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Luminescence of Tb^{3+} doped $TeO_2-ZnO-Na_2O-PbO$ glasses containing silver nanoparticles

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Luminescence properties of Tb^{3+} doped $TeO_2-ZnO-Na_2O-PbO$ glasses containing silver nanoparticles (NPs) were investigated. The absorption band due to the surface plasmon resonance in the NPs was observed. Its amplitude increases with the heat treatment of the samples that controls the nucleation of the NPs. Tb^{3+} emission bands centered at ≈ 485, ≈ 550, ≈ 585, and ≈ 623 nm were detected for excitation at 377 nm. The whole spectrum is intensified by the appropriate annealing time of the samples. Enhancement by $\approx 200\%$ of the Tb^{3+} luminescence at 550 nm was observed for samples annealed at 270 °C during 62 h. This enhancement effect is due to the local field amplitude that increases with the amount of silver NPs and their aggregates. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3010867]

I. INTRODUCTION

The spectroscopic investigation of tellurite glasses containing silver nanoparticles (NPs) is of large interest because the optical properties of such composites can be controlled by appropriate thermal treatment. In general, tellurite based metal-dielectric composites present a large transmittance window (360–4500 nm), low cutoff phonon energy (~ 700 cm^{-1}), high refractive index (~ 2.0), and high nonlinear optical response.[1–11]

Tellurite glasses and composites doped with Tb^{3+} ions deserve particular attention because they have large potential for the development of amplifiers and lasers covering the main telecom windows. In the visible region the emission spectrum of Tb^{3+} ion shows intense fluorescence in the blue-red region and this allows often the use of Tb^{3+} doped materials as phosphors in fluorescent lamps, x-ray intensify screens, and TV tubes.

The nucleation of silver and gold NPs in tellurite glasses was demonstrated recently.[12–15] The growth of silver nanostructures in $TeO_2-PbO-GeO_2$ glass (labeled as TPG glass) originated large luminescence enhancement due to clusters with two or more Pb^{2+} ions.[12] The influence of silver NPs on the luminescence efficiency of Pr^{3+} doped TPG glass was studied in Ref. 13. Enhanced Stokes luminescence and intensified frequency upconversion were observed for samples excited in the visible region. Also recently the luminescence properties of Pr^{3+} doped TeO_2-ZnO containing silver NPs and Eu^{3+} doped TPG with gold NPs were studied in Refs. 14 and 15. In all cases the presence of metallic nanostructures of silver or gold contributed to improve the luminescence characteristics of the samples.

In the present work we report luminescence properties of $TeO_2-ZnO-Na_2O-PbO$ glasses containing Tb^{3+} and silver NPs. It is shown that the luminescence in the blue-red region is enhanced due to the presence of silver NPs. In particular, the green emission at ≈ 550 nm is enhanced by $\approx 200\%$. The luminescence increase that occurs in the whole visible region is controlled by the heat treatment of the sample.

II. EXPERIMENTAL DETAILS

$TeO_2-ZnO-Na_2O-PbO$ glasses were prepared with the starting composition 85.4 TeO_2–6.97 ZnO–4.43 Na_2O–3.20 PbO (in mole percent). The doping species were Tb_4O_7 (5 wt %) and Ag_2O (10 wt %). The reagents were melted in a platinum crucible at 750 °C for 2 h, quenched in air in a heated brass mold, annealed for 2 h at 270 °C, and then cooled to room temperature inside the furnace. The samples were submitted to different heat-treatment times at 270 °C in order to reduce the Ag^+ ions to Ag^0 and to nucleate silver NPs. The amount of NPs increases with the increase in the annealing time.

A 200 kV transmission electron microscope (TEM) was used to investigate the nucleation of NPs; their composition was verified by electron diffraction measurements. Absorption spectra were recorded from 350 to 700 nm using a commercial spectrophotometer. For the photoluminescence measurements the samples were excited using a 30 W xenon lamp (pulses of ~ 3 μs, 80 Hz), and the obtained spectra, excited by radiation at 377 nm, were analyzed by a 0.25 m monochromator.

The optical experiments were performed with the samples having dimensions of $10 \times 10 \times 2$ mm^3 at room temperature.

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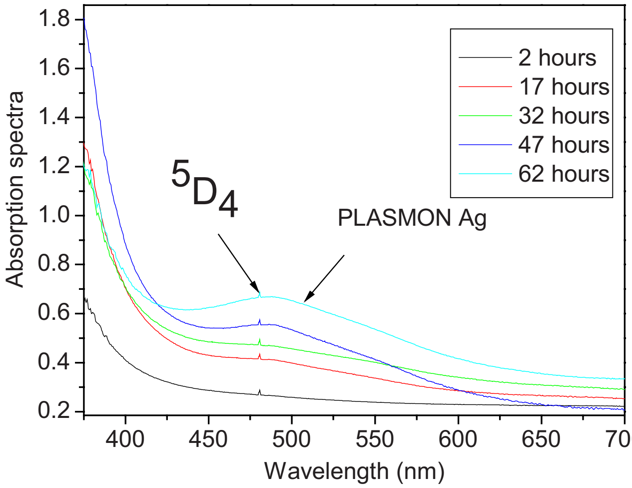

FIG. 1. (Color online) Absorption spectra of Tb^{3+} doped $TeO_2-ZnO-Na_2O-PbO$ samples containing NPs for various heat-treatment times.

III. RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra of the Tb^{3+} doped $TeO_2-ZnO-Na_2O-PbO$ samples, thermally treated at 270 °C during heat-treatment times $\tau_A = 2$, 17, 32, 47, and 62 h. The weak absorption feature at ≈480 nm is due to the ${}^7F_6 \rightarrow {}^5D_4$ electronic transition of Tb^{3+} ions. The broadband centered at ≈490 nm is assigned to the surface plasmon resonance (SPR) associated to the NPs; its amplitude increases with increasing values of τ_A because the concentration of the NPs grows as confirmed by TEM measurements. We recall that the SPR wavelength λ_{SP} depends on the size and shape of the NPs as well as on the dielectric constant of the host.[2,16] In the present case λ_{SP} is located in the expected region and the large bandwidth is attributed to inhomogeneous broadening due to the variety of NPs' sizes and shapes.

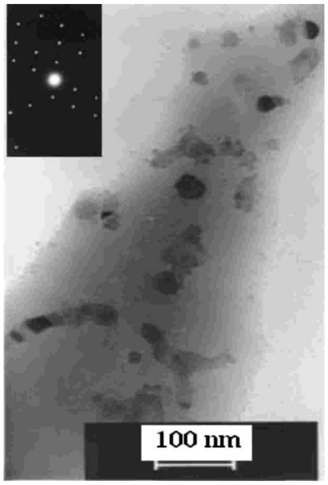

FIG. 2. TEM image of the sample annealed during 62 h. The inset shows the electron diffraction pattern of the silver NPs.

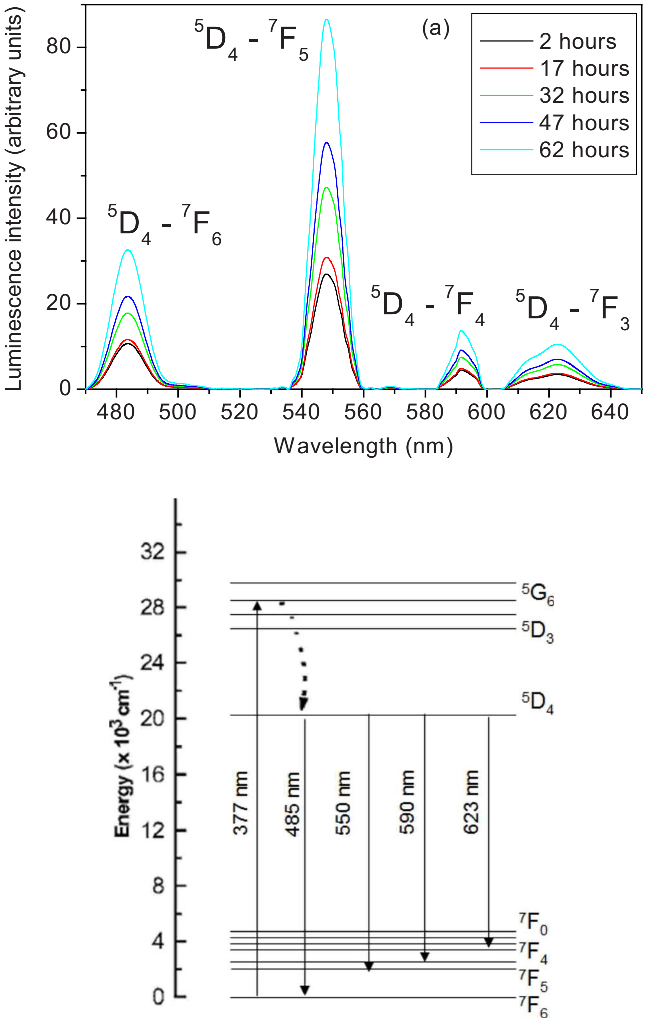

FIG. 3. (Color online) (a) Emission spectra of Tb^{3+} doped $TeO_2-ZnO-Na_2O-PbO$ samples containing silver NPs for different annealing times (excitation wavelength: 377 nm). (b) Simplified energy level scheme of Tb^{3+} ion with indication of the luminescence transitions observed. The dashed line indicates nonradiative decay to level ${}^5D_3$ followed by cross-relaxation among excited ions and neighbors in the ground state according to $({}^5D_3;\ {}^7F_6) \rightarrow ({}^5D_4;\ {}^7F_0)$.

Figure 2 shows a TEM micrograph of a sample heat treated for 62 h demonstrating the presence of silver NPs and aggregates with dimensions in the range of 2–150 nm. Diffraction patterns characteristic of silver crystals were identified. Similar results were obtained for samples heat treated for different values of τ_A. However, the amount of NPs increases with τ_A.

