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Optical and spectroscopic properties of soda lime alumino-silicate glasses doped with erbium and silver

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ABSTRACT

Spectroscopic properties of Ag/Er co-doped soda lime silicate glasses have been studied with the aim of assessing the effective role of silver as a sensitizer for erbium. Changes in spectroscopic properties of Er^{3+} as a function of silver addition to the base composition have been measured. Transmission electron microscopy (TEM), absorption as well as photoluminescence measurements in the visible and infrared spectral region, particularly $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of the Er^{3+} ion were performed; excitation wavelengths in the range from 325 to 808 nm were used. Enhancement of the Er^{3+} luminescence at 1.54 μm was observed when Ag was added.

1. Introduction

Glasses doped with rare earth ions containing metallic nanoparticles have been explored because the rare earth luminescence may be enhanced by the coupling with nanoparticles. This interaction has been attributed to the presence of electronic collective excitations on the surface of the nanoparticles, the so called surface plasmons, whose resonance is typically in the UV spectral region [1]. Several systems containing different combinations of nanoparticles and rare earth ions have been reported in the literature and increase in the luminescence was demonstrated in Er^{3+}, Eu^{3+}, Yb^{3+}/Tm^{3+} and Pr^{3+} [2–5]. In the present work Er^{3+} ions are focused due to the well known infrared emission at 1.54 μm, originated from the $^4I_{11/2} \rightarrow {}^4I_{15/2}$ Er^{3+} transition.

Among the suitable glassy hosts, soda-lime aluminosilicate glasses (SLAS) are attractive materials due to their good chemical durability and adaptability [6]. Low cost integrated optical amplifiers and lasers operating at 1.54 μm can be fabricated. Additionally, silver doping of soda lime silicate glasses have proved to be efficient by several methods, particularly when added by the ion exchange method. Nevertheless, formation of silver nanoparticles has been obtained by exposing the samples to thermal annealing.

In this work the spectroscopic properties of SLAS glasses co-doped with silver and Er^{3+}, namely absorption and emission spectra, were measured. Formation of nanoparticles was investigated without thermal annealing. Attention is focused in the increase of the $^4I_{11/2} \rightarrow {}^4I_{15/2}Er^{3+}$ transition in the infrared region at 1.54 μm when silver is added to the glassy host.

2. Experimental setup

A set of soda lime alumino-silicate (SLAS) glasses doped and codoped with different amounts of erbium and silver ions was produced by conventional melt – quenching process followed by ion exchange process.

The examined compositions are the following ($55SiO_2$–$25Na_2O$–$11CaO$–$8MgO$–$1Al_2O_3$) mol% doping with xEr_2O_3 and yAg_2O. Seven samples were produced with $x = y = 0.0$, $x = 0.0$ and $y = 0.25$, $x = 0.25$ and $y = 0.25$, $x = 1$ and $y = 0.0$ and the last $x = 1.0$ and $y = 0.25$.

The batches were prepared by using reagent grade SiO_2, Na_2CO_3, Al_2O_3, CaO, MgO, $AgNO_3$ and Er_2O_3 starting materials. Previously dried batches were melted in an electrically heated Jung furnace using alumina crucibles, in air, during 4 h at the 1450 °C. The melted batches were quenched in stainless steel.

Optical absorption (OA) spectra of the samples were measured with Perkin–Elmer, lambda nine spectrophotometer in the wavelength range of 300–1800 nm.

The photoluminescence (PL) measurements were performed with a He Cd UV laser tuned at 325 nm (40 mW), and a semiconductor laser emitting at 808 nm. Luminescence signals were collected into a DIGIKROM DK480 monochromator coupled to a

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R928 photomultiplier. All measurements were performed at room temperature.

3. Results

Fig. 1 shows Transmission Electron Microscopy (TEM) images of the following samples (a) SLAS glass with added 0.25 mol% silver and (b) SLAS glass with 0.25 mol% silver and 1 mol% of Er^{3+}. The average size of the observed nanoparticles is about 12 ± 1 nm and 17 ± 1 nm, respectively.

