Study of Er$^{3+}$ fluorescence on tellurite glasses containing Ag nanoparticles

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Abstract. Optical characteristics of tellurite glasses containing silver nanoparticles (NPs) and the influence on the emission spectrum of Er$^{3+}$ ions were studied. The transitions 4f$\leftrightarrow$4f from erbium ions, mainly the $^4I_{13/2}$ $\rightarrow$ $^4I_{15/2}$ transition that involve upconversion energy process, have a strongly dependence with the chemical structure of the rare earth ion. In the present work, silver nanparticles (NPs) embedded in the host vitreous material, show a significant enhance (or quenching) on the erbium fluorescence due the long-range electromagnetic interaction between the plasmon surface energy of the Ag NPs (Localized Surface Plasmon Resonance - LSPR) and the Er$^{3+}$ ions.

1. Introduction

The interaction of light with Er$^{3+}$-doped tellurite glasses containing metallic NPs has attracted much attention due to their relevance for a variety of applications in devices optoelectronic and, photonic including optical telecommunications [1]. However, the transitions intensities have a strongly dependent with the environment around the rare earth ion, for example, when influenced by silver NPs, with the possibility to a significantly increase in the Er$^{3+}$ fluorescence. Furthermore, the controlled production of NPs embedded in glasses matrix is a current challenging with promissory applications [2]. Additionally, alkaline dopants, as Na and K, and some others metal modified the structure of the glass, as well as promoting advantages in optical applications [3]. The NPs growth occurs when the glass is annealed above glass-transition temperature, i.e. when the glass viscosity is sufficient to promote the Ag$^+$ diffusion (Ag$^+$ $\rightarrow$ Ag$^0$).

In the present study, Er$^{3+}$-doped tellurite glasses containing Ag NPs were prepared changing the annealing time. It was also observed the influence of the NPs in the optical characteristics.

2. Experimental

Optically transparent tellurite glasses were prepared by conventional technique of melt-quenching. The starter reagents are TeO$_2$, GeO$_2$, Na$_2$O, ZnO, Er$_2$O$_3$ and AgCl, following the compositional rule: 75TeO$_2$–2GeO$_2$–15Na$_2$O–7ZnO–1Er$_2$O$_3$–0.25AgCl in mol%. The glasses samples were obtained as bulk samples for the samples A025-Z and G025-Z, where Z is the time of annealing at a fixed temperature (above of the glass transition temperature and, Z = 2.5, 5.0, 7.5 and 10.0 hours), the letters
A and G represent the samples prepared without controlled atmosphere and the samples prepared with nitrogen atmosphere into a glove box respectively.

The glass-transition temperature ($T_g$) of the glass samples was determined by Differential Scanning Calorimetry (DSC). The measurement was carried out in nitrogen atmosphere, with heating rate of 10 °C/min. The experimental error in $T_g$ was within ±1 °C. The refractive indices of the glass samples at 543, 632.8, 1305 and 1553.4 nm were measured by prism coupler technique or M-Lines technique (Metricon Model 2010 Prism Coupler). Luminescence spectra were performed using a diode laser at 980 nm (2W), 425 nm output laser with 200 mW, and an InGaAs detector with lock-in technique. For measured the $^{4}I_{13/2}$ level lifetime, the samples were irradiated with a 980 nm laser diode with a train of pulses of 50 µs, with dead time of 100 ms. The emission signal was measured by a 400 MHz oscilloscope (Tektronix TDS 380). TEM photograph was made using a Philips-CM120 operating at 200 kV.

![Figure 1](image-url)

**Figure 1.** Luminescence spectrums and upconversion of Er$^{3+}$ to all samples. The energy levels transitions involved are shown in the graphics. (a) and (b) samples A025-Z pumped at 442 and 980 nm respectively. (c) samples G025-Z and (d) samples A025-Z both pumped with 980 nm.

