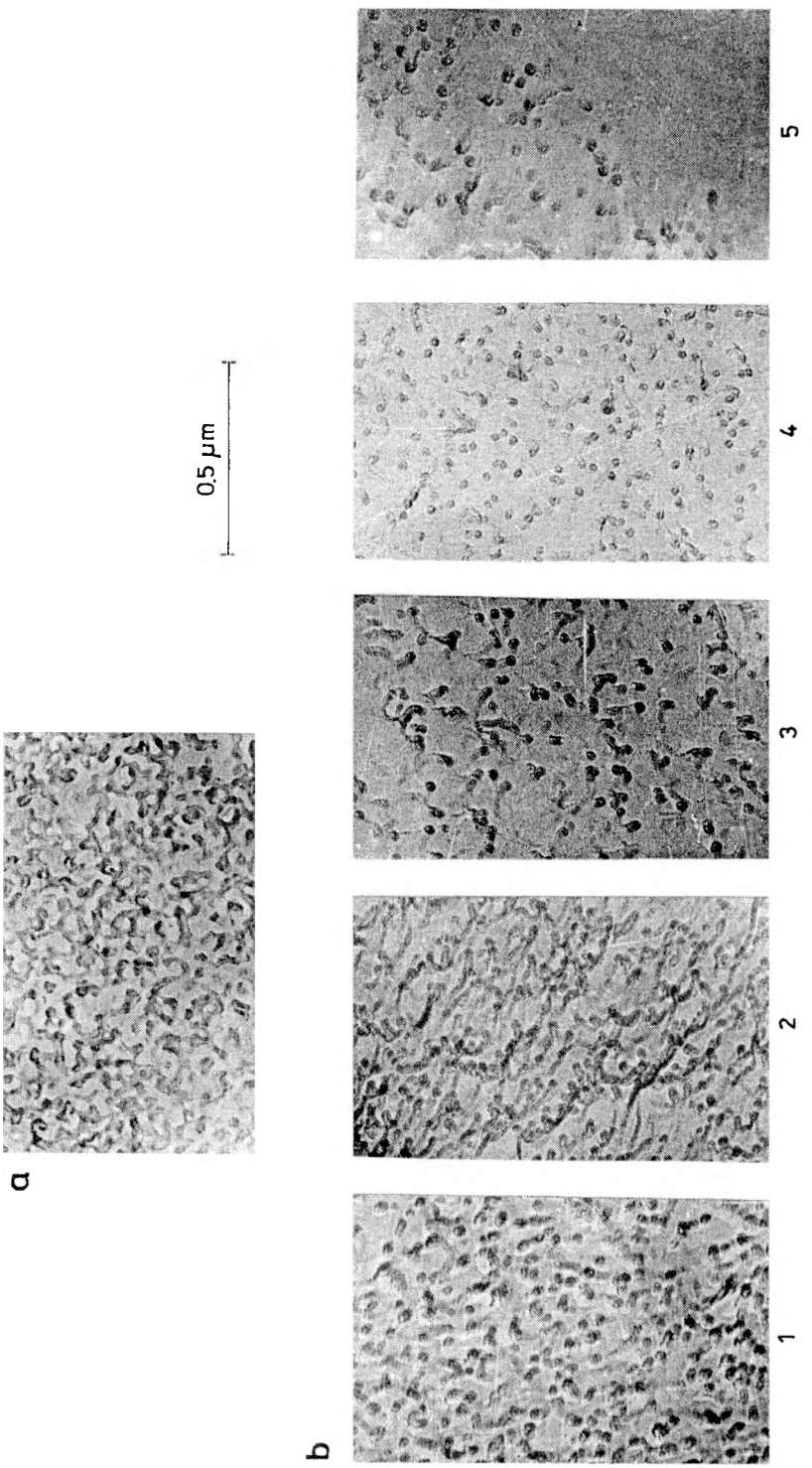

Fig. 3. Electron micrographs of the initial two-phase glass (a) and PG1 (b) (initial thickness $l = 2$ mm) in the planes parallel to the large faces of the sample. The layout of the micrographs from left (1) to right (5) corresponds to the sample areas observed from the periphery to the center.

which are formed as intermediates within the leached layer of two-phase glass, occur in the largest amount and have the highest degree of hydration (see review in [5]). This would decrease the degree of surface hydration of colloidal secondary silica paticles and, therefore, promote the subsequent formation of more homogeneous silica gel precipitates.

