Effects of gold nanoparticles in the green and red emissions of TeO$_2$–PbO–GeO$_2$ glasses doped with Er^{3+}–Yb^{3+}

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ABSTRACT

In the present work it is reported for the first time the effects of gold nanoparticles in the infrared-to-visible frequency upconversion of Er^{3+}–Yb^{3+} co-doped TeO$_2$–PbO–GeO$_2$ glasses. Intense emission bands at 527, 550, and 660 nm were observed corresponding to the Er^{3+} transitions. It is shown that the combined effects of gold nanoparticles and the efficient Yb^{3+} → Er^{+3} energy transfer mechanism change the upconversion visible spectrum. It is then demonstrated that the enhanced local field contribution due to gold nanoparticles and the energy transfer processes between two different rare-earth ions can be used to control and improve the efficiency of luminescent glasses.

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1. Introduction

Vitreous materials containing rare-earth ions and metallic nanoparticles (NPs) have been attracting large interest because of the phenomena related to the increase of the luminescence and to the enhancement of the nonlinear optical properties [1–5] that enables several applications with devices as optical amplifiers, colored displays, lasers, optical limiters among other applications. These phenomena are related to the energy transfer (ET) between metallic NPs and rare-earth ions and/or to the enhancement of local energy field that acts on the rare-earth ions located in proximity of the NPs specifically when the wavelength of the incident light beam, or luminescent wavelength is close to the surface plasmon resonance (SPR) wavelength of the NPs [6,7]. The (SPR) wavelength depends on the host and metal-dielectric functions as well as on the dimensions and shape of the NPs.

Among the materials of interest the heavy metal oxide glasses such as the TeO$_2$ based glasses are known to be excellent materials for photonic applications because of their high refractive index (∼2.0), large transmission window (360–6500 nm), low cutoff photons energy (700 cm^{-1}), large nonlinear optical response, large mechanic resistance, and high chemical durability. Luminescence properties of tellurium oxide glasses were previously reported [8–10]. One approach used to increase the luminescence characteristics of glasses is the appropriate doping with two different rare-earth species. In this case energy transfer (ET) among rare-earth species may favor the luminescence in selected spectral regions. Another possibility is the embedment of metallic nanoparticles close to the emission centers. Indeed the presence of silver nanostructures in TeO$_2$–PbO–GeO$_2$ glass improved the luminescence efficiency of Pb^{2+} clusters [5]. Enhanced Stokes and anti-Stokes luminescence were observed in Pr^{3+} doped TeO$_2$–PbO–GeO$_2$ glass containing silver NPs [5]. Recently enhancement of Pr^{3+} luminescence was presented in TeO$_2$–ZnO–Nb$_2$O$_5$–MoO$_3$ glasses with silver NPs [11].

Recently it was demonstrated the enhancement of the upconversion (UC) efficiency by doping the material with silver NPs and assuming simultaneously the contribution due to ET processes between two different rare-earth ions. Experiments done with TeO$_2$–ZnO–Na$_2$O–PbO glasses containing silver NPs co-doped with Tb^{3+}–Eu^{3+} demonstrated the appropriateness of this approach to control the UC luminescence of glassy materials. However no studies were reported showing if this approach is also appropriated to control the UC luminescence of co-doped glasses with gold NPs.

In the present work it is reported for the first time the infrared-to-visible frequency upconversion (UC) in the Er^{3+}–Yb^{3+} co-doped TeO$_2$–PbO–GeO$_2$ glasses excited in the infrared and the influence of the presence of gold NPs on the UC intensity. It is shown that the combined influence of gold NPs and the efficient Yb^{3+} → Er^{3+} energy transfer mechanism might allow the control of luminescent materials efficiency.

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2. Experimental

Glasses were prepared by adding 0.5 wt.% of Er_2O_3, 2.0 wt.% of Yb_2O_3 and 1.0 wt.% of Au_2O_3 to the base glass composition [33.3 TeO_2–33.3 PbO–33.3 GeO_2 (in wt.%)] using the melt-quenching method. Batches of 7.0 g of high purity (99.999%) compounds were fully mixed in a pure platinum crucible and melted at 1050 °C for 1 h. The melts were then poured into pre-heated brass molds, in air, and annealed at 350 °C for 1 h to release internal stresses. Finally, the glasses were cooled to room temperature following the cooling inertia of the furnace. After cooling the samples were polished and heat treated at 350 °C during 24, 48, and 72 h (three steps of 24 h) to thermally reduce Au^+ and Au^{3+} ions to Au^0 and consequently to nucleate and grow gold NPs.