3. Results

Through DSC analysis, it was possible to obtain the characteristics temperatures of the samples: $T_g = 283 \pm 5$ °C for the glass transition temperature, $T_x = 409 \pm 4$ °C for the onset crystallization temperature. Based on the $T_g$, it was proposed the annealing temperature at 300 °C (just up $T_g$) to perform the formation and growing of the Ag NPs. On the other hand, NPs embedded in the host matrix can induce a significant enhancement or quenching of the erbium fluorescence due to long-range electromagnetic interactions between the LSPR and the Er$^{3+}$ ions. Therefore, the enhancement
and the blue shift in the fluorescence spectrum are resulted of the modification in the local electric field, see Fig. 1 (a) to up (d). Moreover, we considered the luminescence enhancement as the area under the deconvolution peaks ($\lambda$-peak) of the luminescence, i.e., the enhancement is defined by:

\[ I_{\lambda-\text{peak}} = \frac{\text{area}_{\lambda-\text{peak-NPs}}}{\text{area}_{\lambda-\text{peak-without-NPs}}} \]

The measurements of the refractive index of ours samples (see table 1) shown a clearly evidence that the presence of the NPs modifies the medium dielectric permittivity ($\varepsilon(\omega) \approx \sqrt{n(\omega)}$).

Two lasers sources were used to obtain the photoluminescence spectrum. In Fig. 1 (a) the samples A025-Z were pumped with a laser at 442 nm (HeCd). It was possible to observe a pronounced enhancement on $^2H_{11/2} \rightarrow ^4I_{15/2}$, $^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$ level transitions, besides different intensities of the peaks when compared with the spectrum of the Fig. 1 (b), where the samples were excited at 980 nm. The Fig. 1 (c) and (d) show clearly an improvement obtained in the samples manufactured into a glove box under $N_2$ atmosphere (samples G025-Z) in comparison with the ones produced in air atmosphere (samples A025-Z). This is due to the decreasing of hydroxyl groups (-OH) content into the vitreous matrix that promote a photoluminescence enhancement in $^4I_{13/2} \rightarrow ^4I_{15/2}$ level transitions and, an increasing in the $^4I_{13/2}$ lifetime (see Table 1). We can see in this region, for some samples, a quenching process (Fig. 1 (d)) which was verify in the Table 1 ($I_{568\text{-nm}}$).

The LSPR effect on the luminescence is strongly dependent with wavelength excitation and this enhancement (or quenching) depend on the NPs size and shape.

| Sample | $n_{543\text{-nm}}$ | $n_{1550\text{-nm}}$ | $I_{568\text{-nm}}$ | $\tau (\text{ms})$ |
|--------|------------------|---------------------|------------------|------------------|
| A025-2.5 | 2.0205     | 1.9463             | 0.93             | 2.63             |
| A025-5.0 | 2.0214     | 1.9466             | 0.83             | 2.62             |
| A025-7.5 | 2.0213     | 1.9473             | 0.93             | 2.48             |
| A025-10.0 | 2.0208   | 1.9464             | 1.19             | 2.72             |
| G025-2.5 | 2.0208     | 1.9474             | 1.48             | 3.80             |
| G025-5.0 | 2.0188     | 1.9460             | 1.66             | 4.47             |
| G025-7.5 | 2.0211     | 1.9464             | 1.77             | 4.94             |
| G025-10.0 | 2.0206   | 1.9477             | 1.83             | 4.87             |
| Without NPs* | 2.0122 | 1.9405             | 2.74             | ---               |

*in air.

Figure 2. TEM image of the Ag NPs (A025-10.0) showing the dispersed Ag NPs particles into the glass matrix. The maximum diameter (major axis) is 19 to 22 nm with an aspect ratio 1.0–1.2.

We should mention that the growth process of the NPs involves several steps which include the nucleation, growing among others. The diffusion of Ag⁺ ions in the vitreous matrix during the
annealing creates nucleation of clusters by the reduction of these ions to Ag⁺, Fig. 2. The tellurite glasses exhibit a low mobility for the Ag⁺ ions [4].

