

Influence of the heat treatment on the nucleation of silver nanoparticles in Tm^{3+} doped PbO-GeO_2 glasses

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Abstract Nucleation of silver nanoparticles (NPs) in Tm^{3+} doped PbO-GeO_2 (PGO) glass is reported. The influence of the heat treatment on the nucleation of silver NPs is studied by means of transmission electron microscopy and optical spectroscopy. Two heat treatment procedures were applied in order to compare their performance. Observation of infrared-to-visible frequency upconversion (UC) luminescence of Tm^{3+} ions is reported and correlated with the heat-treatment procedure. Enhancement of the UC emission for samples heat treated during various time intervals is attributed to the increased local field in the vicinity of the NPs. Quenching of the UC signal was also observed and correlated with the growth of NPs amount and size.

1 Introduction

Optical materials containing rare-earth ions and metallic nanoparticles (NPs) are attracting large interest because the

presence of the NPs may contribute for intensification of photoluminescence (PL) and enhancement of the nonlinear optical properties [1–7].

Germanium oxide glasses are good candidates for these studies because they exhibit large transmittance window from the visible to the infrared region, low cutoff phonon energy ($\approx 700 \text{ cm}^{-1}$), high refractive index (≈ 2.0), and large chemical stability. The optical and structural properties of GeO_2 -based glasses have been studied by many authors [see, for instance, Refs. [1, 8–13]] but the majority of the studies were performed with samples without metallic NPs.

Nucleation of metallic NPs in PbO-GeO_2 (PGO) glasses was demonstrated recently. Enhancement of Stokes and anti-Stokes luminescence due to silver and gold NPs was reported for PGO glasses doped with Pr^{3+} , Er^{3+} , Eu^{3+} , $\text{Er}^{3+}-\text{Yb}^{3+}$, and $\text{Yb}^{3+}-\text{Tm}^{3+}$ [14–18]. Increase of the PL signals by different factors was observed for different excitation conditions. In all cases the presence of the metallic NPs was essential for improvement of the samples' luminescence. Growth of the near-infrared nonlinearity of PGO films containing Cu NPs was also demonstrated [19]. Enhancement of two orders of magnitude in the figure-of-merit for all optical switching was obtained in comparison with PGO films without metallic NPs.

In the present work we investigate the influence of the heat treatment (HT) of the samples on the nucleation of silver NPs in Tm^{3+} doped PGO glasses, in order to characterize the better conditions to enhance the materials' luminescence properties. Two HT procedures were employed to induce nucleation of Ag NPs in samples containing AgNO_3 . The samples characterization was made using the PL technique and transmission electron microscopy.

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2 Experimental details

The glass samples were prepared by the melting-quenching technique using the following composition: 59PbO-41GeO₂ (in wt.%). The doping species were Tm₂O₃ (1.0 wt.%) and AgNO₃ (5.0 wt.%). The reagents were melted at 1200°C in an alumina crucible for 1 h, quenched in a pre-heated brass mold, annealed at 420°C for 1 h, and cooled to room temperature inside the furnace to avoid internal stress. Glass samples were polished and heat treated during different time intervals to reduce Ag⁺ ions to Ag⁰ to obtain NPs by aggregation of the silver atoms. One set of samples was heat treated continuously during $\tau_{HT} = 12, 24, 48,$ and 72 h. Other samples were prepared using a non-continuous HT consisting of intervals of 12 h, separated by 8 h. This time interval was selected, after many trials, because it allowed efficient nucleation of NPs. A sample prepared without AgNO₃ was used as reference in the optical measurements.

The size distribution of the silver NPs was investigated using a 200 kV transmission electron microscope (TEM). Samples presenting isolated NPs with average diameters from 5 nm to 60 nm were obtained as well as samples containing aggregates with dimensions of ≈ 200 nm.

Absorption spectra were measured with a commercial spectrophotometer and PL spectra were obtained exciting the samples with a CW ytterbium laser operating at 1050 nm, and analyzing the PL in the blue-red region (425–700 nm) using a monochromator coupled to photomultiplier and computer.