A 200 kV transmission electron microscope (TEM) was used to investigate the presence of gold NPs embedded in the glass matrix. Optical absorption spectra were measured at room temperature in the 400–1700 nm range using a commercial spectrophotometer. The UC spectra were excited with a CW diode laser emitting 200 mW at 980 nm. The luminescence signals were dispersed by a monochromator fitted by a S-20 photomultiplier and computer. All measurements were made at room temperature.

3. Results

Fig. 1 shows the TEM image of a sample after heat-treatment during 72 h. The black spots are the gold NPs which average size is ≈10 nm.

Fig. 2 presents the absorption spectra of the Er^{3+}/Yb^{3+} co-doped TeO_2–PbO–GeO_2 with and without gold NPs, and after different annealing time intervals. Absorption bands attributed to $4f$–$4f$ transitions of Er^{3+} ions corresponding to transitions starting from the ground state ($^4I_{15/2}$) to the excited states are observed. The bands centered at 380, 407, 490, 522, 545, 654, and 800 nm are due to the transitions $^4I_{15/2} \rightarrow {}^4G_{11/2}$, $^4I_{15/2} \rightarrow {}^2H_{9/2}$, $^4I_{15/2} \rightarrow {}^4F_{7/2}$, $^4I_{15/2} \rightarrow {}^2H_{11/2}$, $^4I_{15/2} \rightarrow {}^4S_{3/2}$, $^4I_{15/2} \rightarrow {}^4F_{9/2}$, and $^4I_{15/2} \rightarrow {}^4I_{9/2}$, respectively. The small absorption band at ≈450 nm is attributed to the $^4F_{3/2} + {}^4F_{5/2}$ transition. An intense absorption band at ≈980 nm, is mainly due to the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of Yb^{3+} ions that overlaps with the weaker $^4I_{15/2} \rightarrow {}^4I_{11/2}$ transition of the Er^{3+}
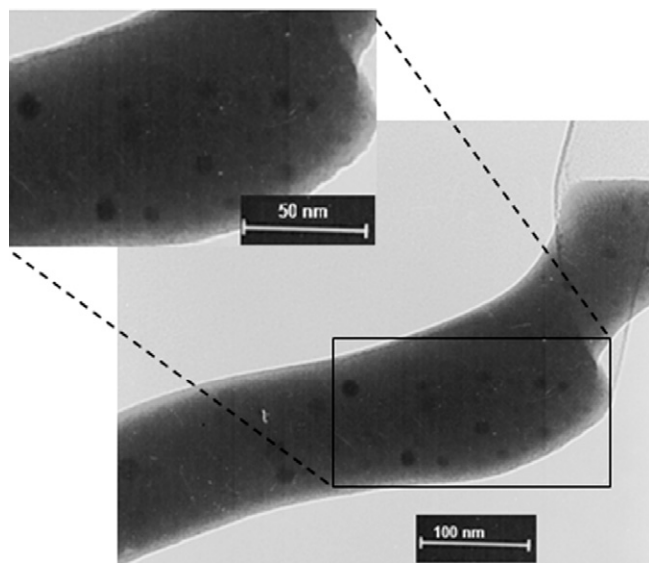

Fig. 1. TEM image of Er^{3+}–Yb^{3+} co-doped TeO_2–PbO–GeO_2 glass containing gold NPs after heat-treatment during 72 h.

ions [8,9]. The absorption band related to the surface plasmon (SP) resonance of the gold NPs was not observed assumedly because of the small amount of gold NPs but the TEM micrographs show their presence. It is estimated that the wavelength corresponding to the surface plasmon resonance of isolated gold NPs is located in the region 500–600 nm based on the dielectric function of gold NPs and the refractive index of TeO_2–PbO–GeO_2 glass (~2.0) [12].

Fig. 3 shows the emission spectra of the Er^{3+}–Yb^{3+} co-doped TeO_2–PbO–GeO_2 glasses with gold NPs for samples heat-treated for 24, 48, and 72 h. The spectrum for a sample without gold NPs is included for comparison. The emission bands centered 527, 550, and 660 nm correspond to the $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$, and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+} ions, respectively. By comparing the samples prepared without gold NPs with the one heat treated during 72 h it can be seen that the $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions with wavelength near the surface plasmon band increases by ~20%. We remark that the changes on the general shape of the emission spectra are related to changes of the local symmetry around Er^{3+} ions [13] due to possible inhomogeneities in the distribution of silver NPs concentration.

