

Structure and spectral properties of the silver-containing high-silica glasses

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Abstract. Silver-containing high-silica glasses were synthesized by an impregnation of the silica porous glasses (PGs) first with AgNO₃ aqueous solution (with or without the presence of the sensitizers, such as Cu(NO₃)₂ or Ce(NO₃)₃), next in the mixed halide salt (NH₄Cl, KBr, KI) solution. Then some part of the samples was sintered at the temperatures from 850 to 900°C up to closing of the pores. The structure of glasses was studied by UV-VIS-NIR and IR spectroscopy and X-ray diffraction (XRD) techniques. According to XRD data the silver-containing high-silica glasses contain the AgBr, AgI, Ag₃PO₄, (CuBr)_{0.75}(CuI)_{0.25} phases. IR spectra confirmed B–O–B, Si–O–Si, P–O–P, O–P–O, O–B–O bonds, (PO₄)³⁻ and P–O⁻ groups in glasses.

1. Introduction

Silver-containing materials and glasses are used as materials for creation of the plasmonic waveguides, 3D laser modified areas, in superlenses and sensors [1–6].

2. Experimental

Synthesis of the silver-containing high-silica glasses was carried out according to the procedure [1, 7–9], which consist in following. At first, PG NFF matrixes (in the form of the rectangular plane-parallel plates in size (1.5±0.03) x (5–15) x (5–25) mm³) were placed in 100 mg/ml AgNO₃ aqueous solution (with or without the presence of sensitizers, such as 10 mg/ml Cu(NO₃)₂ or 10 mg/ml Ce(NO₃)₃). Next the samples were immersed in a mixed halide salt (NH₄Cl, KBr, KI) solution. As the result the samples of photochromic porous glasses (PPGs) with silver halides / with silver and copper halides / with silver and cerium halides were obtained. PPGs were sintered at temperatures from 850 to 900°C for 10–40 minutes which leads to closing of the pores and the photochromic quartz-like glasses (PQGs), i.e. a monolithic high silica material is formed. Depending on the concentration of the impregnating solutions containing silver and sensitizer, in this paper we made the following notation of PPGs and PQGs: 100Ag, 100Ag / 10Cu, 100Ag / 10Ce. 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. %): 0.55 Na₂O, 6.85 B₂O₃, 92.56 SiO₂, 0.04 [F], traces P₂O₅ (PGs), 0.46 Na₂O, 6.42 B₂O₃, 93.09 SiO₂, 0.03 [F], traces P₂O₅ (QGs); (0.43–0.49) Na₂O, (0.52–0.77) K₂O, (5.83–6.39) B₂O₃, (91.00–91.89) SiO₂, (0.02–0.13) [F], (0.08–0.10) P₂O₅, (0.89–1.60) Ag₂O, and in the presence or without the sensitizer (0.02 CuO / 0.04 Ce₂O₃) (PPGs and PQGs).



The synthesized glasses were investigated by various 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. Spectral measurements were conducted at room temperature. X-ray diffraction (XRD) studies were carried out with the D8-Advance “Bruker” powder diffractometer with monochromatic $\text{CuK}\alpha$ -radiation (operating voltage 40 kV, current 40 mA) from the sample surface. Phases were identified using the International Centre for Diffraction Data (ICDD-2006) database.

3. Results and discussion

According to XRD data (figure 1), in all the glasses only phases with cubic structure were found. The **PPGs 100Ag** contain AgBr (Pattern no. 01-071-3754, the unit cell parameter is $a = 5.780 \text{ \AA}$), Ag_3PO_4