Fig. 2 shows the UV–VIS–NIR absorption of soda-lime aluminosilicate glasses, of (a) SLAS base glass, (b) SLAS glass with added 0.25 mol% silver and (c) SLAS glass with 0.25 mol% silver and 0.25 mol% of Er^{3+}. The nondoped sample presents absorption at wavelengths shorter than 600 nm, with two shoulders at about 350 nm and 480 nm. The former may be ascribed to the introduction of small amounts of SiO_2 (1 mol%) [7]. The SLAS 0.25Ag sample presents clearly two peaks at 345 nm and 490 nm, that can be attributed to isolated Ag^+ centers [7] and the surface plasmon resonance absorption [1], respectively. The curve (c) exhibits the characteristic Er^{3+} absorption bands.

Fig. 3 displays the PL spectra excited at 325 nm, with different Ag and Er^{3+} contents. The SLAS matrix has a broad luminescence itself, with bands centered at 520 nm and 690 nm, due to the well known *L* centers in soda lime glasses, characterized by a sodium cation bound to a silanolate center ≡Si—O—Na [8]. The presence of silver results in additional bands ranging from 350 nm to 600 nm and from 600 nm to 800 nm. According to the literature, several silver aggregates may contribute to the PL emission and absorption [6–14]. The band from 400 to 460 nm may be related to the emission of Ag_4 clusters [9], silver dimmers [8], silver monomers (Ag^0) [8,9] and Ag^{2+} [10]. The band in the red-near infrared could be assigned to Ag_3, Ag^{2+} or Ag_3^{2+} [10]. When doping with Er^{3+} ions, there is a strong increase in the Ag luminescence from 350 to 650 nm, allied to the presence of the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ Er^{3+} transition, centered at 540 nm.

Fig. 4 reveals the influence of Ag doping in the Er^{3+} luminescence. Samples were excited at 808 nm, resonant with the $^4I_{15/2} \rightarrow {}^4I_{11/2}$ Er^{3+} transition. Clearly from the Er^{3+} emission $^4I_{13/2} \rightarrow {}^4I_{15/2}$ centered at 1540 nm increases by about 15% when Ag is added. The full width at half maximum (FWHM) is about 26 nm, i. e., larger than conventional soda lime glasses [15,16]. Silver doping did not contribute to changes in the bandwidth, at least up to the doping levels used in the present work. Similar results

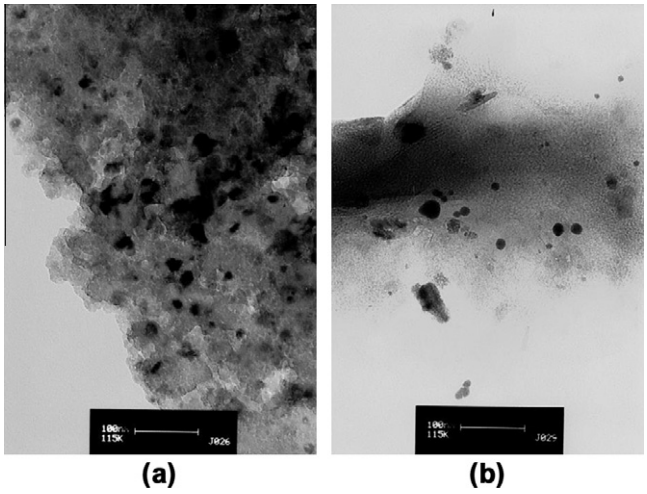

Fig. 1. Transmission electron microscopy of samples: (a) SLAS 0.25%Ag and (b) SLAS 1%Er + 0.25%Ag.

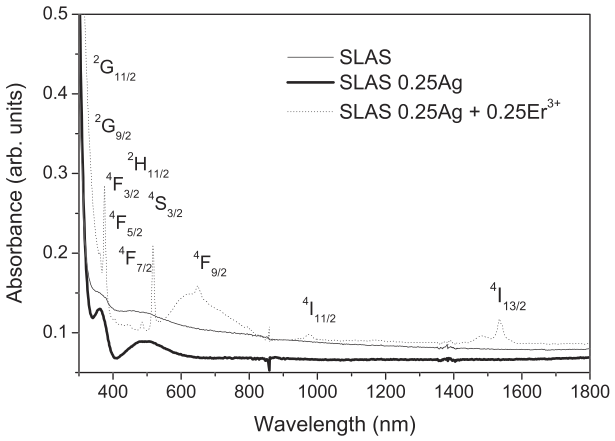

Fig. 2. Absorption spectra of samples SLAS, SLAS 0.25%Er + 0.25%Ag and SLAS 0.25%Ag.