Figure 3 shows the TEM micrographs of the initial two-phase glass (**a**) and of PG1 (**b**) surface sections. The cellulose-carbon replicas were obtained from glass surface freshly cleaved in the plane symmetric about the larger faces of the samples. As is seen from Fig. 3**b**, in passing from center to the outer surface of the PG1 sample the porosity increases while the mean macro-pore diameter (which corresponds to the thickness of liquation channels occupied by the unstable phase of the two-phase glass) remains unchanged (50–60 nm). However, the character of macro-pore distribution is changing: it is important to say about some alternation of the regions of different density. In all likelihood, this alternation is conditioned by the strata formation, *i.e.*, by the recurrent silica gel precipitation during the glass leaching. At the same time, there is not any correlation between the degree of PG homogeneity determined by strata formation and PG light transmission τ (see review in [7]) that may be caused by negligibly small thickness of the strata as compared with λ value.

3.3. Silica spindle-like inhomogeneities

The main source of light decay in PGs is Rayleigh scattering for which the τ value usually decreases in a monotone fashion with increasing α (α – an angle between a normal to the wave front and inhomogeneity axis), Fig. 4, curves 1, 2, 4–6. The decrease in τ with increasing α is related to the increased reflection at the glass-air interface and the increased path length travelled by light in an isotropically

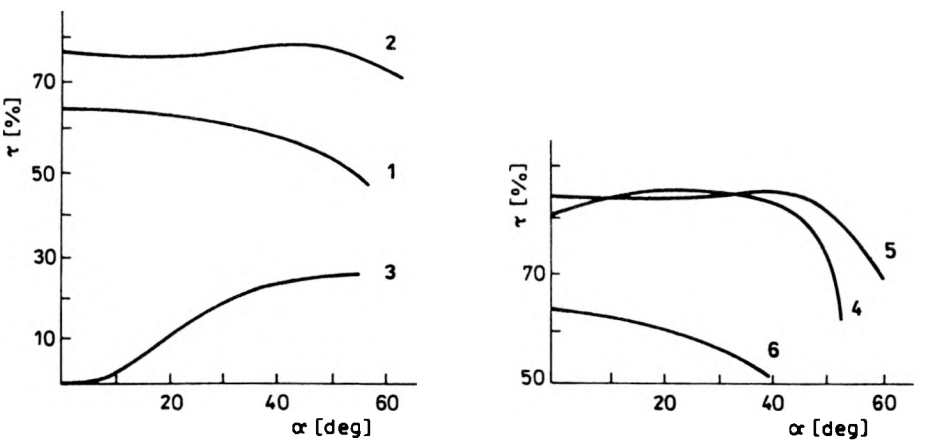

Fig. 4. Transmission τ as a function of the incidence angle α of a light beam (λ = 632 nm), measured from the normal to a larger surface of the porous plates (l = 2 mm), which were obtained by leaching the two-phase glass with (1–3) 1 and (4–6) 3 M HCl at (1, 4) 20, (2, 5) 50, and (3, 6) 100 °C.

scattering medium. However, light scattering in PG samples with spindle-like inhomogeneities apart from strata is characterized by more complex regularities (Fig. 4, curve 3). The silica spindle-like inhomogeneities are responsible for anomalous light propagation in PGs. They align in the direction of light-beam incidence and have an increased refractive index (RI) as compared with adjacent zones [2]. They act as optical wave guides in which light incident along the normal to the wave front, so that the angle α it makes with the axis of the inhomogeneities is less than some critical value, will be captured and scattered at their opposite end. Physicochemical model of the spindle-like inhomogeneity formation is given in some detail in [4], [12]. To summarize briefly, for such inhomogeneities to be formed in a PG, the glass leaching conditions must be such that the pH value of the solution in next to the reaction zone will ensure a sufficiently high solubility of secondary silica, but a relatively short gelatination time, so that these inhomogeneities have enough time to form before the boron-containing precipitates (around which silica gel forms) dissolve.

