

# Frequency upconversion luminescence from $\text{Yb}^{3+}\text{-Tm}^{3+}$ codoped $\text{PbO-GeO}_2$ glasses containing silver nanoparticles

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Infrared-to-visible and infrared-to-infrared frequency upconversion processes in  $\text{Yb}^{3+}\text{-Tm}^{3+}$  doped  $\text{PbO-GeO}_2$  glasses containing silver nanoparticles (NPs) were investigated. The experiments were performed by exciting the samples with a diode laser operating at 980 nm (in resonance with the  $\text{Yb}^{3+}$  transition  ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ ) and observing the photoluminescence (PL) in the visible and infrared regions due to energy transfer from  $\text{Yb}^{3+}$  to  $\text{Tm}^{3+}$  ions followed by excited state absorption in the  $\text{Tm}^{3+}$  ions. The intensified local field in the vicinity of the metallic NPs contributes for enhancement in the PL intensity at 480 nm ( $\text{Tm}^{3+}: {}^1G_4 \rightarrow {}^3H_6$ ) and at 800 nm ( $\text{Tm}^{3+}: {}^3H_4 \rightarrow {}^3H_6$ ). © 2009 American Institute of Physics. [doi:10.1063/1.3211300]

## I. INTRODUCTION

Germanate glasses containing heavy-metal oxides have been attracting the attention of many authors because their physical properties may allow a large variety of photonic applications.<sup>1-10</sup> These glasses present large transmission window from 400 to 4500 nm, low cutoff phonon energy ( $\approx 700 \text{ cm}^{-1}$ ), high refractive index ( $\sim 2.0$ ), large nonlinear response, high chemical durability and thermal stability, and large mechanical resistance. When doped with trivalent rare-earth (RE) ions, germanate glasses exhibit strong photoluminescence (PL) and because of their physical properties, they are strong candidates for application in colored displays, solid-state lasers, optical amplifiers, and optical sensors.<sup>1-10</sup> Therefore, the optimization of the luminescence properties of germanate glasses doped with RE ions is of large interest.

One approach used to increase the PL characteristics of glasses, previously exploited using other glass matrices,<sup>11-13</sup> is the appropriate doping with two different RE species. In this case, energy transfer (ET) among the RE species may favor PL in selected spectral regions. Another possibility is the nucleation of metallic nanoparticles (NPs) inside the matrix and this was demonstrated under different conditions.<sup>14-20</sup> In germanate glasses, enhancement in PL by silver NPs was reported for  $\text{PbO-GeO}_2$  glasses doped with  $\text{Pr}^{3+}$  (Ref. 17) and  $\text{Er}^{3+}$ .<sup>18</sup> Also the large influence of gold NPs in the PL of  $\text{Eu}^{3+}$ -doped  $\text{GeO}_2\text{-Bi}_2\text{O}_3$  was reported.<sup>19</sup>

Recently the combination of RE ions codoping and silver NPs nucleation to improve the efficiency of a frequency upconversion (UC) process was demonstrated. Specifically, enhancement in the infrared-to-visible UC process in  $\text{Er}^{3+}\text{-Yb}^{3+}$  codoped  $\text{PbO-GeO}_2$  glass containing silver NPs was reported in Ref. 20. Increased green-red luminescence

was obtained by the simultaneous exploitation of the enhanced local field due to the metallic NPs and the ET from excited  $\text{Yb}^{3+}$  to  $\text{Er}^{3+}$  ions.

In this work, the UC luminescence observed in  $\text{Yb}^{3+}\text{-Tm}^{3+}$  codoped  $\text{PbO-GeO}_2$  glasses excited in the infrared and the influence of silver NPs nucleation on the UC intensity are investigated. The laser excitation was in resonance with the strong  $\text{Yb}^{3+}$  transition  ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$  at 980 nm. ET from  $\text{Yb}^{3+}$  to  $\text{Tm}^{3+}$  ions followed by excited state absorption in the  $\text{Tm}^{3+}$  ions gives origin to PL bands from  $\approx 400$  to  $\approx 900$  nm. The contribution of ET processes, cross relaxation between  $\text{Tm}^{3+}$  ions, and the influence of silver NPs on the PL spectra were characterized.

