Frequency upconversion properties of Tm^{3+} doped TeO_2–ZnO glasses containing silver nanoparticles

Thiago A.A. de Assumpção[a], Davinson M. da Silva[a,*], Mauricio E. Camilo[b], Luciana R.P. Kassab[b], Anderson S.L. Gomes[c], Cid B. de Araújo[c], Niklaus U. Wetter[d]

[a] Departamento de Engenharia de Sistemas Eletrônicos, Escola Politécnica da USP, 05508-900 São Paulo, SP, Brazil
[b] Laboratório de Tecnologia em Materiais Fotônicos e Optoeletrônicos, Faculdade de Tecnologia de São Paulo, (CEETEPS/UNESP), 01124-060 São Paulo, SP, Brazil
[c] Departamento de Física, Universidade Federal de Pernambuco, 50670-901 Recife, PE, Brazil
[d] Centro de Lasers e Aplicações, Instituto de Pesquisas Energéticas e Nucleares (IPEN – SP), 05508-000 São Paulo, SP, Brazil

ARTICLE INFO

ABSTRACT

Frequency upconversion (UC) properties of Tm^{3+} doped TeO_2–ZnO glasses containing silver nanoparticles (NPs) were investigated. Infrared-to-visible and infrared-to-infrared UC processes associated to the Tm^{3+} ions were studied by exciting the samples with a cw 1050 nm ytterbium laser. The luminescence intensity as a function of laser intensity was also measured using a pulsed 1047 nm Nd^{3+}:YVO laser in order to determine the number of photons participating in the UC processes. Enhancement of the UC signals for samples heat-treated during various time intervals is attributed to the growth of the local field in the vicinity of the NPs. PL enhancement by one-order of magnitude was observed in the whole spectrum of the samples heat-treated during 48 h. On the other hand PL quenching was observed for the samples heat-treated more than 48 h.

1. Introduction

Vitreous materials containing rare-earth (RE) ions and metallic nanoparticles (NPs) are attracting large interest due to prior demonstration of increase in their photoluminescence (PL) properties and the enhancement of their nonlinear optical response [1–5], that enables application of these materials in devices such as optical amplifiers, colored displays, and lasers. PL enhancement has been attributed to energy transfer (ET) from the metallic NPs to the RE ions and to the enhancement of the local field that acts on the RE ions located in proximity of the NPs. On the other hand, the increase of the nonlinear response of the metal–dielectric composites is understood considering the enhanced local field inside the NPs and in their vicinity. The best results are achieved when the frequency of the incident light beam, or the PL frequency, is close to the localized surface plasmon (LSP) resonance frequency of the NPs.

Tellurium oxide glasses are good candidates for these studies because they accept large concentration of RE ions, exhibit a transmittance window from the visible to the near-infrared region, have low cutoff phonon energy, present high refractive index and have large chemical stability [6]. Besides, the nucleation of metallic NPs in tellurium oxide glasses of various compositions using a simple procedure has been recently demonstrated [7–13].

In order to understand the different physical mechanisms underlying the aforementioned optical phenomena, different tellurium oxide based glasses containing silver NPs were studied [7–13]. The presence of Pb^{2+} clusters in TeO_2–PbO–GeO_2 glasses led to enhanced PL in the visible range [7], whereas for Pr^{3+} doped TeO_2–PbO–GeO_2 glass, enhanced Stokes and anti-Stokes luminescence were observed and analyzed [8,10]. Further experiments with TeO_2–PbO–GeO_2 glass doped with Eu^{3+} and containing gold NPs [9] and Tb^{3+} doped TeO_2–ZnO–Na_2O–PbO glass with silver NPs [11] were also reported. In both cases large increase in the samples' luminescence was observed.

The role of ET processes was also exploited in tellurium based glasses containing metallic NPs and co-doped with two different RE species. Enhancement of the frequency upconversion (UC) efficiency by the contributions due to silver NPs and ET processes between two different RE ions were exploited to control the PL of TeO_2–ZnO–Na_2O–PbO glass codoped with Tb^{3+}/Eu^{3+} [12].