3 Results and discussion

Figure 1 shows the absorption spectra of Tm³⁺ doped PGO samples containing silver NPs heat-treated at 420°C using the two different HT procedures mentioned in Sect. 2. Figure 1(a) shows the results for the samples prepared using the non-continuous HT procedure. The curves labeled as (2*12) correspond to HT performed in 2 steps of 12 h each. The curves labeled (4*12) indicate 4 steps of 12 h and (6*12) corresponds to 6 steps of 12 h. Figure 1(b) presents the results for the samples heat treated by the continuous method. The spectrum for the sample without NPs is shown in both curves for reference. Absorption bands associated to Tm³⁺ ions starting from the ground state (³H₆) are observed in both figures. Small changes in the amplitude of the Tm³⁺ bands are observed but negligible energy shifts occur even for the samples heat treated for long times. An absorption band related to the surface plasmon (SP) resonance is not observed because the amount of silver NPs is not enough to present a noticeable signal. Considering the dielectric function of silver [20] and the refractive index of the PGO glass the SP band should be located in the range ≈ 420 nm to

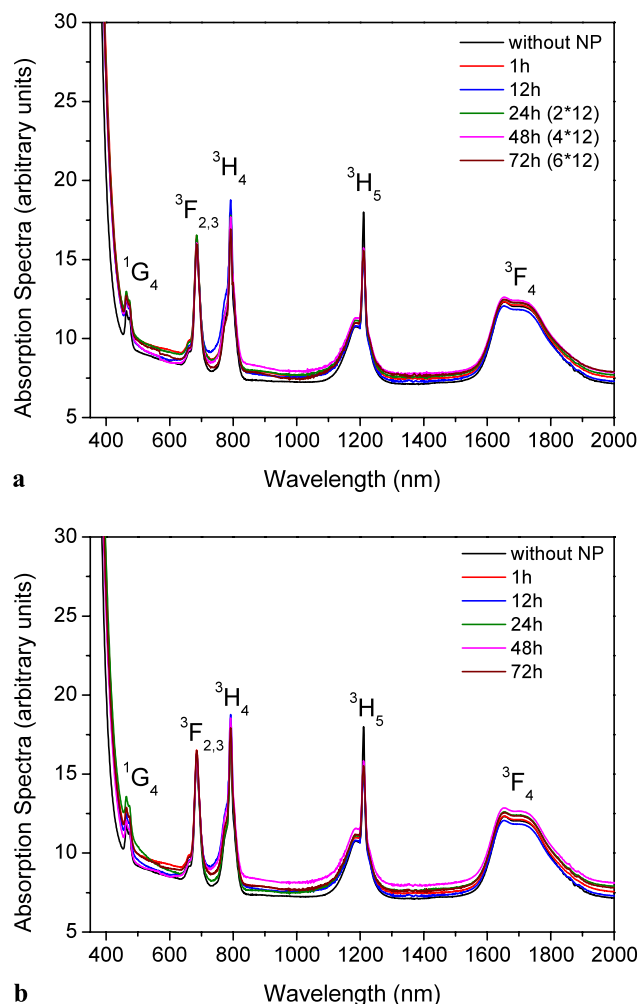


Fig. 1 Absorption spectra of Tm³⁺ doped PbO-GeO₂ samples containing silver NPs. The spectrum for a sample without NPs is also shown for reference. **(a)** Continuous HT. **(b)** Non-continuous HT

≈ 500 nm. This band was observed in previous publications using PGO samples [15, 18]. However, the presence of silver NPs in the present case was confirmed through TEM images, as shown in Fig. 2. The influence of different NPs and aggregates is discussed below. The silver composition of the NPs was corroborated through energy-dispersive spectroscopy (EDS).

Figure 3 shows the UC spectra of Tm³⁺ ions for samples heat treated during various times, τ_{HT} , and for the sample without NPs. The results for the samples heat treated by the non-continuous method are shown in Fig. 3(a) while the spectra for the samples heat treated by the continuous method are shown in Fig. 3(b). The bands centered at 454, 477, and 652 nm correspond to transitions ¹D₂ → ³F₄, ¹G₄ → ³H₆, and ¹G₄ → ³F₄, respectively. The highest intensity enhancement is obtained for the samples heat treated during 24 h; the PL signals observed from the samples heat treated for longer times are partially quenched.

