Study of red up-conversion mechanism in Er^{3+}/Yb^{3+} co-doped Germanate glasses

J. Jakutis and N. U. Wetter

Centro de Lasers e Aplicações, IPEN – São Paulo, SP

jjneto@ipen.br ; nuwetter@ipen.br

L. R. P. Kassab and F. A. Bonfim

Laboratório de Vidros e Datação, FATEC-SP – São Paulo, SP

Abstract

This paper presents a study of the up-conversions (525, 550 and 660 nm) of Er^{3+} co-doped with Yb^{3+} in a germanate host, GeO_2-PbO-Ga_2O_3. Lower phonon energy (~700 cm^{-1}), high refractive index (~2) and large transmission window (400 nm - 4500 nm) were some characteristics of this glass. As a result we observe an increase of the erbium transition $^4F_{9/2} \rightarrow {}^4I_{15/2}$ (660 nm) with higher Yb^{3+} concentration in the host.

Introduction

Er^{3+}doped glasses have attracted much interest due to their important optical properties for use in lasers, photonic devices and other communications devices. When 980 nm laser diodes were developed, these interests were stimulated, from the application point of view, since Mears *et al*.[1] reported the operation of the Er-doped fiber amplifier pumped at 980 nm.

Since the spectral region of the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ 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 to Er transfer mechanism of the excitation energy[2].

In addition, the up-conversion luminescence from Er^{3+} doped glass has attracted attention for the purpose of developing infrared laser pumped solid state up-conversion lasers [3]. An efficient up-conversion laser at 540 nm when pumped with a laser diode at 800 nm has been realized and has shown a higher efficiency than harmonic generation techniques[4]. Hosts based on fluoride systems have been used for this purpose due to its lower phonon energy. However oxides are much more appropriate as host materials for practical applications because they are easy to fabricate, and have high mechanical resistance, high chemical durability, and thermal stability.

This work reports the up-conversion emissions of Er^{3+} and Yb^{3+} ions co-doped germanate glass, GeO_2-PbO-Ga_2O_3 (GPG), under the excitation of a 980 nm diode laser at room temperature and the influence of the Yb^{3+} concentration on the visible red emission.

Experimental Setup

The germanate glasses were prepared adding 0.5 wt% of Er_2O_3 and different concentrations of Yb_2O_3 (1 to 5 wt%), with the host composition 17.0GeO_2 – 72.8PbO -10.2Ga_2O_3 (weight %); next, this mixture of powders (high purity, 99.999%) was melted in a pure platinum crucible at 1200 ºC, during one hour and then quenched in a heated brass molds, in air, and annealed at 392 ºC for one hour. Finally the glasses were cooled to room temperature inside the furnace.

After cooling, the samples were polished to acquire an optical quality surface for absorption and emission measurements. The luminescence was obtained with 7 W of pulsed (50 % duty cycle) diode laser excitation at 980nm, dispersed by a monochromator and collected by a S-20 photomultiplier. All measurements were made at room temperature.

Results and Discussions

The co-doped samples increases the population efficiency of the $^4I_{11/2}$ (Er^{3+}) level , due to the fact that the Yb^{3+} cross section is higher than the one of Er^{3+} and an efficient energy transfer mechanism $Yb^{3+} \rightarrow Er^{3+}$ enables the increase of the visible and infrared emitting level population.

As a result, we measure the up-conversion emissions of the five glasses described above and we compare them at 550 nm normalized spectra together. This gives us the relations of green to red emission for each of the glasses. The spectra are shown in figure 1 below.

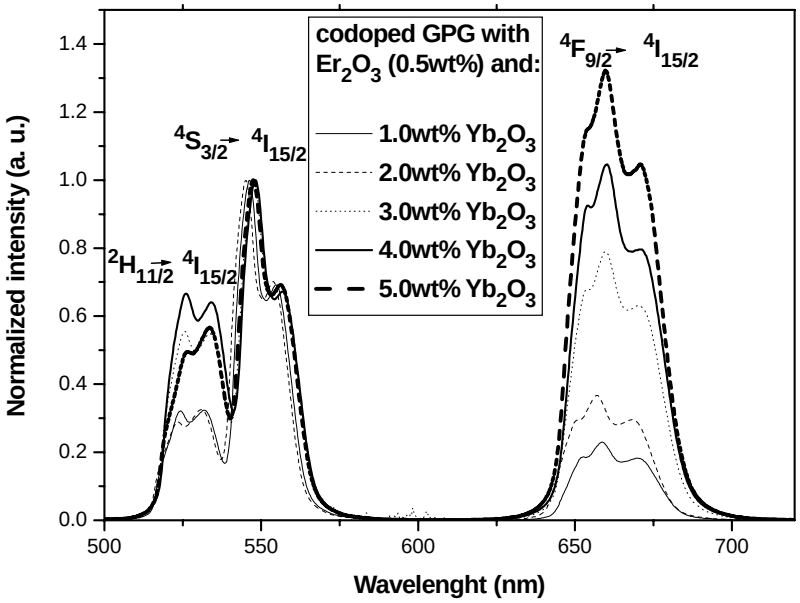

Figure 1: Up-conversion emission spectra of the five glasses.