The luminescence spectra of the Tb^{3+} doped metal-dielectric composite for excitation at 377 nm (${}^7F_6 \rightarrow {}^5G_5$ transition) exhibit strong emission bands due to the $4f-4f$ transitions of Tb^{3+} ions. Figure 3(a) presents spectra corresponding to the transitions: ${}^5D_4 \rightarrow {}^7F_6$ (≈485 nm), ${}^5D_4 \rightarrow {}^7F_5$ (≈550 nm), ${}^5D_4 \rightarrow {}^7F_4$ (≈585 nm), and ${}^5D_4 \rightarrow {}^7F_3$ (≈623 nm). Because of the large energy gap between levels ${}^5D_4$ and ${}^7F_0$ (≈17 300 cm^{-1}) the quantum efficiency for luminescence originating from the ${}^5D_4$ level is almost 100%.

Luminescence transitions originating from the ${}^5D_3$ level are not observed because of a cross-relaxation $({}^5D_3,\ {}^7F_6) \rightarrow ({}^5D_4,\ {}^7F_0)$ among Tb^{3+} ions in the ${}^5D_3$ level and neighbor ions in the ground state. This cross-relaxation process was observed in different glasses having Tb^{3+} concentration larger than 0.5%.[17,18] The probability of multiphonon relaxation among the ${}^5D_3$ and ${}^5D_4$ levels is very small because of the large energy gap (≈5800 cm^{-1}).

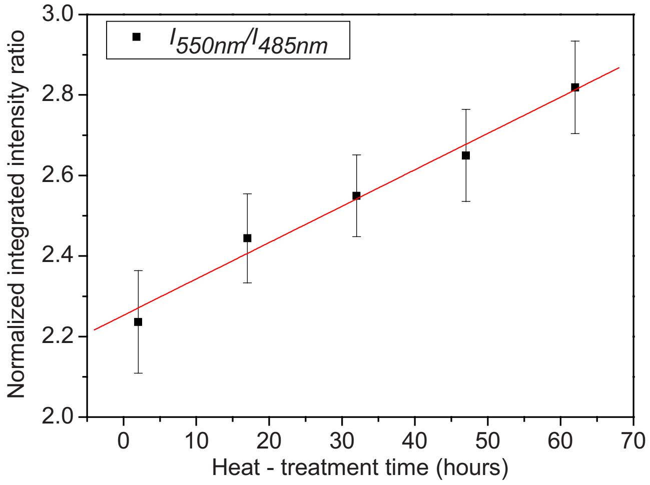

FIG. 4. (Color online) Normalized integrated intensity ratio between the luminescence at 550 and at 485 nm $R=I_{550\ \mathrm{nm}}/I_{485\ \mathrm{nm}}$ as a function of the annealing time.

A simplified energy level scheme for Tb^{3+} ions with indication of the emissions detected in the experiments is shown in Fig. 3(b).

The spectra in Fig. 3(a) correspond to various values of τ_A that correspond to different amounts of silver nanostructures. It can be noted that there was an intensification of ≈200% for the luminescence signal centered at ≈550 nm, corresponding to $\tau_A=62$ h, with respect to the sample heat treated during 2 h. We recall that previous studies with tellurite glass without metallic NPs[14] indicate that the heat treatment under the present conditions does not change the symmetry around the trivalent rare-earth ions; the changes observed in Fig. 3(a) are attributed to the influence of the NPs that changes the local field in the Tb^{3+} ions location.

Figure 3(a) allows the determination of the integrated intensity ratio $R=I_{550\ \mathrm{nm}}/I_{485\ \mathrm{nm}}$ for different values of τ_A. The results are given in Fig. 4 which shows the behavior of R as a function of τ_A. We observe that the emission at ≈550 nm is more sensitive to the presence of silver NPs than the fluorescence band at ≈485 nm. This is due to the fact that electric dipole transitions are more sensitive to the local field change than magnetic dipole transitions. Similar results were obtained in Eu^{3+} doped tellurite glasses containing gold NPs.[15]

It is also important to remark that luminescence enhancement occurs even for the emissions centered at ≈585 and ≈623 nm. This is understood considering the influence of aggregates that usually originate hot spots of the electromagnetic field[19] that may originate the main contribution for intensification of the orange and red spectrum.[13,14] This effect was also reported for lead-germanate glasses.[20]

IV. SUMMARY

In summary, the present results show that the nucleation of silver NPs in Tb^{3+} doped TeO$_2$–ZnO–Na$_2$O–PbO glass contributes for the enhancement of Tb^{3+} luminescence corresponding to wavelengths in the visible spectrum. The luminescence enhancement is due to the local field growth that occurs because of the mismatch between the dielectric function of the NPs and the host glass. The Tb^{3+} ions located in the vicinity of the NPs are in the presence of an intensified local field and consequently the luminescence efficiency increases.

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