

Upconversion Photoluminescence of Cerium Doped Cobalt Tungstate Nano Materials

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ABSTRACT

In this work nano range CoWO₄ powder samples doped with different concentrations of Ce³⁺ ions were prepared by coprecipitation method. The samples were also sintered at various temperatures and characterized using XRD, TG/DTA methods. It was found that the nano particle size increased with increase in sintering temp. The variation in optical absorption due to variation in sintering temperatures and variation in dopant Ce³⁺ concentration were directly reflected on the PL emissions. Upconversion PL is also reported for the Ce³⁺ doped samples.

Keywords— Room temperature (RT); Photoluminescence(PL); Tungstates; Doping; Upconversion.

1. INTRODUCTION

Tungstates belong to an important family of inorganic materials having potential applications in areas like photoluminescence, microwaves, optical fibers, scintillator materials etc. As a self activating phosphor, tungstate have advantages of high chemical stability, high average refractive index, high X-ray absorption co-efficient, high light yield, short decay time, and low after glow to luminescence. Nanosized phosphors have attracted researchers, as the understanding of effect of nano size particles on luminescence property is yet to be fully developed. In this communication we report about the photoluminescence and upconversion luminescence studies carried out on undoped and Ce³⁺ ions doped CoWO₄ nanomaterial.

1.1 Experimental

Nanoparticle undoped and Ce³⁺ ion doped samples of CoWO₄ were prepared by co-precipitation method. The samples were sintered at 400, 500 & 600 °C and characterized using XRD and TG/DTA methods. The XRD patterns were recorded using a Rigaku Miniflex Diffraction with Cu K α radiation filtered through Ni absorber. Optical absorption in the uv-vis range (200-800nm) was measured at room temperature (RT) using Shimadzu UV 2450 uv-visible spectrometer equipped with a diffuse reflection holder. The luminescence properties of the materials were studied by analyzing the photoluminescence (PL) spectra of the materials in the visible range from 400nm to 750nm. The PL spectra and the corresponding excitation spectra were recorded at room temperature (RT) using Shimadzu RF-5301PC spectrofluorophotometer with xenon flash lamp. The samples were loaded on a powder sample holder provided by Shimadzu for the purpose. Up-conversion photoluminescence study was done by irradiating the samples with 600 nm Xe lamp with emission spectra recorded in the range of 400nm to 500nm.

2. RESULTS AND DISCUSSIONS

The XRD patterns of undoped CoWO₄ samples sintered at 400, 500 & 600 °C suggests that (JCPDS 15-0867) the samples are monoclinic with P_{2/a} space group possessing wolframite structure phase. Decreasing full width at half maximum (FWHM) of XRD peaks with increasing sintering temperature shows improvement in crystallinity of the material. Appearance of a new peak in the XRD patterns at $2\theta = 29^\circ$ indicates formation of secondary phase [WO₆]⁶⁻ complex which is found to increase with increasing Ce³⁺ doping and sintering temperature. Similar effect was noted for BaWO₄: Tm³⁺ phosphors also [1]. Particle size calculated using Scherrer's formula for undoped and samples sintered at various temperatures was found to increase with increasing sintering temperature. Similar effects are also reported in the literature [2].

The intensity of the optical absorption band between 220 nm to 450 nm for CoWO₄ samples sintered at 600 °C varies with the concentration of Ce³⁺ doping Fig.1. This suggests that this absorption band may be directly related to the formation of the secondary phase [WO₆]⁶⁻ complex.

