

Infrared studies and spectral properties of photochromic high silica glasses

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The structure of photochromic high silica glasses (PHSGs) was studied by UV–VIS–NIR and IR spectroscopy, transmission electron microscopy (TEM) and X-ray diffraction (XRD) techniques. PHSG plates were obtained by impregnation of silica porous glasses at first with AgNO_3 aqueous solution (in or without the presence of the sensitizers, such as $\text{Cu}(\text{NO}_3)_2$ or $\text{Ce}(\text{NO}_3)_3$), next in the mixed halide salt (NH_4Cl , KBr , KI) solution. Then a part of the samples was sintered at temperatures from 850 to 900 °C up to closing of the pores. The results of TEM study have shown that the PHSG plates have two-phase structure with inclusions of the size of 10–100 nm. According to XRD data, the PHSGs contain the AgBr phase. IR spectra confirmed the presence of AgI , AgCl , CeO_2 , CuCl_2 , CuCl phases in PHSGs.

Keywords: silica porous glass, photochromic high silica glass, transmission electron microscopy (TEM), X-ray diffraction (XRD), UV–VIS–IR transmission spectra.

1. Introduction

We have synthesized and investigated the samples of photochromic high silica glasses (PHSGs) which are the photochromic porous glasses (PPGs) and photochromic quartz-like glasses (PQGs) obtained by sintering of PPGs up to closing of the pores. PHSG is new photosensitive composite material, which possesses a number of properties inherent to quartz glass [1]. PHSGs are usually obtained by impregnation of the silica porous glasses (PGs) with photosensitive silver halides phases (AgCl , AgBr , AgI) [1–3]. The materials of this kind are used for creation of the plasmonic waveguides, in the optical data storage, in superlenses and sensors [4–13]. Formation of these microoptical elements occurs due to the use of laser irradiation [4, 11, 14]. In the case of PHSGs, the photochemical properties can be improved through variation in PG plate thickness and conditions of their preparation, as well in solution composition of impregnant and sintering modes [2].

2. Experiment

2.1. Synthesis of the glasses

Synthesis of PHSGs was carried out according to the procedure [1–3], which consists in following. At first, PG samples (in the form of the rectangular plane-parallel plates of the size of $(1.5 \pm 0.03) \times (10–15) \times (15–25)$ mm³) were placed in AgNO₃ aqueous solution (in or without the presence of sensitizers, such as Cu(NO₃)₂ or Ce(NO₃)₃). Next the samples were submerged in a mixed halide salt (NH₄Cl, KBr, KI) solution. As the result, the samples of PPGs were obtained. PPGs were sintered at temperatures from 850 to 900 °C for 10–40 minutes [2]; owing to that, a closing of the pores and formation of a monolithic high silica material, *i.e.*, PQG, took place. The pure quartz-like glasses (QGs) were prepared from PGs without impregnation under the same sintering conditions. The glasses under investigation have following compositions (as analyzed, wt%): 0.30 Na₂O, 3.14 B₂O₃, 0.11 Al₂O₃, 96.45 SiO₂ (PGs) [3], 0.20–1.05 Na₂O, 0.39–0.48 K₂O, 3.07–3.45 B₂O₃, 94.11–96.09 SiO₂, 0.33–1.25 Ag₂O (with/without ≤ 0.1 Al₂O₃), and in or without the presence of a sensitizer (0.03–0.04 CuO, 0.02–0.03 Ce₂O₃) – PHSGs. The copper quantity was determined by the flame photometry method on iCE of 3000 Series spectrometer, cerium – by inductively coupled plasma mass spectroscopy (ICP-MS) on Elan 6100 drc.

