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Photoluminescence enhancement by gold nanoparticles in Eu$^{3+}$ doped GeO$_2$–Bi$_2$O$_3$ glasses

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We report large photoluminescence (PL) enhancement in Eu$^{3+}$-doped GeO$_2$–Bi$_2$O$_3$ glasses containing gold nanoparticles (NPs). Growth of $\approx1000\%$ in the PL intensity corresponding to the Eu$^{3+}$ transition $^5D_0 \rightarrow ^7F_2$, at 614 nm, was observed in comparison with a reference sample that does not contain gold NPs. Other PL bands from 580 to 700 nm are also enhanced. The enhancement of the PL intensity is attributed to the increased local field in the Eu$^{3+}$ locations due to the presence of the NPs and the energy transfer from the excited NPs to the Eu$^{3+}$ ions. © 2009 American Institute of Physics. [DOI: 10.1063/1.3097241]

To enhance the photoluminescence (PL) properties of glasses doped with rare-earth ions (REI), samples containing metal nanoparticles (NPs) have been investigated by various authors. The increase of the local field due to the NPs has been accounted as a possible cause for the PL enhancement. Because of the mismatch between the dielectric function of the metallic NPs and the host glass, there is a confinement of the electromagnetic field near the NPs’ surface originating enhanced near-field intensities. Then the REI located nearby the metallic NPs contribute for the enhanced PL. Another possible way for PL enhancement involves the absorption of light by the NPs followed by energy transfer to the REI. Since the light absorption cross section of the NPs is larger than for the REI, this PL excitation route may be more efficient in some cases.

The PL enhancement factor (the ratio between the luminescence intensity from samples with and without metallic NPs) $\eta$ depends on the volume fraction of the sample occupied by the NPs, the so-called filling fraction, and light wavelength. When the incident light or the PL has wavelength close to the NPs surface plasmons (SPs) resonance wavelength $\lambda_{SP}$, the factor $\eta$ can be considerably large. The value of $\lambda_{SP}$ depends on the host and the metal dielectric functions, as well as on the size and shape of the NPs.

Since heavy-metal oxide glasses are suitable materials for photonic devices, we have studied their PL properties using REI doped samples containing silver and gold NPs. Heavy-metal oxide glasses present high refractive index and broad transparency window from the visible to the middle infrared. When doped with REI heavy-metal oxide glasses become highly luminescent due to the low cutoff phonon energy of the host matrix that significantly decreases nonradiative transition rates of the REI electronic levels in comparison with other glasses.

Nucleation of silver NPs was reported for Pr$^{3+}$ doped GeO$_2$–PbO glasses, and PL enhancement was observed for samples with different concentrations of Pr$^{3+}$ and silver NPs. Intensified infrared-to-visible frequency upconversion in Eu$^{3+}$ doped GeO$_2$–PbO glasses containing silver NPs was observed corresponding to $\eta=100\%$ for PL in the green region. The influence of silver NPs was exploited to obtain enhancement of the whole frequency upconversion spectra from 500 to 700 nm in Yb$^{3+}$–Er$^{3+}$ doped GeO$_2$–PbO glasses. The increase of Eu$^{3+}$ luminescence due to the presence of gold NPs in tellurite glasses was reported in Ref. 10. The Eu$^{3+}$ hypersensitive transition $^5D_0 \rightarrow ^7F_2$ at 614 nm was enhanced by $\sim100\%$.

Due to the increasing use of Eu$^{3+}$ in photonic applications, other glass matrices have to be investigated for identification of more appropriate hosts. Therefore, in this letter, we report on the characteristics of Eu$^{3+}$-doped GeO$_2$–Bi$_2$O$_3$ glass containing gold NPs. This glass has been studied by other authors because of its large potential for many applications (see, for instance, Refs. 11–14). We discovered that GeO$_2$–Bi$_2$O$_3$ glass allowed more efficient nucleation of gold NPs than the previously reported materials. Consequently, an enhancement factor $\eta=1000\%$ for the PL at 614 nm was obtained for samples heat treated at 420 $^\circ$C for 3 h. The whole PL spectrum from 580 to 700 nm is intensified.

