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SHORT COMMUNICATION

Structural Characteristics and Electrokinetic Potential of Silicate Porous Glasses Doped with Silver Iodide

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Abstract—The structural (volume porosity, specific surface area, and average pore radius) and electrokinetic characteristics are studied for silicate and AgI-doped microporous glasses and quartz-like nanocomposites based on them. The change in the structure and surface parameters is analyzed for vitreous materials by doping with silver iodide in the porous space and high-temperature treatment of the initial and doped materials.

Keywords: porous silicate glass, nanocomposite, quartz-like, silver iodide, electrokinetic potential

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The interest in the porous and monolithic nanostructured vitreous materials doped with metals and metal compounds is caused by both the practical importance of novel metamaterials and the necessity of the development of fundamental concepts of the structure of nanomaterials with a mosaic surface–electrolyte solution interface. The impregnation of high-silica porous matrices with salts of different metals followed by additional treatment (temperature, laser, etc.) is the most common method of obtaining porous composites and quartz-like nanostructured materials. Photosensitive glasses doped with silver are promising materials for photonics, laser technology, optical instrumentation, and solar energy [1–3]. Processing photochromic quart-like glasses doped with silver halides by ultraviolet laser irradiation results in the separation of quasi-metallic silver nanoparticles [4–6], which provides a high resolution of these glasses and makes their application possible for image fixation and storage, as well as recording volumetric phase holograms. The growing interest in glasses doped with nanosized silver is caused by their applicability in nanobiotechnology, sensorics, and photonics [1, 7, 8] due to the plasmonic resonance at the absorbance of light by nanoparticles enclosed in the dielectric matrix. When in contact with biological objects, plasmonic effects significantly expand their detection, identification, and diagnostics [9]. Porous quartz-like glasses impregnated with silver halide can be considered as a promising material for plasmon waveguides, which are functional elements of integrated optical circuits that can be suitable for focusing, collimating, and branching laser beams, for matching optical fibers in fiber-optic communication lines and telecommunications, etc. [10, 11].

The functional characteristics of the materials during use in contact with electrolyte solutions depend on the processes on the interface. The study of the structural and electrokinetic parameters characterizing the state of the surface of the synthesized materials in a liquid medium is required to develop the methods of direct synthesis of porous glasses (PGs) doped with silver compounds and quartz-like materials based on them.

The so-called microporous (MIP) glasses were chosen for investigation; these glasses are called according to the classification proposed by S.P. Zhdanov for PG obtained by leaching two-phase sodium borosilicate (SBS) glasses in acid solutions [12] independently of the pore size. The MIP PG samples were prepared in shape polished discs and plates with a thickness of ~1 mm from two-phase 8V-NT glass with the composition (mol %) of $8Na_2O{\cdot}22B_2O_3{\cdot}70SiO_2$ by leaching in aqueous 3M solutions of acidic or hydrochloric acids followed by rinsing with distilled water and drying at 120°C. The obtained MIP glasses were used to obtain quartz-like glass (QG-8V-NT) by the heat treatment of the samples at 875 ± 5°C and nanocomposites. Doped porous samples of 8V-NT MIP-Ag were obtained by the technique described in [13]. The 8V-NT MIP samples were impregnated for one day in an aqueous $AgNO_3$ solution (0.6 M) at a temperature of 20°C and, after that, for 35–60 min in an aqueous KI solution (0.6 M) at 50°C. The following reaction occurred in the porous space of the glass:

Table 1. Structural characteristics of porous vitreous materials

Material designation	Pore space parameters		
	porosity W, cm^3/cm^3	specific surface area, S_0, m^2/g	average pore radius, r_{S_0}, nm
8V-NT MIP [16]	0.236	219	1.3
8V-NT MIP-Ag	0.245	145	2.0

$$AgNO_3 + KI \rightarrow AgI\downarrow + KNO_3. \quad (1)$$

The samples were dried at 120°C after each impregnation. To obtain Ag-containing quartz-like nanocomposite (QG-Ag), the porous sample was heated and sintered at $T = 875 \pm 5$°C, which led to the decomposition of salts (AgI at $T > 560$°C and $AgNO_3$ at $T > 300$°C) with the formation of metallic silver.

The porous structure of MIP glasses of different compositions was studied by scanning electron microscopy (SEM) using a Merlin (Zeiss) microscope. The volume porosity W of MIP samples was also determined by the weighting method [12] using an Al 204 balance (Mettler Toledo); the accuracy was ±1–2%). Specific surface S_0 of pores was determined by heat nitrogen desorption by chromatographic recording; the accuracy of S_0 determination was 1–1.5 m^2/g. These structural characteristics were used to calculate the average pore radius r_{S_0}:

$$r_{S_0} = \frac{2W}{(1-W)\rho_S S_0}, \quad (2)$$

where ρ_S is the density of the silica framework.