We observe an increase of the red emission around 660 nm, proportionally to the increase of the Yb^{3+} concentration. For 4.0 wt% of Yb_2O_3 we already achieve a higher peak emission of the red emission band when compared to the green emission. Through the area of the red band we can show a linear correspondence between the concentration and the intensity of this emission.

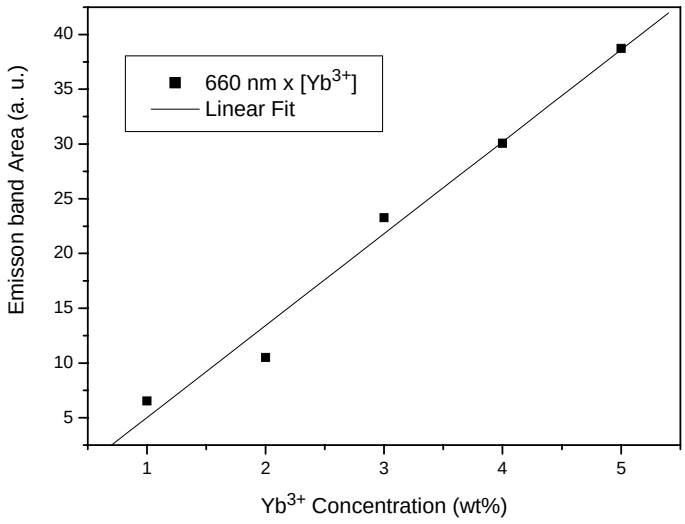

Figure 2: Linear behavior of the red emission as a function of Yb^{3+} concentration.

The up-conversion processes involve a sequential two-photon absorption for the red and green emissions (for germanate glasses [5], 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 3.

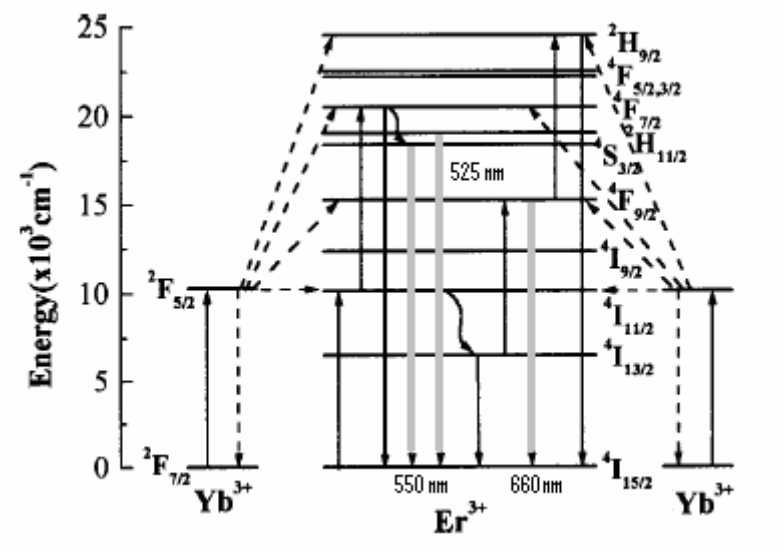

Figure 3: Energy level scheme of a co-doped system with Er^{3+}/Yb^{3+} [6].

The increase in the relative red emission intensity compared to the green emission indicates an independent channel of population of the $^4F_{9/2}$ multiplet.

This experimental evidence could be explained considering the population of the $^4F_{9/2}$ level via an additional transfer channel, shown in figure 4. 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 of around 1000 cm^{-1} [7], and it has been previously reported to occur in Er^{3+}/Yb^{3+} co-doped phosphate glasses [8]. This additional mechanism provides simultaneously a direct path of population for the $^4F_{9/2}$ level. Besides, a lengthening of its lifetime occur due to the involvement of the long-lived $^4I_{13/2}$ erbium metastable level and it is another way to prove this phenomenon ($\tau_{exp} \approx 3ms$[9]).

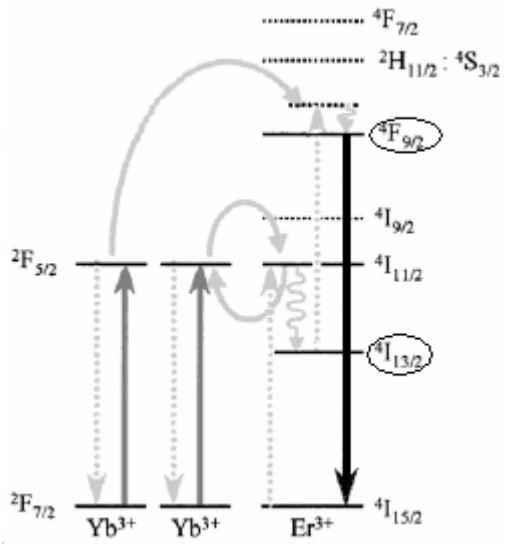

Figure 4: A model proposed to explain the mechanism of the red up-conversion emission [7].

Conclusions

We present in this work a Er^{3+}/Yb^{3+}co-doped germanate glass system which has lower phonon energy (~700 cm^{-1}), high refractive index (~2) and a large transmission window (400 nm - 4500 nm). The main characteristic is the capacity of increasing the red emission compared to the green emission, through an increase of the Yb^{3+} concentration. This effect expands the applications of this glass to other developments in photonic devices, like i.g. the study of red up-conversion lasers.

Acknowledgements
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