## II. EXPERIMENTAL DETAILS

Samples with composition 59  $\text{PbO}$ -41  $\text{GeO}_2$  (in wt %) were prepared using the melt-quenching technique. The doping species were  $\text{Tm}_2\text{O}_3$  (0.5 wt %),  $\text{Yb}_2\text{O}_3$  (2.0 wt %), and  $\text{AgNO}_3$  (3.0 wt %). The reagents were melted at 1200 °C in an alumina crucible for 1 h, quenched in a preheated brass mold, annealed at 420 °C for 1 h, and cooled to room temperature inside the furnace to avoid internal stress. The glass samples were polished, cut, and then submitted to different heat-treatment periods of time ( $T_{\text{ht}}=24, 30, \text{ and } 60 \text{ h}$ ) to thermally reduce  $\text{Ag}^+$  to  $\text{Ag}^0$ , and to nucleate silver NPs. A simple calculation, assuming that all silver ions are reduced, allows an estimate of the maximum NPs volume fraction that could be obtained as 1.24% for the sample heat treated during 60 h.

The absorption spectra was measured with a commercial spectrophotometer and the emission spectra were obtained exciting the samples with a cw diode laser operating at 980 nm, in resonance with the  $\text{Yb}^{3+}$  transition  ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ . The PL was analyzed through a spectrometer attached to a photomultiplier and computer.

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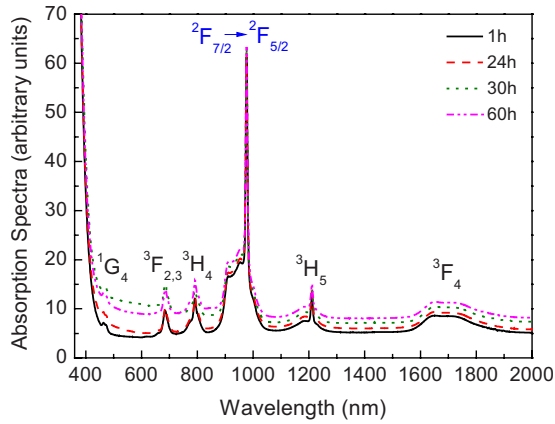


FIG. 1. (Color online) Absorption spectra of  $\text{Tm}^{3+}/\text{Yb}^{3+}$  codoped  $\text{PbO-GeO}_2$  samples containing silver NPs for various heat-treatment times.

A 200 kV transmission electron microscope (TEM) was used to investigate the size distribution of silver NPs. Isolated silver NPs with average diameter of  $\approx 10$  nm and large NPs aggregates of  $\approx 80$  nm were observed.

### III. RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra of  $\text{Yb}^{3+}-\text{Tm}^{3+}$  codoped  $\text{PbO-GeO}_2$  samples containing silver NPs heat treated during different times. Absorption bands associated to  $\text{Tm}^{3+}$  ions, starting from the ground state ( $^3\text{H}_6$ ), are observed as well as the band centered at 980 nm, corresponding to the transition  $^2\text{F}_{7/2} \rightarrow ^3\text{F}_{5/2}$  of  $\text{Yb}^{3+}$  ions. An absorption band related to the surface plasmon resonance (SPR) in the NPs is not observed because the amount of NPs is not large. With basis on the dielectric function of silver<sup>21</sup> and the refractive index of  $\text{PbO-GeO}_2$  glass ( $\approx 2$ ), we estimate that the wavelength corresponding to the SPR in the isolated NPs is located in the range of  $\approx 420$  to  $\approx 500$  nm. The presence of silver NPs is confirmed through TEM measurements. The aggregates of NPs also observed by TEM originate a background in the optical spectra that extends from the blue to the infrared region. Similar behavior was demonstrated experimentally and theoretically for aggregates of gold and silver NPs in liquid suspensions.<sup>22</sup>

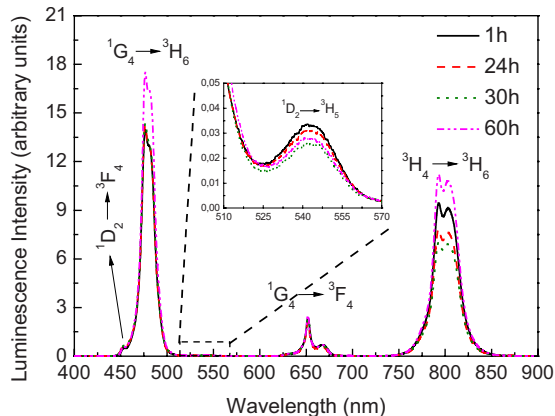


FIG. 2. (Color online) Emission spectra of  $\text{Tm}^{3+}/\text{Yb}^{3+}$  codoped  $\text{PbO-GeO}_2$  samples containing silver NPs obtained by pumping the samples with a diode laser operating at 980 nm ( $\approx 100$  mW).

