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Citation: *J. Appl. Phys.* **105**, 103505 (2009); doi: 10.1063/1.3126489

View online: <http://dx.doi.org/10.1063/1.3126489>

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# Enhanced luminescence of Tb<sup>3+</sup>/Eu<sup>3+</sup> doped tellurium oxide glass containing silver nanostructures

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(Received 2 March 2009; accepted 2 April 2009; published online 20 May 2009)

We report on energy transfer studies in terbium (Tb<sup>3+</sup>)—europium (Eu<sup>3+</sup>) doped TeO<sub>2</sub>–ZnO–Na<sub>2</sub>O–PbO glass containing silver nanostructures. The samples excitation was made using ultraviolet radiation at 355 nm. Luminescence spectra were recorded from ≈480 to ≈700 nm. Enhanced Eu<sup>3+</sup> luminescence at ≈590 nm (transition <sup>5</sup>D<sub>0</sub>–<sup>7</sup>F<sub>1</sub>) and ≈614 nm (transition <sup>5</sup>D<sub>0</sub>–<sup>7</sup>F<sub>2</sub>) are observed. The large luminescence enhancement was obtained due to the simultaneous contribution of the Tb<sup>3+</sup>–Eu<sup>3+</sup> energy transfer and the contribution of the intensified local field on the Eu<sup>3+</sup> ions located near silver nanostructures. © 2009 American Institute of Physics.

[DOI: 10.1063/1.3126489]

## I. INTRODUCTION

Nonradiative energy transfer (ET) processes involving rare-earth (RE) ions in solids have been widely studied because of the special optical properties of the RE ions and their photonic applications. In principle ET processes may favor particular applications (such as the operation of anti-Stokes emitters<sup>1,2</sup>) but it may be detrimental as in the case of RE based lasers because interactions among the active ions contribute for the increase of the laser threshold.<sup>1,2</sup> In particular the study of ET processes in glasses having frequency gap in the visible region deserves large attention because when doped with RE ions some glasses may present efficient visible luminescence.<sup>1–13</sup>

Tellurium oxide glasses are very good candidates for these studies because they accept large concentration of RE ions, exhibit large transmittance window (from the visible to the infrared region), have low cutoff phonon energy (~700 cm<sup>-1</sup>), present high refractive index (~2.0) and show large chemical stability. Luminescence properties of tellurium oxide glasses doped with RE ions were reported by various authors.<sup>1–3,7,8,13</sup>

Recently nucleation of metallic nanoparticles (NPs) inside tellurium oxide glasses was reported.<sup>14–18</sup> In all cases studied the presence of NPs contributes to enhance the material's luminescence efficiency either due to ET from the NPs to the RE ions or by influence of the large local field on the RE ions positioned in the vicinity of the NPs. Indeed the presence of silver nanostructures in TeO<sub>2</sub>–PbO–GeO<sub>2</sub> glass improved the luminescence efficiency of Pb<sup>2+</sup> clusters.<sup>14</sup> Enhanced Stokes and anti-Stokes luminescence were observed in Pr<sup>3+</sup> doped TeO<sub>2</sub>–PbO–GeO<sub>2</sub> glass containing silver NPs.<sup>15,16</sup> More recently, experiments with TeO<sub>2</sub>–PbO–GeO<sub>2</sub>

glass doped with Eu<sup>3+</sup> and containing gold NPs (Ref. 17) and Tb<sup>3+</sup> doped TeO<sub>2</sub>–ZnO–Na<sub>2</sub>O–PbO glass with silver NPs (Ref. 18) were reported. However, experiments with tellurium based glasses containing metallic NPs and codoped with two different RE species were not reported.

In this work we present the first luminescence study of Tb<sup>3+</sup>/Eu<sup>3+</sup> doped TeO<sub>2</sub>–ZnO–Na<sub>2</sub>O–PbO glass containing silver NPs. In the experiments we excited the samples using ultraviolet light with frequency larger than the frequency band gap of the glass. The wavelength used was 355 nm which is possibly in resonance with a Tb<sup>3+</sup> transition originating from the ground state. Luminescence bands from ≈480 to ≈700 nm were observed due to radiative transitions associated to the RE ions. The contribution of ET processes and the intensified local field due to the NPs allowed obtaining enhanced luminescence in the orange-red spectral region.