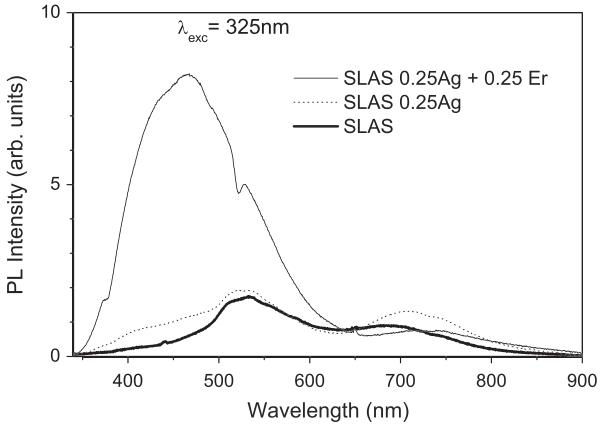

Fig. 3. Luminescence of SLAS, SLAS 0.25%Er + 0.25%Ag and SLAS 0.25%Ag in the visible and near infrared range, excited at 325 nm.

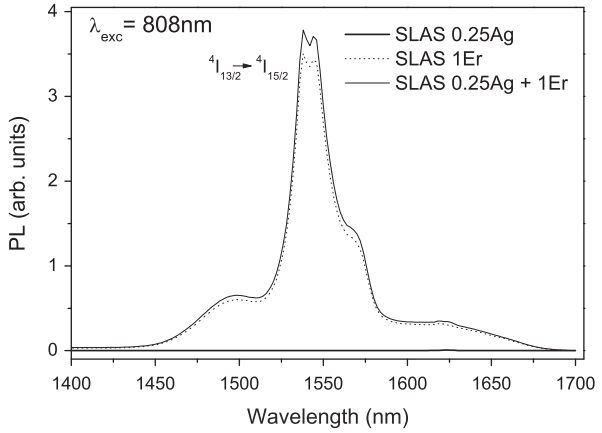

Fig. 4. Luminescence of SLAS 0.25%Ag, SLAS 1%Er and SLAS 1%Er + 0.25%Ag in the near infrared range, excited at 808 nm.

were found with laser pumping in the UV region (325 nm) (not shown). In this case the Er^{3+} luminescence increased by about 20%.

Fig. 5 shows the lifetime of the $^4I_{11/2} \rightarrow {}^4I_{15/2}$ Er^{3+} transition, excited by a HeCd UV laser for samples co-doped with (0.25Er, 0.25Ag, 1Er and 1Er 0.25Ag) mol%. The most important feature to be pointed out is that the sample with lower Er^{3+} content (0.25Er and 0.25Ag) mol% presents the higher lifetime (7.5 ms). When

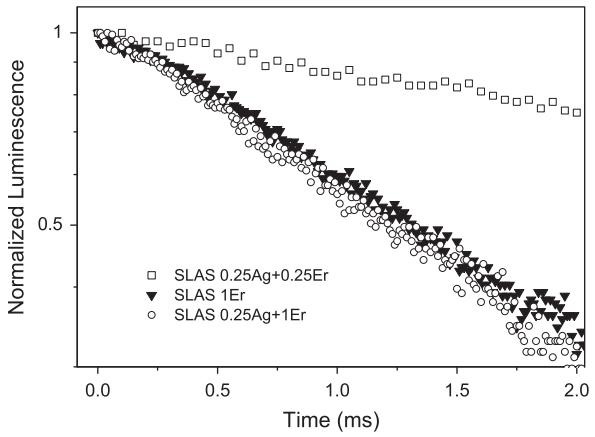

Fig. 5. Lifetime of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ Er^{3+} transition in the SLAS 0.25%Er + 0.25%Ag, SLAS 1%Er and SLAS 1%Er + 0.25%Ag samples, excited at 325 nm.

Er^{3+} concentration increases to 1% lifetime goes to 1.64 ms in the case of codoping with 0.25Ag mol% and to 1.58 ms when only Er^{3+} is present.

4. Discussion

Plasmon resonance may be produced by nucleation and growth of particles reaching the radii >5–10 Å by means of appropriate thermal treatments and exposure to laser light irradiation.