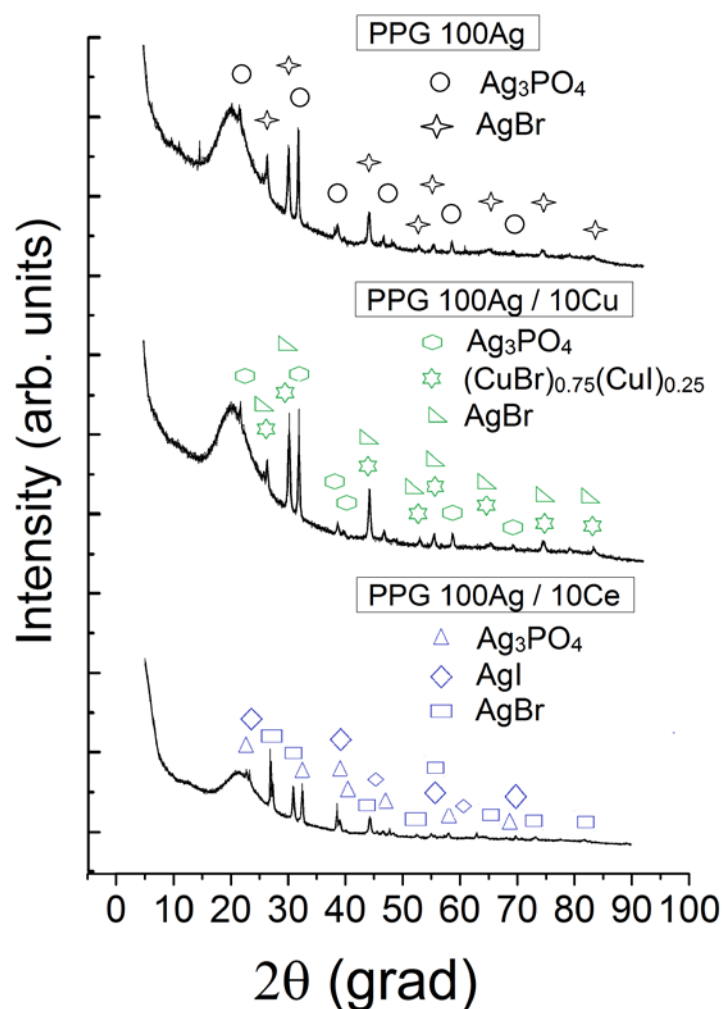


Figure 1. X-ray diffraction spectra of the photochromic porous glasses.

(Pattern no. 00-030-1137, $a = 7.720 \text{ \AA}$) phases, the **PPGs 100Ag / 10Cu** – AgBr (Pattern no. 01-079-0148, $a = 5.769 \text{ \AA}$), Ag_3PO_4 (Pattern no. 00-030-1137, $a = 7.752 \text{ \AA}$) and $(\text{CuBr})_{0.75}(\text{CuI})_{0.25}$ (Pattern no. 01-077-2388, $a = 5.772 \text{ \AA}$) phases, **PPGs 100Ag / 10Ce** – AgBr (Pattern no. 01-071-3754, $a = 5.766 \text{ \AA}$), Ag_3PO_4 (Pattern no. 00-030-1137, $a = 7.768 \text{ \AA}$), and AgI (Pattern no. 01-071-3829, $a =$

6.606 Å) phases. The glasses additionally doped with copper or cerium have smaller unit cell parameter of AgBr and larger unit cell parameter of Ag_3PO_4 , which may be due to the influence of sensitizers. Such reduction of the unit cell parameters can be explained by the fact that for mixed crystals of the silver halides the superimposition and shift of the diffraction peaks are characteristic [8].

IR and UV-VIS-NIR transmission spectra of the glasses are shown in figure 2. In the IR spectra (figure 2a) of all types of glasses (PG and PPGs) the absorption bands are observed at: 3676–3672,

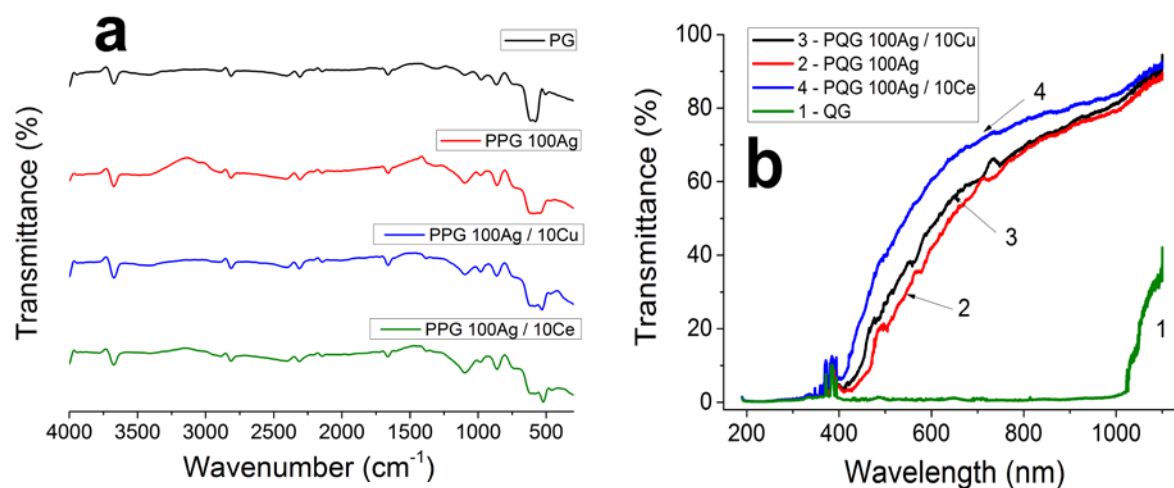


Figure 2 (a, b). (a) IR transmission spectra of the glasses; (b) UV-VIS-NIR transmission spectra of the glasses.