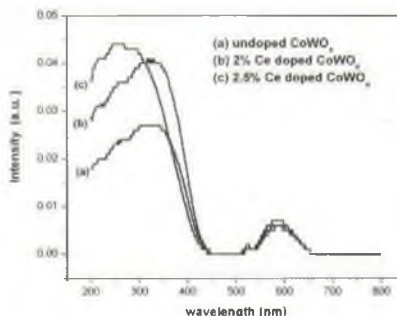


Fig. 1: Absorption spectra of CoWO₄ measured at RT

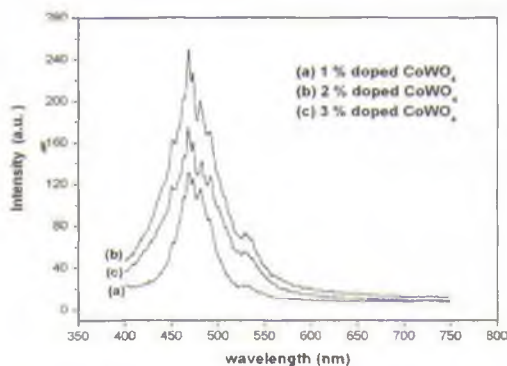


Fig. 2: PL spectra measured at RT with excitation at 220nm

The absorption band centered around 600 nm which does not shift with Ce^{3+} doping may be related to the intermediate levels inside the band gap of the host material due to Co^{3+} & W^{5+} defects [3]. The structure and spectral position of the absorption bands of undoped and 2.0% Ce^{3+} doped samples are same. When the Ce^{3+} doping is increased beyond 2.0% a blue shift appears in the band absorption maxima. The intensity of the absorption maxima increases with increase in Ce^{3+} doping. These effects are directly reflected in the PL spectra of Ce^{3+} doped CoWO_4 samples sintered at 600 °C Fig. 2. The intensity of the PL band spectrum increases for increase in Ce^{3+} doping and decreases beyond 2.0% Ce^{3+} doping. The emitting centers for the PL spectra are the same for the undoped & Ce^{3+} doped samples, because none of the PL peak positions vary with changes in Ce^{3+} doping as well as varying sintering temperatures. The PL spectra have maximum intensity for 600 °C sintered samples doped with 2.0% Ce^{3+} ions. The optical absorbance of undoped and doped samples occurs in the same spectral region. This indeed shows the overlapping of the 5d states of Ce^{3+} with conduction band of the CoWO_4 resulting in the delocalization and transport of energy through the conduction band to the host emitting center. This may be the reason for enhanced luminescence intensity for 2.0% Ce^{3+} doped CoWO_4 compared to the undoped CoWO_4 and also due to the increase in WO_6 phase due to the increase in Ce^{3+} ions concentration. This is in accordance with the earlier theory [4] that the intrinsic luminescence is caused by the annihilation of a self-trapped exciton, which formed excited $[\text{WO}_6]^{6*}$ complex which can be excited either in the excitonic absorption band or in the recombination process due to the wolframite-structured products. If the Ce^{3+} doping is increased beyond 2% there is

a decrease in the PL spectral intensity and correspondingly blue shift in the absorption maxima which can be interpreted as due to the change in geometry of the system because of the increased Ce^{3+} ions substitution for Co^{2+} ions (radius of Ce^{3+} is 1.143 Å & that of Co^{2+} is 0.72 Å).

The increase in PL intensity with increase in sintering temperature for Ce^{3+} doped samples may be due to increase in nano particle size and due to the increase in the formation of the secondary phase $[\text{WO}_6]^{6*}$ at higher temperature and higher concentration of Ce^{3+} ions. Similar results were obtained by [2] for undoped CoWO_4 material.

Upconversion PL band emissions were observed between 400nm & 500 nm, when the irradiated wavelength was 600 nm. This emission has the same spectral properties and intensity dependence on the concentration of Ce^{3+} ions like the PL emission bands due to 220 nm irradiation Fig.2. But the total intensity of the upconversion spectrum is only one third of the intensity of the PL emission spectrum due to 220 nm irradiation which indicates that the emitting centers are the same in both the cases. The upconversion process may be explained with the help of anti-Stokes two photon theory. When the samples are irradiated at 600nm the first photon pumps the electrons from the conduction band to the intermediate level formed due to Co^{3+} (formed by the oxidation of Co^{2+}) and the compensating W^{5+} (formed by the reduction of W^{6+}) defects [3]. The second photon ionizes the electrons to the conduction band. When the electrons are recaptured or transfer energy in the valence band, intrinsic emission occurs, while the recombination or transfer of energy in the intermediate level gives emission at higher wavelength.

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