## II. SAMPLES PREPARATION

Samples having compositions 85.4 TeO<sub>2</sub>–6.97 ZnO–4.43 Na<sub>2</sub>O–3.20 PbO (in wt %) were prepared using the melt-quenching method. The doping species were 2.0 wt % of Tb<sub>4</sub>O<sub>7</sub>, 1.0 wt % of Eu<sub>2</sub>O<sub>3</sub>, and 4.0 wt % of AgNO<sub>3</sub>. The high pure 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. Afterwards the samples were submitted to different heat-treatment times at 270 °C in order to reduce the Ag<sup>+</sup> ions to Ag<sup>0</sup> and to nucleate silver NPs. Samples doped with Tb<sup>3+</sup> and Eu<sup>3+</sup> without AgNO<sub>3</sub> and two samples containing only Eu<sup>3+</sup> (1.0 and 5 wt %) were also prepared to be used as references. Heat treatment during time intervals τ<sub>A</sub>=2, 17, 32, 47, and 62 h were performed.

A 200 kV transmission electron microscope (TEM) was used to investigate the nucleation of NPs. Also electron diffraction measurements and energy dispersive x-ray spectroscopy

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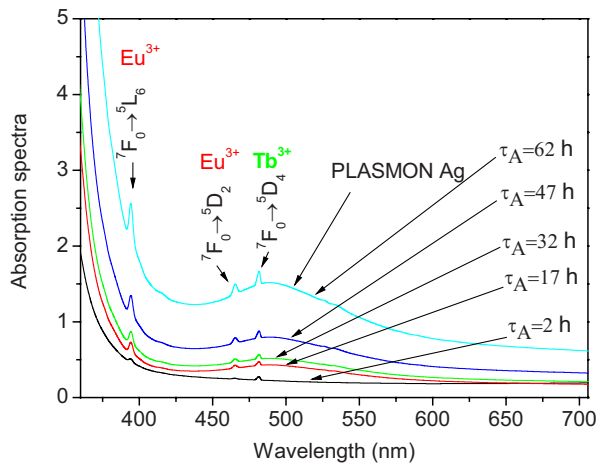


FIG. 1. (Color online) Absorption spectra of the samples heat-treated during different times. The broadband centered at  $\approx 490$  nm is due to the SP resonances in the metallic nanostructures.

copy were employed to determine the composition of the NPs. Isolated NPs with a variety of sizes and shapes, and aggregates with dimensions from 10 to 30 nm were observed. The EDS analysis showed the presence of silver, Te, Zn, and Pb in the NPs. For the optical experiments the samples had dimensions of  $10 \times 10 \times 2$  mm<sup>3</sup>.

### III. RESULTS AND DISCUSSIONS

Figure 1 shows the absorption spectra from 350 to 700 nm obtained using a commercial spectrophotometer. Transitions originating from the ions ground state are observed at 480 nm ( $\text{Tb}^{3+}: {}^7\text{F}_6 - {}^5\text{D}_4$ ), 465 nm ( $\text{Eu}^{3+}: {}^7\text{F}_0 - {}^5\text{D}_2$ ), and 395 nm ( $\text{Eu}^{3+}: {}^7\text{F}_0 - {}^5\text{L}_6$ ). The broadband centered at  $\approx 490$  nm, observed in the samples heat treated for times longer than 2 h, is attributed to surface plasmon (SP) resonances. Its amplitude increases for longer heat-treatment times due to the increase of the NPs volume fraction. The large SP bandwidth is attributed to the variety of shapes and sizes of the NPs and the presence of aggregates of NPs.

Photoluminescence was excited using a 15 W xenon lamp (pulses of 3  $\mu\text{s}$  at 80 Hz), followed by a 0.2 m monochromator to select the wavelength at 355 nm. The luminescence spectra in Fig. 2, exhibit bands due to  $4f-4f$  transitions associated to  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  ions. Results for different values of  $\tau_A$  are shown and it is observed that the luminescence in the orange-red region is enhanced while increasing the volume fraction occupied by the NPs. No luminescence signal in this spectral range was detected when the samples containing only  $\text{Eu}^{3+}$  were excited under the same conditions. Moreover, previous studies with tellurium oxide glasses indicated that the symmetry around the RE ions does not change with the heat treatment.<sup>17,18</sup> Therefore the results indicate that the simultaneous presence of  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  ions is essential to observe the strong luminescence in the orange-red region.

