

Luminescent study of SnO₂:Eu³⁺ nanopowders prepared by Pechini method

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Abstract – Nanopowders of SnO₂:Eu³⁺ are prepared by Pechini method. X-ray diffraction and infrared spectroscopy are used to characterize the material. The results show that Eu³⁺ ions induce lower crystallite sizes and promote basicity of the surface. Photoluminescent properties are studied based on 4f⁶-intraconfigurational transitions, showing the existence of two types of local environments around Eu³⁺ ion.

There is an advantage of using rare earth ions as additives on semiconductors due to the combination of optical properties of rare earth ions and electrical properties of semiconductors. SnO₂ is a very important n-type semiconductor and is widely used as sensor, catalytic ceramic and conductive film.

In this work, nanopowders of SnO₂ doped with Eu³⁺ ion, in concentrations of 1, 5 and 10% are prepared by Pechini method^[1] with heating at low temperature (500 °C). In sequence, these luminescent materials are characterized by X-ray diffraction and infrared spectroscopy. XRD patterns of SnO₂:Eu³⁺ show broadening of the FWHM as increasing of Eu³⁺ concentration, indicating lower crystallites sizes. IR spectra show a slight increasing of the intensity band at 3700 cm⁻¹, corresponding to the basic hydroxyls groups on the surface^[1], with increasing of Eu³⁺ concentration. Thus, rare earth ion doped into SnO₂ matrix promotes higher basicity of the surface.

Excitation spectrum of SnO₂:Eu³⁺ 5% system (Fig. 1) recorded at 77 K shows a broad band around 310 nm, assigned to matrix host band ($\lambda_{em} = 615$ nm) and narrow lines assigned to the ⁷F₀→⁵L_J transitions (J=0-6) of Eu³⁺ ion, with maximum on ⁷F₀→⁵D₂ transition (464 nm). On the other hand, the broad band is not observed in the spectrum obtained at room temperature, which indicates that the energy transfer from the host to Eu³⁺ ion is higher and more efficient when the spectrum is obtained at 77 K. Fig. 2 presents the emission spectra of the europium-doped system with excitation monitored at 310 nm of SnO₂ and 394 nm of Eu³⁺ ion. These spectra present different behaviors, depending on the excitation wavelength. When the excitation is monitored at Eu³⁺ ion, ⁵D₀→⁷F_J (J=0-4) transitions are observed, with ⁵D₀→⁷F₂ transition dominating the intensity (peak around 615 nm). However, when the excitation is monitored at SnO₂ band, the peaks attributed to ⁵D₀→⁷F₀, ⁵D₀→⁷F₂ and ⁵D₀→⁷F₄ transitions shows lowering of intensities compared to the intensity of magnetic dipole transition ⁵D₀→⁷F₁, indicating that Eu³⁺ ions occupy two different symmetry where one of them has center of inversion. Therefore, it is possible to conclude the existence of two types of local environments around Eu³⁺ ion, probably located into lattice of tin oxide and segregated on the surface of SnO₂. This phenomenon is also observed in luminescence decay curves which present a bi-exponential behavior. The SnO₂:Eu³⁺ 5% presents emission quantum efficiency around $\eta = 15\%$, demonstrating that energy transfer from the matrix host (SnO₂) to Eu³⁺ ions is not efficient.

The segregation of Eu³⁺ ions on SnO₂ surface lead these materials to be used as potential gas sensors once they can give information about some adsorbed gases on the SnO₂ surface.

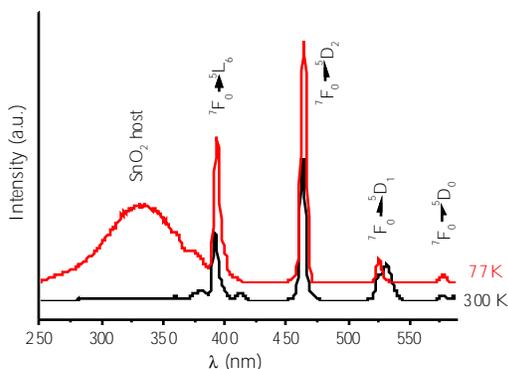


Fig. 1. Excitation spectra of SnO₂:Eu³⁺ material ($\lambda_{em} = 615$ nm) obtained at 77 and 300 K.

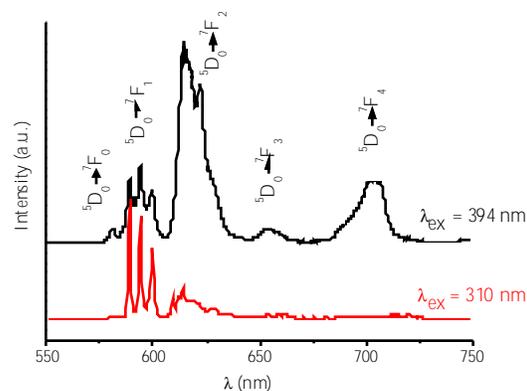


Fig. 2. Emission spectra of SnO₂:Eu³⁺ material at 77 K, with excitation monitored at 310 and 394 nm.

References

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