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## Journal of Luminescence

journal homepage: [www.elsevier.com/locate/jlumin](http://www.elsevier.com/locate/jlumin)Upconversion luminescence of cerium doped CoWO<sub>4</sub> nanomaterialsUma Subramanian<sup>a,\*</sup>, S.J. Naik<sup>b</sup>, R.B. Tangsali<sup>a</sup>, A.V. Salker<sup>b</sup><sup>a</sup> Department of Physics, Goa University, GOA-403 206, India<sup>b</sup> Department of Chemistry, Goa University, GOA-403 206, India

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## ABSTRACT

In this paper we report the bluish green upconversion intrinsic photoluminescence (PL) observed at room temperature (RT) 300 K for the nanorange (27–50 nm) Ce<sup>3+</sup> doped and undoped CoWO<sub>4</sub> powder samples sintered in air at 600 °C. Excitation by Xenon lamp at 600 nm was done and the emission was observed between 400 nm and 550 nm. Co<sub>1-x</sub>Ce<sub>x</sub>WO<sub>4</sub> [where x=0.00, 0.02, and 0.03] compounds were prepared by the solution based co-precipitation method and characterised by X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The surface morphology of the compounds was examined by scanning electron microscopy (SEM) techniques. Optical absorption and photoluminescence behaviour of the compounds in the rigid matrix were studied. High emission intensity and easy preparation make these systems potential candidates for application as luminescent materials.

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## 1. Introduction

Tungstates are self activating phosphors and have applications in areas like photoluminescence, microwaves, electro-optics, scintillator materials etc. [1–3]. Majority of the tungstates have wolframite or scheelite structures depending on their cationic radii. Small radii (< 0.077 nm) are in favour of forming wolframite structure and large radii (> 0.099 nm) favour scheelite structure [4,5]. In wolframite structured tungstates the intrinsic luminescence is caused by the annihilation of self-trapped exciton, which forms excited [WO<sub>6</sub>]<sup>6-</sup> complex that can be either excited in the absorption band or in the recombination process [6]. There are many reports on the luminescence study of various tungstates [1–7]. But only a few workers have reported the luminescence of CoWO<sub>4</sub> samples [3,8–10]. In our earlier communication we have reported the intrinsic PL emissions observed at RT for Ce<sup>3+</sup> doped and undoped CoWO<sub>4</sub> nanopowder samples sintered at different temperatures [11]. Maximum PL emission was observed for nanosamples doped with 1.5–2% Ce<sup>3+</sup> ions and sintered at 600 °C. This was attributed to the presence of balanced amounts of [WO<sub>4</sub>]<sup>2-</sup> and [WO<sub>6</sub>]<sup>6-</sup> clusters and bigger particle size. For bulk samples PL intensity was 40 times less than that of the nanosamples and insensitive to Ce<sup>3+</sup> doping concentrations. In this communication we report the upconversion intrinsic luminescence observed for the first time in undoped and Ce<sup>3+</sup> doped nano-CoWO<sub>4</sub> powder samples excited by 600 nm xenon

lamp. The samples were prepared by the co-precipitation method and sintered in air at 600 °C for 5 h. However no upconverted intrinsic luminescence was observed for bulk samples sintered at 1000 °C.

## 2. Experimental

Nanomaterials of Co<sub>1-x</sub>Ce<sub>x</sub>WO<sub>4</sub> solid solution (x=0.00, 0.02, and 0.03) were prepared by using the co-precipitation method. In a typical synthesis, the stoichiometric amounts of cobalt nitrate, sodium tungstate and cerium nitrate were dissolved in minimum quantity of water. After getting a clear solution, the metal nitrates were added to the sodium tungstate solution. A blue colour precipitate obtained was continuously stirred and after several hours the solid product Co<sub>1-x</sub>Ce<sub>x</sub>WO<sub>4</sub> was collected by filtration, washed with distilled water, dried at 80 °C and calcined at temperatures 400 °C, 500 °C, 600 °C and 1000 °C for 5 h.

