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Influence of the modifier cation in the photoluminescent emission of $Zn_{1-X}Co_XWO_4$

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Abstract – $Zn_{1-X}Co_XWO_4$ was synthesized by the polymeric precursor method, being characterized by XRD, Raman, UV-vis spectroscopy and PL emission. PL emission in different regions for cobalt rich and zinc rich samples were assigned to redox reactions (Co^{3+} / W^{5+}) and to WO_4/WO_6 polyhedra, respectively.

Tungstates display excellent optical properties, being applied as optical fibers [1], photoluminescent materials, lasers, scintillators and detectors. Photoluminescent (PL) evaluation of $ZnWO_4$ and $CdWO_4$ was done by Lou et al [2], who showed that these materials have blue-green emission, being the green one assigned to a disorder in the crystalline structure due to $(WO_6)^{6-}$ polyhedra.

In the present work, the influence of the modifier cation in the PL emission of $Zn_{1-x}Co_xWO_4$, obtained by the polymeric precursor method, was evaluated. Samples were heat treated at 500 °C and characterized by X-ray diffraction (D-5000, Siemens), FT-Raman spectroscopy (RFS/100/S, Bruker) between 50 and 1000 cm^{-1} and UV-vis spectroscopy (5G, Cary). PL emission was evaluated using a U1000 Jobim-Yvon double monochromator coupled to a GaAs photomultiplier.

A meaningful change in the PL emission region was observed when zinc was replaced by cobalt in the crystalline structure, with the disappearance of the blue, green and yellow emission, besides the appearance of a red one. All samples were crystalline, with a high long range order. In relation to the short range order, Raman spectra showed that zinc rich samples were more disordered than cobalt rich ones. It was also observed that Co^{2+} was partially oxidized to Co^{3+} being probably compensated by the partial reduction of W^{6+} to W^{5+}. These results indicated that different PL emission mechanisms were present in zinc rich and cobalt rich tungstates. In the first ones (X = 0.0; 0.2; 0.4), PL emission with higher energy values was probably due to the disorder in the former region, with WO_4, WO_5, WO_6 groups, as already observed for tungstates with scheelite structure [2] or for $ZnWO_4$ and $CdWO_4$ [3]. For cobalt rich samples (X = 0.6; 0.8; 1.0), low energy PL emission was probably due to the Co^{3+} and W^{5+} defects, leading to intermediate levels inside the band gap.

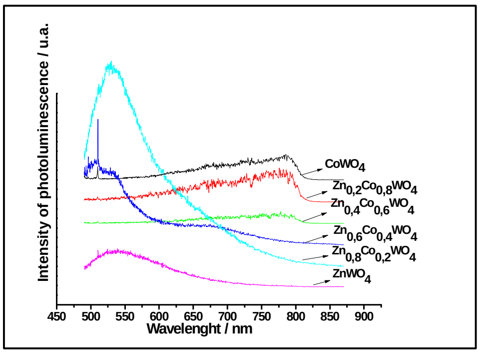

Figure 1: PL emission spectra of $Zn_{1-X}Co_XWO_4$ heat treated at 500 °C.

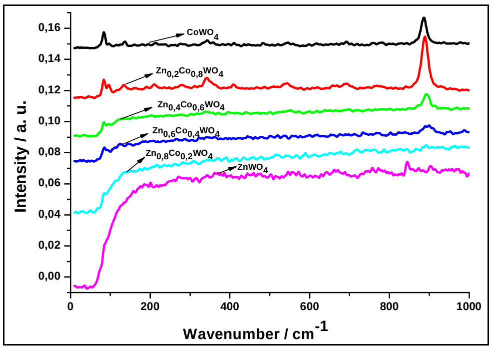

Figure 2: Raman spectra of $Zn_{1-X}Co_XWO_4$, heat treated at 500 °C.

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