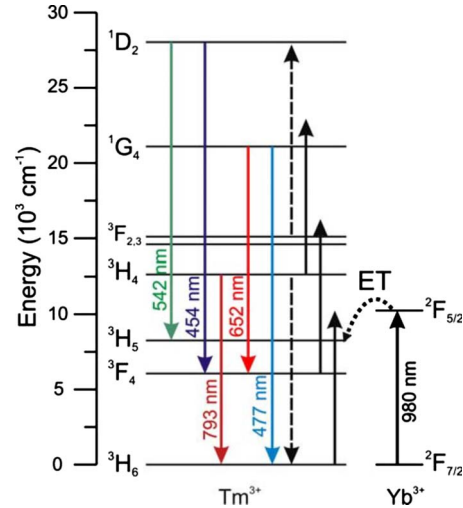


FIG. 3. (Color online) Energy level scheme of  $\text{Tm}^{3+}$  and  $\text{Yb}^{3+}$  ions with indication of the luminescence observed. Dashed arrows indicate cross relaxation among the excited  $\text{Tm}^{3+}$  ions. Dotted arrow indicates ET from  $\text{Yb}^{3+}$  to  $\text{Tm}^{3+}$  ions. Solid arrows represent radiative transitions.

Figure 2 shows UC luminescence spectra for different heat-treatment times. PL bands centered at  $\approx 454$ ,  $\approx 477$ ,  $\approx 542$ ,  $\approx 652$ , and  $\approx 800$  nm are observed corresponding to the  $\text{Tm}^{3+}$  transitions  $^1\text{D}_2 \rightarrow ^3\text{F}_4$ ,  $^1\text{G}_4 \rightarrow ^3\text{H}_6$ ,  $^1\text{D}_2 \rightarrow ^3\text{H}_5$ ,  $^1\text{G}_4 \rightarrow ^3\text{F}_4$ , and  $^3\text{H}_4 \rightarrow ^3\text{H}_6$ , respectively.

Figure 3 shows a simplified energy level diagram of  $\text{Tm}^{3+}$  and  $\text{Yb}^{3+}$  ions with arrows describing the pathway of excitation and luminescence transitions. The upward arrows represent laser- induced transitions. Promotion of  $\text{Tm}^{3+}$  ions from the ground state to state  $^3\text{H}_5$  due to ET from the excited  $\text{Yb}^{3+}$  ions is represented by the dotted line. The dashed lines indicate a cross-relaxation process as discussed below.

To identify the mechanism of UC for each transition, the dependence of the UC intensities with the laser power was measured and the results are shown in Fig. 4. For the present experimental conditions using a low intensity diode laser, we do not expect saturation of transitions. Therefore, the UC signals satisfy the expression  $I_{\text{UC}} \propto I^m$ , where  $I_{\text{UC}}$  represents the UC intensity,  $I$  is the laser intensity, and  $m$  is the number of photons participating in the UC process. The slope deter-

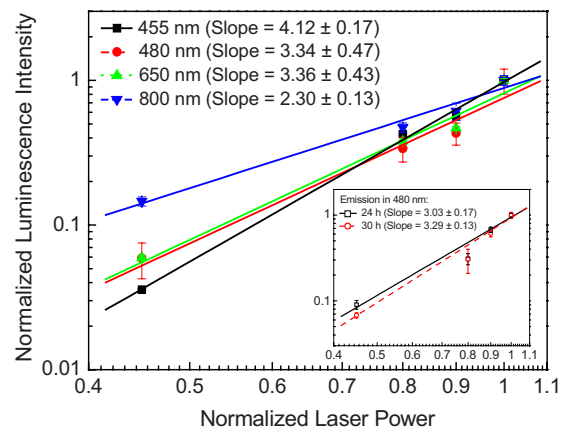


FIG. 4. (Color online) Luminescence intensity of  $\text{Tm}^{3+}$  ions as function of the laser power for samples containing silver NPs heat treated for 1, 24, and 30 h.

