Synthesis and spectral-optical properties of composite materials based on high-silica porous glasses doped by iodides of silver and erbium

M A Girsova¹, T V Antropova¹, G F Golovina¹, I N Anfimova¹, L N Kurilenko¹, M Yu Arsent’ev²
¹Laboratory of Physical Chemistry of Glass, Grebenshchikov Institute of Silicate Chemistry RAS, Saint-Petersburg 199034, Russia
²Laboratory of Research of Nanostructures, Grebenshchikov Institute of Silicate Chemistry RAS, Saint-Petersburg 199034, Russia
E-mail: girsovamarina@rambler.ru

Abstract. Composite materials (CMs) doped by iodides of silver and erbium were synthesized on the base of the thermally modified high-silica porous glasses (PGs) with small additions of P₂O₅ and fluoride ions. CMs were manufactured by two-stage impregnation of the PGs first with AgNO₃ aqueous solution (with or without Er(NO₃)₃), next in the halide salt (0.6 M KI) aqueous solution. Then the samples of composites were heat treated at the temperatures from 120 to 870 °C up to their sintering and closing of the pores. The structure of composites was studied by X-ray powder diffraction (XRD) technique. According to XRD data the CMs doped by iodides of silver and erbium contain the AgI phase. Spectral-optical properties of CMs were investigated by UV-VIS-NIR spectroscopy. Optical density spectra in UV-VIS region have the bands corresponded with the absorption of silver molecular clusters. Peaks at 377, 448, 450–453, 485, 611–622, 647, 668–684 nm answered to the absorption of erbium ions were found. According to NIR transmission spectra, bands caused by the absorption of Si–OH, B–OH and Na–OH groups are found.

1. Introduction
It is known that the simultaneous presence of silver nanoparticles and rare earth (RE) ions in the material leads to energy transfer processes, where silver and RE ions can be sensitizers [1, 2]. Besides that the role of RE ions depends on their concentration in material [3].

2. Experimental
In this work, composite materials (CMs) were synthesized based on matrices from thermally modified porous glasses (PGs) with small additions of P₂O₅ and fluoride ions (PG-NFF) [4, 5]. Thermal modification of PG-NFF was carried out by its heating within wide temperature (T) range from 120 °C (PG-NFF-120) to 700 °C (PG-NFF-700) in accordance with the procedure first proposed in [4]. It was found that with PG’s temperature increasing, the pore specific surface area (SA) decreases from ~ 65 to ~ 37 m²/g, the average pore diameter D increases from ~ 10 to ~ 17 nm while maintaining the porosity W ~ 0.30 cm³/cm³. The values of W were determined by gravimetric method,
and SA by thermal desorption of nitrogen at 77 K (BET) method. The values of D were calculated in accordance with the procedure described in [4].

Additional heat treatment of PG-NFF-120 samples at T = 870 ± 5 °C leads to complete pore collapse and the formation of quartz-like glass QG-NFF. According to chemical analysis, the basic porous matrices PG-NFF-120 and QG samples contain (wt. %) (0.46–0.55) Na2O, (6.42–6.85) B2O3, (92.56–93.09) SiO2, (0.03–0.04) |F|, ≤0.01 P2O5 [5].

Synthesis of the CMs was carried out by two-stage impregnation of PG-NFF. At first, PG-NFF matrices (in the form of the rectangular plane-parallel plates in size (5–15) x (5–25) x (1.5±0.15) mm³) were placed in 100 mg/ml AgNO3 aqueous solution (with or without the presence of sensitizers, such as 10 mg/ml Er(NO3)3). Next the samples were immersed in a halide salt (0.6 M KI) aqueous solution. Then CMs were heat treated at the temperatures from 120 to 870°C for 15–160 minutes. Such heat treatment of CMs and PGs leads to their sintering with closing of the pores, i.e. a monolithic high silica material is formed.

In the CM samples of series (50 Ag, 100 Ag, 100Ag/10Er) based on PG-NFF-120 matrices doped with silver iodide with or without erbium iodide, the content of silver and alkali metals (wt. %) is (0.45–0.56) Na2O, (0.49–0.57) K2O, (0.68–1.02) Ag2O as determined by flame photometry on an iCE of 3000 Series spectrophotometer.

XRD study of the CMs (on example 100Ag/10Er series based on PG-NFF-120 matrix, heat-treated in air at 120 °C) was carried out on D8-Advance “Bruker” X-ray diffractometer (monochromatic CuKα radiation, operating voltage of 40 kV at a current of 40 mA in the angle range 2θ = 20–60 °) using the database ICDD-2006 on the samples previously powdered.