The thermal behaviour of the samples was investigated using thermal techniques (TG/DTA/ NETZSCH STA49A). 10 mg of the precursor material was placed in an alumina sample pan which was then heated up to 1000 °C with the heating rate maintained at 10 °C/min, in flowing synthetic air. The weight loss of the precursor sample at the thermal event was recorded during heating. The XRD patterns were recorded using a Rigaku Miniflex Diffractometer with CuK $\alpha$  radiation filtered through Ni absorber. The optical absorption measurements at room temperature were recorded by reflectance UV–vis spectroscopy on Shimadzu UV 2450 UV–visible spectrometer in the wavelength range of 200–800 nm. The PL emission spectra of the samples were measured

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between 400 nm and 750 nm with 220 nm excitation and the upconverted emissions were recorded from 400 nm to 570 nm for excitation wavelength of 600 nm using a Shimadzu RF-5301PC spectrofluorophotometer, with a Xenon flash lamp (UV-35 filter was used at the excitation slit to avoid the harmonic effects from the grating). The samples were loaded on a powder holder provided by Shimadzu and was mounted at about 45° to the excitation source for PL measurement. The emission slit width was 1.5 nm for PL measurements and 3 nm for upconversion measurements. The XPS data were recorded with the sample mounted on a specially designed sample holder [12] using an ALKalpha laboratory X-ray source operated at 150 W and an electron energy analyser with five channeltrons from Specs GmbH, Germany. The data were recorded with 20 eV pass energy with 1 eV energy resolution. The chamber pressure was  $6 \times 10^{-11}$  mbar.

### 3. Results and discussion

The X-ray diffraction patterns of  $\text{Ce}^{3+}$  doped and undoped  $\text{CoWO}_4$  samples sintered at 600 °C are shown in Fig. 1(a). The pattern corresponds to  $\text{CoWO}_4$  [JCPDS card no 72-0479] with monoclinic crystalline structure of wolframite type oxides. The patterns of the cerium doped  $\text{Co}_{1-x}\text{Ce}_x\text{WO}_4$  (where  $x=0.02, 0.03$ )

show formation of  $\text{Ce}_2\text{WO}_6$  phase with peak around 28° (JCPDS No. 25-1445) which increases with an increase in Ce content. Also the  $(\text{WO}_6)^{6-}$  phase increased with an increase in the sintering temperature [11].

TEM image of undoped  $\text{CoWO}_4$  sintered at 500 °C is shown in Fig. 1(b). The average particle size measured for an ensemble of 35 particles from this image is 45.22 nm with a standard deviation of  $\pm 11.76$  nm. The particle size calculated from the XRD pattern given in our earlier paper [11] for the same sample is  $33 \pm 0.02$  nm.

Surface morphologies observed by SEM for undoped  $\text{CoWO}_4$  and 2%  $\text{Ce}^{3+}$  doped samples sintered at 600 °C are shown in Fig. 2(a) and (b) respectively. These pictures show that the grain formation is better, the boundaries are distinct and the grain surface appears quite smooth in the  $\text{Ce}^{3+}$  doped sample (Fig. 2(b)) as compared to the undoped sample (Fig. 2(a)).

The optical absorption spectra of  $\text{Ce}^{3+}$  doped bulk  $\text{CoWO}_4$  samples sintered at 1000 °C are shown in Fig. 3(a). There is a broad absorption band between 200 nm and 450 nm, a small peak of very low intensity around 475 nm and a broad peak centred around 600 nm with a shoulder at 525 nm. The absorption intensity of the broad band centred around 600 nm is greater than that of the band between 200 nm and 450 nm. The optical absorption spectra of  $\text{Ce}^{3+}$  doped nano- $\text{CoWO}_4$  samples sintered at 600 °C are shown in Fig. 3(b). The absorption intensity of nanosamples is