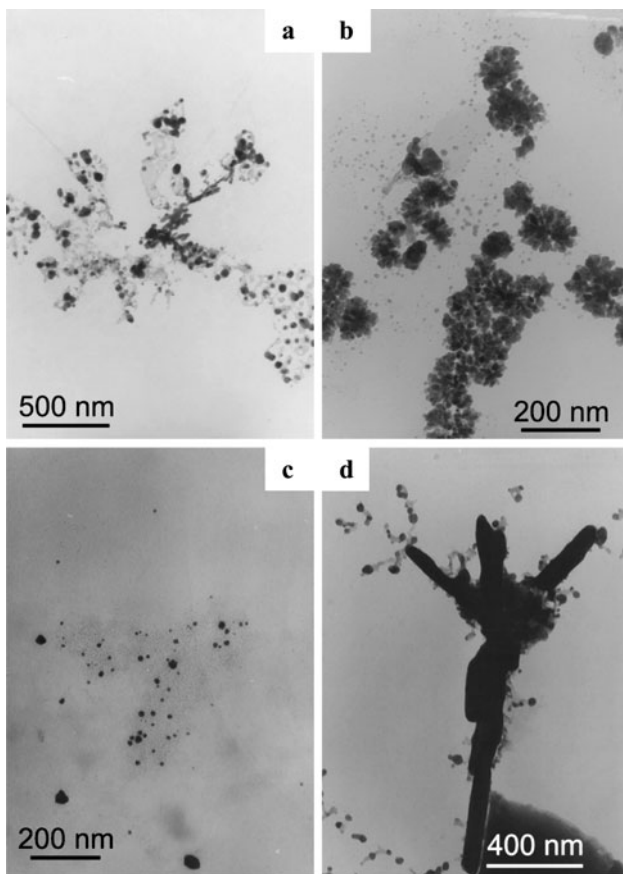
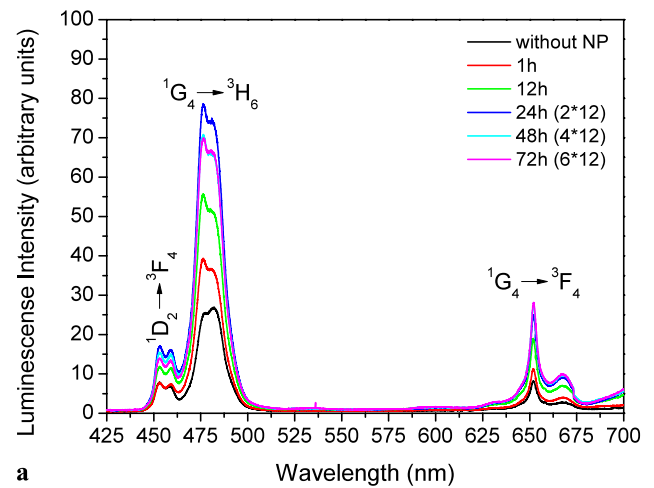
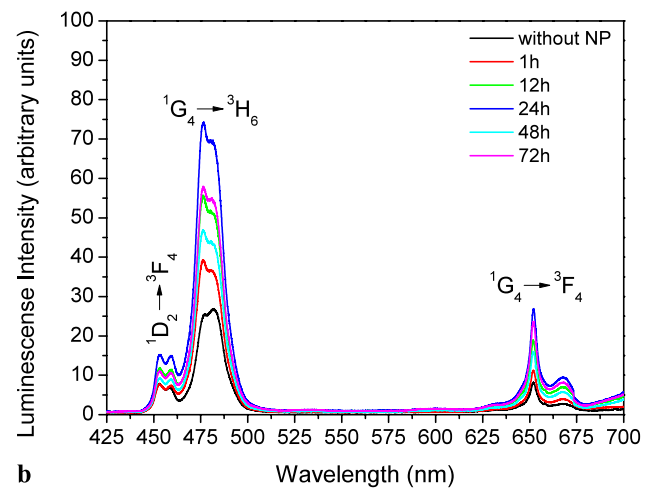


Fig. 2 Transmission electron microscope images of samples. (a) Continuous HT during 24 h. (b) Non-continuous HT during 24 h. (c) Continuous HT during 72 h. (d) Non-continuous HT during 72 h

