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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 PL 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 $^5\text{D}_0 \rightarrow ^7\text{F}_2$ 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 $\text{O}(2p) \rightarrow \text{Ti}^{IV}$. 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 $\text{O}^{2-} \text{Ti}^{IV} \rightarrow \text{O}^- \text{Ti}^{3+}$ [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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