Temperature-dependent luminescent properties of the sodium decatungstoeuropate

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Abstract

Eu^{3+} luminescence was used as analytical-structural probe to investigate the temperature-dependent emission in LnPOM.

Introdução

Lanthanide-based polyoxometalates (LnPOM) are multifunctional materials with electrical, optical and magnetic properties with large technological interest[1]. Among LnPOM materials, sodium decatungstoeuropate, $Na_9[Eu(W_5O_{18})_2].14H_2O$, presents intense red emission with color purity and high luminescence quantum efficiency under ultraviolet (UV) excitation[2]. The study of the luminescent properties as a function of temperature is important for application of materials in optical devices. In this context, the aim of this work is to evaluate the luminescent properties of the solid $Na_9[Eu(W_5O_{18})_2].14H_2O$ at different temperatures, using the Eu^{3+} luminescence as analytical-structural probe.

Resultados e Discussão

Sodium decatungstoeuropate was prepared by mixing sodium tungstate and europium nitrate solutions in suitable temperature and pH, as described in the literature[3]. Photoluminescence measurements at different temperatures (-100 to 350°C) were recorded in FLUOROLOG HORIBA JOBIN YVON fluorimeter using cryostat-furnace accessory projected and developed by Luminescent Materials Laboratory and Microtube Company. Emission spectra were recorded with excitation at 275 nm, ligand to metal charge transfer band, LMCT, and 394 nm, $^7F_0 \rightarrow {}^5L_6$ intraconfigurational transition of Eu^{3+} ion.

Photoluminescence measurements of the solid sample evidence the presence of Eu^{3+} ions at least two non-centrosymmetric sites. With increasing temperature, the distortions caused by thermal vibration and dehydration process decrease the local symmetry around the Eu^{3+} at both sites. As a consequence, the line assigned to $^5D_0 \rightarrow {}^7F_2$ transition increases with relation to the line assigned to $^5D_0 \rightarrow {}^7F_1$ transition, as shown in the Figure 1(a).

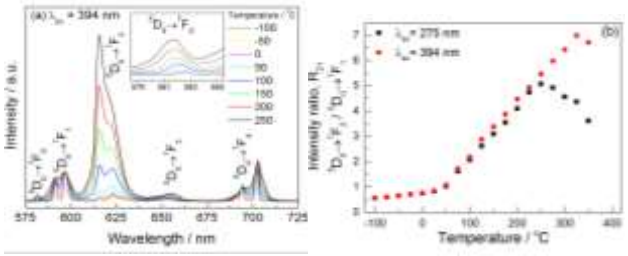

Figure 1. (a) Emission spectra of the $Na_9[Eu(W_5O_{18})_2].14H_2O$ at different temperatures with excitation at 394 nm. (b) Intensity ratio R_{21} as a function of the temperature.

The R_{21} parameter, given by the ratio between the integrated area under lines assigned to $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ transitions, provides information about the local symmetry around Eu^{3+} ions and are showed at Figure 1(b). The R_{21} increases with the temperature, indicating symmetry decreasing, especially above 100°C, because dehydration process starts at this temperature. Above 200°C, R_{21} decreases with excitation at 275 nm, probably because after dehydration process, the symmetry of one site increases again. The Eu^{3+} ions in this site are preferentially excited by LMCT process.

Conclusões

Eu^{3+} luminescence has been successfully used as analytical-structural probe and showed that structure of the $Na_9[Eu(W_5O_{18})_2].14H_2O$ solid changes with the temperature. It was possible to correlate the spectral changes with the symmetry, dehydration process and preferential energy transfer from LMCT states to one of the sites in the sodium decatungstoeuropate solid.

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