Increasing Er^{3+} Up-Conversion Intensities By Co-Doping Telluride Glasses With Yb^{3+}

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Abstract. This work presents an analysis of Erbium visible up-conversions in TeO_2-GeO_2-PbO glasses codoped with Yb^{3+}. These glasses have low phonon energy (~700 cm^{-1}), high refractive index (~2), large transmission window (350 nm - 6500 nm) and can be easily fibered. As a result we observe an increase of the green and red up-conversion intensities when the concentration of Yb^{3+} increases.

Keywords: Spectroscopy, Laser, Rare earth, Telluride Glasses.

INTRODUCTION

Erbium doped materials have been used in many optical fields, such as active media in solid state lasers and photonic and communication devices, due to their visible and infrared emission lines. One of the absorption lines of Er^{3+} is around 980 nm; laser diodes have been developed at 980 nm and nowadays can achieve high powers with low costs.

Since the spectral region of the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ (~980 nm) transition of the Yb^{3+} ion overlaps that of the $^4I_{15/2} \rightarrow {}^4I_{11/2}$ transition of the Er^{3+} ion, it becomes possible to achieve an effective Yb^{3+} to Er^{3+} transfer mechanism for the excitation energy [1], which increases the absorption of the pump wavelength due to higher absorption cross section at 980 nm in Yb^{3+} when compared to Er^{3+}.

Telluride hosts are excellent for rare earths ions, because they present low phonon energy (~700 cm^{-1}) that increases the fluorescence efficiency, high refractive index (~2) adequate for non linear effects (second harmonic generation), large transmission window (350 nm - 6500 nm), suitable for hosting several rare earth ions and can be easily fibered. Fluoride hosts have been used for developing infrared diode-laser pumped solid state up-conversion lasers, due to their lower phonon energy. An efficient, 800 nm diode-pumped up-conversion laser at 540 nm has been realized and has shown a higher efficiency than harmonic generation techniques [2]. However oxides are much more appropriate as host materials for practical applications because they are easy to fabricate, have high mechanical resistance, high chemical durability and thermal stability.

This work reports the up-conversion emissions of Er^{3+} in a co-doped (Er^{3+}/Yb^{3+}) telluride host, TeO_2-GeO_2-PbO (T1), under the excitation of a 960 nm diode laser at room temperature; the influence of the Yb^{3+} concentration on the visible emissions is reported.

EXPERIMENTAL SETUP

The telluride glasses were prepared adding 0.5 wt% of Er_2O_3 and different concentrations of Yb_2O_3 (1 to 5 wt%, in steps of 1 wt%), to the host composition TeO_2-GeO_2-PbO (T1). Next, this mixture of powders (high purity, 99.999%) was melted in a pure platinum crucible at 1050 ºC, during one hour and then quenched in a heated brass mold, in air, and annealed at 350 ºC for one hour. Finally the glasses were cooled to room temperature inside the furnace.

CP992, *RIAO/OPTILAS 2007*, edited by N. U. Wetter and J. Frejlich
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After cooling, the samples were polished to acquire an optical surface quality for absorption and emission measurements. The luminescence was obtained with 3 W of pulsed (50 % duty cycle) diode laser excitation at 960 nm, dispersed by a monochromator and collected by a S-20 photomultiplier. All measurements were made at room temperature.

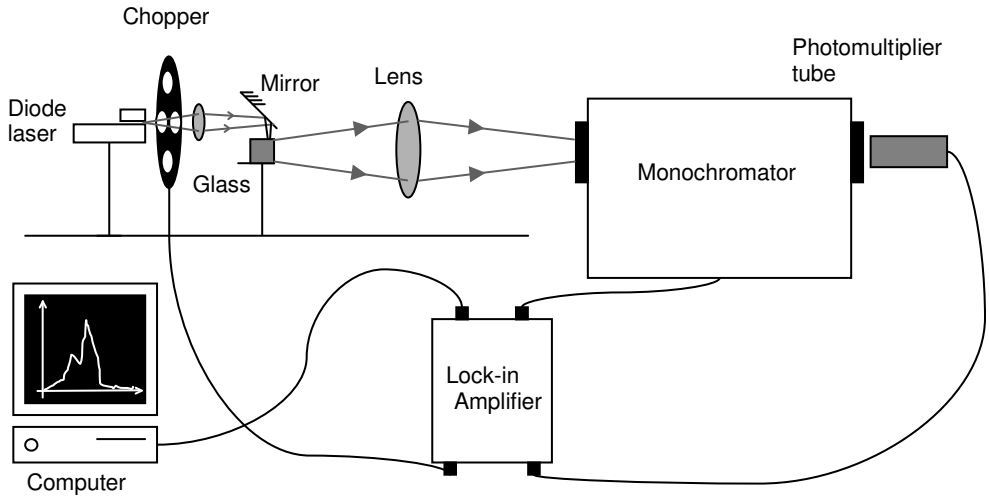

FIGURE 1. System for emission measurements.