The TEM examination of PGs related some features pertaining to pore structure of PG samples differing in optical properties due to various conditions of their preparation [6]. The replicas were obtained from the PG surface cleaved in the plane perpendicular to the large faces of the sample (Fig. 5). In the central zone of PG1 sample which shows anomalous light scattering (Fig. 5**a**, photo 3) the high dense regions perforated with lower density structures (the so-called chains) are detected. The chains are oriented in the direction preferential for the mass transfer of interchanging agents during the glass leaching. The sizes of dense regions between chains, $1-3$ μm, are comparable with those of spindle-like inhomogeneities $2-5$ μm, which cause anomalous light propagation in PGs [2]. In ordinary scattered PG2 sample the cellular structures are not found (Fig. 5**b**). It may be suggested that there is a certain correlation between PG optical properties and the presence of the above-mentioned cellular structures oriented along the incidence direction of the light beam whose action reveals the effect of anomalous scattering in PG. However, the fact that chain diameters in the cross-section direction are considerably smaller than the wavelength of the beams considered did not allow us to unambiguously consider chains as wave guide claddings by assuming for wave guide core more dense (and thus higher reflecting) silica regions. It is not ruled out that anomalous scattering in some PGs is associated with the channelling of light between the above chains. Such a PG light scattering may be influenced by stresses, which lead to formation of regions differing in RI values owing to local formation of quartz microcrystals (see Fig. 1) [13]. Figure 6 presents the transmission spectra (relative to initial two-phase glass) of the PG1 (curve 1) and PG2 (curve 2) as well as their first derivatives (relative to air) [9]. The observed abnormally high relative transmission of PG1 gives evidence for the existence of the spatially irregular structures. To reveal an anomalous transmission and scattering of PGs we estimated the ratio of transmission at fixed (non-zero) incidence angle to transmission at normal light beam incidence. Spectral dependences of such standardized estimations provide evidence for anomalous transmission peaks (Fig. 7), which confirms the hypothesis of waveguide structures in some PGs.

