Influence of silver nanoparticles in Tm3+/Er3+/Yb3+ doped germanate glasses for colorful display

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### ABSTRACT

We report on the influence of silver nanoparticles in germanate glasses (GeO2 - PbO) doped with Tm3+, Er3+ and Yb3+. All samples produced showed emission at 477 nm (blue light) from the Tm3+ ion, at 530 and 550 nm (green light) from the Er3+ ion and at 660 nm (red light) from both. The enhancement of the luminescence was probably caused by increased local field in the vicinity of rare-earth ions due to the presence of silver nanoparticles. The absorption band related to the surface plasmon resonance of the silver nanoparticles was observed in the range of 420 to 500 nm. Enhancement of about 60% was observed, in the presence of silver nanoparticles, for samples heat-treated during 48h. The intense red, green and blue upconversion luminescence of these glasses might allow the development of potential three-dimensional display

### INTRODUCTION

Germanate glasses doped with rare earth íons and metalic nanoparticles have attracted interest due to the intensification of the luminescence of rare earth ions caused by the influence of nanoparticles, and also by the increase of the nonlinear optical properties [1].

Germanate glasses were chosen because of the high high refractive index ( ~2), good mechanical strength, chemical durability, low phonon energy as compared to silicates and borates and wide transmission window, from the visible to the mid-infrared region (400 – 7000 nm) [2]. The upconversion process that occurs between the rare-earths Tm 3+/Yb3+/Er3+ enables the emission of the three primary colors. For this reason they are strong candidates for application in colorful displays, solid state lasers, optical amplifiers and optical sensors [3]. We recently reported the enhancement of the luminescence of rare earth íons in PbO-GeO2 (GP) glasses due to nucleation of silver and gold nanoparticles [4]. The influence of silver nanoparticles were reported in samples doped with Pr3+ [5], Er3+ [6], and Tm3+ [1]. Also it was reported the influence of silver nanoparticles in the upconversion process in samples codoped with Er3+/Yb3+ [7] and the influence of gold NPs in Eu3+ doped germanate glasses [8]. On the other hand near-infrared third-order nonlinearity of PGO films containing Cu, Cu2O and Au NPs indicated a large potential for all-optical switching [9,10]. More recently the enhancement of the infrared-to-visible upconversion (UC) process in Tm3+/Yb3+ codoped PGO glass containing silver NPs was also reported [11]. The present work reports, for the first time, the influence of silver nanoparticles in the Tm3+/Yb3+/Er3+ upconversion process of PbO-GeO2 glasses, excited by 980 nm laser

### EXPERIMENTAL DETAILS

Samples with composition 60 PbO – 40 GeO2 (in wt%) were prepared using the melt-quenching technique. The dopping species were Yb2O3 (3.0 wt %), Tm2O3 ( 0.25 wt %), Er2O3 (0.5 wt %) and AgNO3 (4.0 wt %). The reagents were melted at 1200º C in alumina crucible for 1 h, quenched in preheated brass mold, annealed at 420º C for 1h, and cooled to room temperature inside the furnace to avoid internal strees. The samples were polished, cut and submitted to different heat-treatment periods of time (12h, 24h and 48h). The absorption spectra was measured with commercial spectrophotometer and emission spectra were obtained exciting the samples with a cw diode laser operating at 980 nm, in resonance with the Yb3+ transition 2F7/2 → 2F5/2. The PL was analyzed through a spectrometer attached to a photomultiplier and computer. A 200 KV transmission electron microscope (TEM) was used to investigate the presence of silver nanoparticles in the samples.

### RESULTS AND DISCUSSION

Fig 1 shows the TEM images of the sample heat-treated for 48h. We observe that the nanoparticles average size is about 20 nm.

 

*Fig 1:* *Transmission electron* *microscope image of the sample heat-treated for 48h at 500ºC.*

Fig 2 and Fig 3 show the absorption spectra from the visible to the infrared of all the samples produced. The results for the sample prepared without silver NPs is shown as reference. The absorption bands related to Tm3+, Yb3+ and Er3+are observed. The bands centered at 680, 800 and 1200 are due to the following Tm3+ transitions 3H6 →3F2,3, 3H6 → 3H4 and3H6 → 3H5 respectively. The bands related to Er3+ íons are centered at 490, 520, 545, 650, 800, 980 and 1550 nm and are associated to transitions 4I15/2 → 4F7/2, 4I15/2 → 2H11/2, 4I15/2 → 4S3/2, 4I15/2 → 4F9/2, 4I15/2 →4I9/2, 4I15/2 → 4I11/2 and 4I15/2 → 4I13/2,respectively. The transition associated to the ~~of~~ Yb3+ íons is centered at 980 nm (2F7/2 →2F5/2). The absorption band related to the surface plasmon resonance of the silver nanoparticles is in the range of 400 ~ 500 nm for samples annealed for 48h. This band was also observed in Er3+ doped PbO-GeO2 glasses with silver NPs [7]. The presence of this band is related to the large efficiency of silver ions reduction and corroborates the nucleation of silver NPs that is observed by TEM measurements.



Fig 2: Absorbance spectra of the Tm 3+/Yb 3+/Er3+ doped PbO-GeO2 glasses containing silver nanoparticles for different periods of time; the sample without silver NPs is shown as reference (400-900nm)  Fig 3: Absorbance spectra of the Tm3+/Yb3+/Er3+ doped PbO-GeO2 glasses containing silver nanoparticles for different periods of time; the sample without silver NPs is shown as reference (900-1700 nm).