In this paper we report the observation of infrared-to-visible and infrared-to-infrared UC processes in Tm^{3+} doped TeO_2–ZnO glass containing silver NPs. The choice of Tm^{3+} was motivated by the large infrared-to-visible UC efficiency reported for other tellurite glassy hosts and by the several applications already demonstrated

* Corresponding author. Tel.: +55 1133222278.
E-mail address: davinsonm@gmail.com (D.M. da Silva).

for Tm^{3+} doped glasses [14–19]. The infrared lasers used, operating at 1050 nm and 1047 nm, are widely available for optical telecom studies allowing the exploitation of the present results for photonic applications.

2. Experimental details

The samples studied were prepared by the melting–quenching technique starting with the following composition (in wt%): 85TeO$_2$–15ZnO. The doping species were 0.5 Tm$_2$O$_3$ and 2.0 AgNO$_3$ (in wt%). The reagents were melted at 800 °C in a platinum crucible for 20 min, quenched in a pre-heated brass mold, annealed at 325 °C for 2 h, and cooled to room temperature inside the furnace to avoid internal stress. Glass samples were polished and heat-treated for different periods of time, t_{ht}, to reduce the silver ions (Ag$^+$) to obtain Ag^0, enabling the nucleation of silver NPs. The samples were heat-treated for 24, 48 and 72 h to obtain different NPs concentrations. A sample annealed for 2 h was used as reference because the concentration of silver NPs is negligible.

Absorption spectra were measured with a commercial spectrophotometer and the PL spectra were obtained exciting the samples using a cw ytterbium laser operating at 1050 nm, and analyzing the PL from 400 nm to 900 nm. The PL intensity dependence with the laser intensity was determined using a Nd^{3+}:YVO pulsed laser operating at 1047 nm.

A 200 kV transmission electron microscope (TEM) was used to investigate the nucleation of the silver NPs and their size distribution.

3. Results and discussions

Fig. 1 shows the absorption spectra of the Tm^{3+} doped TeO$_2$–ZnO samples containing silver NPs, for different heat-treatment times, t_{ht}, at 325 °C. Absorption bands associated to Tm^{3+} ions starting from the ground state (^{3}H$_6$) to the excited states ^{1}G$_4$, ^{3}F$_{2,3}$, and ^{3}H$_4$ are indicated in Fig. 1. The absorption band related to the LSP resonance is not observed because the amount of NPs is not enough to show a noticeable band. With basis on the dielectric function of silver [20] and the refractive index of the TeO$_2$–ZnO glass ($\approx$2) we estimate the wavelength of LSP resonance of isolated NPs to be located in the range from $\approx$420 to $\approx$500 nm. However, the presence of silver NPs is confirmed by the TEM images.

Fig. 2 shows a TEM image obtained for the sample heat-treated for 48 h at 325 °C corresponding to one region with large concentration of NPs. Energy dispersive X-ray spectroscopy (EDS) was performed during TEM analysis in order to confirm the presence of silver NPs. The EDS spectrum is also shown in the inset of Fig. 2. Isolated silver NPs with diameters from $\approx$10 nm to $\approx$50 nm were observed but the spatial distribution of NPs is not uniform. The TEM images also show aggregates and isolated NPs with various shapes that contribute for the background observed in the whole spectra of Fig. 1.

Fig. 3 shows that the PL bands centered in $\approx$477, $\approx$650 and $\approx$800 nm, corresponding to the transitions ^{1}G$_4 \rightarrow {}^3$H$_6$, ^{1}G$_4 \rightarrow {}^3$F$_4$