Figure 4 presents a simplified energy diagram of Tm³⁺ ions with indication of the excitation pathway and the PL transitions observed. The dependence of the PL intensities with the laser intensity was analyzed to identify the energy pathway that originates each UC transition. The results are shown in Fig. 5 where the slopes indicate the number of photons absorbed in each process. The straight line corresponding to transition $^1D_2 \rightarrow ^3F_4$ (454 nm) presents a slope ≈ 4 , while the slope corresponding to transitions $^1G_4 \rightarrow ^3H_6$ (477 nm) and $^1G_4 \rightarrow ^3F_4$ (652 nm) is ≈ 3 . Therefore, we concluded that transitions $^1G_4 \rightarrow ^3H_6$ and $^1G_4 \rightarrow ^3F_4$ are due to the absorption of three laser photons starting from the ground state 3H_6 as indicated by upward solid arrows in Fig. 4. On the other hand, transition $^1D_2 \rightarrow ^3F_4$ correspond the absorption of four photons. In this case the most probable excitation pathway is the absorption of two photons by two ions from state 3H_6 to state $^3F_{2,3}$, followed by a cross-relaxation corresponding to $(^3F_3, ^3H_4) \rightarrow (^3H_6, ^1D_2)$ as indicated in Fig. 4 by dashed arrows. The population of level 3H_4 is due to nonradiative decay from levels $^3F_{2,3}$ that are directly excited through excited state absorption from level 3F_4 . This mechanism of cross-relaxation, responsible



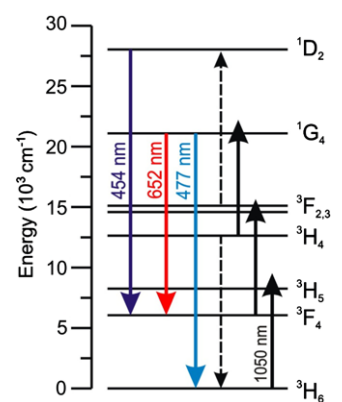
a



b

Fig. 3 Emission spectra of Tm³⁺ doped PbO-GeO₂ samples with and without silver NPs obtained upon excitation of the samples with a CW ytterbium laser at 1050 nm. Laser intensity: ≈ 1 W. (a) Continuous HT. (b) Non-continuous HT

Fig. 4 Simplified energy levels diagram of Tm³⁺ ions



for excitation of level 1D_2 , was previously identified in other glasses doped with Tm³⁺ ions [21–23].

Figure 6 shows that the UC emission follows a nonlinear dependence with τ_{HT} . Continuous and non-continuous HT lead to similar increase of the integrated PL signals

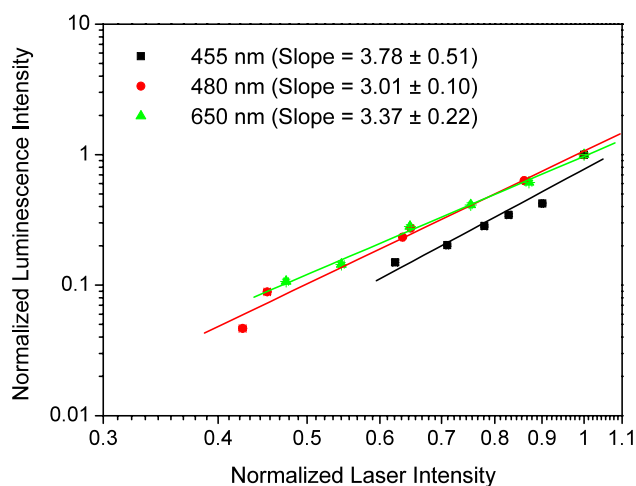


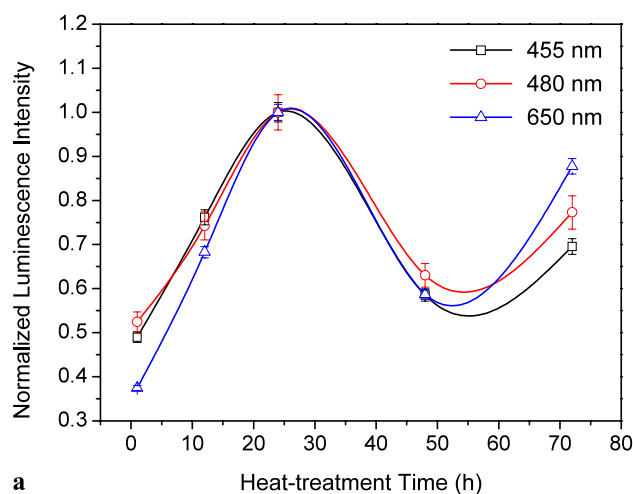
Fig. 5 Upconversion luminescence intensity as a function of the laser intensity

for $\tau_{HT} \leq 24$ h. For the non-continuous HT it is observed a small reduction in the growth rate for $\tau_{HT} > 24$ h while for the samples heat treated continuously the PL signals decrease for $25 \text{ h} < \tau_{HT} < 50$ h and increase for $\tau_{HT} > 50$ h.