2.2. Methods of glass characterization

The synthesized glasses were investigated by the following techniques:

- IR transmission spectra were obtained with SPECORD M-80 spectrophotometer in the range of 4000 to 300 cm⁻¹ at the spectral resolution of 4 cm⁻¹. For measurements of IR spectra, the glasses were powdered and mixed with KBr in order to obtain thin pellets by vacuum pressing.
- Transmission spectra were measured by SF-2000 UV/VIS spectrophotometer in the wavelength range of 190–1100 nm with a step of 0.115 nm.
- TEM images were obtained by the well-known method of cellulose-carbon replicas with EM-125 electronic microscope at an accelerating voltage of 75 kV [1].
- X-ray diffraction studies were carried out on the DRON-2 device with monochromatic CuK_α-radiation (rotation speed of the counter was 2 °C/min).

3. Results and discussion

3.1. The structure of the glasses under investigation

The electron micrographs of the synthesized samples are presented in Fig. 1. It is seen that the structure images of the PQGs with different dopants are various. The separate inclusions in the size of 10–100 nm are observed inside a silica matrix in the cases of impregnation of PG by silver halides (Fig. 1a) or by silver and copper halides (Fig. 1b). In pure QGs, such inclusions were not observed [1].

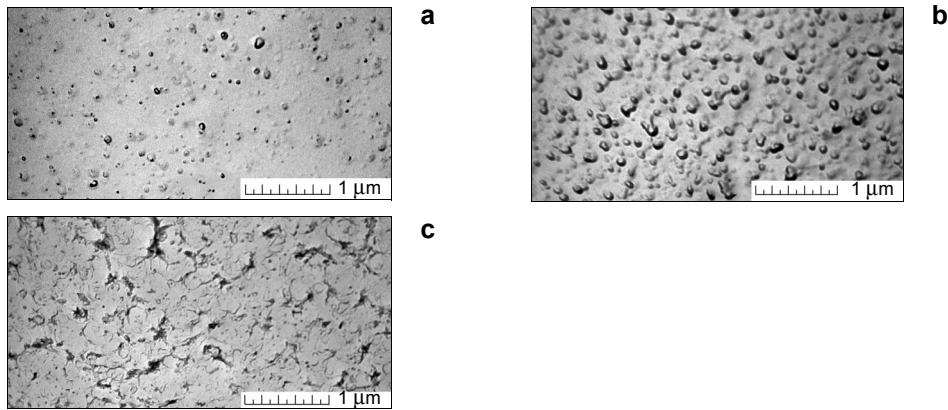


Fig. 1. TEM photographs of the photochromic quartz-like glasses with: silver halides (a); silver and copper halides (b); silver and cerium halides (c).

It is necessary to notice that according to TEM study, the QGs have a structure of a “micro-liquation” type [1]. It gives the grounds to assume that the inclusions are formed by a photosensitive phase. It is visible that the total amount of inclusions in PQGs doped with silver and copper halides (Fig. 1b), is greater than in PQGs doped only with silver halides (Fig. 1a), and reaches ~45%. However in the case of PQG doped with silver and cerium halides, a characteristic pattern of crystallized material [15, 16] is visible (Fig. 1c).

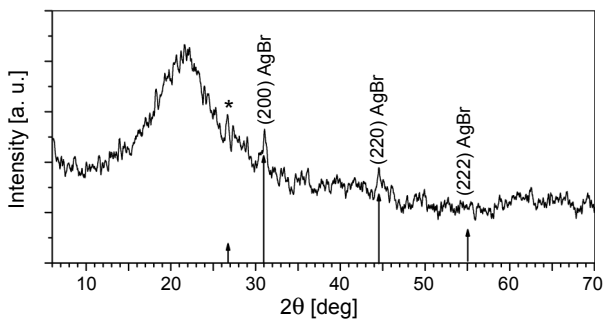


Fig. 2. Typical X-ray diffraction spectrum of the photochromic quartz-like glasses. An asterisk indicates the strongest line of quartz.