3500–3476, 3428–3404, 2896–2888, 2824–2812, 1664–1660, 1388–1368, 1100–1096, 984–972, 864–856, 732–724, 692–684, 476–472, 464–456 cm^{-1} . Broad bands placed at 3676–3672, 3500–3476, 3428–3404, 1664–1660 cm^{-1} are assigned to stretching vibrations of hydroxyl and water groups [10–11]. Two bands at 2896–2888 and 2824–2812 cm^{-1} are associated with hydrogen bonds [10]. The band at 3428–3404 cm^{-1} is due to Si–OH stretching and also due to vibrational structure of Si–O–Si [12]. The band located at 1388–1368 cm^{-1} is assigned to B–O asymmetric stretching vibrations in BO_3 units [13]. The absorption band at 1100–1096 cm^{-1} is connected with Si–O–Si asymmetric stretching and assigned to P–O^- groups, the phosphate non-bridging oxygen portion of PO_4 tetrahedra in a chain structure [14–16]. Bands have been found in the range 984–972 cm^{-1} assigned to the stretching and deformation modes of $(\text{PO}_4)^{3-}$ groups and confirming the presence of P–O^- groups in the glasses [15–16]. Stretching vibrations of B–O bonds in BO_4 units are responsible for band at 864–856 cm^{-1} [13]. The band observed at 732–724 cm^{-1} suggest the presence of symmetric stretching modes of the linear P–O–P linkages, ν_{sym} (P–O–P) [15, 17]. The absorption band at 692–684 cm^{-1} is assigned to ν_{sym} (P–O–P) and B–O–B bond bending vibrations of the borate network [17–19]. The two weak bands appearing at 472 cm^{-1} and in the range 464–456 cm^{-1} , which may be attributed to bending vibrations δ (Si–O–Si), δ (O–P–O) and δ (O–B–O) linkages [12, 15, 17–18].

All samples of PQGs are highly transparent in the range 370–1100 nm (figure 2b). QG has low transparency (strong absorbance) from 190 nm to 370 nm and from 395 nm to 980 nm. Other character of light transmittance of the QG plates may be caused by a formation scattering and absorbing structure (possible microcrystalline inhomogeneities) [20]. The broad absorption band from 190 to 322 nm and the maxima at 344, 352, 364, 379, 392–393 nm (in all glasses) are associated with the glass matrix. The absorption bands at 395 nm (curve 4), 410 (curves 2, 3), 505, 577, 722 nm (curve 2) are conditioned by silver. Several absorption bands around 481, 559, 712, and 748 nm (curve 3) are caused by the presence of copper. The spectra showed three surface plasmon resonance peaks two of

which centered at 395 and 410 nm corresponding to the silver and the another centred at 559 nm to that of copper in the glasses [21–23].

It should be noted that the given results (figure 2) obtained at the study of the PPGs and PQGs on the basis of PG NFF matrixes differ from data for the similar samples received on the basis PG 8V-NT [8].

The optical absorption spectra of PPGs are shown in figure 3. A plurality of absorption bands were

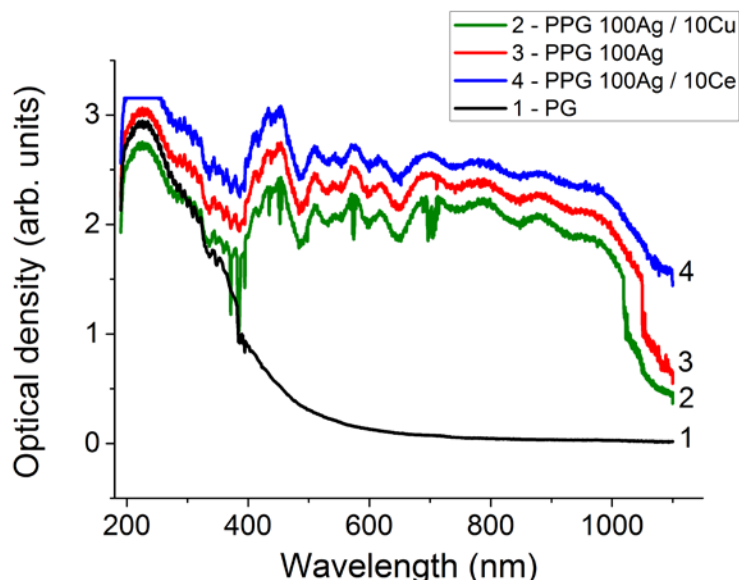


Figure 3. Absorption spectra of the photochromic porous glasses in comparison with porous glass.

detected on absorbance spectra. The maxima at 364, 376–379, 396, 410–411, 433–434, 454, 511–514, 539–544, 570, 617–620, 693–698, 779–780, 875–876, 966–971 nm (curves 2–4) can be connected with presence of silver inside matrix of PPGs. The peaks observed at 581, 689, 720, 789 nm (curve 2) could be corresponding to the presence in the glasses of divalent copper ions [23]. Absorption band centered 789 nm which is due to the characteristic ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transition of Cu^{2+} ions in a distorted octahedral site [19].

4. Conclusion

X-ray diffraction spectra of PPGs show that they contain AgBr, AgI, Ag_3PO_4 , $(\text{CuBr})_{0.75}(\text{CuI})_{0.25}$ phases in the cubic system. According to IR transmission spectra, PPGs contain B–O–B, Si–O–Si, P–O–P, O–P–O, O–B–O bonds, $(\text{PO}_4)^{3-}$ and P–O^- groups in glasses. UV–VIS–NIR transmission spectra have shown that PQGs are transparent throughout the visible and near infrared spectral range. Optical absorption spectrum in PPG 100Ag / 10Cu shows broad band at 789 nm which is due to the characteristic ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transition of Cu^{2+} ions.

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