At this point it should be emphasized that contrary to previous works, [18] significant surface plasmon resonance of silver nanoparticles was observed in the absorption measurements (Fig. 2), where the corresponding nanoparticles were identified in the TEM images (Fig. 1). Varma et al. [10] have shown the formation of nanoparticles with diameter about 50 nm in soda lime glasses with similar composition with the ones used in the present work for temperatures higher than 500 °C (irrespective of time), without post-exchange annealing treatment. In our case, the band centered at about 495 nm (Fig. 2) in the absorption spectra was attributed to plasmon resonance from nanoparticles [1]. The peak position of the plasmon resonance may be used to determine the nanoparticles dimensions. The model, proposed by Mie, uses the classical electromagnetic theory to determine the absorption and scattering of an electromagnetic plane wave by a nanometer spherical particle embedded in a transparent host [1]. The model considers that the dimensions of the particles are much smaller than the light wavelength. Several authors have demonstrated the validity of this procedure. It should be noted that absorption is the main mechanism for particles with radii $R < 500$ Å. Rayleigh scattering is relevant only when the particle size is comparable to the wavelength of the incident light. Since in the present work the peak position of the plasmon absorption is centered at about 495 nm (Fig. 2), it suggests that nanoparticles with radii about 45 nm are formed [17]. The Half Width at Half Maximum (HWHM), given by 100 nm is also in agreement with the Mie theory [1]. TEM results shown in Fig. 1 are consistent with the average size estimated from the absorption peak, considering the large dispersion given by the HWHM.

The luminescence excited at 325 nm can be understood considering that such pumping is resonant with the glass absorption and the $^4I_{15/2} \rightarrow {}^2G_{11/2}$ Er^{3+} absorption. So, it is a result of a mixed emission from the SLAS glassy host, silver aggregates and Er^{3+}. Fig. 3 suggests that there is energy transfer from Er^{3+} ions to silver aggregates in the visible spectral range. The PL excitation at $\lambda = 325$ nm lies in the conduction band of the SLAS glass where are available a continuum of empty levels which can accept a reasonable population of photoelectrons, which relax successively being transferred to the $^2G_{11/2}$, $^2G_{9/2}$, $^2H_{11/2}$, $^2F_{5/2}$, $^4F_{5/2}$ Er^{3+} states, by means of the glass lattice, until they are trapped by the Ag particles that emit in the range from 350 nm to 650 nm.

The results of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ Er^{3+} infrared emission pumped at 325 nm, 532 nm and 808 nm suggest that the main Er^{3+} sensitizer mechanism comes from the local field enhancement due to the surface plasmon resonance of the silver nanoparticles that increases the absorption probability in the well known absorption bands of Er^{3+} ions. Similar results were found by Marques et al. in Ag doped sol–gel planar waveguides [19]. In fact, the plasma band is far from resonance with the excitation laser (808 nm) and therefore the only level capable of accept photoelectrons is the $^4I_{11/2}$ Er^{3+} level. The infrared luminescence shown in Fig. 3 was obtained with excitation energy that lies in a very transparent region inside the glass band gap. As there are not existing Ag^+ levels in the range of $\lambda > 808$ nm, the small Er^{3+} luminescence enhancement can be produced by traces of Ag^0 atoms, since the silver nanoparticles are not resonant. On the other hand, when the pumping wavelength goes to 325 nm, it is near the Plasmon absorption, so the increase in the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ Er^{3+} transition is more significant (20%).

Effects of Er concentration have not been investigated yet. Low Er^{3+} doping levels were chosen since for higher concentrations other effects are expected such as dipolar interactions, luminescence quenching, etc., that may produce undesirable attenuations.

The role of silver in the green emission of Er^{3+} ions were also observed with laser excitation tuned at 532 nm. In this case only Er^{3+} emission was detected. Nevertheless, no upconversion was measured when pumping the samples with laser excitation at 808 nm. We believe that this is due to the high non-radiative effects in the samples. Strong absorption from OH radicals was observed in the infrared absorption measurements (not shown). As such absorption is characterized by energy at about 3300 cm^{-1} it practically quenches all effects that could be observed in the green emission. In this case, the gap to be overcome is about 3000 cm^{-1} ($^4S_{3/2} \rightarrow {}^4I_{9/2}$).

5. Conclusions

In summary, the role of Ag in the Er^{3+} luminescence was investigated in SLAS glasses. From PL measurements it was concluded that there is emission from several Ag aggregates. Additionally, the presence of plasmons from Ag nanoparticles with radii at about 45 nm was also confirmed from absorption in the UV–VIS region and TEM images. The infrared luminescence from the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ Er^{3+} transition was enhanced up to 20% when Ag was added. The effect was attributed to the local field enhancement due to surface plasmon resonance.

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