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## Energy transfer mechanism of titanium to rare earth ions in $Y_2O_3$

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### Abstract

In this work, Ti, Eu and EuTi doped  $Y_2O_3$  luminescent nanoparticles were synthesized through the proteic sol-gel method. X-ray powder diffraction (XRD) showed the only  $Y_2O_3$  single crystal phase. Transmission electron microscopy (TEM) showed that the samples presented high crystallinity degree, and some families of  $Y_2O_3$  crystallographic planes were identified. The Ti valence was investigated through X-ray absorption near edge spectroscopy (XANES) and it was stabilized in a mix of valences between  $Ti^{3+}$  and  $Ti^{IV}$ . The  $Ti^{IV}$  was the most observed oxidizing state in samples, mainly in the EuTi doped  $Y_2O_3$ . It occurs due to the affinity of  $Y_2O_3$  which it is an oxide (hard base) with  $Ti^{IV}$ , a hard acid. Doped yttrium oxide optical behavior was investigated through X-ray excited optical luminescence (XEOL) and photoluminescence (PL) under UV-Vis and vacuum ultraviolet (VUV) excitation. The results indicated the  $Eu^{3+}$  is the main emitter center in samples doped with Eu and EuTi and the  $^5D_0 \rightarrow ^7F_2$  transition—maximum emission at 612 nm—was the most intense peak observed in the emission spectra of Eu and EuTi doped samples. The Ti-doped samples exhibited a broadband with maximum around 520 nm. It might correspond the  $Ti^{3+}$  characteristic emission but since in both cases, there is a large amount of  $Ti^{IV}$  in the samples it can also be due to the ligand to metal charge transfer transition  $O(2p) \rightarrow Ti^{IV}$ . Finally, in the EuTi-doped  $Y_2O_3$  system,  $Ti^{3+}$  (or  $Ti^{IV}$ ) excitation was observed but no Ti emission was present, indicating an energy transfer process from Ti to Eu via charge transfer band (CTB) to the  $Eu^{3+}$ . These results present the unprecedented Ti to Eu energy transfer in Yttrium Oxide host, aiding the development of new efficient materials.

### Key words:

nanoparticles, energy transfer, titanium.

### Introduction

Persistent luminescent nanoparticles have been used to develop bioimaging methods to observe specific biological tissues. The region of emission of materials, which must occur in the region between 600 and 900 nm, where there is a window of transparency in biological tissues. Another feature is the luminescence time decay that may allow the observation of a functionalized nanoparticle follow in the biological tissue [1].

In this work, we have proposed the synthesis and the study of the structural, morphological and optical properties of  $Y_2O_3$  doped with Eu and Ti and the main goal is to obtain nanoparticles with emission in the near infrared red region and persistent luminescence decay for bio applications and describing their luminescence mechanisms under visible, UV and X-rays excitation.

### Results and Discussion

The samples were produced via proteic sol-gel method and they were calcined at 1000°C under reducing and static air atmospheres. The XRD results showed in all cases it was formed only the  $Y_2O_3$  crystalline phase. The TEM revealed samples nanostructured with average size of ~60nm. XANES results around the Ti K edge suggest a mix of  $Ti^{3+}$  and IV valences in all preparations. In the EuTi-doped  $Y_2O_3$ , the XANES showed the Ti is more than 85%  $Ti^{IV}$ , and it probably occurs due the chemical affinity between a hard base, the host, and a hard acid, the Ti IV. Optical properties were investigated through PL UV-Vis, PL VUV and XEOL and the results indicated the main optical center in Eu and EuTi doped samples is the  $Eu^{3+}$ . The Ti-doped  $Y_2O_3$  presented a typical  $Ti^{3+}$  emission. The

PL UV-Vis excitation spectra showed that even the Ti emission is not observed in the EuTi emission spectra, there is a Ti CTB that transfers energy to the Eu optical center and it favors the Eu emission and the persistent decay. Ti is mainly in the Ti IV form in all samples and it does not present optical activity due to its electronic structure, however the observed  $Ti^{3+}$  emission in Ti-doped  $Y_2O_3$  may be a consequence of an energy transfer mechanism based on the Ti charge transfer band from  $O^{2-} Ti^{IV} \rightarrow O^- Ti^{3+}$ [2,3]. It also may come the 3d-3d  $Ti^{3+}$  transitions or both mechanisms. The  $Y_2O_3$  optical band gap was also mapped and it is around 5.8 eV and the general optical behavior under and above the gap was similar.

### Conclusions

Eu, Ti and EuTi doped  $Y_2O_3$  were successfully produced and their optical morphological and optical characteristics reveal potential materials for bioimaging applications. In this specific discussion, a mechanism of energy transfer between a 3d ion,  $Ti^{IV}$  and rare earth,  $Eu^{3+}$ , was presented and the luminescence mechanism of this set under UV-Vis, VUV and X-rays irradiation was discussed.

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