As shown in Refs. [6,7] the proximity of the luminescence of the infrared-to-visible frequency upconversion with the plasmon absorption band favors the intensity enhancement that is due to the intensified local field effect. This explains the fact that $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition is less influenced by the presence of gold NPs than the other observed transitions. We remark that the enhancement obtained in the presence of gold NPs for the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions is of the same order of magnitude as the one measured in Yb^{3+}–Er^{3+} co-doped TeO_2–PbO–GeO_2 glass, prepared without gold NPs but with higher concentration of Yb^{3+} (5.0 wt.%) [14]. This fact also shows the role of gold nanoparticles in the energy luminescence of the infrared-to-visible frequency upconversion of Er^{3+}/Yb^{3+} co-doped TeO_2–PbO–GeO_2.

4. Discussion

To identify the mechanism of the UC emission for each transition, the dependence of the UC intensities with the laser intensity was analyzed, and it is shown in Fig. 4. The slopes shown represent the number of photons absorbed in each process. A slope ~2.0 is observed for $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions for the samples with and without gold nanoparticles indicating that two photons are participating in the UC emission. Then the introduction of gold nanoparticles does not affect the dependence of the upconversion intensities with the laser intensity. This mechanism was identified for Er^{3+} doped PbO–GeO_2 glasses with silver NPs [15].

Fig. 5 presents the energy level diagram of Er^{3+} and Yb^{3+} ions illustrating possible UC pathways for Er^{3+}–Yb^{3+} co-doped glasses. It is well known that the energy transfer efficiency depends on the relative concentration of Er^{3+} and Yb^{3+} and the lifetime of the levels participating in the ET process. Therefore we consider that the ET pathways indicated in Fig. 5 by the dashed lines (1), (2) and (3) represent the dominant processes because in the present work the Yb^{3+} concentration is six times larger than the Er^{3+} concentration. The green emissions are mainly originated by the following process: Yb^{3+} ions when excited under 980 nm transfer the stored energy to the Er^{3+} ions that are promoted to the $^4I_{11/2}$ state. Then, by means of pathways (1) and (2), Er^{3+} ions are promoted from the $^4I_{11/2}$ to the $^4F_{7/2}$ level. Then the Er^{3+} ions relax non-radiatively to the $^2H_{11/2}$ and $^4S_{3/2}$ levels and the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions originate the green emissions at 527–550 nm. The red emission at 660 nm is due to the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition. Besides the feeding of the $^4F_{9/2}$ level through
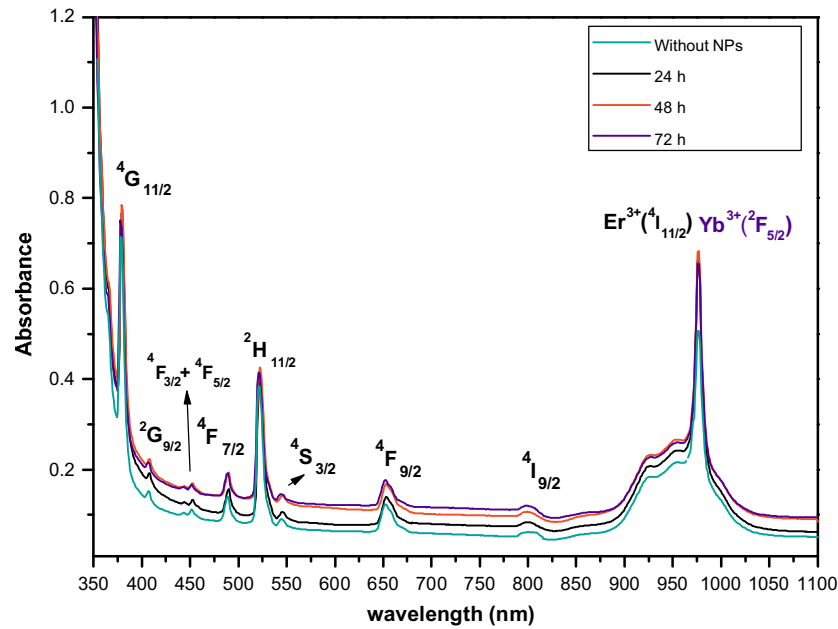
Fig. 2. Absorbance spectra of the Er^{3+}–Yb^{3+} co-doped TeO_2–PbO–GeO_2 glass containing gold NPs heat-treated for different times.
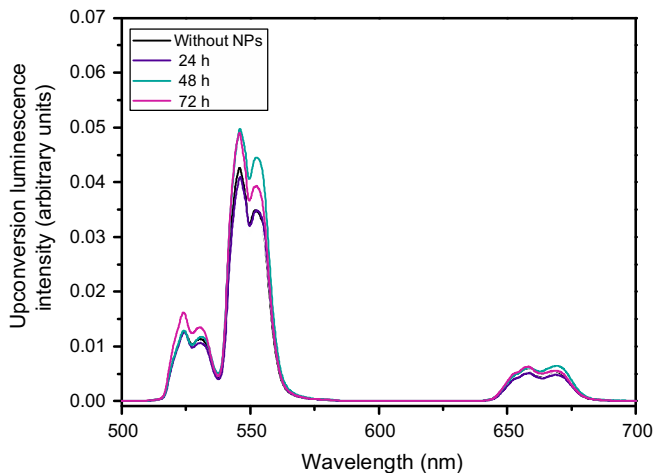

