

Investigation of blue emission in Tm:Yb and Tm:Nd germanate glasses

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Abstract

Infrared-to-visible upconversion (UPC) of GeO₂-PbO glasses codoped with Tm:Yb, and Tm:Nd were investigated. Absorption spectra of the samples confirmed the presence of the rare-earth ions in trivalent form. Strong blue emission (480nm) was observed in Tm:Yb samples pumped with a high power cw diode laser of 960nm. The upconversion mechanism was due to the excited state absorption of three photons. When pumped with a diode laser of 792nm, Tm:Nd glasses also presented 480nm emission, but with lower intensity.

Introduction

The upconversion (UPC) process in solid state materials doped with rare earth ions has been investigated for many applications. The main applications in the last years have been chemical sensors, high density optical data storage, biomedicine, solid state lasers, color displays and optical communications. Thulium doped glasses have been largely studied due to its blue emission, that can be used in the fabrication of blue lasers, color displays and chemical sensors [1].

Germanate glasses are good candidates for these applications, since they have a large transmission window (400 – 4500 nm), low phonon energy ($\sim 700\text{ cm}^{-1}$) and high refractive index (~ 2.0). Besides germanate glasses have been used for the nucleation of metallic nanoparticles [2] and for the deposition of thin films using the sputtering technique. For these films high nonlinear refractive index have been measured in the picosecond and femtosecond regimes [3-4]. Ytterbium and Neodimium are good energy

donators and in this work the main interest is related to the increase of the blue emission from Tm^{3+} ions. Through the study of Tm^{3+} , Yb^{3+} and Nd^{3+} energy levels we could determine the correct wavelength to pump the samples and the processes of energy transfer.

In Tm:Yb codoped samples, the process to obtain blue emission occurs through the energy transfer between Yb^{3+} and Tm^{3+} when Tm^{3+} absorbs three fotons of same the energy from Yb^{3+} ions excited at 960 nm, as seem in Figure 1; then the energy absorbed is emitted in a single foton, with higher energy and minor wavelength (UPC process). In Tm:Nd codoped samples, both ions are excited at 792 nm; then the excited Tm^{3+} ion absorbs one of the probable fotons that can be emitted from Nd^{3+} , as seem in Figure 2. Then the UPC process occurs but in this case with the absorption of two fotons of different energies.

Experimental and Results

The samples were prepared using the following composition: 41GeO₂ – 59PbO (%mol). The codoped glasses were prepared with Tm₂O₃ (0.5 wt%), Yb₂O₃ (2.0 and 3.0 wt%) and Nd₂O₃ (1.0 and 2.0 wt%). The reagents were melted in an alumina crucible, for 1h at 1100 °C, quenched in a preheated brass mold, and annealed at 420 °C for 1h to reduce internal stress. After polishing, absorption spectra of the samples were obtained to verify the incorporation of the rare earth ions in the trivalent form; the emission measurements were performed to verify the intensity of the blue emitted light.

The absorption spectra showed absorption bands related to the transitions of Tm^{3+} , Yb^{3+} and Nd^{3+} . The emission spectra of Tm:Yb codoped glasses were obtained using a 960 nm high power cw diode laser; a strong blue emission centered in 480nm due to the UPC of Tm^{3+} was observed. For Tm:Nd glasses the same blue emissions were observed by pumping the samples with a high power cw diode laser at 792 nm, but with lower intensity. The energy transfer processes, for both cases, are shown in Figures 1 and 2 and the emission spectra are presented in Figure 3.

Conclusion

Infrared-to-visible upconversion of GeO₂-PbO glasses codoped with Tm:Yb, and Tm:Nd were investigated. The Tm:Yb codoped samples showed stronger blue emission than the Tm:Nd codoped samples. Nd^{3+} ion has many probables transitions when excited with 792 nm, so the resulting energy transfered to Tm^{3+} ions is lower than the one related to the Tm:Yb codoped samples. So germanate glasses codoped with Tm:Yb are adequate hosts for technological applications with blue emission.

Acknowledgement

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Figures

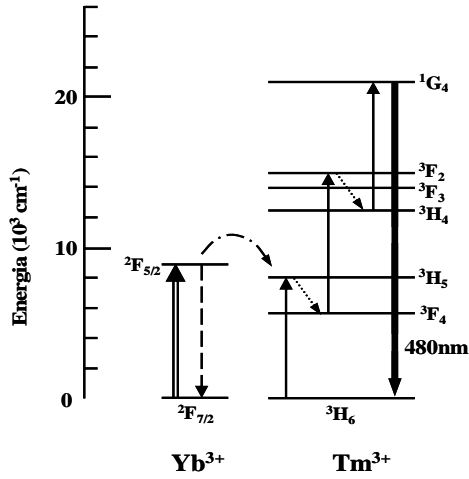


Figure 1 – Simplified energy-level diagram for Yb^{3+} and Tm^{3+} . Double-arrow stands for 960 nm pumping and thicker arrow stands for the UPC emission.

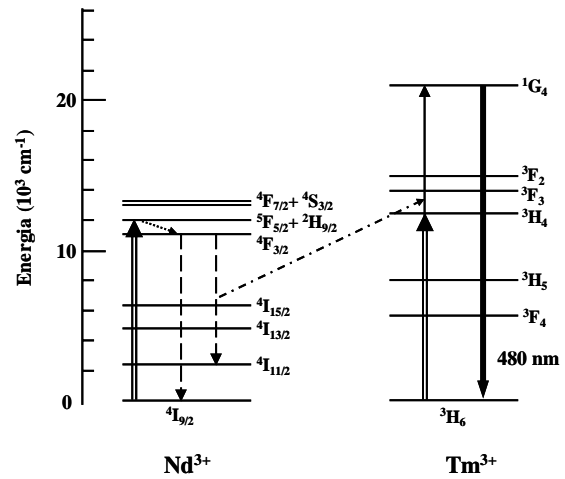


Figure 2 – Simplified energy-level diagram for Nd^{3+} and Tm^{3+} . Double-arrow stands for 792 nm pumping and thicker arrow stands for the UPC emission.

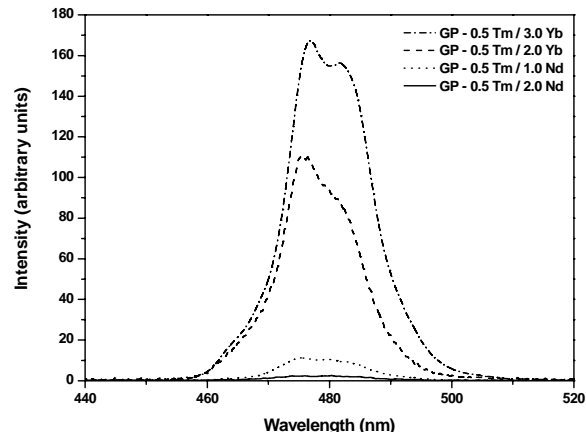


Figure 3 – UPC emission spectra of $\text{Tm}:\text{Yb}$ and $\text{Tm}:\text{Nd}$ germanate glasses. The feature corresponds to the ${}^1\text{G}_4 \rightarrow {}^3\text{H}_6$ transition.

References

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