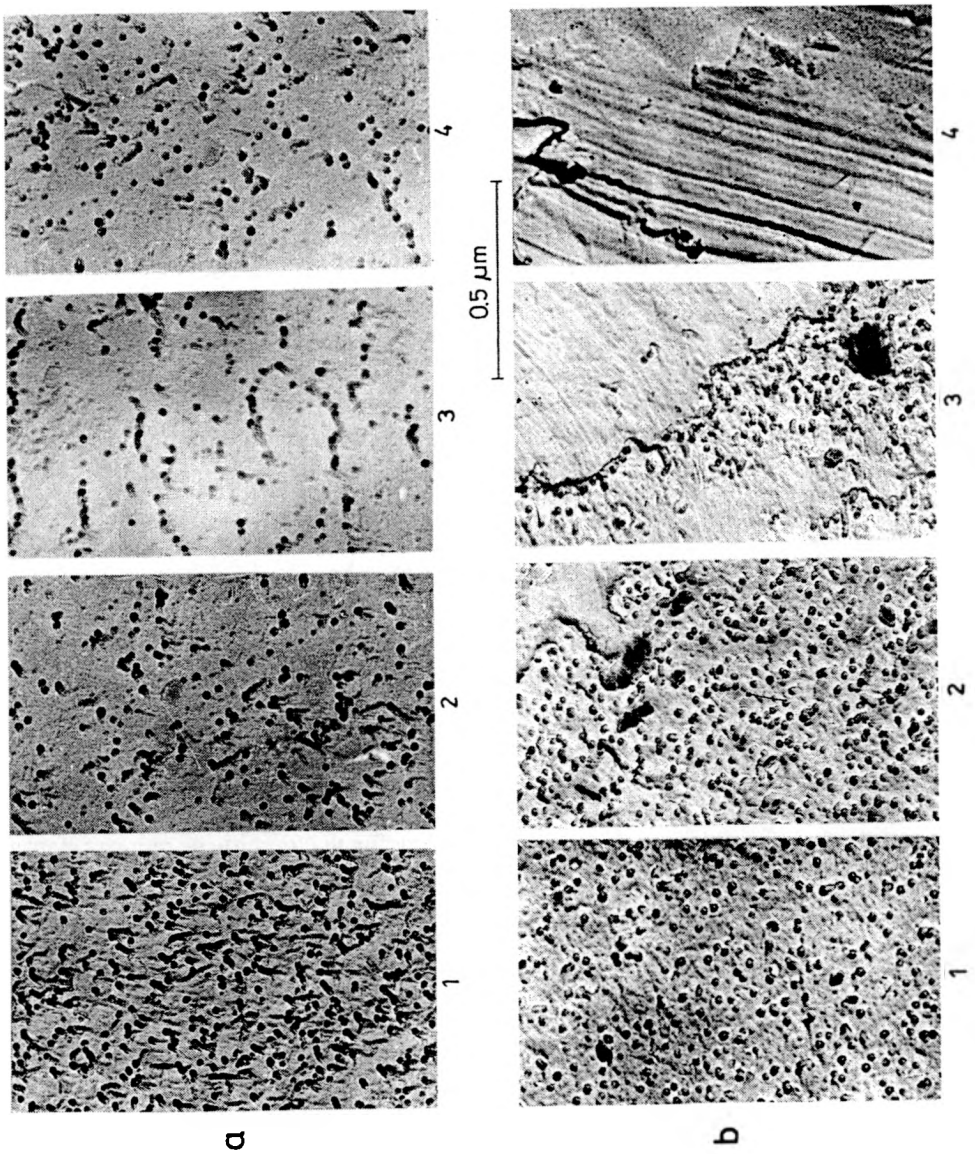

Fig. 5. Electron micrographs of porous glasses (l = 2 mm) PG1 (a) and PG2 (b) in the planes perpendicular to the large faces of the sample. The layout of the micrographs from left to right corresponds to the sample areas observed from the periphery to the center.