Fig. 3. UC emission spectra of Er^{3+}–Yb^{3+} co-doped TeO_2–PbO–GeO_2 glasses containing gold NPs for different heat treatment times; the UC emission of the sample without gold NPs is shown as reference.
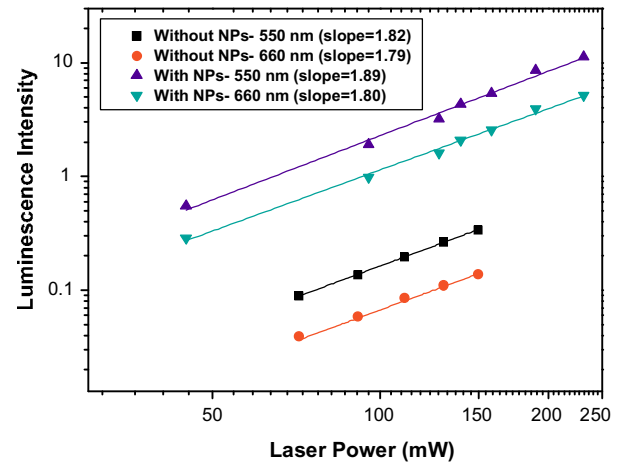

Fig. 4. UC emission intensity as a function of the laser power for the samples with and without gold NPs heat treated during 72 h.

the non-radiative relaxation from the $^4S_{3/2}$ level, by means of pathway (3) in Fig. 5, the non-radiative transition $^4I_{11/2} \rightarrow {}^4I_{13/2}$ may occur and promotes the ions to the $^4F_{9/2}$ level. The longer lifetime of the $^4I_{13/2}$ level when compared with the lifetime of the $^4I_{11/2}$ level [9] makes the pathway (3) dominant over the pathways (1) and (2).

It is observed that the excited state absorption between the Er^{3+} levels involved in the UC pathway described above may also takes place; however, we believe that in the present work the ET processes are dominant due to the large concentration ratio of $[Yb^{3+}]:[Er^{3+}]$ (6:1).

The nucleation of metallic NPs contributes either for quenching or enhancement in luminescence [1]. If the distance between the rare-earth ion and the metallic NPs is very small (<5 nm) multipole interactions are increased and the ET from an excited rare-earth ion to the metallic structure may be very efficient. In this case the contribution of the increased local field for luminescence enhancement may not be dominant [1]. For distances in the range
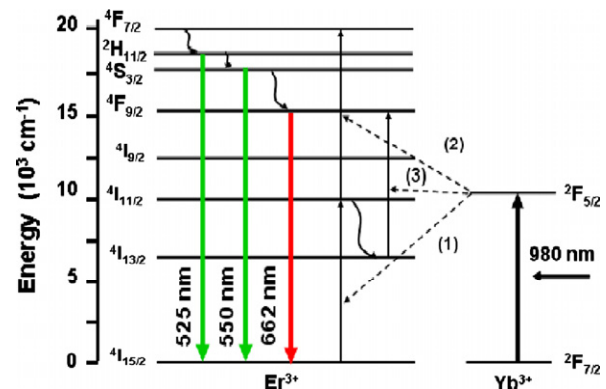

Fig. 5. Energy level diagram of Er^{3+} and Yb^{3+} ions illustrating possible UC pathways for Er^{3+}–Yb^{3+} co-doped TeO_2–PbO–GeO_2 glasses with gold NPs. The solid straight lines with upward and downward arrows indicate optical transitions; dotted lines and wavy arrows denote ET processes and non-radiative relaxation, respectively.