To understand the spectra of Fig. 2 it is useful to consider the  $\text{Tb}^{3+}/\text{Eu}^{3+}$  energy level scheme shown in Fig. 3. Since no emission in the orange-red region was observed from the sample that does not contain  $\text{Tb}^{3+}$ , we assume that the incident light at 355 nm is not in resonance with  $\text{Eu}^{3+}$  transitions starting from the ground state. Accordingly, con-

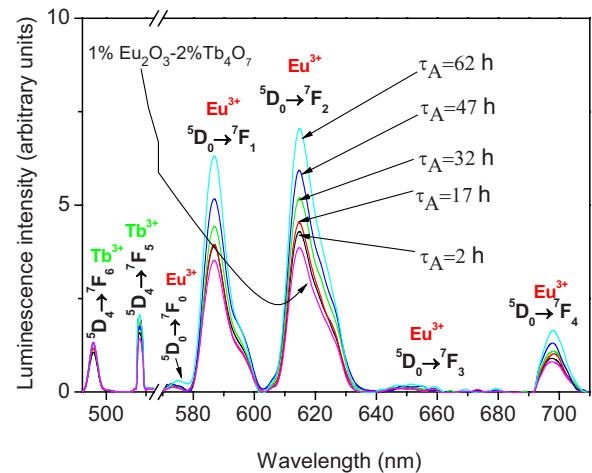


FIG. 2. (Color online) Luminescence spectra for excitation at 355 nm. The corresponding heat-treatment time  $\tau_A$  is indicated.

sidering excitation of  $\text{Tb}^{3+}$  ions, two different pathways for the absorbed energy may be followed. One pathway is due to ET from the  ${}^5\text{D}_3$  ( $\text{Tb}^{3+}$ ) level to the energy level  ${}^5\text{L}_6$  ( $\text{Eu}^{3+}$ ). From this level, after nonradiative relaxation, the  $\text{Eu}^{3+}$  ion excitation reaches level  ${}^5\text{D}_0$  from where radiative transitions to  $\text{Eu}^{3+}$  levels  ${}^7\text{F}_J$  ( $J=0-4$ ) occur. Another energy pathway starts with nonradiative relaxation from level  ${}^5\text{D}_3$  ( $\text{Tb}^{3+}$ ) to  ${}^5\text{D}_4$  ( $\text{Tb}^{3+}$ ). Then, radiative relaxations from  ${}^5\text{D}_4$  ( $\text{Tb}^{3+}$ ) to  $\text{Tb}^{3+}$  levels  ${}^7\text{F}_J$  ( $J=0-6$ ) may occur corresponding to emissions in the blue-red spectral region; also quasis resonant cross-relaxation (CR) to  $\text{Eu}^{3+}$  levels  ${}^5\text{D}_J$  ( $J=0, 1, 2$ ) occurs, as indicated in Fig. 3. This efficient CR process was well characterized for  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  in different hosts<sup>2,19-21</sup> and considering the large concentration of RE ions it is very probable in the present case. Following the CR, radiative decay corresponding to  $\text{Eu}^{3+}$  transitions  ${}^5\text{D}_0 - {}^7\text{F}_J$  ( $J=0-4$ ) takes place. We note that the  $\text{Tb}^{3+}$  emissions at  $\approx 485$  nm (transition  ${}^5\text{D}_4 - {}^7\text{F}_6$ ) and  $\approx 545$  nm (transition  ${}^5\text{D}_4 - {}^7\text{F}_5$ ) are weak. It is important to note that these emissions are weaker than in the  $\text{Tb}^{3+}$  doped sample<sup>18</sup> because of the ET to  $\text{Eu}^{3+}$

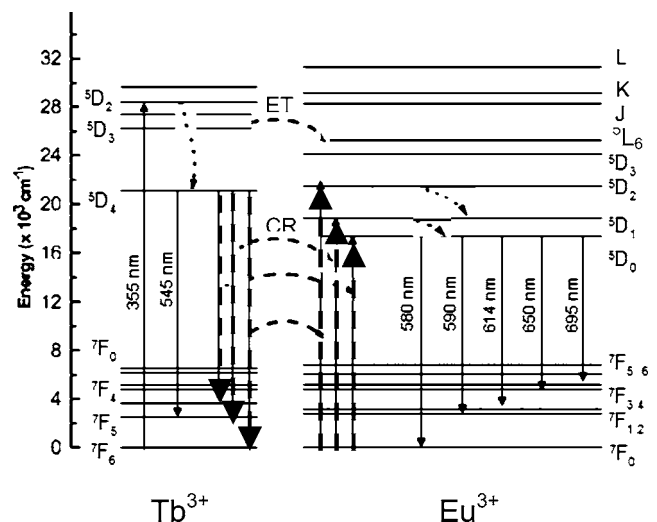


FIG. 3. Energy level scheme of  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  ions. The solid lines represent radiative transitions. Dotted lines represent phonon relaxation processes. Dashed lines represent CR and ET processes.