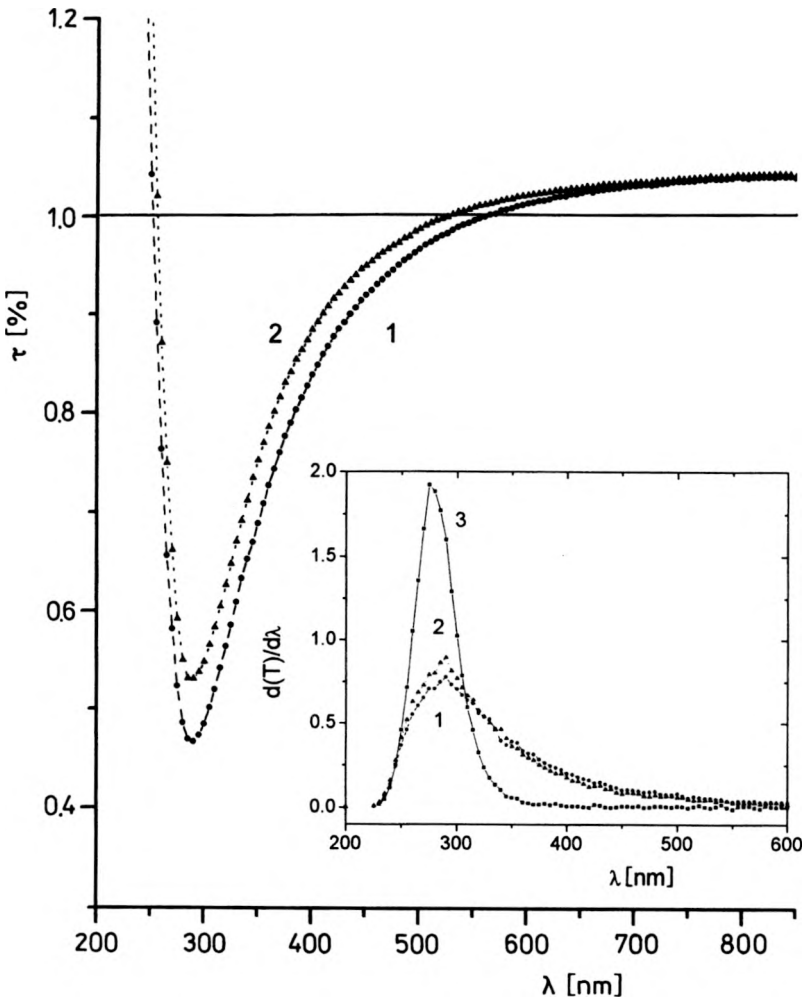

Fig. 6. Transmission spectra of the PG1 (1) and PG2 (2) (relative to initial two-phase glass (3)) as well as their first derivatives (relative to air).

Comprehensive investigation of the spectral dependences of light transmission, depolarization of transmission and reflectance of PGs (see Figs. 6–9) allow us to estimate the RI values. Figure 10 demonstrates the RI spectral dependences for PG1 (curves 1, 3) and PG2 (curves 2, 4) determined by two procedures used in [9]. As is seen from Fig. 10, the mean RI values for each of the PGs taken in adequate spectral regions are closely related but are not in line. The reasons of these distinctions are discussed in some detail in [9]. Nevertheless, the data obtained allow us to assess the dimensions of waveguide structures causing an increase of PG transmission at $\lambda = 250$ nm (see Fig. 6). For this purpose we used the model of the planar waveguide, which lay perpendicular to the sample surface. It was suggested that a waveguide was single mode and symmetrical one consisting of a substance

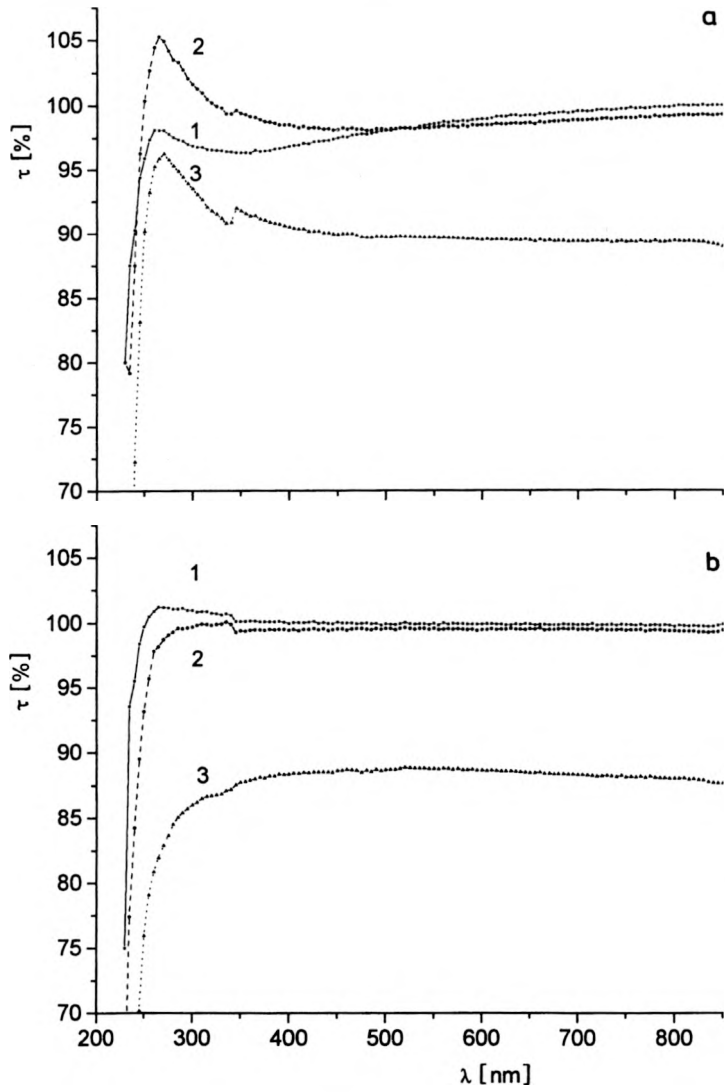

Fig. 7. Spectral transmission dependence of PG1 (a) and PG2 (b) at the different angles of incidence α of a light beam, measured from the normal to a larger surface of the porous plates (l = 2 mm). Incidence angle α, degrees (1) 10, (2) 20, (3) 30.

