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Luminescence of Silver Nanoclusters Formed by Ion Exchange Method in Cerium-doped and Undoped Glasses

Y.M. Sgibnev*, A.I. Ignatiev†, N.V. Nikonorov‡, A.I. Sidorov§

Saint-Petersburg National Research University of Information Technologies, Mechanics and Optics, 49, Kronverkskiy Pr., 197101 Saint-Petersburg, Russia

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The paper describes the research of influence of cerium ions in a silicate glass composition on the process of formation silver nanoclusters and their optical properties. Effect ion exchange time and subsequent heat treatment at temperature below transition temperature were investigated. The paper shows that in cerium-doped glasses the rate of formation of silver nanoclusters higher than in the glass without cerium. It explained by the shift of redox reaction of cerium and silver ions towards formation of atomic silver

Keywords: Silver nanoclusters, Ion exchange, Cerium-doped glasses.

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1. INTRODUCTION

Neutral molecular clusters of silver have a broad and intensive luminescence in the visible region. It makes them promising candidate for down-converters for solar cells and phosphors for white LEDs [1]. The molecular silver clusters in glass host can be formed by high temperature synthesis or low temperature ion exchange. The ion exchange technique is more attractive because it allows getting high concentration of silver ions on the surface of the glass. The Ce-doped glasses have radiation-resistance properties. Therefore it use in aerospace industry and understanding of effect cerium ions in glasses on the luminescence of silver nanoclusters is important for use the solar cells in space.

2. OBJECT OF RESEARCH

The aim of this work was research the influence of cerium ions on the luminescent properties of silicate glasses with molecular silver clusters formed by ion exchange. We investigated the optical glass K8 (SiO_2 – B_2O_3 – BaO – K_2O – Na_2O – As_2O_3) and its cerium-doped radiation-resistant analogue K208 (CeO_2 = 0.74% mol).

3. EXPEREMENTAL TECHNIQUE

Silver was introduced into the glass by low temperature ion exchange in a mixture of nitrates (5%$AgNO_3$ and 95%$NaNO_3$) at 320 °C, time was variety (1, 4, and 18 hours). After cooling, washing and drying were measured absorption and photoluminescence spectra. Recording the optical density spectra was conducted with Perkin-Elmer Lambda 650 double-beam spectrophotometer in the 200-800 nm wavelength region with a step by wavelength of 1 nm. For measurement luminescence spectra at a fixed excitation wavelength used fiber spectrometer EPP2000-UVN-SR (StellarNet) with excitation semiconductor laser (λ = 405 nm). After ion exchange samples were heat treated at T = 400 °C (below transition temperature T_g = 550 °C).

4. RESULTS OF EXPERIMENTS

Effect of cerium in the glass composition is shown in the ion exchange step. As seen from absorption spectra (Figs. 1, 2), in Ce-doped glasses formation of silver nanoclusters takes places with greater speed than undoped glasses.

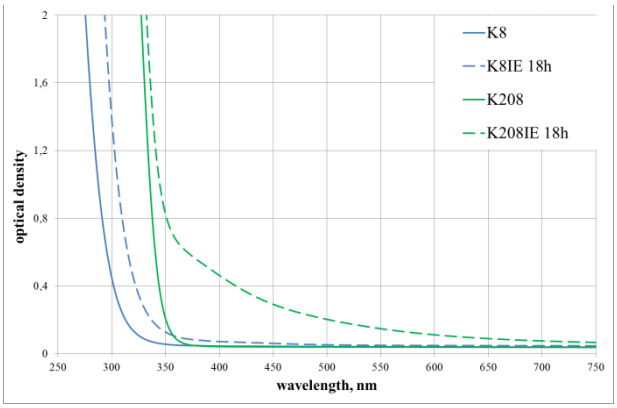

Fig. 1 – Optical density spectra of the samples before and after the silver ion exchange during 18 hours

The subsequent heat treatment at temperature T = 400 °C of the samples after ion exchange led to increase of nanoclusters size and formation of silver nanoparticles (in Ce-doped glasses) or increase of concentration of silver nanoclusters (in undoped glasses).

In case of undoped glasses intensity of photoluminescence grows with increasing ion exchange time. Subsequent heat treatment at temperature T = 400 °C increase intensity of photoluminescence too.

Photoluminescence of silver nanoclusters in Ce-doped

* sgibnevem@gmail.com
† ignatiev@oi.ifmo.ru
‡ nikonorov@oi.ifmo.ru
§ aisidorov@qip.ru

glasses reduces with increasing ion exchange time.