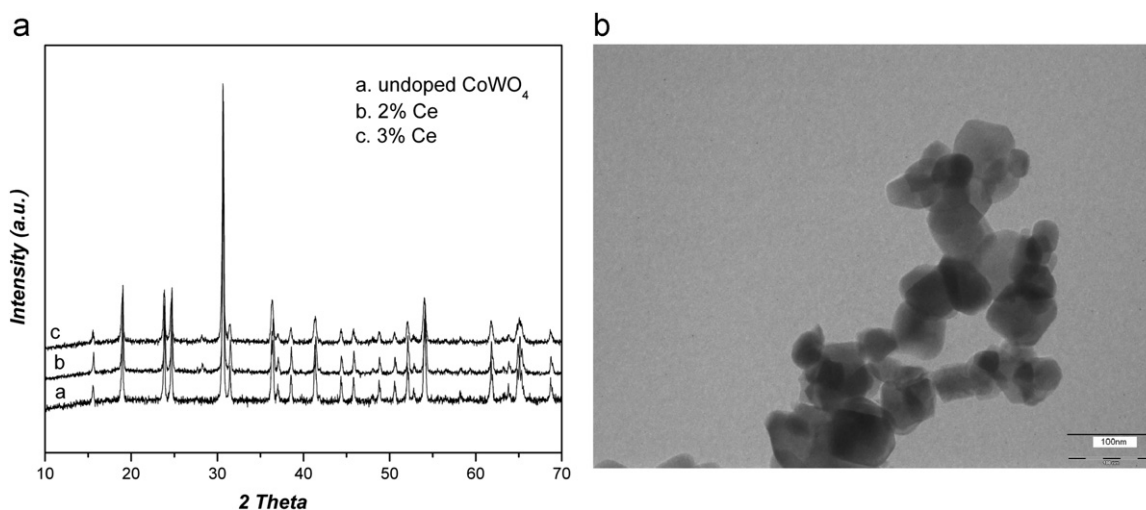


Fig. 1. (a) XRD patterns of  $\text{CoWO}_4:\text{Ce}^{3+}$  sintered at 600 °C. (b) TEM image of undoped  $\text{CoWO}_4$  sintered at 500 °C.

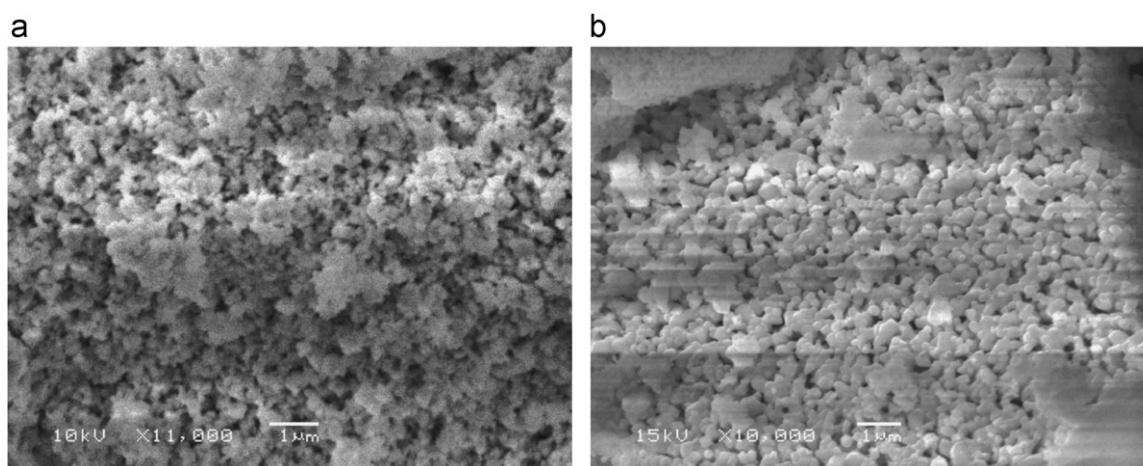


Fig. 2. (a) SEM image of undoped  $\text{CoWO}_4$  sintered at 600 °C. (b) SEM image of  $\text{CoWO}_4:\text{Ce}^{3+}$  2% sintered at 600 °C.