with refractive index $n_1 = 1.5$ (as for SiO_2) (a), and it was placed into medium with low RI value (equal 1) (b). Then the cross-section size of the waveguide can be estimated by equation

$$d = \frac{\lambda\varphi}{\pi \cos\theta} \tag{1}$$

where the connection of mode angle θ to incidence angle on waveguide side $\alpha_{max} = 20°$ is established by correlation

$$\theta = \frac{1}{2}\left[\pi - \arcsin\left(\frac{1}{n_1}\sin\alpha_{\max}\right)\right],$$

a phase shift φ on the waveguide boundary for the TE and TM polarization is expressed by:

$$\varphi_{TE} = \frac{\sqrt{n_1^2 \sin^2\theta_1 - 1}}{n_1 \cos\theta}, \quad \varphi_{TM} = n_1 \frac{\sqrt{n_1^2 \sin^2\theta_1 - 1}}{\cos\theta}. \tag{2}$$

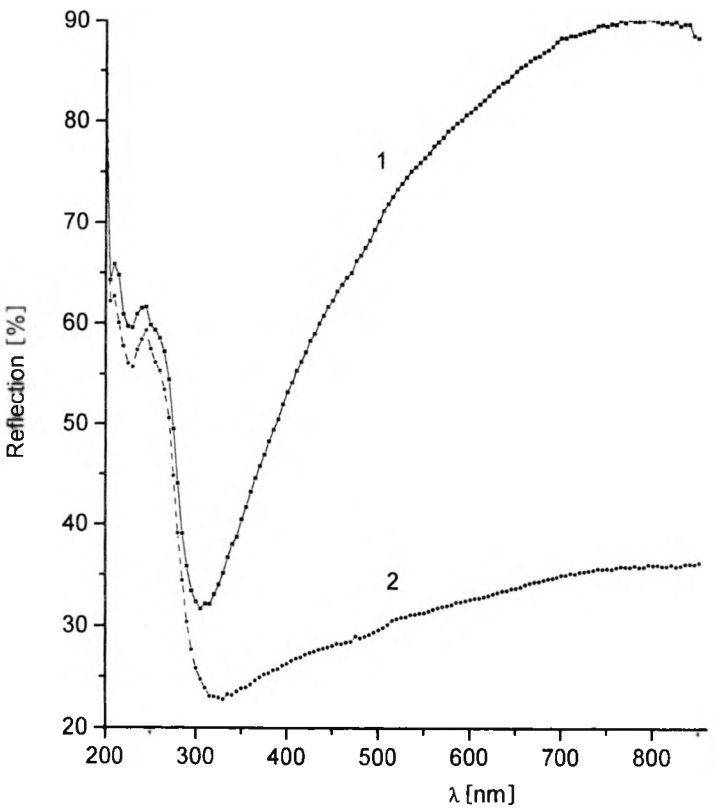

Fig. 8. Spectral reflectance dependences of the PG1 (1) and PG2 (2) (relative to reflectance of the initial two-phase glass).

As was calculated from Eqs. (2), $d \leqslant 1000$ nm, which is in agreement with results of our TEM study of PGs (Fig. 5) and with available data of [2] as well.

Figure 11 presents the RI dependences of glasses under study on the light beam incidence angle obtained by reflectance ellipsometry operating at 632.8 nm wavelength. This method was chosen as alternative one as regards optical spectroscopy. The principle of the method consists in measurement of the elliptical angles Ψ and Δ at fixed light incidence angle α on the sample. Correlation between elliptical angles and an elliptical function ρ can be specified by equation