5–20 nm the luminescence enhancement predominates and this is the case of the samples heat treated during 48 and 72 h, respectively. The relative location of the rare-earth ion with respect to the metallic NPs is difficult to be controlled. However, by using the step-by-step heat treatment procedure for nucleation (three steps of 24 h instead of 72 h continuously) [16], as it is the case of samples studied in this work, it is possible to avoid the formation of aggregates that can be responsible for the energy transfer from the rare-earth ions to metallic NPs and consequently to the quenching of the luminescence, as explained above.

The present work demonstrated the simultaneous contribution of the ET from Yb^{3+} to Er^{3+} and the intensified local field effect resulting from the mismatch between the dielectric functions of the gold NPs that influences the luminescence of the materials. Also, this work shows that the presence of gold NPs nucleated after heat treatments, makes possible the use of Yb^{3+} lower concentrations to optimize the luminescence efficiency of Yb^{3+}–Er^{3+} co-doped TeO_2–PbO–GeO_2 glasses.

5. Conclusion

The energy transfer (ET) between different rare-earth species in tellurium based glasses containing gold NPs has been shown. The effects of gold NPs in the infrared-to-visible frequency upconversion of Er^{3+}–Yb^{3+} co-doped TeO_2–PbO–GeO_2 glasses is due to the increased local field in the Er^{3+} ions locations and the close values between the luminescence wavelengths and the NPs surface plasmon resonance. The preparation of tellurite samples with gold NPs describes a routine to optimize the luminescence of Yb^{3+}–Er^{3+} co-doped TeO_2–PbO–GeO_2 glasses and can be applied to other glasses containing gold NPs and co-doped with different rare-earth ion.

References

[1] P.N. Prasad, Nanophotonics, Wiley, New York, 2004.
[2] G. Fu, W. Cai, C. Kan, C. Li, L. Zhang, Appl. Phys. Lett. 83 (2003) 36.
[3] T. Som, B. Karmalar, J. Opt. Soc. Am. B 26 (2009) 20.
[4] T. Som, B. Karmakar, Spectrochim. Acta, Part A 75 (2010) 640.
[5] L.R.P. Kassab, C.B. de Araújo, in: V.P. Nilsson (Ed.), Photonics Research Developments, Nova Science Publishers, Inc., New York, 2008.
[6] D.M. da Silva, L.R.P. Kassab, S.R. Lüthi, C.B. de Araújo, A.S.L. Gomes, M.J.V. Bell, Appl. Phys. Lett. 90 (2007) 081913.
[7] L.R.P. Kasssab, D.S. da Silva, C.B. de Araújo, J. Appl. Phys. 107 (2010) 113506.
[8] M.J.F. Digonnet (Ed.), Rare-Earth Doped Fiber Lasers, Amplifiers, Marcel Dekker, New York, 1993, and references therein.
[9] See, for instance M. Yamane, Y. Asahara, Glasses for Photonics, Cambridge University Press, Cambridge, UK, 2000.
[10] R. El-Mallawany, A. Patra, C.S. Friend, R. Kapoor, P.N. Prasad, Opt. Mater. 26 (2004) 267.
[11] G. Lakshminarayana, J. Qiu, J. Alloys Compd. 478 (1–2) (2009) 630.
[12] E.D. Palik, Handbook of Optical Constants of Solids, Academic Press, New York, 1985.
[13] M. Letz, U. Peuchert, B. Schreder, K. Senescal, R. Sprengard, J.S. Hayde, J. Noncryst. Solids 351 (2005) 1067.
[14] J. Jakutis, L. Gomes, C.T. Amâncio, L.R.P. Kassab, J.R. Martinelli, N.U. Wetter, Opt. Mater. 22 (2010) 107.
[15] L.R.P. Kassab, F.A. Bonfim Junior, J.R. Martinelli, N.U. Wetter, J. Jakutis Neto, C.B. de Araújo, Appl. Phys. B 94 (2009) 239.
[16] T.A.A. de Assumpção, L.R.P. Kassab, A.S.L. Gomes, C.B. de Araújo, Appl. Phys. B, in press, doi:10.1007/s00340-010-4258-5.