mined from the log-log plot of Fig. 4 gives the value of  $m$ . It can be seen that for transitions  $^1D_2 \rightarrow ^3F_4$  ( $\approx 454$  nm) and  $^1D_2 \rightarrow ^3H_5$  ( $\approx 542$  nm), we have  $m=4$  indicating that four laser photons are involved in excitation process. On the other hand, transitions  $^1G_4 \rightarrow ^3H_6$  ( $\approx 477$  nm) and  $^1G_4 \rightarrow ^3F_4$  ( $\approx 652$  nm) present cubic dependence with the laser power. In the case of transition  $^3H_4 \rightarrow ^3H_6$  ( $\approx 800$  nm), two laser photons participate in the excitation process corresponding to  $m=2$ . In all cases, one laser photon is resonantly absorbed by the  $\text{Yb}^{3+}$  ions that transfer the stored energy to  $\text{Tm}^{3+}$  ions originally in the ground state. The  $\text{Tm}^{3+}$  ions excited to level  $^3H_5$  decay to level  $^3F_4$  and from there they are excited by the incident laser to higher energy states. Due to the energy mismatch between the laser photon energy and the energy gap for transitions  $^3F_4 \rightarrow ^3F_{2,3}$  and  $^3F_{2,3} \rightarrow ^1G_4$ , we consider that phonons are generated when the ions make the upward transitions. This explains the cubic dependence observed for transitions  $^1G_4 \rightarrow ^3H_6$  ( $\approx 477$  nm) and  $^1G_4 \rightarrow ^3F_4$  ( $\approx 652$  nm). The emission corresponding to  $^3H_4 \rightarrow ^3H_6$  is due to the excitation of level  $^3F_{2,3}$  by the absorption of two photons followed by nonradiative relaxation from level  $^3F_{2,3}$  to  $^3H_4$ . The laser intensity dependence of the UC signals at 542 and 454 nm cannot be understood considering the absorption of a fourth laser photon because the frequency mismatch between the photon energy and transition  $^1G_4 \rightarrow ^1D_2$  is too large. In previous experiments with tellurite glass excited by an infrared laser, the generation of light from level  $^1D_2$  was explained considering cross relaxation between  $\text{Tm}^{3+}$  pairs.<sup>23</sup> This is the dominant mechanism also in the present case and the dashed lines in Fig. 3 represent this process.

It is important to notice that level  $^1D_2$  has energy larger than the optical gap of the glass matrix. Although the transitions  $^1D_2 \rightarrow ^3F_4$  ( $\approx 454$  nm) and  $^1D_2 \rightarrow ^3H_5$  ( $\approx 542$  nm) are weak (probably due to reabsorption by the glass matrix) they are clearly recognized. This behavior indicates that the 4f states of  $\text{Tm}^{3+}$  ions in  $\text{PbO-GeO}_2$  glass, as well as in tungstate glasses,<sup>24</sup> have little overlap with the extended Bloch waves of the glass host.

As shown in Fig. 2, the UC luminescence is dependent on the heat treatment of the samples. Nucleation of silver NPs contributes either for quenching or enhancement in luminescence. If the distance between the RE ion and the metallic particle is very small, ET from an excited RE ion to the metallic structure may be very efficient and the contribution of the increased local field for PL enhancement may not be dominant.<sup>25</sup> It can be seen in Fig. 2 that transition  $^1G_4 \rightarrow ^3H_6$  having wavelength near the SPR wavelength increases by  $\approx 30\%$  for heat-treatment time varying from 1 to 60 h. Although transition  $^3H_4 \rightarrow ^3H_6$  is also increased for heat treatment in the same time interval, its intensity is smaller for shorter treatment times due to ET from the  $\text{Tm}^{3+}$  ions to silver aggregates. However the understanding of the full PL behavior is not simple because it is affected by the nucleation of large silver NPs, formation of aggregates, and fragmentation of metallic structures. These processes have been observed for silicate<sup>16,26–28</sup> and tellurium-lead-germanate<sup>29,30</sup> glasses. Using x-ray photoelectron spectroscopy, the authors of Refs. 26 and 27 were able to demonstrate the effect of different silver concentration on the clustering of NPs. For

$\text{PbO-GeO}_2$ , glasses we expect important influence of the silver concentration as well as large influence of the heat-treatment procedure on the aggregation and fragmentation of the NPs but the investigation of these processes is beyond the scope of this article. Also the possibility of ET from the RE ions to the aggregates of NPs and the relative location of the RE ions with respect to the aggregates cannot be controlled. More systematic studies will be performed in the future to characterize the luminescence behavior as a function of the heat-treatment processing.

In summary, we studied the luminescence properties of  $\text{Yb}^{3+}\text{-Tm}^{3+}$  codoped  $\text{PbO-GeO}_2$  glasses containing silver NPs upon infrared excitation. Frequency UC luminescence due to the ET from excited  $\text{Yb}^{3+}$  ions to  $\text{Tm}^{3+}$  ions followed by excited state absorption in the  $\text{Tm}^{3+}$  ions was observed. Enhancement or quenching of the luminescence spectra are observed due to competition between the effects of the increased local field in the location of  $\text{Tm}^{3+}$  ions or ET from the excited ions to silver NPs aggregates.

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