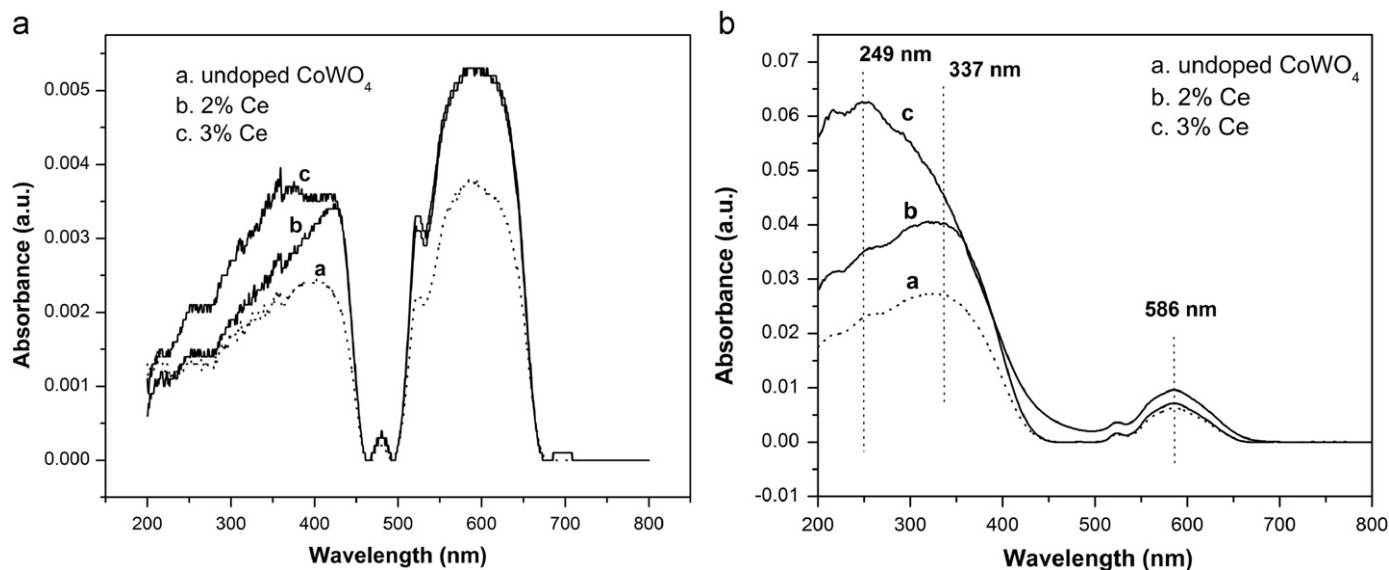


Fig. 3. (a) Absorption spectra of bulk  $\text{CoWO}_4:\text{Ce}^{3+}$  sintered at  $1000\text{ }^\circ\text{C}$ . (b) Absorption spectra of nano- $\text{CoWO}_4:\text{Ce}^{3+}$  sintered at  $600\text{ }^\circ\text{C}$ .