In the Table 1 is shown the lifetime for the samples A025-Z. These modifications are related to the radiative decay rate $\Gamma_r$ and nonradiative decay rate $\Gamma_{nr}$. Thus:

$$\Gamma_r^{\text{eff}} = \frac{3}{2} \sum_{m} (2l+1) \left\{ \left( \frac{j_{l}(kr) + b_{l}h_{l}^{\text{even}}(kr)}{kr} \right)^{2} + \left( \frac{\zeta_{l}(kr) + b_{l}h_{l}^{\text{odd}}(kr)}{kr} \right)^{2} \right\},$$

$$\Gamma_{nr}^{\text{eff}} = \frac{3}{2} \sum_{m} (2l+1) \left\{ \left( \frac{j_{l}(kr) + a_{l}h_{l}^{\text{even}}(kr)}{kr} \right)^{2} + \left( \frac{\zeta_{l}(kr) + a_{l}h_{l}^{\text{odd}}(kr)}{kr} \right)^{2} \right\}$$

there are two possible dipole orientations: radial and tangential and $\Gamma_r^{\text{eff}}$ refers to radiative decay rate for the dipole located in the embedding (nonabsorbing) medium in the absence of the NPs [5]. Bessel and Hankel functions, $\psi_{l}(x)=xj_{l}(x)$, $\zeta_{l}(x)=xh_{l}^{(1)}(x)$. $a_{l}$ and $b_{l}$ are Mie scattering coefficients of a sphere, $l$ is the angular mode number, and $r$ is the distance to the sphere surface. Therefore the presence of Ag NPs modified the quantum efficiency: $\eta = \Gamma_{r}^{\text{eff}}(\Gamma_{r} + \Gamma_{nr})$ in the matrix host (dielectric). This approach provides physical insight on the extent of radiative and nonradiative rate decay enhancements was intrinsically linked. The Fig. 3 shows the results obtained from our simulation of the quantum efficiency of system keeping in mind the coupling interaction between the NPs and the Er³⁺ ions, where we were considerate the physical parameters of the A025-10.0 sample (refraction index, Mie scattering coefficients and others). For this the optical data of Ag were taken from Palik [6]. For the carried out simulations the value of refractive index is adjusted through the dispersion equation of Sellmeier [7].

![Figure 3](image)

**Figure 3.** The $\eta_{\perp}$ and $\eta_{\parallel}$ data normalized for radiative decay rate in the absence of sphere (a), and (b) as a function of the excitation wavelength for dipole, quadrupole and octupole. The NPs size is fixed in 20 nm. Dipole emitted (c) and (d) in function of the distance to the sphere surface with size of NPs, i.e. $2d$, with wavelength fixed in 980 nm. Where: $\Gamma_{r}^{\text{eff}} = 100\%$.

We should mention that the obtained value for $r = (1/N)^{1/3}$ [8], where $N$ is the concentration of ion (atoms/cm²) for our glasses, from ours experimental parameters is: $21 \pm 2$ Å.

From Fig. 3 (a) and (b) we can say that in our glasses the dipoles formation are more favorable in comparison with the other configurations (quadruple or octupole), just as it is shown in those figures, for different wavelengths, and verified by the emission spectrum (see Fig. 1 (a) and (b)). In the same way, we can observed that the quantum yield of the tangential and radial components are 20% and 39% respectively, finding good agreement with the obtained values of $I_{l=568-nm}$, see Table 1. Moreover, Fig. 3 (c) and (d) show the dependence of NPs size versus the quantum efficiency of an emitter dipole with the two possible orientations to a fixed wavelength at 980 nm. From these results, we can
conclude that the NP size increasing to the quantum efficiency also rises, that it can be attributed to electromagnetic properties of the radioactive emission of the emitter dipoles providing modifying the local field inside the vitreous matrix. In this sense, the existence of a good size is independent of the dispersion caused by the NPs. Comparing the size of 22 nm obtained through the TEM (Fig. 2) for the sample A025-10 and of the result shown in the figure 3 (c) and (d) with quantum efficiency among 20 to 40%, we obtain a good agreement with the experimental result obtained in the Table 1 with an increment of intensity of 19%.

4. Conclusions

To summarize, the DSC technique was essential to establish the temperature range, where the growth process of the NPs is more appropriately. We show that Er$^{3+}$-doped tellurite glass is a good host matrix that permits the formation of NPs. Of course the size the NPs is mainly dependent on annealing time and the controlled atmosphere ($N_2$) permits increment the lifetime of these glasses due the decrease of the group -OH content. Finally, the photoluminescence enhancement observed in the experimental results is verified in the Fig. 3 with excellent concordance, where is assuming the idea of an emitter dipole (from an electric dipole).

Acknowledgments

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