RESULTS AND DISCUSSIONS

We measured the five co-doped glasses and one doped solely with Er^{3+}. As a result, the increase of the Yb^{3+} concentration causes an enhancement of the up-conversion emissions in the visible region as shown in Figure 2.

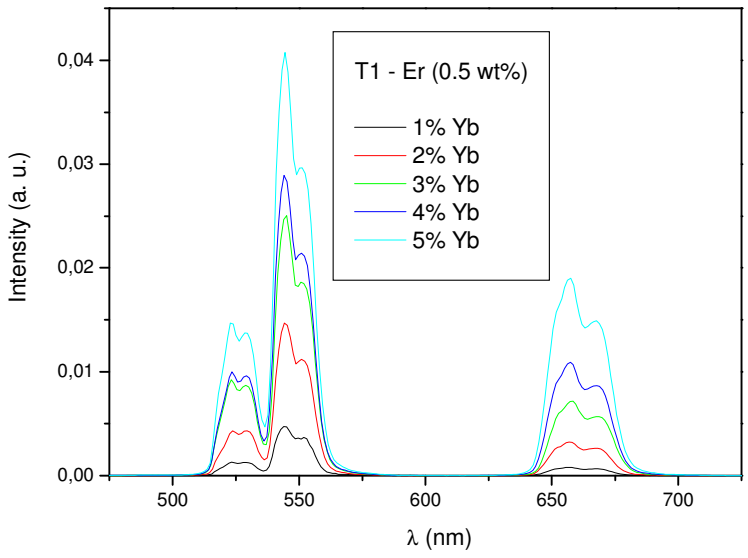

FIGURE 2. Up-conversion emissions in the green and red of Er^{3+}-Yb^{3+} co-doped T1 as a function of the Yb^{3+} concentration.

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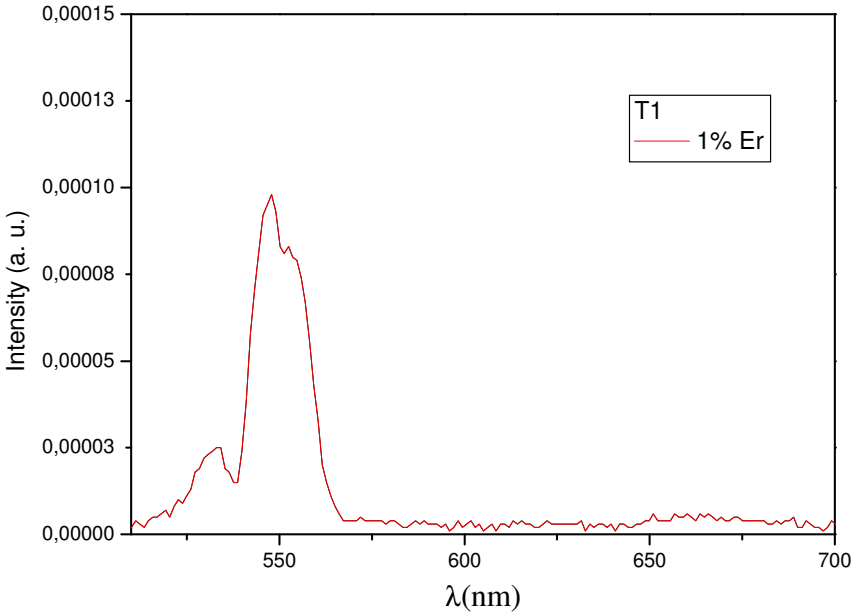

FIGURE 3. Up-conversion emission of singly Er^{3+} doped T1.