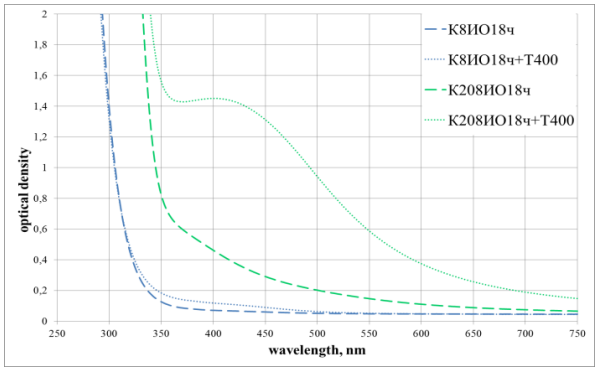

Fig. 2 – Optical density spectra of the samples after the silver ion exchange during 18h and subsequent heat treatment at temperature T = 400 °C during 3 hours

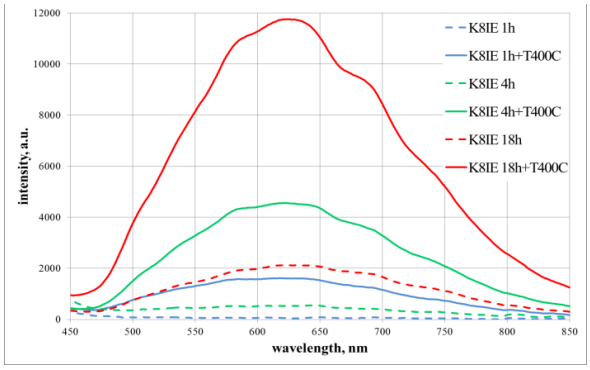

Fig. 3 – Luminescence spectra K8 samples depending on the time of ion exchange and subsequent heat treatment at temperature T = 400 °C. Excitation wavelength λ = 405 nm.

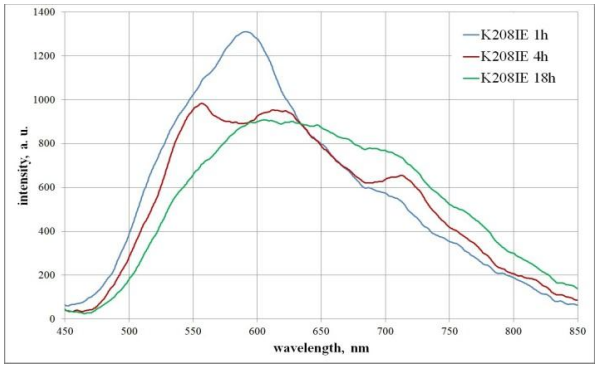

Fig. 4 – Luminescence spectra K208 samples depending on the time of ion exchange. Excitation wavelength λ = 405 nm

Heat treatment of K208 samples decreases photoluminescence intensity in many times. Therefore those luminescence spectra aren't shown in Fig. 4.

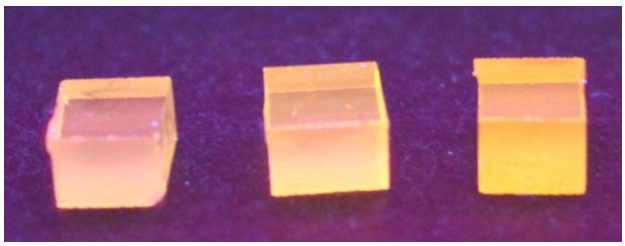

Fig. 5 – Photo of K8 samples after ion exchange (1, 4 and 18 hours right to left) and subsequent heat treatment. Excitation wavelength λ = 365 nm

5. DISCUSSION

Absorption spectra of the undoped glasses after silver ion exchange have a weak band in optical range 300-500 nm. Molecular silver clusters absorb exactly in this optical range[2, 3]. Such clusters can form by the reduction of silver ions in glass defects to atomic state and subsequent association with silver ions:

$$nAg^0 + mAg^+ \rightarrow Ag^{m+}{}_n.$$

Concentration of silver nanoclusters increases after heat treatment, that's why intensity of luminescence increases also.

Cerium ions in glass can reduce silver ion to the atomic state:

$$Ce^{3+} + Ag^+ \leftrightarrow Ce^{4+} + Ag^0.$$

During silver ion exchange process the increase concentration of silver ions shifts chemical equilibrium to the right. It explains the presence of wide absorption band (which belong to different silver molecular clusters) in Fig. 1. Intensity of photoluminescence declines because absorption increases.

AKNOWLEDGEMENTS

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