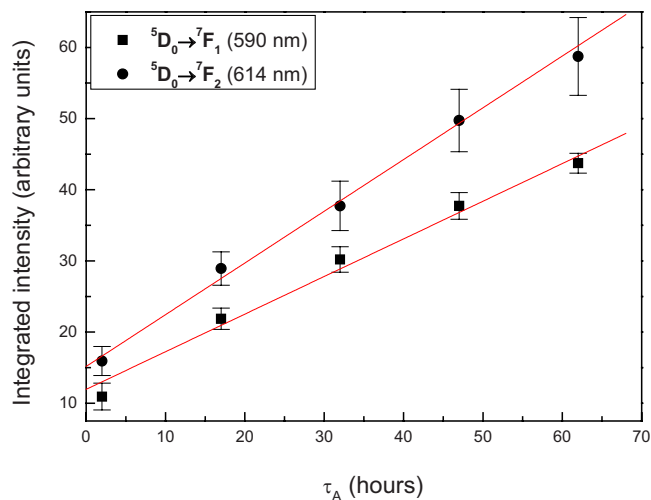


FIG. 4. (Color online) Integrated luminescence intensity for  $\text{Eu}^{3+}$  transitions  ${}^5\text{D}_0\text{--}{}^7\text{F}_1$  and  ${}^5\text{D}_0\text{--}{}^7\text{F}_2$  as a function of the heat-treatment time  $\tau_A$ .

ions. Of course we may not discard possible contribution of  $\text{Tb}^{3+}$  ions to the luminescence centered at  $\approx 590$  nm (transition  ${}^5\text{D}_4\text{--}{}^7\text{F}_6$ ) and  $\approx 614$  nm (transition  ${}^5\text{D}_4\text{--}{}^7\text{F}_5$ ). These  $\text{Tb}^{3+}$  transitions were reported in Ref. 18 and their amplitudes are sensitive to the presence of the metallic NPs. However due to the efficient CR between  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  ions and because of the quenching observed for the  $\approx 545$  nm emission, we conclude that the emissions at  $\approx 590$  and  $\approx 614$  nm are mainly due to  $\text{Eu}^{3+}$  ions.

The influence of the metallic NPs is clearly seen in Fig. 2. The emissions originating from level  ${}^5\text{D}_0$  grows with the increase of  $\tau_A$  reaching an enhancement of  $\approx 100\%$ . As observed in Fig. 1 the SP band overlaps with the  ${}^5\text{D}_0$  ( $\text{Eu}^{3+}$ ) level and then an increase in the  $\text{Eu}^{3+}$  luminescence is expected due to the enhanced local field in the proximity of the NPs. Figure 4 summarizes the relative increase of the luminescence bands at  $\approx 590$  and  $\approx 614$  nm as a function of  $\tau_A$ . The results indicate that a large number of  $\text{Eu}^{3+}$  ions are properly located nearby the metallic NPs. However, if the distance between the RE ion and the NP (or metallic aggregate) is very small the dipole-dipole interaction between them may contribute for ET from the RE ion to the metallic structure and the luminescence band is quenched.<sup>22</sup> Of course some ions are not in favorable positions and this may be the cause for not obtaining a giant luminescence enhancement as in experiments with single emitters placed near a NP.<sup>22</sup> Finally we note that enhancement of the emission centered at  $\approx 698$  nm is also observed. Although this wavelength is far from the central wavelength of the SP band, the luminescence enhancement at  $\approx 698$  nm may be due to aggregates that contribute for SP band tail extending to the red region as observed in Fig. 1.

#### IV. SUMMARY

In summary, we studied luminescence properties of  $\text{Tb}^{3+}/\text{Eu}^{3+}$  doped  $\text{TeO}_2\text{--ZnO--Na}_2\text{O--PbO}$  glass prepared with and without silver NPs upon excitation of the samples by ultraviolet light. Europium luminescence due to ET from excited  $\text{Tb}^{3+}$  ions was identified. Luminescence enhancement in the orange-red spectral region was observed being controlled by the heat-treatment time of the samples. The present work reports the first observation of ET between different RE species in tellurium based glasses containing silver nanostructures.

#### ACKNOWLEDGMENTS

We acknowledge the financial support from the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), and Fundação de Amparo à Ciência e Tecnologia de Pernambuco (FACEPE). The Laboratório de Microscopia Eletrônica (IFUSP) is acknowledged for TEM images. This work was performed under the Nanophotonics Network Program.

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