Surface-plasmon-enhanced frequency upconversion in Pr3+ doped tellurium-oxide glasses containing silver nanoparticles

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A frequency upconversion process in Pr^{3+} doped TeO$_2$–ZnO glasses containing silver nanoparticles is studied under excitation with a nanosecond laser operating at 590 nm, in resonance with the $^3H_4 \rightarrow {}^1D_2$ transition. The excited Pr^{3+} ions exchange energy in the presence of the nanoparticles, originating efficient conversion from orange to blue. The enhancement in the intensity of the luminescence at ∼482 nm, corresponding to the $^3P_0 \rightarrow {}^3H_4$ transition, is due to the influence of the large local field on the Pr^{3+} ions, which are located near the metallic nanoparticles. © *2008 American Institute of Physics.* [DOI: 10.1063/1.2919566]

I. INTRODUCTION

The study of glasses doped with rare earth ions are of significant interest due to their potential applications in many optical devices.[1–3] Specifically, heavy metal oxide (HMO) glasses doped with trivalent rare earth ions are very important because they show strong luminescence due to their small cutoff phonon frequencies.[1] However, in order to make devices with enhanced optical characteristics, the concentration of rare earth ions has to be low enough so that luminescence quenching is minimized. It is also possible to prevent the quenching effect by modifying the environment felt by the luminescent ions.[4–6] Therefore, glasses containing metallic nanoparticles doped with low concentration of rare earth ions are of particular interest because the large local field acting on the ions positioned near the nanoparticles may increase the luminescence efficiency when the optical frequency of the excitation beam and/or the luminescence frequency are near resonance with the surface plasmon frequency of the nanoparticles.[7]

Recently, the luminescence properties of HMO glasses doped with rare earth ions and containing metallic nanostructures have been investigated. Initially, optical absorption and Stokes luminescence were investigated in Pr^{3+} doped PbO–GeO$_2$ glasses containing silver nanoparticles.[8] The luminescence efficiency of Pr^{3+} ions was influenced by the nanoparticle concentration, which was controlled by the appropriate heat treatment of the samples. The influence of silver nanoparticles on the luminescence of Pr^{3+} doped TeO$_2$–PbO–GeO$_2$ was investigated in Ref. 9. Enhancement of Stokes emissions and frequency upconversion (UC) intensity were characterized for different nanoparticle concentrations. In another work, the luminescence properties of Eu^{3+} doped TeO$_2$–PbO–GeO$_2$ glasses containing gold nanoparticles were also investigated.[10] The emission spectra of the samples exhibited an enhancement of Eu^{3+} luminescence due to the presence of gold nanoparticles. The emission at 614 nm due to the Eu^{3+} hypersensitive transition $^5D_0$-$^7F_2$ was influenced by the gold nanoparticles and increases by ≈100% for samples heat treated at 350 °C for 41 h.

In the works referred above, detailed measurements of the Stokes luminescence were performed to characterize the influence of the isolated metallic nanoparticles and their aggregates on the optical properties of the systems. On the other hand, the influence of metallic nanoparticles on the UC luminescence of HMO doped with rare earth ions was not much exploited. The infrared-to-visible UC of Er^{3+} doped PbO–GeO$_2$ was reported in Ref. 11. The experiments were made, wherein the samples were excited with a cw diode laser (980 nm) and the red and green luminescence due to the Er^{3+} ions were recorded. The excitation mechanism for UC generation was found to be the excited state absorption in isolated ions. UC in Pr^{3+} doped TeO$_2$–PbO–GeO$_2$ glasses, excited at 520 nm (off resonance), was also reported.[9] The generation of the signal was attributed to a phonon-assisted optical transition from the Pr^{3+} ground state ($^3H_4$) to the [^3P_J ($J=0,1,2$), $^1I_6$] manifold simultaneously with phonon annihilation, which was corroborated by the fact that the dependence on the incident light intensity of the UC intensity was linear.

This paper reports a study of UC processes in Pr^{3+} doped TeO$_2$–ZnO (Pr^{3+}:TZO) containing silver nanoparticles. In this case, the Pr^{3+} ions are excited in resonance with the $^3H_4 \rightarrow {}^1D_2$ transition, and the main goal is to investigate the influence of the metallic nanoparticles on the UC emission that corresponds to the $^3P_0 \rightarrow {}^3H_4$ transition. The UC process studied here is different from the ones reported in Refs. 9 and 11 because the interaction between two Pr^{3+} ions plays the essential role in the process and its efficiency depends on the strength of the interaction between Pr^{3+} ions. The metallic nanoparticles contribute for a luminescence enhancement of ≈120% with respect to the UC emission observed for samples without metallic nanostructures.