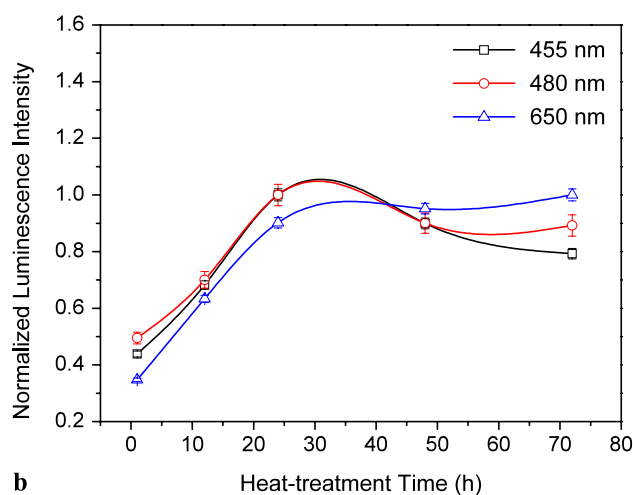
To correlate the HT procedure with the PL properties we first note that TEM images corresponding to samples heat treated for 24 and 72 h at 420°C , using the two HT procedures, present different results. In the samples heat treated by the non-continuous procedure the silver NPs have average diameter of ≈ 15 nm for $\tau_{HT} = 24$ h [Fig. 2(a)] and ≈ 5 and ≈ 15 nm for $\tau_{HT} = 72$ h [Fig. 2(b)]. For the continuous HT procedure we observe average diameter of ≈ 20 nm for $\tau_{HT} = 24$ h [Fig. 2(c)] and larger than ≈ 200 nm for $\tau_{HT} = 72$ h [Fig. 2(d)]. The proximity between the average NPs diameters obtained with both HT procedures for $\tau_{HT} = 24$ h explains the similar increase of the PL signal observed in Fig. 3. However a tendency for NPs aggregation is noticed when the continuous HT procedure is used.

Continuous and non-continuous HT performed at 48 and 72 h originate different UC enhancement when compared with samples heat treated during 24 h, as shown in Fig. 3. When both HT procedures are performed during 72 h, it is observed that UC luminescence decreases in both cases. This result can be attributed to the nucleation of larger NPs and formation of aggregates larger than 200 nm, as shown in Fig. 2(d).

The PL bands at 454 and 477 nm are more influenced when $\tau_{HT} = 24$ h while the emission at 652 nm presents the highest enhancement for $\tau_{HT} = 72$ h for the non-continuous HT. To understand the origin of the PL growth we recall that in the case of blue emission the proximity of the PL wavelength to the region where the SP band is located favors the enhancement. Concerning the emission at 652 nm the presence of larger NPs with ≈ 80 nm and aggregates contributes to the PL enhancement in the red region. It is known that



a



b

Fig. 6 Normalized integrated UC intensity. (a) Continuous HT. (b) Non-continuous HT procedure

the surface plasmon resonance is red-shifted for larger NPs [2, 6, 7].

In all cases we attribute the PL enhancement to the increased local field effect resulting from the mismatch between the dielectric functions of the silver NPs and the glass. On the other hand, quenching is attributed to the increased proximity between the Tm^{3+} ions and silver NPs as a consequence of the growth in the amount of NPs. The small distance between the ions and the silver structures contributes to increase multipole interactions that favor energy transfer from the Tm^{3+} ions to the silver particles. This phenomenon of PL quenching was identified for different fluorophores in the proximity of metallic films and NPs [24, 25].

In summary, we observed that when applying the continuous HT procedure, the NPs tend to aggregate, and in the non-continuous HT procedure, the period of time chosen for the steps (12 h) was enough to prevent aggregation of particles. With the present results we demonstrated the contribution of silver NPs of different sizes for enhanced PL of

Tm³⁺ in the blue-red region upon excitation of samples by infrared light and describe a routine to obtain Tm³⁺-doped PGO samples without much aggregation of Ag particles.

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