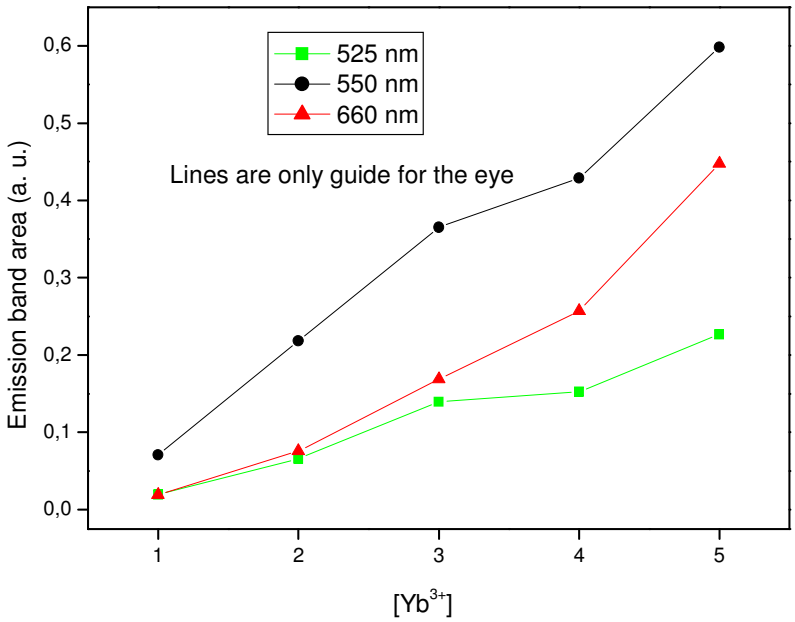

FIGURE 4. Integrated emission for the three up-conversions as a function of the Yb^{3+} concentration.

Comparing figures 2 and 3 we observe that the up conversion emission is 400 times higher for 5% of Yb^{3+} (same scale is used for both figures). The up-conversion emission behaviors are shown in Figure 4, which show the area of beneath the emission curves as a function of Yb^{3+} concentration. When comparing the area of the red (660 nm) and the green (550 nm) emission band, it is seen that the slope of the red emission increases faster with higher concentrations of Yb^{3+}, as shown in Figure 5. A similar behavior was observed for germanate glasses [3].

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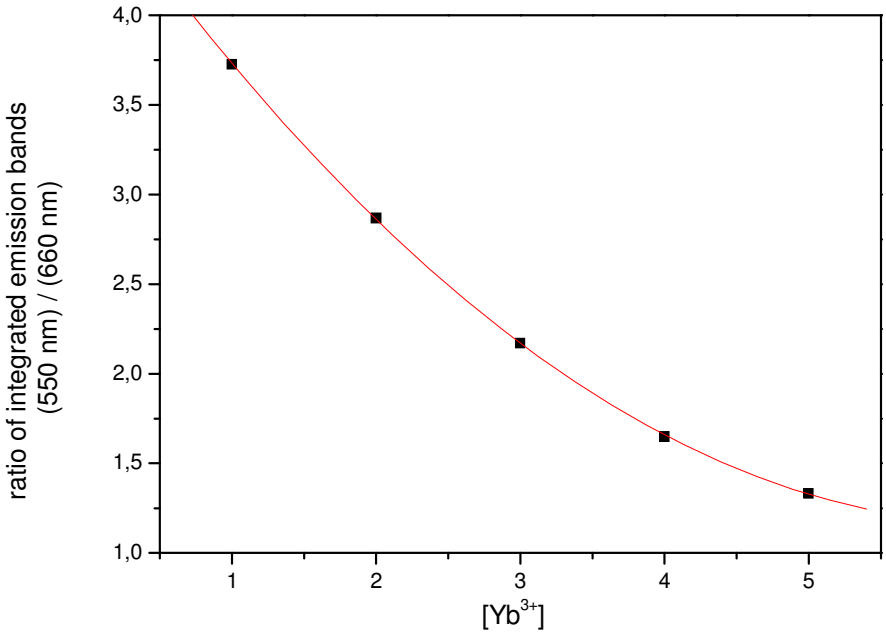

FIGURE 5. Ratio between the integrated emissions at 550 nm and 660 nm as a function of Yb^{3+} concentration.