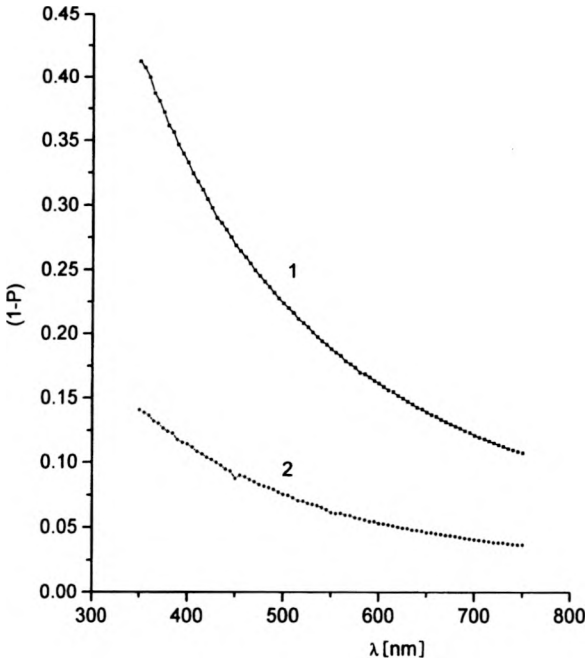

Fig. 9. Spectral depolarization dependences of PG1 (1) and PG2 (2).

$$\rho = \tan \Psi \cdot \exp(i\Delta). \tag{3}$$

In the case of semi-infinitely medium model the correlation between a complex refractive index n, a function ρ and angle α is defined as

$$n = n_1 \sqrt{\left(\frac{\rho-1}{\rho+1}\right)^2 \tan^2 \alpha + 1}. \tag{4}$$

Figure 11 shows that two-phase ABS glass is characterized by RI values from 1.471 to 1.477. The observed insignificant distinction of RI values upon the change of incidence angle can be ascribed to existence of the transition layer on the sample surface or to some inhomogeneity of the sample structure. The PG1 is characterized by dramatic RI dependence on the incidence angle. At $\alpha \approx 50$ degrees the RI value ranges up to 1.47 – 1.50, at larger angles – up to 1.24 – 1.30. This result gives evidence for distinct correlations in distribution of pores and elements of the matrix skeleton. Owing to that the effect of the localization of incident light by the structure inhomogeneities (in kind as a waveguide one) can come about at angles of less than 50 degrees. These results are in good agreement with data obtained when studying such PGs by other methods [2], [7], [12]. The PG2 is characterized by RI values from 1.24 to 1.27, which is interpreted within the framework of effective medium model as an increase of the porosity part in the formation of optical properties of the material [9].

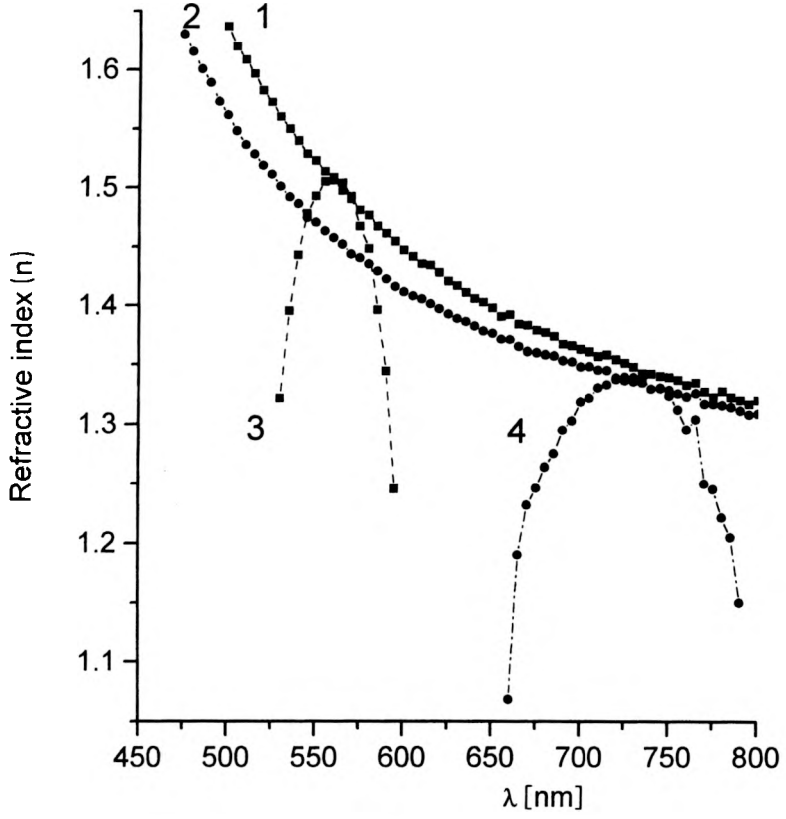

Fig. 10. Spectral dependences of the refractive index of PG1 (1, 3) and PG2 (2, 4). For explanation, see the text and [9].

