Optical properties of antimony-borate glass rods co-doped with Eu^{3+}/Ag^{+} ions

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Received October 12, 2021; accepted December 02, 2021; published December 31, 2021

Abstract—This paper presents the results of research on the luminescent properties of antimony-borate glass rods doped with europium and silver ions. The reduction of silver ions to a form of nanoparticles was carried out and the occurrence of localized plasmon resonance was demonstrated, which caused changes in the Eu^{3+} luminescence signal at a wavelength of 613 nm. The effect of the concentration of silver ions dopant at a constant content of europium ions on the luminescence and absorption characteristics of the produced samples was investigated. In the examined doping range, no large dependencies of spectral changes as a function of silver ions concentration were found. Clear quenching of luminescence was observed due to the heating time of doped glass matrices for energy transition ($^5D_0 \rightarrow {}^7F_2$).

The technology of nanocomposite glasses containing noble metal nanoparticles is widely researched due to the possibility of overcoming typical limitations of fused quartz (for instance, bandwidth, luminescence efficiency, and nonlinearity) and high application potential. Optical fibers based on this technology combine both the mechanical and chemical properties of a glass matrix with extended spectroscopic properties of embed metal nanoparticles (NPs) [1–4]. Therefore, in the technological process of glass synthesis, in addition to active doping (rare earth elements), noble metal ions are introduced into the structure, and then, as a result of controlled thermal treatment, metallic NPs are formed. As a result of collective oscillations of free electrons, plasmons are formed on the surface of metal nanoparticles. Such a phenomenon is referred to as localized surface plasmon resonance (LSPR) [6]. The effect of the surface plasmon resonance depends on the type of material, shape and dimension of NPs, as well as dielectric features and index of refraction. Therefore, the change of geometry (rods, sphere) of metallic nanoparticles and the physicochemical properties of the host, in which it is located, leads to changes in the interaction of metallic nanoparticles with optical radiation resulting from the plasmon localized on the surface of metallic nanoparticles. In the literature, there are many studies on obtaining localized surface plasmon resonance in many glasses, including antimony [5], tellurium [6], phosphate [7] or lead-germanium [9].

Sb_2O_3 has a chemical potential that allows the reduction of silver ions directly in the process of thermochemical synthesis. The heating process, in which nanoparticles are formed at a temperature above glass transformation, increases the concentration of nanoparticles in the glass structure. According to the energy structure of europium ions it is possible to obtain a plasmonic effect and energy transfer between Ag NPs and Eu^{3+} ions, which allow the enhancement or quenching of the luminescence. This mechanism is strongly depended on the concentration of Ag NPs and the heating time. Also, Schneider *et al.*, report non-conventional silver nanoparticle growth on the surface of lead–germanate oxide glasses which can be used as an active layer in plasmonic sensors [9]. The article presents research on obtaining the plasmonic effect in glass rods with different content of silver ions and heating time. The produced glass rods were doped with Eu^{3+} ions whose excited-state absorption band harmonizes with the plasmon band of silver nanoparticles. Moreover, as a result of heating, a surface reduction of silver ions was observed, which can be used as active layers in optoelectronic sensors.

Antimony-borate glass rods were made from glass composition [%mol]: $25Sb_2O_3$-$25GeO_2$-$45B_2O_3$-$5Na_2O$ – $xAgNO_3$ – $0.5Eu_2O_3$, where x = 0.5; 1; 1.5. The homogenized sets were melted in a platinum crucible at 1450°C. Next, the glass was cast in a brass mold and annealed in a furnace at 380°C for 12 hours. The preform prepared in this way was processed into glass rods with a diameter of 1 mm and length of 100 mm (Fig. 1). The observed brown color of (c) rod stems from partial reduction of nanoparticles during thermal drawing. Measurements of optical properties in the visible range were carried out by using a Stelarnet GreenWave optical spectrometer and a laser diode emitting at a wavelength of 395 nm. Surface changes were recorded using electron scanning microscopy SEM.

Figure 2 shows the luminescence spectra of antimony-borate glass rods doped with 0.5 mol.% Eu_2O_3 and with a different content of silver ions, obtained with excitation of

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395 nm laser radiation. The europium ion luminescence bands in the visible range at the wavelengths of 570 nm, 590 nm, 613 nm, 660 nm and 700 nm are assigned to the corresponding radial transitions from the $^5D_0$ level to the baseline levels $^7F_0$, $^7F_1$, $^7F_2$, $^7F_3$, $^7F_4$, respectively.