Figure 6 presents the intensity of the 550 nm emission as a function of the pump power, in log scale. The slope of these curves indicates the number of photons that participate in the absorption process. In all the cases the slope is around 2, indicating that two photons are present in the process; non radiative processes may participate in some cases and contribute for the decrease of the slope to 1.5. The same was observed for the 660 nm emission shown in Figure 7.

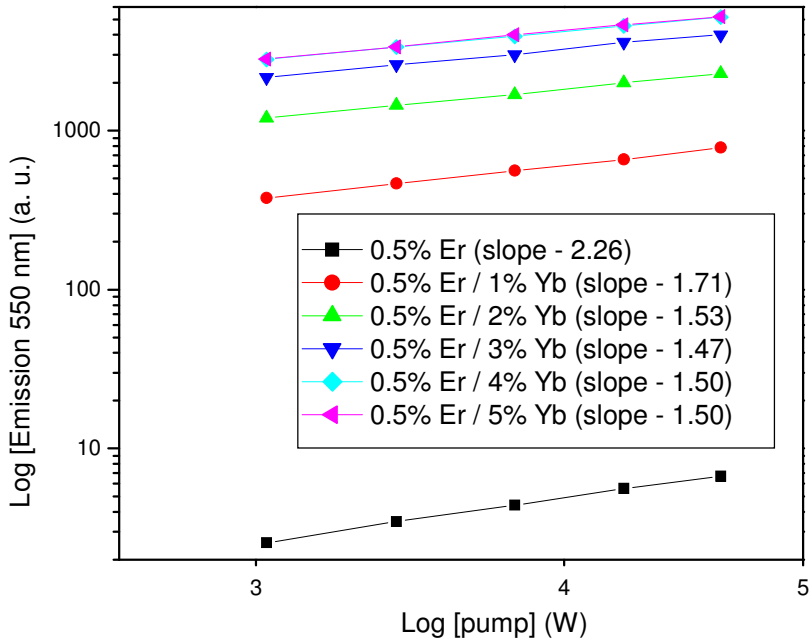

FIGURE 6. Emission intensity (at 550 nm) as a function of the pump power.

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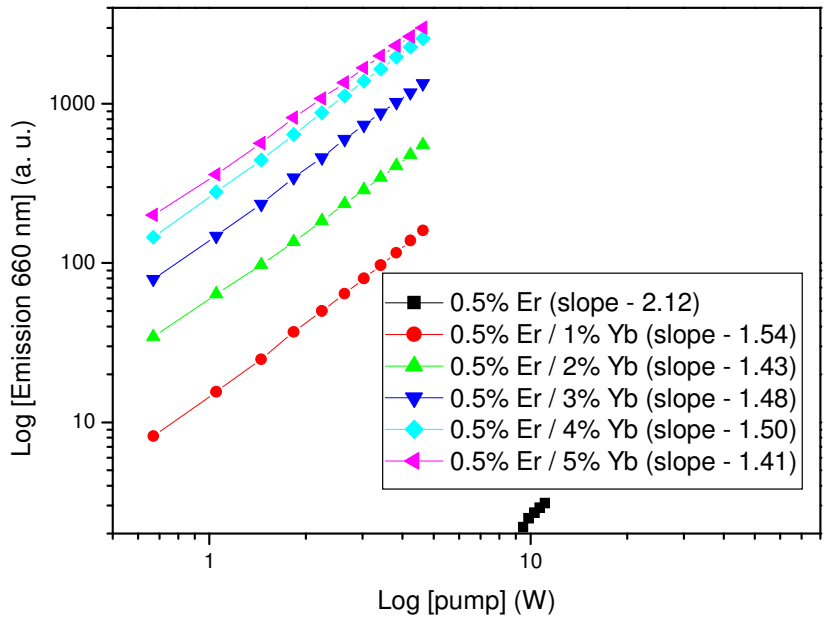

FIGURE 7. Emission intensity as a function of the pump power (at 660 nm).

The up-conversion processes involve a sequential two-photon absorption for the red and green emissions [4] (other hosts could present a three-photon up-conversion) using the energy transferred from Yb^{3+} to Er^{3+}. In sequence, three radiation transitions occur, emitting red and green photons: $^4H_{11/2} \rightarrow {}^4I_{15/2}$ (525 nm), $^4S_{3/2} \rightarrow {}^4I_{15/2}$ (550 nm) and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ (660 nm). These processes are shown in Figure 8.

