



ICAM2009

11<sup>th</sup> International Conference  
on Advanced Materials

Rio de Janeiro Brazil  
September 20 - 25

## Study of structural, optical properties and the Eu<sup>3+</sup> site distribution in Eu<sup>3+</sup>-doped BaWO<sub>4</sub> nanoparticles prepared by a wet chemical route

J. H. S. Romero<sup>(1)</sup>, G. Gasparotto<sup>(2)</sup>, H. H. S. Oliveira<sup>(1)</sup>, M. A. Cebim<sup>(1)</sup> and M. R. Davolos<sup>(1)\*</sup>

(1) UNESP - São Paulo State University, Institute of Chemistry, Luminescent Materials Laboratory, Araraquara, Brazil.

(2) UNESP - São Paulo State University, Institute of Chemistry, LIEC, Araraquara, Brazil.

\* davolos@iq.unesp.br

**Abstract** – BaWO<sub>4</sub> and Eu<sup>3+</sup>-doped BaWO<sub>4</sub> are compounds with potential application in the scintillation area and Eu<sup>3+</sup> ions also act as a spectroscopic probe for structural investigation in the materials. In this work, it is investigated the structural and spectroscopic properties of pure and Eu<sup>3+</sup>-doped BaWO<sub>4</sub> nanoparticles obtained by the Pechini method. The crystalline single-phase BaWO<sub>4</sub> was obtained at 700, 900 and 1100°C. It was shown by the spectroscopic data that Eu<sup>3+</sup> are distributed in two types of sites and the Eu<sup>3+</sup> distribution in the sites are highly dependent on its concentration and the firing temperature.

The use of nanoparticles in scintillator devices have gained crescent attention in the last years, which is being accompanied by the interest in the understanding of scintillation mechanism and the determination of specific values of its efficiency in such structures [1]. In general, as crystals and ceramics are traditionally used in these devices, the nanoparticles introduce new possibilities in the development of hybrid (organic-inorganic) or in thin films-based detectors [2]. Since the dopant gives rise to suitable spectroscopic properties to this kind of scintillator material, the dopant distribution into nanoparticle sites plays a major role in the development of nanoparticles-based devices. In this way, using the well-know probe features of Eu<sup>3+</sup> as a dopant, the aim of the present work is the study of structure and optical properties, as well as the determination of Eu<sup>3+</sup> site distribution in Eu<sup>3+</sup>-doped BaWO<sub>4</sub> prepared by the Pechini method. This method allows the preparation of crystalline nanoparticles with relatively low firing temperatures. BaWO<sub>4</sub> and Eu<sup>3+</sup>-doped BaWO<sub>4</sub> (1.0, 3.0 and 5.0 at-%) were successfully prepared at three firing temperatures: 700, 900 and 1100°C. In accordance to the XRD data, the fully crystalline single-phase BaWO<sub>4</sub> was obtained at 700°C. The FT-IR profile spectra exhibit strong bands in 400-1000 cm<sup>-1</sup> range which are attributed to metal-oxygen vibrations of WO<sub>4</sub><sup>2-</sup> group and weak bands related the residual organic matter on the particles surface. The band gap energy of the compounds was calculated by diffuse reflectance measurements and is 3.3 eV for pure BaWO<sub>4</sub> and has higher values for doped samples, due to defects caused by the presence of Eu<sup>3+</sup> ions in the host. A probable cause for the diminution of the bandgap in doped samples is the decrease of the mean particle size diameter, which reflects the influence of the dopant in the formation of the particle. In relation to luminescence spectroscopy data, two emission spectra were observed for the samples fired at 900°C (also at 1100°C), that is, (i) when the excitation is fixed in the tungstate group (275-300 nm) and (ii) when the excitation is fixed directly in the Eu<sup>3+</sup> ion (394 nm). In the first case (i), the emission is related to Eu<sup>3+</sup> ions occupying a high symmetric site, since the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>1</sub> (0-1) transition, centered at 584 nm, have a higher intensity than the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> (0-2) transition, centered at 614 nm, and the (0-2)/(0-1) intensity ratio vary in the range 0.4-0.6. In the second case (ii), the 0-2 transition is more intense than the 0-1 transition, the ratio (0-2)/(0-1) is ~2, and this can be explained by the occupation of Eu<sup>3+</sup> ions in at least one site with low symmetry. Independently of the Eu<sup>3+</sup> amount, in the samples fired at 900 and 1100°C, Eu<sup>3+</sup> emissions always prevails. On the other hand, the samples fired at 700°C present emissions (excitation fixed in the range 275-300 nm) related to both the Eu<sup>3+</sup> ion and the tungstate group (centered at 500 nm). These emission spectra have a low intensity and the Eu<sup>3+</sup> spectral profile also indicates the occupation of a site with low symmetry. In relation to excitation spectra, the emission was fixed in Eu<sup>3+</sup> (584 and 614 nm), and bands related to the Eu<sup>3+</sup> ion and the tungstate group were observed. These two types of bands have a comparable intensity when the dopant amount is 3 at-% and the firing temperature is 900°C. Furthermore, the Eu<sup>3+</sup>-O<sup>2-</sup> charge transfer band is centered below 270 nm and is partially overlapped with the excitation band of the tungstate group. Finally, after the gathering of structural and spectroscopic data, it was possible to describe essential optical characteristics of the pure and Eu<sup>3+</sup>-doped BaWO<sub>4</sub>, along with the site distribution of Eu<sup>3+</sup> ions, which are important properties for the assembly of nanoparticles-based scintillation detectors.

### References

- [1] S. Galkin, et al. Nano-size effect in the semiconductor scintillators, In: Proceedings of the International Conference on Inorganic Scintillators and Their Applications, 2009, paper LBNL-T13-3.
- [2] A. Peurrung. Materials Today, 11 (2008) 50-54.