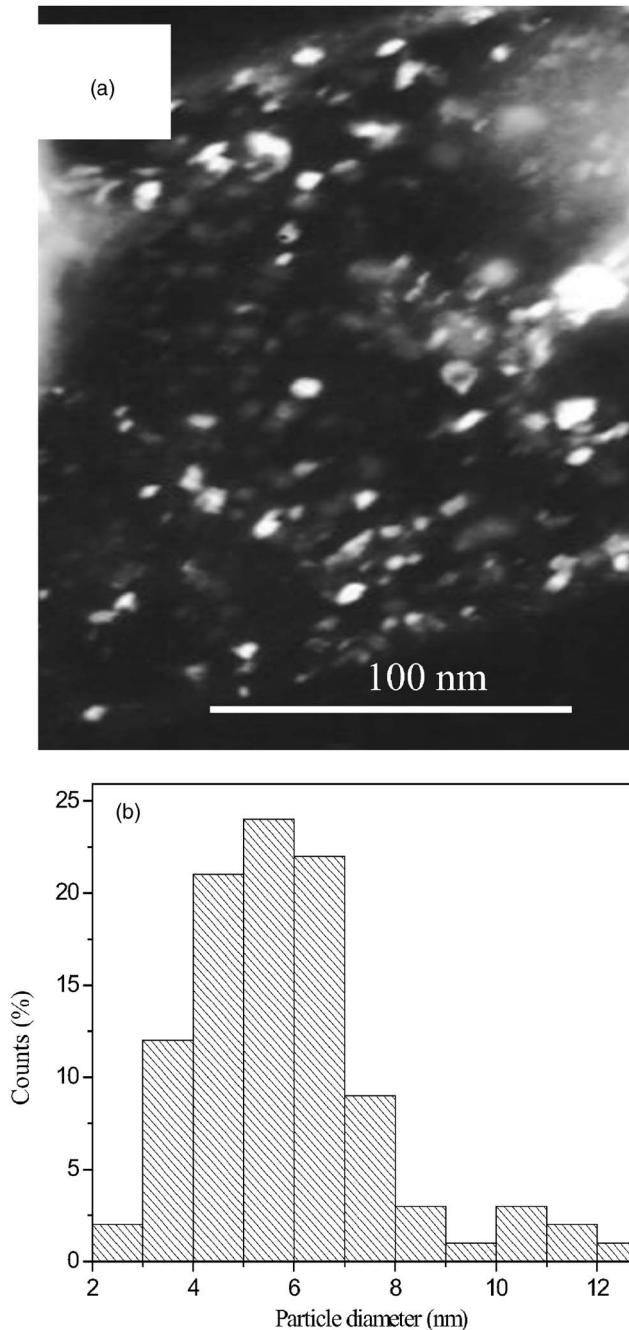a)Author to whom correspondence should be addressed. Electronic mail: cid@df.ufpe.br.

FIG. 1. TEM image of the sample annealed for 20 h (sample D). (b) Histogram of the size distribution of the metallic NPs. Average diameter: 6 nm.
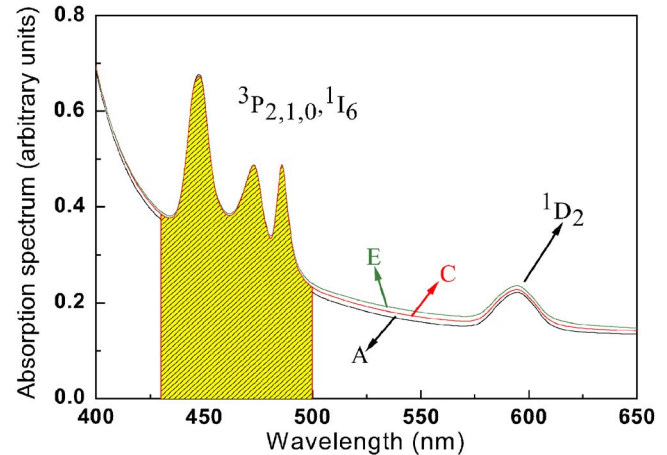

FIG. 2. (Color online) Absorption spectra of samples A, C, and E. The features are due to transitions in the Pr^{3+} ions. The shaded area indicates the expected location of the surface plasmon band.