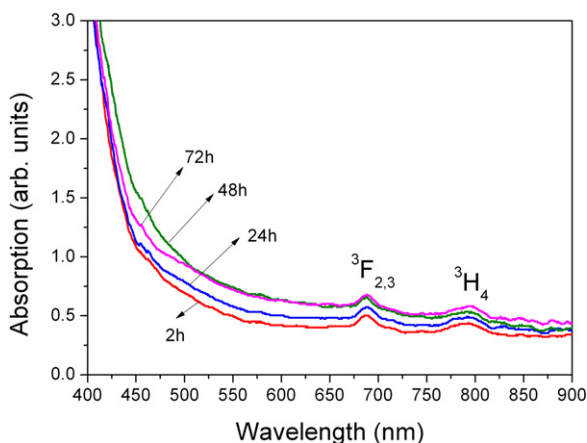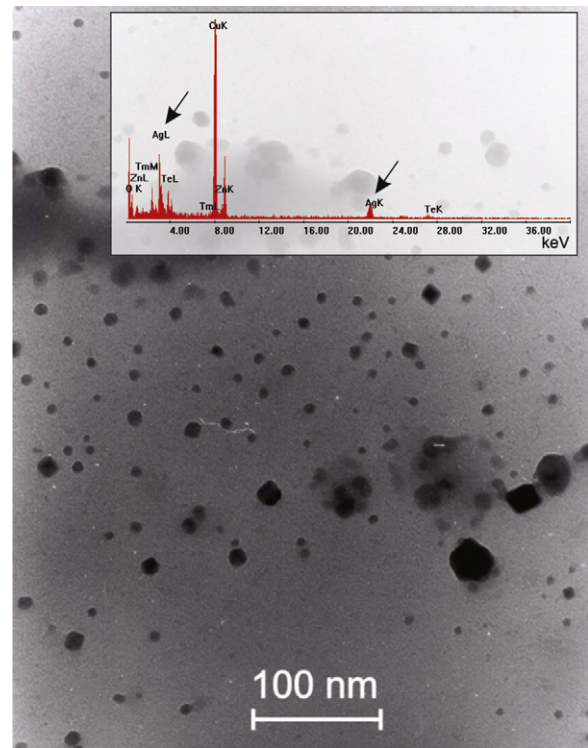**Fig. 2.** TEM image of the sample heat-treated during 48 h. The inset shows the EDS spectrum obtained during TEM analysis.

Fig. 1. Absorption spectra of Tm^{3+} doped TeO$_2$–ZnO samples containing silver NPs for different heat-treatment times.

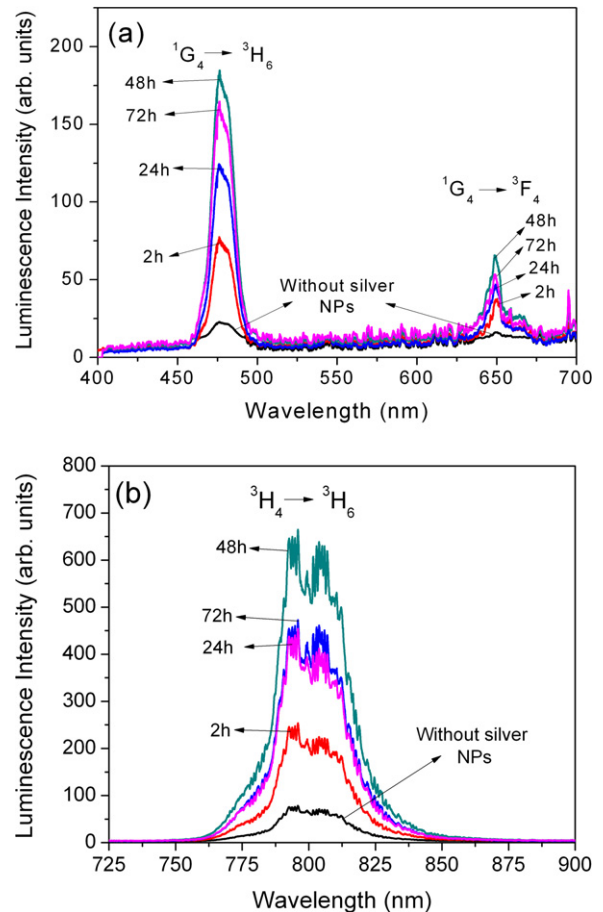**Fig. 3.** Emission spectra of Tm^{3+} doped TeO$_2$–ZnO samples containing silver NPs excited with a cw ytterbium laser at 1050 nm ($\approx$1 W).
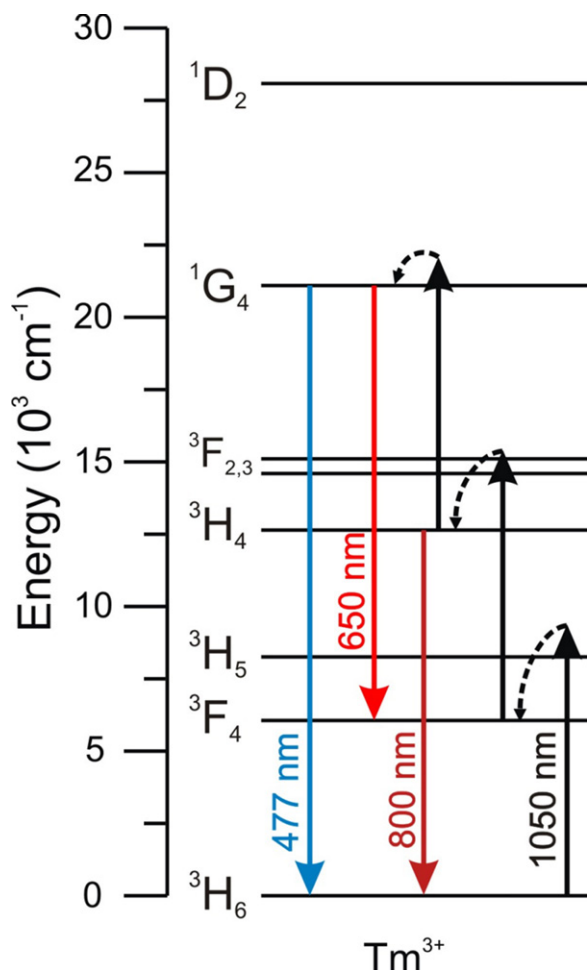
Fig. 4. Simplified energy level diagram of Tm^{3+} ions with indication of the UC pathways and wavelengths.