X-ray diffraction spectrum of PQG samples under study is shown in Fig. 2. Our measurements indicated that all three types of the PQGs contain silver bromide in the cubic system. In the case of PQG doped with silver halides without sensitizers, the diffraction spectra have the peaks (200) AgBr, (220) AgBr and (222) AgBr. The unit cell parameter of AgBr crystallites equals $a = 5.775 \text{ \AA}$ and is slightly lower than the table value (Database PDF-2 file No. 79-0149). The glasses additionally doped with copper

or cerium have even smaller unit cell parameter of AgBr, namely $a = 5.704 \text{ \AA}$ and $a = 5.648 \text{ \AA}$, correspondingly. Such reduction of the unit cell parameters can be explained by the fact that for mixed crystals of the silver halides, the superimposition and the shift of the diffraction peaks are characteristic. At that it is necessary to notice that the diffraction peaks of AgCl, AgI and AgBr phases have a close location [17].

3.2. UV–VIS–NIR and IR transmission spectra investigation

The transmission spectra of PGs, QGs and PQGs are given in Fig. 3. It is seen that in the case of QGs, the cut-off was observed at $\lambda = 206 \text{ nm}$, which shifted to $\lambda = 233 \text{ nm}$ for PGs and to $\lambda = 267 \text{ nm}$ for PQGs. The transmittance of PQGs is reduced as compared with PGs and QGs. At that PQGs doped with silver and cerium halides have the lowest transmittance value in the spectral range 395–1100 nm in comparison with other glasses. Also for given glass, an intermittent increase in transmittance in the spectral range 300–395 nm is observed (Fig. 3, black solid line). This result can be caused by absorption of cerium nanoparticles as well by a formation of silver colloidal nanoparticles [18, 19].

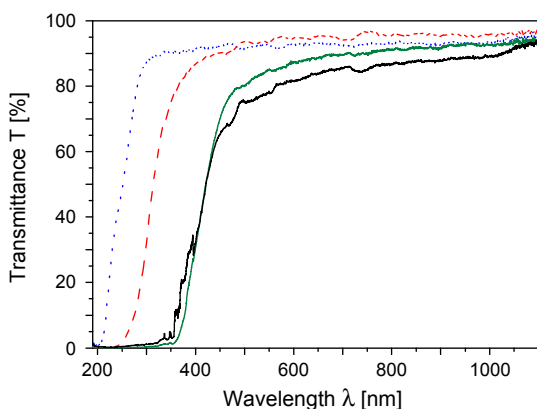


Fig. 3. Transmission spectra of the glasses: silica porous glass (dash line), quartz-like glass (dot line), and photochromic quartz-like glasses: doped with silver halides (green solid line), doped with silver and cerium halides (black solid line).

IR transmission spectra of glasses under investigation are shown in Figs. 4 and 5. It was found that all types of glasses have eight fundamental absorption bands at 3684–3672, 3520–3472, 3432–3420, 2928–2916, 2824–2820, 1668–1652, 1392–1376, 1108–1080 cm^{-1} . On the basis of the literary data [19–37], the following structural groupings can be identified on characteristic peaks.

Broad-bands placed at 3684–3672, 3520–3472, 3432–3420, 1668–1652 cm^{-1} are assigned to stretching vibrations of hydroxyl groups and water. The broad-band at 3432–3420 cm^{-1} is due to Si–OH stretching of surface silanols hydrogen and also due to vibrational structure of Si–O–Si. Two bands at 2928–2916 and 2824–2820 cm^{-1} are connected with hydrogen bonds. The band at 1392–1376 cm^{-1} is connected with

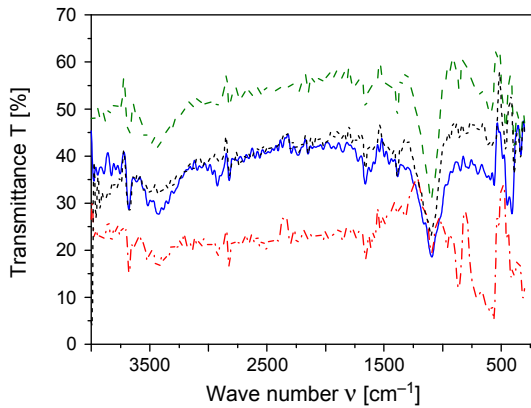


Fig. 4. IR transmission spectra of the glasses: silica porous glass (dash-dot line), and photochromic porous glasses: doped with silver halides (short-dash line), doped with silver and copper halides (solid line), doped with silver and cerium halides (dash line).