II. EXPERIMENTAL

The samples were fabricated by the melt-quenching method with the following composition: 85.5 TeO_2–14.5 ZnO (in wt %). The doping components were Pr_2O_3 (1.0 wt %) and $AgNO_3$ (1.0 wt %). The reagents were melted in a platinum crucible at 800 °C, quenched inside a brass mold, annealed at 350 °C, and then cooled to room temperature. Sample A (with Pr^{3+} and without Ag) and sample B (containing Pr^{3+} and Ag) were annealed for 1 h. Three samples were submitted to heat treatment at 350 °C for 10 h (sample C), 20 h (sample D), and 40 h (sample E) to thermally reduce the Ag^+ ions into Ag^0, which is needed to nucleate metallic nanoparticles.

A 200 kV transmission electron microscope (TEM) was used to investigate the nucleation of metallic nanoparticles. Optical absorption spectra were measured with a double-beam spectrometer operating in the visible range. For excitation within the $^1D_2$ band of the Pr^{3+} ions, a dye laser ($\approx$590 nm, pulses of 8 ns, peak power of $\sim$20 kW, and linewidth of $\sim$0.5 cm^{-1}) pumped by the second harmonic of a Nd:YAG (yttrium aluminum garnet) laser was used. The excitation beam was focused onto the sample with a 5 cm focal length lens, and the fluorescence was collected in a direction perpendicular to the incident beam; the signal was analyzed by a 0.5 m spectrophotometer (resolution of 0.5 nm) attached to a photomultiplier tube. The signals were recorded by using a digital oscilloscope connected to a computer. The experiments were made with the samples at room temperature.

III. RESULTS AND DISCUSSION

Figure 1(a) shows one representative TEM image of a sample that contains metallic nanoparticles, while the corresponding histogram of their sizes is shown in Fig. 1(b). The average diameter of the nanostructures is $\approx$6 nm. The absorption spectra of three Pr^{3+}:TZO samples are shown in Fig. 2. The bands are due to Pr^{3+} transitions starting from the ground state ($^3H_4$) to final excited states, as indicated. The surface plasmon band is not seen because the nanoparticle concentration is small and, as a consequence, the amplitude of the Pr^{3+} bands does not change for different samples. The spectra of the other samples are similar. The shaded area in Fig. 2 indicates the expected location of the surface plasmon band based on the results of Refs. 8 and 11.