Synthesized CMs were investigated by optical spectroscopy methods in UV-VIS-NIR spectral regions, depending on composition and temperature of heat treatment of them (120–870 °C), as well as of the PG-NFF matrices. Samples of PG-NFF with different thermal history and QG-NFF were chosen as the objects of comparison. The measurements were carried out at room temperature on the samples with a thickness of 1.00 and 1.50 mm (± 0.15 mm). The optical density spectra were obtained in the spectral range 270–1100 nm on SF-2000 spectrophotometer, and FTIR transmission spectra in the range 7500–4000 cm⁻¹ on FSM-2211 spectrophotometer.

3. Results and discussion

According to XRD data, crystalline phase of the hexagonal modification AgI (No. 01-078-1614) with average crystallite size of 26 nm was estimated by the Scherer method (Fig. 1).
Fig. 2 shows the optical density spectra of thermally modified porous glasses in the spectral region 270–1100 nm. The presence of UV absorption which is possibly associated with silicon defect centers [6] in PG-NFF matrices, has been established.

![Fig. 2. Optical density spectra of thermally modified PGs](image)

Figure 3 and Figure 4 show the optical density spectra of the CMs of series 50Ag, 100Ag and 100Ag/10Er samples obtained on the PG-NFF-120 matrices, depending on their heat treatment temperature.

![Fig. 3. Optical density spectra of the CMs of series 50Ag and 100Ag depending on the temperature of their heat treatment (120–870 °C)](image)

The spectral dependences revealed absorption bands at the wavelength 340–346 nm (~ 3.58–3.65 eV), 351–354 nm (~ 3.50–3.53 eV), 372–385 nm (~ 3.22–3.33 eV), 483–485 nm (~ 2.56–2.57 eV), 504–512 nm (~ 2.42–2.46 eV), 544 nm (2.28 eV), 611–622 nm (~ 1.99–2.03 eV), which corresponded with the absorption of silver molecular clusters [7, 8]. It has been established that in most of the CM samples the peaks appear at the wavelengths 395–455 and 564–575 nm, which may
Fig. 4. Optical density spectra of the CM 100Ag/10Er depending on the temperature of their heat treatment (120–870 °C)

indicate the formation of AgI nanocrystals and interspersed silver nanoparticles with plasmon resonance [9–12]. With increase in the temperature of heat treatment of CMs from 120 to 870 °C, a change in the position of the absorption bands (or their disappearance) associated with silver presence is observed at the spectra. The peaks at the optical density spectra of CMs at 377, 448, 450–453, 485 and 611–622, 647, 668–684 nm can also be associated with the absorption of erbium ions that relate to transitions $^4I_{15/2} \rightarrow ^2G_{11/2}$, $^4I_{15/2} \rightarrow ^4F_{3/2}$, $^4I_{15/2} \rightarrow ^4F_{5/2}$, $^4I_{15/2} \rightarrow ^4F_{7/2}$ and $^4I_{15/2} \rightarrow ^4F_{9/2}$ respectively [12–16].

Figure 5 and Figure 6 show typical transmission spectra of the CMs of series 50Ag and 100Ag/10Er based on PG-NFF-120 matrices in the near infrared region. Most of the CM samples exhibit absorption bands at the frequency range 7332–7315 cm$^{-1}$ (stretching vibrations of OH and Si–OH groups), 7189–7116 and 5281–5261 cm$^{-1}$ (absorption of OH groups and water molecules), at 4686–4646 cm$^{-1}$ (stretching vibrations of B–OH groups), 4536–4503 cm$^{-1}$ (deformation vibrations of Si–OH groups, vibrations of OH and Na–OH groups), 4453–4437 and 4192–4155 cm$^{-1}$ (vibrations of OH and Si–OH groups) (see the overview in [5]). It should be noted that absorption bands in the

Fig. 5. Transmission spectra of the CM 50Ag depending on the temperature of their heat treatment
frequency range 6583–6486 cm\(^{-1}\) (\sim 1519–1542 nm), characteristic for erbium ions [12–15], were not detected.

4. Conclusion
XRD spectra of the synthesized CM’s powders show that they contain AgI phase of the hexagonal modification. According to NIR transmission spectra, CMs contain Si–OH, B–OH, Na–OH groups. Optical absorption spectra of the CM 100Ag/10Er show the bands at 377, 448, 450–453, 485 and 611–622, 647, 668–684 nm corresponded with the absorption of erbium ions (transitions \(^4I_{15/2}\) \rightarrow \(^4G_{11/2}\), \(^4I_{15/2}\) \rightarrow \(^4F_{3/2}\), \(^4I_{15/2}\) \rightarrow \(^4F_{5/2}\), \(^4I_{15/2}\) \rightarrow \(^4F_{7/2}\) and \(^4I_{15/2}\) \rightarrow \(^5F_{9/2}\) respectively).

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