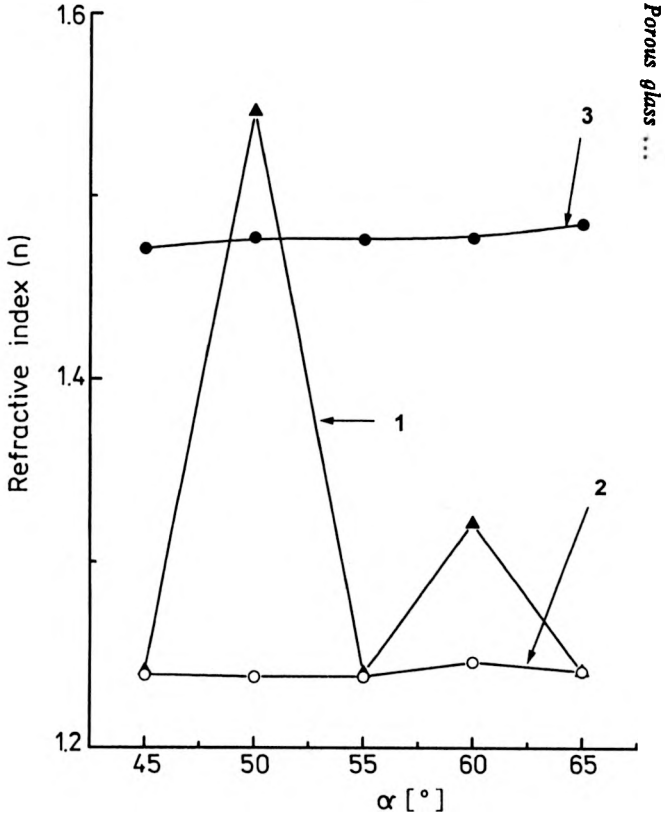

Fig. 11. Dependences of the refractive index of glasses under study from the light beam incidence angle α obtained by reflectance ellipsometry operating at 632.8 nm wavelength.

Pore concentration was determined within the above mentioned model by equation

$$\varepsilon = w\varepsilon + (1-w) \tag{5}$$

where $\varepsilon = n^2$ is a dielectric constant of "glass – air" mix, w is a volume part of the pores. According to our calculations the value w (*i.e.*, a relative volume of the macro-pores that is adequate for volume of the liquation channels in two-phase glass) is in the range from 45% for PG1 (a distribution of the macro-pores over the volume is strongly correlated) to 65% for PG2 (macro pores are accidentally distributed). These data are consistent with results obtained by TEM methods [6] as well as by immiscibility diagram of the glass system under consideration (50–55%), [1].

4. Conclusions

We have discussed the features of the porous glass structure consisting in formation of the different types of inhomogeneity during the leaching of the two-phase glass.

It was shown that different silica and boron-containing microcrystalline phases can be detected in X-ray amorphous porous glasses depending on concentration of the leaching acid solution.

Irregular precipitation of the secondary silica gel inside pores during two-phase glass leaching in the plane parallel to sample surface (strata formation) depends on the temperature and concentration of the leaching solution.

Much attention was given to the so-called spindle-like inhomogeneities formed by secondary silica gel in the plane perpendicular to the large faces of the glass samples. The existence of the spatially irregular structures in porous glasses was proved by results of their study by optical spectroscopy and reflective ellipsometry methods. These inhomogeneities cause the anomalous light transmission through the porous glasses. The ranges of an abnormal light transmission and light scattering were detected.

The comprehensive approach to definition of optical characteristics of porous glasses allowed obtaining the information on their possible structure parameters. The results of different methods of investigation were observed to be in agreement.

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