

Rio de Janeiro Brazil September 20 - 25

Synthesis and Structural Characterization of Nanostructured Zn₇Sb₂O₁₂ Semiconductor doped with Eu(III) (1- 5%)

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Abstract –This work reports on XRD, FTIR and PL studies of $Zn_7Sb_2O_{12}$ doped with 1-5% of Eu(III) prepared from Pechini's method in order to investigate the influency of Eu(III) in the lattice local symmetry. XRD data ensured the spinel inverse phase formation and both spectroscopic techniques employed indicated that Eu(III) cause a slight distortion of local lattice symmetry, preferentially in [SbO₆] sites, but also occupying other available places in the open structure.

The oxide of some rare-earth (RE) elements, as well known, are considered excellent host lattices for trivalent activators ions, displaying luminescent properties [1]. The spectral lines of Eu(III) in general are narrow ones and sensible to the crystalline field around the metallic ions, due to spin-orbital coupling. This fact allow to use Eu(III) as a doping ion in order to investigate the local symmetry and geometry acting as a structural probe. [2]. The matrix used in this work is the semiconductor Zn₇Sb₂O₁₂ with inverse spinel structure, that has been mainly studied due to its electrical properties as temperature sensor [3]. Therefore, this semiconductor was doped with 1-5% of Eu(III) in order to verify its availability to be applied as luminescent material as well as to use such RE as structural probe. Samples of this semiconductor, with or without Eu(III) content, were prepared by Pechini's method and heated to 1020°C in air atmosphere. Photoluminescent spectroscopy (PL), FTIR and X-ray Diffraction (XRD) and Transmission Electron Microscopy (TEM) techniques were used to monitor the influence of Eu(III) in the lattice local symmetry. TEM results showed that particle size varies from 40 to 100 nm. XRD data certified the desired phase formation, whereas in Fig. 1 it can be viewed a representative sample. Fig. 2 shows the FTIR spectra of other representative sample, and it is possible to observe that after heating the excess of organic matter from polymeric resin was completely eliminated. The detailed comparison among the IR absorption band assigned to [SbO₆] group observed in the FTIR spectra of all samples suggests that the inclusion of Eu(III) in the Zn₇Sb₂O₁₂ lattice leads to a slight local distortion. In Fig. 3 it is shown the excitation spectra of the sample that presented the higher relative emission intensity, i.e., the one doped with 4% of Eu(III). The differences in the spectral features under different emission positions suggest that must be occurring an occupation of Eu(III) in different symmetry sites. From emission spectra analysis, the systematic detection of all set of Eu(III) transitions confirms that there must be an occupation of sites with low symmetry in the semiconductor crystalline structure, whereas considering FTIR discussion, the [SbO₆] site could be the preferential one.



Figure 1: XRD pattern of $Zn_7Sb_2O_{12}$: Eu(2%).

Figure 2: FTIR spectra of $Zn_7Sb_2O_{12}$:Eu(1%) before and after heating at 1020°C.

Figure 3: Room temperature excitation spectra of $Zn_7Sb_2O_{12}$:Eu(4%) with different emission positions (612, 596 and 627 nm).

References

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