Figures 3(a)–3(c) show the luminescence spectra for samples A, C, and E. The dye laser wavelength at 590 nm was in resonance with the $^3H_4 \rightarrow {}^1D_2$ transition. The two bands are observed to peak at $\sim$486 and $\sim$692 nm and are attributed to the $^3P_0 \rightarrow {}^3H_4$ and $^1D_2 \rightarrow {}^3H_5$ transitions, respectively. The behavior of the UC luminescence intensity at $\sim$486 nm versus the laser intensity is quadratic, showing that the excitation of the $^3P_0$ state is due to the absorption of two photons; the temporal behavior of the UC signal shows
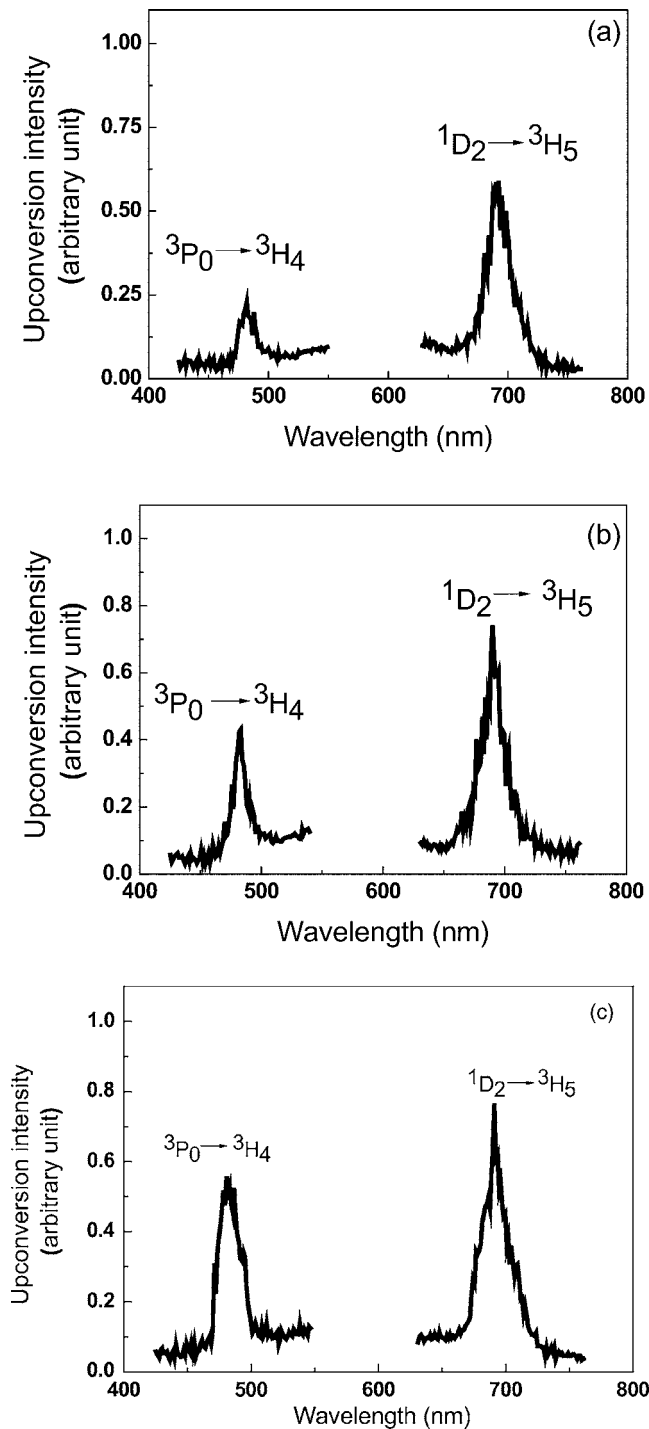
TABLE I. Ratio R between the integrated intensities corresponding to $^3P_0 \to \, ^3H_4$ and $^1D_2 \to \, ^3H_5$ transitions for samples heat treated at different times.

Sample	Heat-treatment time (h)	R
A	1	0.29
B	1	0.42
C	10	0.47
D	20	0.52
E	40	0.64

The dependence of the ratio R between the integrated intensities of transitions $^3P_0 \to \, ^3H_4$ and $^1D_2 \to \, ^3H_5$ as a function of the heat-treatment time was determined. The results are shown in Table I, where it can be seen that R increases by more than $\sim 120\%$ for sample E in comparison to sample A. The UC enhancement is due to the proximity between the surface plasmon band and the $[^3P_J \, (J=0,1,2); \, ^1I_6]$ manifold. The intensity of the emission centered at 692 nm was not affected by the presence of the metallic nanoparticles because the $^1D_2$ multiplet is located far from the surface plasmon band. Pr^{3+}:TZO samples (without silver) were heat treated for different time intervals, but no variation in the luminescence intensity was observed. This result confirms that the enhancement of the UC intensity in the other samples is due to the presence of the metallic nanoparticles and not due to changes in the glass structure.

In conclusion, we remark that a comparison between the optical absorption spectra and the luminescence results illustrates the larger sensitivity of the UC process to changes in the environment of the rare earth ions hosted in glasses with metallic particles. This is clearer when energy levels closer to the surface plasmon resonance participate in the UC process. Finally, the present results suggest that the presence of silver nanoparticles may enhance UC processes of high order, such as the ones involving triads and quartets of Pr^{3+},[19,20] by a factor much larger than is shown here for ion pairs.

FIG. 3. Luminescence spectra. (a) Sample A, (b) sample C, and (c) sample E. Excitation wavelength: 590 nm. The elastic scattered signal centered at 590 nm was removed from the spectra.

rise and decay times of ≈ 10 and $\approx 100 \, \mu s$, respectively. This process was already observed in other glassy systems and vitreous ceramics, which was attributed to an energy exchange process involving a pair of Pr^{3+} ions.[12–18] Accordingly, two ions initially excited to level $^1D_2$ exchange energy in such a way that one ion is promoted to the $[^3P_J \, (J=0,1,2), \, ^1I_6]$ manifold, while the other nonradiatively decays to lower energy levels. On the other hand, the intensity of the emission corresponding to the $^1D_2 \to \, ^3H_5$ transition linearly depends on the laser intensity.

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