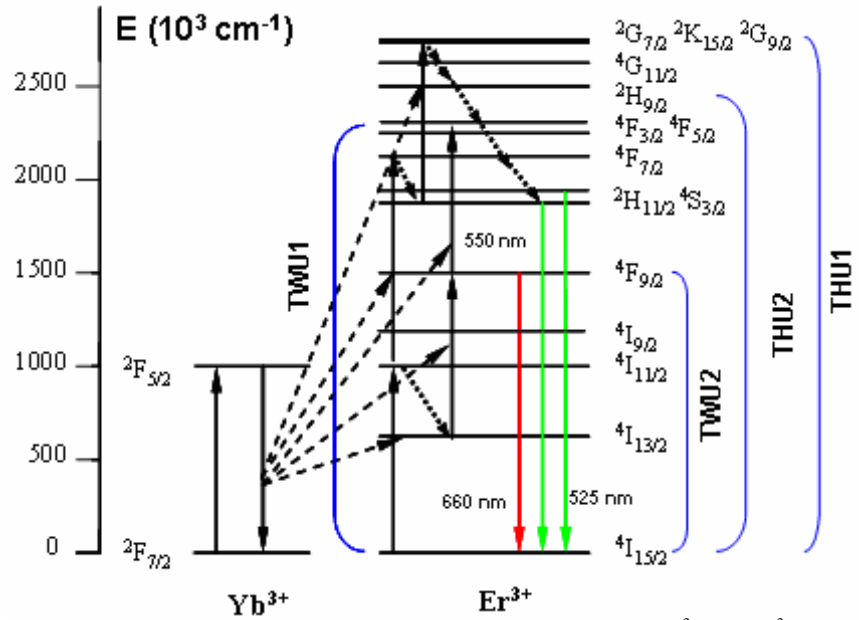

FIGURE 8. Energy level scheme of a co-doped system with Er^{3+} and Yb^{3+}.

In this system, energy transfer from Yb^{3+} to Er^{3+} occurs. More specifically, this exchange is due to a spectral overlap between the transitions $^2F_{7/2} \rightarrow {}^2F_{5/2}$ of Yb^{3+} with $^4I_{15/2} \rightarrow {}^4I_{11/2}$ of Er^{3+}. This kind of interaction can occur for other levels, too. There are many possible energy transfer mechanisms from Er^{3+} to Yb^{3+}, but just some of them do

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happen frequently. TWU1 (two photon up-conversion 1) and TWU2 (two photon up-conversion 2) are the most probable mechanisms to occur. In figure 8, THU1 and THU2 represent three photon up-conversions.

The experimental evidence of the enhancement of the red emission when compared to the green could be explained considering the population of the $^4F_{9/2}$ level via an additional transfer channel, TWU2, shown in Figure 8. This non-resonant mechanism involves the interaction between the Yb^{3+} excited state and the first Er^{3+} excited multiplet: $^2F_{5/2} \rightarrow {}^2F_{7/2}$ (Yb^{3+}): $^4I_{13/2} \rightarrow {}^4F_{9/2}$ (Er^{3+}). The energy mismatch of this process is around 1000 cm^{-1} [5] and it has been previously reported to occur in Er^{3+}-Yb^{3+} co-doped phosphate glasses [6] and in oxyfluoride glasses [7]. This additional mechanism provides simultaneously a direct path of population for the $^4F_{9/2}$ level. This result possibly indicates that the quantities of Er^{3+} ions in $^4I_{11/2}$ level that relax non-radiatively to the lower $^4I_{13/2}$ level are much greater than those excited to the upper $^4F_{7/2}$ level. In other words it possibly results from the longer lifetime of $^4I_{13/2}$ level that makes non-radiative relaxation $^4I_{11/2} \rightarrow {}^4I_{13/2}$ more easily to arise.

CONCLUSIONS

The enhancement of Er^{3+} visible up-conversion in telluride glasses in the presence of Yb^{3+} ions is reported; for 5% of Yb^{3+} this increase is 400 times. The red emissions respond better than the green ones with the increase of the Yb^{3+} concentration; power dependent studies reveal that both green and red emissions result from two-photon processes. This glass proved to be an excellent option for optical applications, like active media, photonic devices and for infrared sensors in general.

ACKNOWLEDGMENTS

The authors thank Fundação de Amparo a Pesquisa de São Paulo (FAPESP) and CNPq.

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