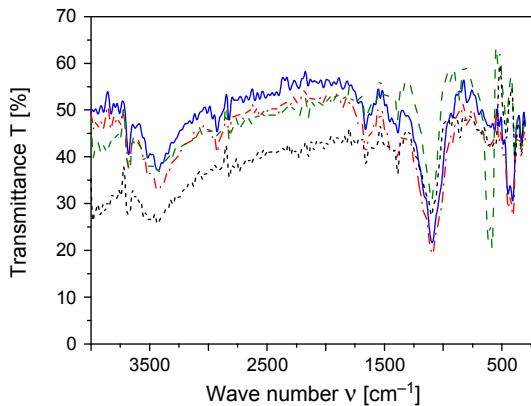


Fig. 5. IR transmission spectra of the quartz-like glass (dash-dot line), and photochromic quartz-like glasses: doped with silver halides (short-dash line), doped with silver and copper halides (solid line), doped with silver and cerium halides (dash line).

asymmetric stretching vibrations of $[\text{BO}_3]$ unit. Broad-band placed at $1108\text{--}1080\text{ cm}^{-1}$ is associated with Si–O–Si asymmetric stretching.

Apart from the absorption bands mentioned above, the PPGs and PQGs have the following bands. The shoulders at $1320\text{--}1316$ and $1100\text{--}1088\text{ cm}^{-1}$ became broader (Figs. 4 and 5). This result was due to the interaction between the AgCl/Ag particles and the matrix of the glass and due to the addition of AgI, which induces a change in the spectra in this range of the frequencies. The band at $860\text{--}848\text{ cm}^{-1}$ in PPGs (Fig. 4, solid line) and PQGs (Fig. 5, short-dash and dash lines) indicates some effect of the AgI on the glass structure. The band at $792\text{--}776\text{ cm}^{-1}$ (Fig. 4, short-dash and solid lines) is associated with the symmetric stretching mode of Ag–O–Si bonds, showing that the Ag clusters have oxygen as an adsorbate atom/surrounding atom. The weak

shoulder at 704–688 cm^{-1} is assigned to Si–O–Al deformation and also due to bending of B–O–B linkages in the borate network. The shoulder at 616–608 cm^{-1} (Fig. 4, short-dash and dash lines) is assigned to vibration of Ag–O bonds. The band at 536–528 cm^{-1} which is observed in Fig. 5 (dash line) can be attributed to the Ce–O stretching vibration. The sharp peaks in 560–400 cm^{-1} range (Figs. 4 and 5, solid lines) show the copper halide linkages (CuCl, CuBr, CuI) whereas halides behave as a bridging ligand. The bands at 516 and 408 cm^{-1} (Fig. 4, solid line) can be attributed to the CuCl_2 and CuCl phases. The band at 452–444 cm^{-1} is attributed to δ (Si–O–Si) symmetric stretching and bending vibrations. The symmetric and asymmetric Ag–O stretching bands were observed at 464–460, 392–384 and 336–332 cm^{-1} .

4. Conclusions

UV–VIS–NIR transmission spectra have shown that PGs, QGs and PQGs are transparent throughout the visible and near infrared spectral range. The intermittent increase in transmittance at $\lambda = 300\text{--}395$ nm in PQGs doped with silver and cerium halides is connected with the absorption of cerium nanoparticles.

According to TEM data, a structure of PHSGs has a “micro-liquation” type with the inclusions of a photosensitive phase, a portion of which depends on the kind of the entered sensitizer. Crystallization is characteristic for samples which are doped by silver and cerium halides.

X-ray diffraction spectra of PQGs show that they contain AgBr phase in the cubic system. According to IR transmission spectra, all samples of PHSGs contain AgI, AgCl, Ce–O, Ag–O, Ag–O–Si, Si–O–Al units; copper halide linkages (CuCl, CuBr, CuI), CuCl_2 and CuCl phases.

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