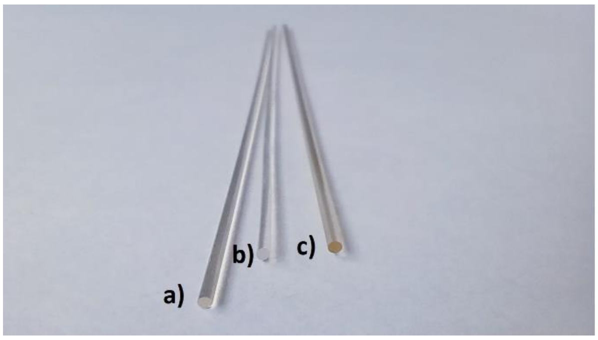

Fig. 1. Fabricated glass rods of antimony-borate glasses (a) SGBNa_1.0Ag_0.5Eu, 9b) SGBNa_0.5Ag_0.5Eu, (c) SGBNa_1.5Ag_0.5Eu.

Established on the spectral analysis of the produced glass rods, it was observed that an increase in the concentration of silver causes a slight decrease in the level of luminescence. It is strictly related to the partial reduction of silver ions to the form of nanoparticles in the rod forming process, which was confirmed by absorption measurements (Fig. 3). It is clearly visible that the absorption band with the maximum at a wavelength of 460 nm grows with the increase in the concentration of silver ions. The appearance of the plasmon band also confirms the obtaining of silver nanoparticles in the antimony-borate glass.

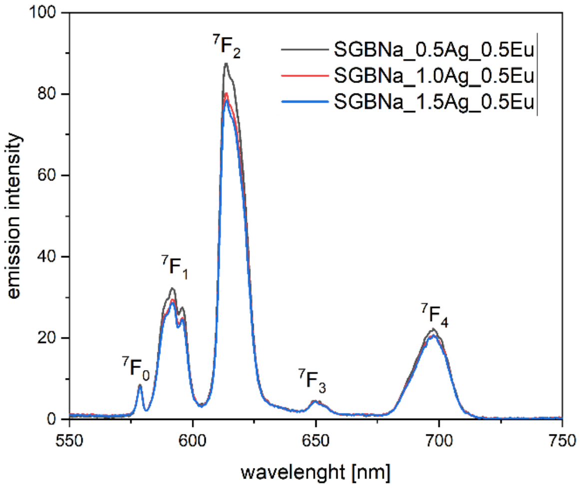

Fig. 2. Luminescence spectrum of SGB glass rods co-doped with $0.5Eu_2O_3$ and three concentrations of Ag ions.

Due to the strong quenching of the luminescence signal, glass rods doped with 0.5 mol% $AgNO_3$ were selected in the next stage of the study, which was heated at the temperature of 400°C for 60 minutes (heating in a furnace for 15 minutes, then taking measurements, and again in the same order for a total of 60 minutes). The Figure indicates analogous luminescence spectra obtained when the rods are excited with laser radiation at a wavelength of 395 nm. As it can be seen, additional heating of the produced rods causes an increase of luminescence after 15 min which suggests that a plasmon effect occurred. For longer heating time the intensity decrease, which is related to the undesirable energy back-transfer between europium ions and silver nanoparticles.

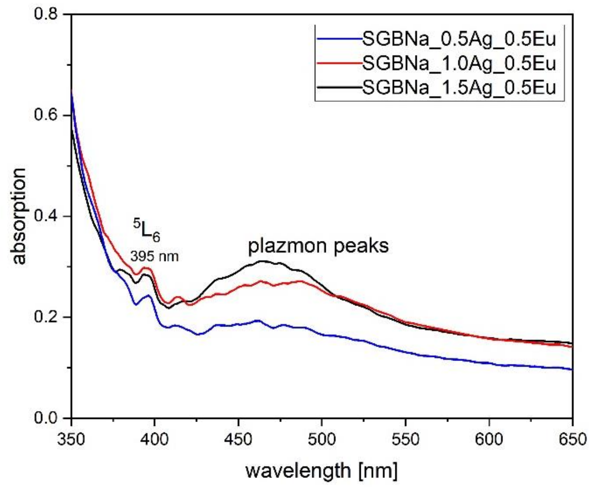

Fig. 3. Absorption spectrum of SGB glass rods doped with $0.5Eu_2O_3$ and three concentrations of Ag ions.

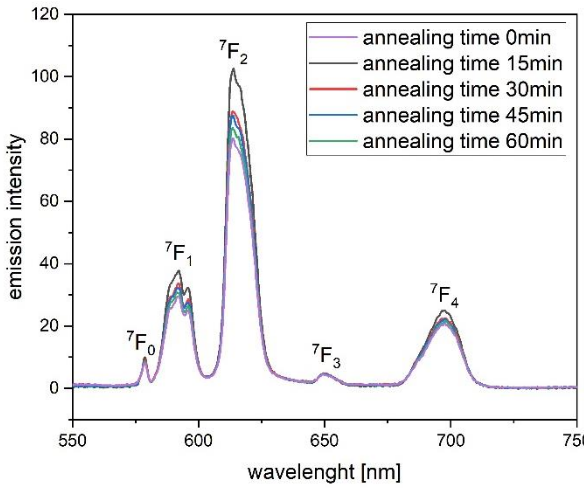

Fig. 4. Luminescence spectrum of SGBNa_0.5Ag_0.5Eu glass rod in relation to the annealing time.