Fig 4 shows the luminescence spectra of the samples heat-treated for 12, 24 and 48h under 980 nm pumping. The spectrum of a sample without silver nanoparticles is included for comparison. The emission bands centered at 477 and 652 nm correspond to the Tm3+ transitions, 1G4 → 3H6 and 1G4 → 3F4 respectively. The emissions corresponding to Er3+ ions are centered at 530, 550 and 660 nm and related to 2H11/2 → 4I15/2, 4S3/2 → 4I15/2 and 4F9/2→ 4I15/2 transitions respectively. The luminescence intensity of all wavelengths for samples containing silver nanoparticles was enhanced. We observe enhancement of about 60% for emissions at 477, 550 and 660 nm.

 *Fig 4: Emission spectra of Tm*3+*/Er*3+*/Yb*3+ *doped PbO-GeO2 samples containing silver NPs obtained by excitation at 980 nm. The result of the sample without silver NPs is shown as reference.*

As show in figure 4 the upconversion luminescence depends on the heat treatment time of the samples. Therefore one of the important steps to obtain large luminescence enhancement is related to the nucleation of the metallic NPs through controlled heat treatment of the samples. The optimum distance between silver NPs and rare earth ions for larger luminescence enhancement is ≈15 nm [12]. When the distance is smaller quenching due to energy transfer from the rare earth ion to the NP is dominant. The influence of the NPs on the luminescence efficiency of the rare-earth ions is larger when the incident light and the photoluminescence wavelength are near resonance with the the localized surface plasmon (LSP) represented by wsp. The 980 nm excitation wavelength is far for the LSP resonance wavelength, and the probability of the excitation of the plasmon band is very small. So the intensity enhancement is attributed to the increased local field in the vicinities of the silver NPs. The probability of energy transfer from the NPs to the Er3+ and Tm3+ ions is negligible and the proximity between the luminescence wavelengths and the plasmon absorption band, favors the enhancement of the upconversion emissions due to the intense local field effect [6]. So the most important contribution from the NPs is due to the Purcell effect for the emissions with frequencies near to wsp [13].

Fig 5 presents a simplified energy level diagram of Tm3+/Yb3+/Er3+ ions illustrating the possible upconversion processes between Yb3+ - Er3+ and Yb3+ - Tm3+ doped glasses. The arrows describe the pathways of excitation (upward arrows) and luminescence transitions (downward arrows). The dotted arrows indicate energy transfer from Yb3+ to Tm3+ and Er3+ ions. Dashed arrows indicate non-radiative transition. The Tm3+ emissions are originated by the following process: one laser photon of 980 nm is absorbed by the Yb3+ ions that transfer the stored energy to the Tm3+ ions that are promoted from the ground state 3H6 to the 3H5 level, and then decay to 3F4 level. Then they are excited by the incident laser, due to the absorption of another photon that promotes the Tm3+ ions to 3F2,3 level. Then a non-radiative~~ly~~ decay occurs to the 3H4 level and the Tm3+ ions are promoted to1G4 level by the energy transfer from Yb3+ ions. The blue and red emissions that come from Tm3+ ions are related to the 1G4 → 3H6 and 1G4 → 3F4 transitions, respectively. The Er3+ emissions are originated by the following process: Yb3+ ions when excited under 980 nm transfer the stored energy to Er3+ ions that are promoted to level 4I11/2, and then to 4F7/2 level by the absorption of another photon. The Er3+ ions relax non-radiatively to the following levels: 2H11/2, 4S3/2 and 4F9/2. From these levels, it is obtained the green emission related to the transitions 2H11/2→4I15/2 and 4S3/2→4I15/2, and the red emission to the transition 4F9/2→4I15/2. Another pathway for this transition is related to the population of 4I11/2 level followed by a decay to 4I13/2 level and the absorption of another photon that promotes Er3+ to 4I9/2 level.



Fig. 5 Energy level diagram of Tm3+/Yb3+/Er3+ ions. Solid arrow represent radiation transitions, dotted arrows indicate energy transfer from Yb3+ to Tm3+ and Er3+ ions. Dashed arrows indicate non radiative transitions [14].

To identify the upconversion mechanism for each transition, the dependence of the upconversion intensities with the laser power excitation was analyzed and the results are shown in Fig 6. The intensity of the upconversion process, Iucp, depends on the laser power Ip by the relation Iucp ~ Ip n where n represents the number of photons that participates into the process. The slope determined from the log-log plot of Fig 6 shows the value of n. Figure 6 shows that two photons are associated to 550 and 660 nm emissions and three photons are involved on the excitation process related to 480 nm emission. Although the red emission is due to 1G4 → 3F4 and 4F9/2→4I15/2, transitions associated to Tm3+ and Er3+ respectively.

 Fig.6: Dependence of the upconversion intensity with the laser power excitation.

#### CONCLUSION

The influence of silver nanoparticles (NPs) on the frequency upconversion luminescence in Er3+ and Tm3+ doped PbO-GeO2 glass is reported. The growth of silver NPs inside the glasses was obtained using ~~on~~ the melt-quenching method followed by controlled heat-treatment in order to obtain nucleation of the metallic NPs. Enhancement of about 60% was observed for the upconverted emissions at 477, 550 and 660 nm, when a laser at 980 nm was used for excitation. The laser frequency is far from the NPs surface plasmon resonance frequency and the luminescence enhancement is attributed to the local field increase in the proximity of the NPs. This is the first observation of luminescence enhancement due to silver NPs in a germanate glass doped with three different rare-earth ions. The present results describe a method that can be used for the development of colorful displays with enhanced performance.

ACKNOWLEDGMENTS

The authors would like to thank the support from the National Institute of Photonics/CNPq

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