and $^3H_4 \rightarrow {}^3H_6$, respectively, change their amplitude for different t_{ht} values. Notice that all PL bands increase with t_{ht} up to 48 h. One-order of magnitude enhancement is observed for the whole PL spectra that is a remarkable result in comparison with our previous reports for other RE ions [8–13]. The spectra corresponding to $t_{ht} = 72$ h show partial quenching of the PL intensity. To understand this behavior we recall that when the distance between a RE ion and a metallic NPs is very small (<5 nm), ET from the excited RE ion to the NP may be efficient and the contribution of the increased local field for PL enhancement is not dominant. Heat-treating the samples for very long times leads to large NPs concentration and the relative distances between the Tm^{3+} ions and the NPs are reduced. Then the excited Tm^{3+} ions transfer the energy absorbed from the laser beam to the NPs which dissipate the energy by heat.

The dependence of the UC signals with the laser intensity was analyzed to identify the routes corresponding to each UC emission. A log–log plot of the UC intensity corresponding to transitions $^1G_4 \rightarrow {}^3H_6$, $^1G_4 \rightarrow {}^3F_4$ and $^3H_4 \rightarrow {}^3H_6$ presents slopes of ≈ 2.7, ≈ 2.8, and ≈ 1.8, respectively. These results indicate that the PL bands at 477 nm and 650 nm are due to the absorption of three laser photons while the transition $^3H_4 \rightarrow {}^3H_6$ is due to the absorption of two photons. Considering the mismatch between the incident photon energy and the energy levels we conclude that the UC processes occur because the intermediate steps are phonon-assisted. Even the excited state absorption $^3F_4 \rightarrow {}^3F_{2,3}$ which is resonant is followed by emission of phonons due to the decay from level $^3F_{2,3}$ to the level $^3H_4$.

Fig. 4 presents a simplified energy diagram for the Tm^{3+} ions with indication of the excitation pathways and the PL transitions observed.

4. Summary

The present results demonstrate the large influence of silver NPs in the infrared-to-visible and infrared-to-infrared UC luminescence of Tm^{3+} doped TeO_2–ZnO glasses. Enhancement of the UC emission for the heat-treated samples is attributed to the increase of the local field on the Tm^{3+} ions locations, in the vicinity of the NPs. The 10-fold enhancement obtained for the whole PL spectrum is an important result that illustrates the potential of using metal–dielectric composites to improve the performance of luminescent materials containing RE ions.

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