The electrophoretic mobility of particles (U_e) was measured on the particles of the porous and bulk materials obtained by grinding the samples in an agate mortar. The measurements were carried out by Doppler electrophoresis using a ZS Malvern (Zetasizer Nano) analyzer at a temperature of 20°C in a universal capillary U-shaped polycarbonate cuvette (DTS1060) with integrated gilded electrodes. The electrokinetic

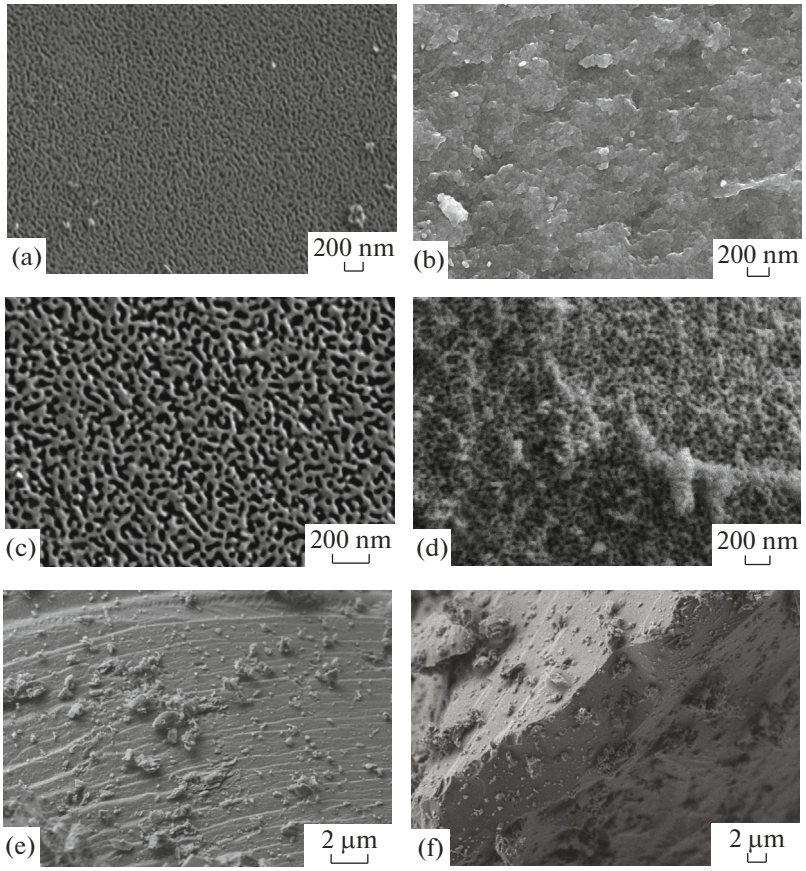

Fig. 1. SEM images of the studied samples of 8V-NT MIP (a, b), 8V-NT MIP-Ag (c, d), and QG-Ag (e, f): surface (a, c, e) and cleavage face (b, d, f).