The samples were prepared by the melt-quenching method using the starting composition 58.4 GeO$_2$–41.6 Bi$_2$O$_3$ in wt %. The doping species were Eu$_2$O$_3$ (0.5 wt %) and Au$_2$O$_3$ (3.0 wt %). The reagents were melted in an alumina crucible for 1 h at 1100 $^\circ$C, quenched in air in a preheated brass mold, and annealed. Heat treatment of the samples is made to minimize internal stress and to thermally reduce the Au$^+$ and Au$^{3+}$ ions for nucleation of gold NPs. The samples studied were annealed at 420 $^\circ$C for 3, 24, 48, and 72 h.

A 200 kV transmission electron microscope (TEM) was used to investigate the nucleation of NPs. A representative TEM image is presented in Fig. 1 showing that gold NPs and some NPs’ aggregates are nucleated inside the glass.

Figure 2 shows the absorption spectra of the samples containing Eu$^{3+}$ and gold NPs. The spectrum of a sample without gold NPs and doped with 0.5 wt % of Eu$_2$O$_3$ is shown for reference. Features associated to the Eu$^{3+}$ 4$f$-4$f$ transitions are observed for the sample with gold NPs.
transitions originated from the ground state \( (7F_0) \) are observed. The broad absorption band centered at \( \approx 500 \) nm is attributed to the SP resonance. Its amplitude does not change much with the heat-treatment time, and this indicates that all gold ions are chemically reduced for 3 h of heat treatment. Note that some Eu\(^{3+} \) transitions overlap with the SP band.

PL was excited using a 15 W xenon lamp followed by a 0.25 m monochromator equipped with a holographic grating. The spectra obtained for excitation at 405 nm, in resonance with the Eu\(^{3+} \) transition \( 7F_0 - 5D_2 \), is shown in Fig. 3. The emission bands centered in \( \approx 585, \approx 595, \approx 614, \approx 655, \) and \( \approx 700 \) nm, correspond to Eu\(^{3+} \) transitions \( 5D_0 - 7F_J \) \((J=0, 1, 2, 3, \text{and} 4)\). A simplified energy level scheme for the Eu\(^{3+} \) ions and the optical transitions observed in Fig. 3 are indicated in Fig. 4.

The results of Fig. 3 indicate that the PL bands are affected by the presence of gold NPs. For instance, the signal centered at 614 nm, for the samples heat-treated for 3 h, is approximately \( \approx 10 \) times larger than the signal observed for the sample that does not contain gold NPs. Since the incident light can be absorbed by the NPs, we attribute the PL increase not only to the enhanced local field but also to energy transfer from the NPs to the Eu\(^{3+} \) ions. PL enhancement is partially due to the increased Eu\(^{3+} \) absorption due to the gold NPs. Note that the amplitude of the \( 7F_0 - 5D_2 \) transition in Fig. 3 is larger in the heat-treated samples. On the other hand, the dependence with the PL wavelength is clear because the bands associated to the electric-dipole transitions \( 5D_0 - 7F_2,4 \) increased by \( \approx 1000\% \) while the magnetic-dipole transitions \( 5D_0 - 7F_1,3 \) increased by \( \approx 500\% \). The other transitions are enhanced by different factors. The small PL quenching observed for heat treatments longer than 3 h is probably because, with the increasing of the heat-treatment time, more Eu\(^{3+} \) ions become so near from the NPs that energy transfer occurs from the directly excited ions to the NPs. This is expected when the distance between the REI and the NPs is smaller than 5 nm because at short distances the dipole-dipole interaction between REI and NP becomes large. Therefore we should consider that most of the excited NPs transfer the absorbed energy to the glass matrix. Measurements with Eu\(^{3+} \)-doped samples without gold NPs do not

![FIG. 2. TEM image of the sample heat treated for 24 h.](image-url)

![FIG. 3. Color online] PL spectra of the samples heat-treated for different times (excitation at 405 nm). The spectrum for the sample doped with 0.5 wt % of Eu\(_2\)O\(_3\) and no metal NPs is also shown to illustrate the luminescence enhancement.](image-url)

![FIG. 4. Simplified energy levels scheme of Eu\(^{3+} \) ions with indication of the radiative transitions observed. The shaded area indicates the SPs band location.](image-url)
show dependence of PL signals with the heat treatment demonstrating the essential role due to the NPs.

In summary, the present results show that the nucleation of gold NPs in Eu$^{3+}$ doped GeO$_2$–Bi$_2$O$_3$ glass is more efficient than in tellurite glasses. Because larger gold NPs filling fractions are obtained the PL enhancement in the orange-red spectral region is the largest observed for the different glasses previously studied.

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