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Photo-Induced Solution Deposition of Silver Nanoparticles on a Tb^{3+} Doped SiO_2-GeO_2-Na_2O Glass

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Incorporation of Ag or Au nanoparticles (NPs) in rare earth doped glasses has attracted attention the last decades because of the enhancement on optical properties ought to the localized surface plasmon resonance of the NPs, open the possibility to a wide range of new applications [1]. However, in the case of traditional melt quenched glasses is not an easy task to incorporate noble metal nanoparticles, methods like thermochemical reaction, ion implantation and ion exchange are used for this purpose. Ion exchange is the most used method, where Na^+ ions in the glass matrix are exchanged by Ag^+ ions by dipping the glass in a molten mixture of $AgNO_3/KNO_3$ at around 400°C. Afterwards, thermal treatments for the nucleation and growth of Ag nanoparticles are carried out [1]. Another method is the thermochemical reduction of Ag^+ to Ag^0 with the aid of a polyvalent ion like Sn, Sb or Pb and thermal treatments of the glass for several hours [2]. In this regard, our work is focused on using a photo-induced synthesis of silver NPs as an alternative to ion exchange incorporation of silver ions and subsequent formation of nanoparticles on the glass surface. This method uses light to produce metal NPs by either direct photoreduction of the metal ions or photosensitization of radicals or molecules to reduce the metal ions [3]. By using photochemical synthesis, is not necessary to immerse the glass in a molten bath of salts that could produce damage like surface cracking on the glass and it will be more safe for glasses of low glass transition temperature.

A glass with a composition of $(40 - x)SiO_2$-$40.GeO_2$-$20.Na_2O$ in % mol, where x is 0.3% mol of Tb^{3+} ions (labeled as SGN-Tb), was fabricated as it was previously reported in [4]. Afterwards, to proceed with the photochemical synthesis of NPs, the sample was immersed in an aqueous solution of 0.1 mmol $AgNO_3$ and 6 mmol sodium citrate, and irradiated for 40 minutes with an Argon ion laser of 488 nm using a power of 130 mW. Optical absorption was examined in a PerkinElmer UV/Lambda45 spectrometer to follow up the Ag nanoparticles surface plasmon resonance (SPR) appearance. A Field-emission scanning electron microscope JEOL 4800 was used to perform microstructure observation of the glass surface and nanoparticle formation, as well as EDS analysis. Photoluminescence (PL) of the samples was acquired in a Jobin Ybon FluoroLog-3 Fluorometer using an excitation wavelength of 378 nm.

In Figure 1a), optical absorption of the glass as cast and after photochemical deposition are very similar showing only the absorption bands corresponding to the $^7F_5 \rightarrow {}^5D_4$ and $^7F_6 \rightarrow {}^5D_4$ transitions of Tb^{3+} ions at 378 and 488 nm, respectively. To promote the growth of Ag NPs, a thermal treatment at 380°C for 61 hours was carried out, as a result, in Figure 1 a) it can be observed that the spectrum of the SGN-Tb glass shows the absorption band of the SPR of Ag NPs located around 400 nm. FE-SEM imaging evidenced that, after the thermal treatment Ag NPs growth superficially on the glass and some are embedded more deep within the surface (Figure 2 a and b). It is possible that during photochemical deposition Na^+/Ag^+ ion exchange occurred and Ag^+ ions diffused into the glass, and the thermal treatment promoted the nucleation and growth of the Ag NPs. Figure 1 b) shows the PL emission of the

SGN-Tb glass with and without Ag NPs showing that due to the incorporation of the NPs the emission bands corresponding to $^5D_3 \rightarrow {}^7F_{5,4,3}$ transitions of Tb^{3+} almost vanished. These bands are located in the range of 400 to 470 nm, which coincides with the region where Ag SPR band appears.

Finally, the method proposed in this work has the advantage of using just the necessary amounts of Ag source without the need to dip the glass in molten salts that can cause surface cracking. Thus, photochemical deposition of Ag NPs could be a feasible alternative to traditional ion exchange method.