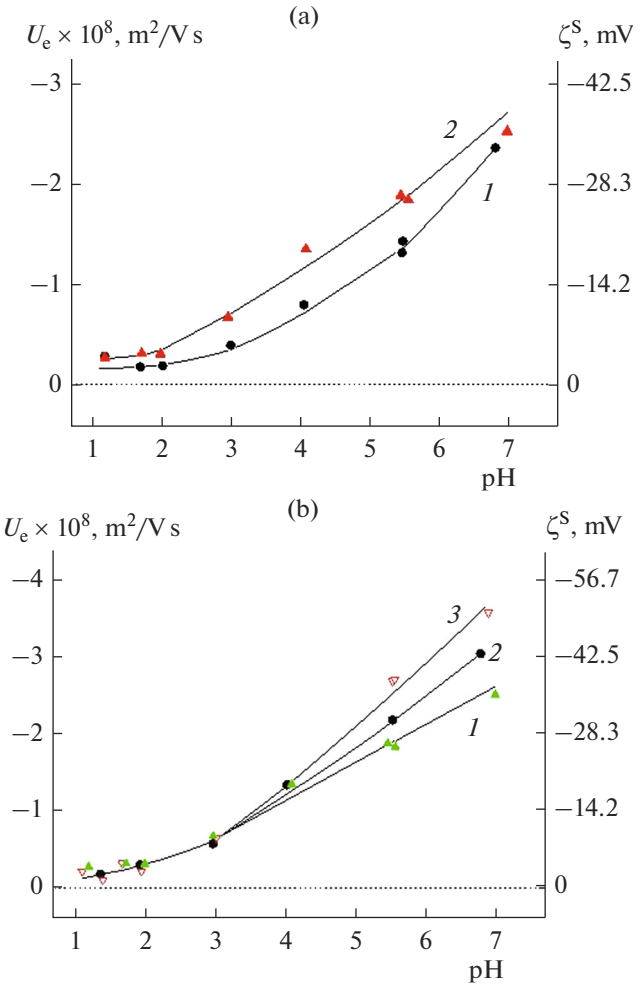

Fig. 2. Dependences of electrophoretic mobility and electrokinetic potential of particles of vitreous materials on pH against the background of a $NaNO_3$ solution (10^{-2} M): (*1*) 8V-NT MIP; (*2*) MIP-Ag (a); (*1*) MIP-Ag; (*2*) QG-8V-NT; (*3*) QG-Ag (b).

characteristics were studied against the background of $NaNO_3$ solutions with a concentration of 10^{-2} M in a pH range from 1 to 7.5. The electrolyte was chosen because sodium nitrate is indifferent both for the silica surface and for silver iodide.

The values of the electrokinetic potentials were calculated by the Smoluchowski equation:

$$\zeta^S = \frac{\eta}{\varepsilon\varepsilon_0} U_e, \qquad (3)$$

where η is viscosity; and ε and ε_0 are the dielectric permittivity of the medium and vacuum, respectively.

It should be noted that for the studied MIP glasses, the intrinsic conductivity of the particles and electroosmosis in pores insignificantly affect their electrophoretic mobility [18, 19]. Therefore, the values of the electrokinetic potential of porous and monolithic materials should mainly depend on the surface chemistry and the structure of the surface layer.

The suspension's pH was measured using a Seven Multi S47-K (Mettler Toledo) pH meter (the measurement error did not exceed 0.1 pH unit). The solutions were prepared using analytical or reagent grade chemicals using deionized water obtained by the UVOI-M-F installation for obtaining purified water, with specific electrical conductivity $\kappa_V \le 1.5 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$.

The results of the investigation of the structural parameters of the initial and doped MIP samples are given in Figs. 1a–1d and Table 1. As can be seen, no significant changes are observed on the surface (Figs. 1a, 1c) or cleavage face (Figs. 1b and 1d) SEM images after doping with silver iodide. For both samples, the structure of the surface layer and volume phase is typical. The SEM images of the QG-Ag quartz-like glasses (Figs. 1d, 1f) indicate the complete collapse of the pore channels during sintering, i.e., obtaining a monolithic vitreous material.

The SEM results of porous materials agree with the data from the direct measurements. It is seen from the table that the volume porosity of AgI-doped samples is slightly higher than that for the initial glass. These changes are within the permitted error of the method. The character of the change in the volume porosity after doping corresponds to reality; and this is confirmed by the redistribution of the surface areas of the pores. The significant decrease in the S_0 value and, correspondingly, the growth of the average pore radius of the 8V-NT MIP-Ag sample are apparently related to the partial washing out of the secondary silica from the pore space of the 8V-NT MIP glass while holding the MIP glass in the concentrated electrolyte solution.

Figure 2 presents the results of the measurements of the electrophoretic mobility of the particles and the calculation of the electrokinetic potentials for the studied vitreous materials. Against the background of an indifferent electrolyte in the studied pH range, the electrokinetic potentials are negative for all the studied systems. The isoelectric point ($\zeta^S = 0$) is in the area of pH < 1, which is characteristic of porous silicate glasses. Doping microporous glass with silver leads to an increase in the absolute values of the particle mobility and electrokinetic potentials at pH = const (Fig. 2a), which indicates a change in the electrosurface characteristics of particles during doping.

The comparison of electrokinetic characteristics of the porous composite and quartz-like glasses demonstrates (Fig. 2b) that the electrokinetic potentials almost coincide for all the studied samples in the acid pH area (pH ≤ 3). On shifting to the neutral pH area, the $|\zeta^S|$ values of both quartz-like glasses exceed that of the doped microporous sample. The ratio of the electrokinetic potentials for the initial QG-8V-NT material and composite QG-Ag quartz-like material is similar to that for nanoporous materials. An increase in the $|\zeta^S|$ value on the transition from porous glass to

quartz-like glass (at the same chemical composition) can be related to the change in the structure of the electric double layer under treatment at a high temperature, which causes the sliding boundary to approach the surface due to the sintering of the secondary silica which was in the pore space.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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