What is more, the most visible changes take place at a wavelength of 612 nm (Fig. 4), corresponding to the energy transition from $^5D_0 \rightarrow {}^7F_2$. Based on the observation of the annealed rods, it was determined that the decrease in luminescence is caused by the growth of nanoparticle structures and the formation of conglomerates on the material surface. As a result, small rods changed their color. While examining the absorption spectra for the SGB_0.5Eu_0.5Ag rod, it was observed that the absorption band corresponding to the plasmon vibration increased for the first 45 minutes and then remained constant.

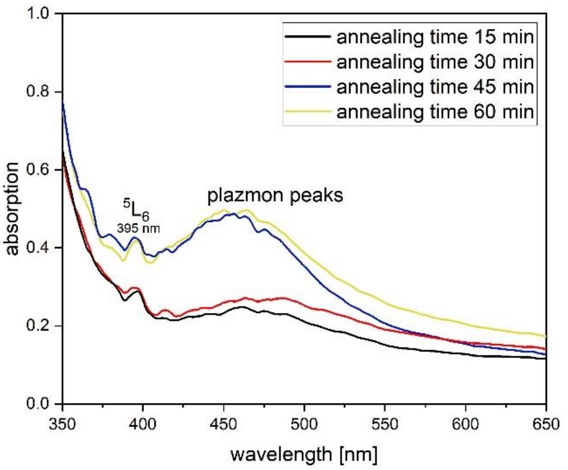

Fig. 5. Absorption spectrum of SGB_0.5Ag_0.5Eu glass rod in relation to the annealing time.

The observed phenomenon was described by the Schneider *et al.*, where, as a result of the migration of silver ions, their self-organization took place on the surface of lead-germanium glasses [9]. Heating time favors the formation of continuous metallic layers on the glass surface and thus the local electric field decreases and, consequently, the level of luminescence decreases. In order to confirm the plasmonic effect and surface reduction of silver ions, surface morphology studies were performed using electron scanning microscopy (SEM). Figure 6 shows photographs that were taken for the surface of the SGBNa_0.5Ag_0.5Eu rod immediately after production and after additional one-hour heating at 400°C. The scale of measurement was the same, hence easy comparison of the size on nanoparticles was made.

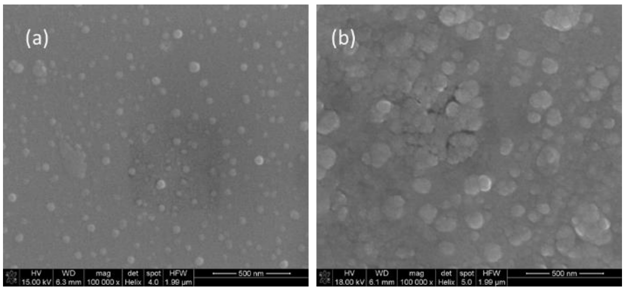

Fig. 6. SEM photo of the surface of glass rod SGB_0.5Ag_0.5Eu a) after fabrication, b) after annealing.

Based on the measurements and EDS analysis, it was found that spherical silver nanoparticles were formed on the surface of the produced antimony-borate rods. Their arrangement is relatively homogeneous, which confirms the stability of used technology. In the parent glass rod the particle size was estimated approx. at 60 nm (Fig. 6a) and after the annealing process (Fig. 6b) the NPs size increased up to 130 nm. Also, it is worth noticing that the warming-up process leads to the accumulation of nanoparticles. Their large increase was caused by their being pushed to the upper glass layer and a significant increase in their size compared to the initial size.

In summary, in the article we present research on the optical properties of antimony-borate rods doped with Eu ions and various concentrations of silver ions. Antimony glasses are characterized by high thermal stability, which is a promising matrix for the production of optical fibres with suspended metallic nanoparticles. In the absorption spectrum, characteristic plasmon peaks for the wavelength of 460 nm originating from silver ions were observed. The phenomenon of luminescence quenching indicated the migration of energy from europium ions to silver ions, which depends on the larger volume fraction, and as a result of heating a larger size of silver nanoparticles formed. The highest dependence of luminescence suppression due to warming up was observed for the wavelength of 613 nm. Furthermore, as a result of heating the developed antimony-borate rods, the ability of self-organization of nanoparticles on the material surface was demonstrated.

The project was funded by National Science Centre (Poland) granted on the basis of the decision No. DEC-2016/21/D/ST7/03453 and partially by Bialystok University of Technology from grant No. WZ/WE-IA/3/2020.

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