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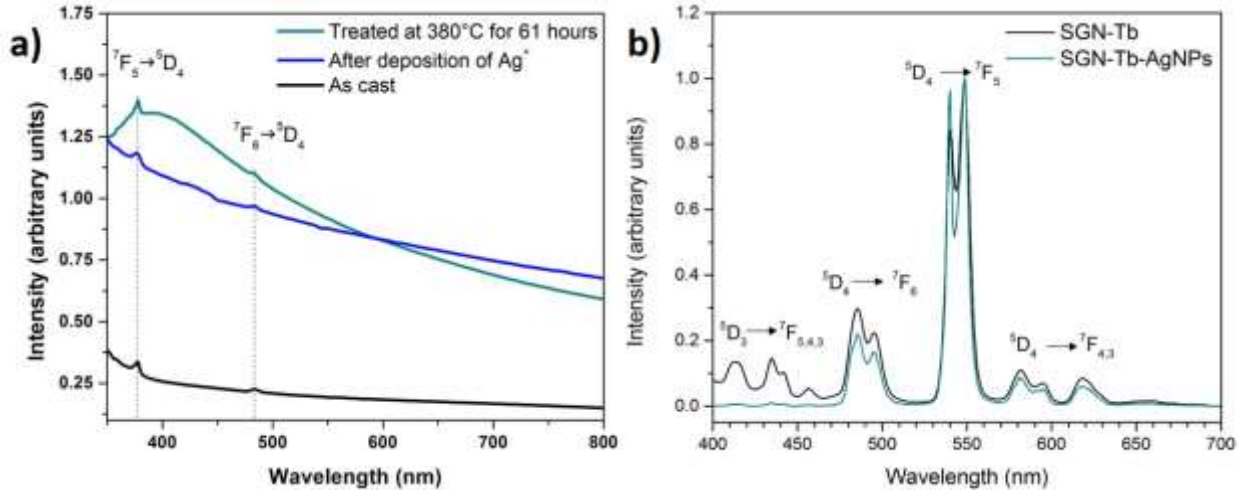

Figure 1. a) Optical absorption of the glass as cast, after photochemical deposition and after thermal treatment at 380°C for 61 hours. b) Photoluminescence of the glass with and without Ag NPs.

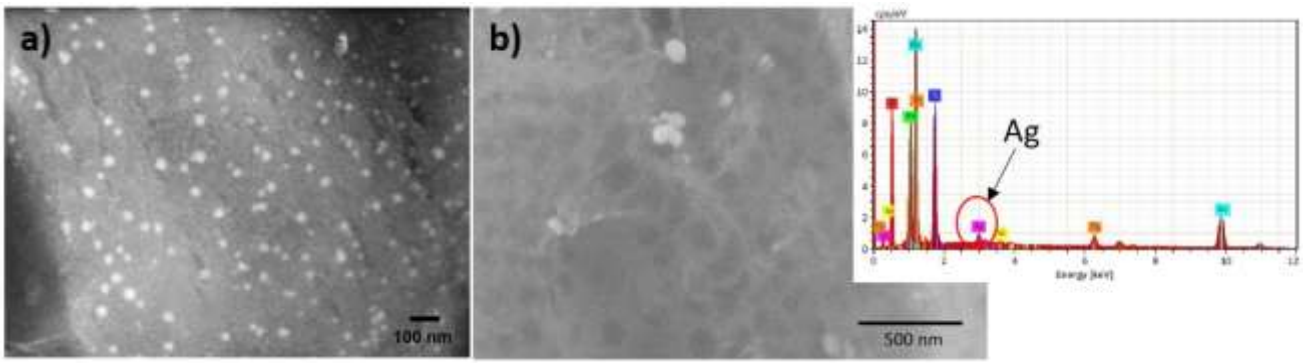

Figure 2. a) Micrograph of Ag nanoparticles superficially formed on the glass surface; and b) micrograph showing some Ag nanoparticles formed deep within the glass [5].

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