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Luminescence of Tb$^{3+}$ doped TeO$_2$–ZnO–Na$_2$O–PbO glasses containing silver nanoparticles

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Luminescence properties of Tb$^{3+}$ doped TeO$_2$–ZnO–Na$_2$O–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 $\approx$485, $\approx$550, $\approx$585, and $\approx$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 in the visible region and this allows often the use of Tb$^{3+}$ doped materials as phosphors in fluorescent lamps, x-ray intensify screens, and TV tubes.

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. 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. The influence of silver NPs on the luminescence efficiency of Pb$^{2+}$ 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 Pb$^{2+}$ 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.

II. EXPERIMENTAL DETAILS

TeO$_2$–ZnO–Na$_2$O–PbO glasses were prepared with the starting composition 85.4 TeO$_2$–6.97 ZnO–4.43 Na$_2$O–3.20 PbO (in mole percent). The doping species were Tb$_4$O$_7$ (5 wt %) and Ag$_2$O (10 wt %). The reagents were melted in a platinum crucible at 750 °C for 2 h, quenched in air in a heated brass mould, 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.

In the present work we report luminescence properties of TeO$_2$–ZnO–Na$_2$O–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 $\approx$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.
III. RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra of the Tb\(^{3+}\) doped TeO\(_2\)–ZnO–Na\(_2\)O–PbO samples, thermally treated at 270 °C during heat-treatment times \(\tau_h = 2, 17, 32, 47,\) and 62 h. The weak absorption feature at \(\approx 480\) nm is due to the \(^7F_6 \rightarrow ^5D_4\) electronic transition of Tb\(^{3+}\) ions. The broadband centered at \(\approx 490\) nm is assigned to the surface plasmon resonance (SPR) associated to the NPs; its amplitude increases with increasing values of \(\tau_h\) because the concentration of the NPs grows as confirmed by TEM measurements. We recall that the SPR wavelength \(\lambda_{SP}\) depends on the size and shape of the NPs as well as on the dielectric constant of the host.\(^2\) In the present case \(\lambda_{SP}\) is located in the expected region and the large bandwidth is attributed to inhomogeneous broadening due to the variety of NPs’ sizes and shapes.

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 \(\tau_h\). However, the amount of NPs increases with \(\tau_h\).

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: \(^5D_4 \rightarrow ^7F_6\) (\(\approx 485\) nm), \(^5D_4 \rightarrow ^7F_5\) (\(\approx 550\) nm), \(^5D_4 \rightarrow ^7F_4\) (\(\approx 585\) nm), and \(^5D_4 \rightarrow ^7F_3\) (\(\approx 623\) nm). Because of the large energy gap between levels \(^5D_4\) and \(^7F_0\) (\(\approx 17300\) 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 \((^5D_3, ^7F_4)\) \(-\rightarrow\) \((^5D_4, ^7F_0)\) 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 (\(\approx 5800\) cm\(^{-1}\)).
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 \(\tau_A\) that correspond to different amounts of silver nanostructures. It can be noted that there was an intensification of \(\approx 200\%\) for the luminescence signal centered at \(\approx 550\) 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 \(R = I_{550\text{ nm}}/I_{485\text{ nm}}\) for different values of \(\tau_A\). The results are given in Fig. 4 which shows the behavior of \(R\) as a function of \(\tau_A\). We observe that the emission at \(\approx 550\) nm is more sensitive to the presence of silver NPs than the fluorescence band at \(\approx 485\) 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 \(\approx 585\) and \(\approx 623\) 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 Te\(_2\)O\(_2\)–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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