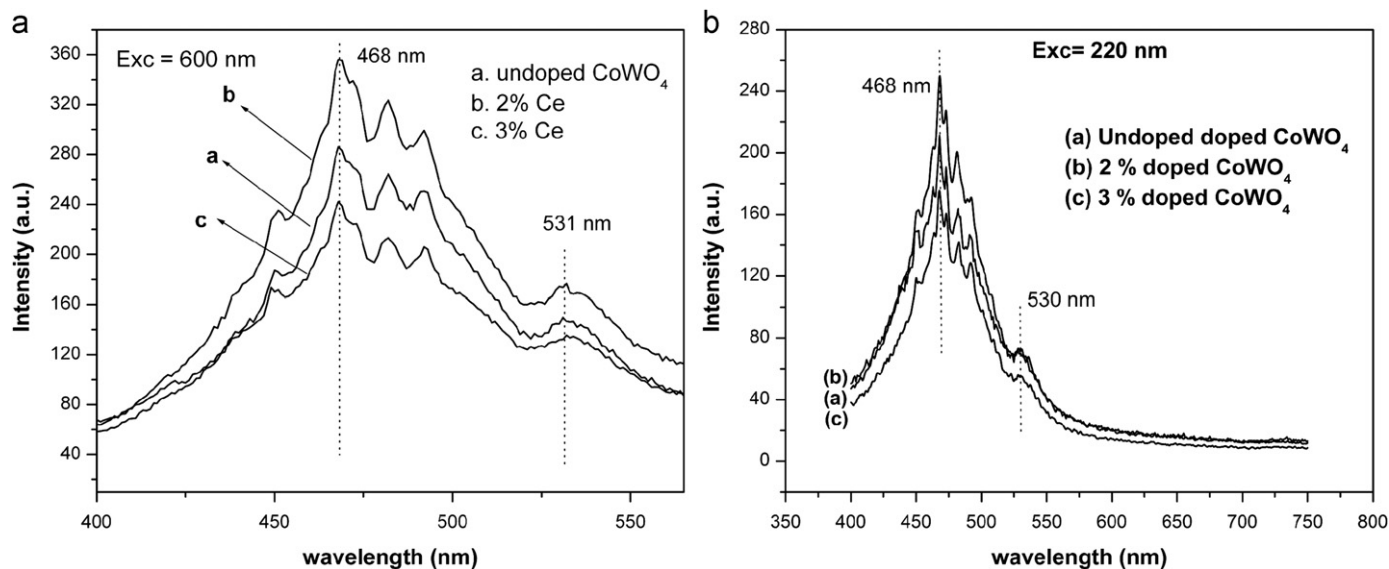


Fig. 4. (a) Upconversion PL spectra of nano- $\text{CoWO}_4:\text{Ce}^{3+}$  sintered at  $600\text{ }^\circ\text{C}$  and  $\lambda_{\text{exc}}=600\text{ nm}$ . (b) PL spectra of nano- $\text{CoWO}_4:\text{Ce}^{3+}$  sintered at  $600\text{ }^\circ\text{C}$  and  $\lambda_{\text{exc}}=220\text{ nm}$ .

approximately 10 times higher than that of the bulk samples and there is a broad band between 200 nm and 450 nm, a small shoulder around 525 nm and a broad peak around 586 nm. Also the absorption intensity of the band between 200 nm and 450 nm is much greater than that of the band centred around 586 nm. There is a blue shift in the absorption maxima and edge for nanosamples as compared to the bulk samples i.e. from 425 nm to 337 nm for undoped and 2%  $\text{Ce}^{3+}$  doped samples and from 425 nm to 249 nm for 3%  $\text{Ce}^{3+}$  doped samples. There is also a blue shift in the higher wavelength peak from 600 nm to 586 nm for all the samples. The peaks around 600 nm for the bulk and 586 nm for the nanosamples is due to the d–d transitions from  $4A_2 \rightarrow 4T_1(P)$  levels of the  $\text{Co}^{2+}$  ions.

Fig. 4(a) shows the upconversion intrinsic luminescence spectra of  $\text{Ce}^{3+}$  doped nano- $\text{CoWO}_4$  samples sintered at  $600\text{ }^\circ\text{C}$  for the excitation wavelength of 600 nm. There is a broad emission band between 400 nm and 570 nm which has a prominent peak around 468 nm (blue–green) and shoulder around 531 nm (green).

Same pattern of intrinsic PL emission spectra is observed for 220 nm excitation (Fig. 4(b)). Similar PL spectrum has been reported for Cd, Mg, Zn and Co tungstates by others [7,9,3]. Maximum emission intensity occurs for the 2%  $\text{Ce}^{3+}$  doped sample. However the upconversion intensity due to 600 nm excitation is only one third of the PL emission intensity due to 220 nm excitation. The similarity of PL spectra and upconverted spectra for the nanosamples suggests that the emission centres are the same in both cases. In wolframite structured tungstates the intrinsic luminescence is caused by the annihilation of self-trapped exciton, which forms excited  $[\text{WO}_6]^{6-}$  complex that can be either excited in the absorption band or in the recombination process [6].

The excitation spectra of  $\text{Ce}^{3+}$  doped nano- $\text{CoWO}_4$  samples sintered at  $600\text{ }^\circ\text{C}$  for the emission at 468 nm are shown in Fig. 5. Similar excitation spectra were observed for 531 nm emission. It is a band spectra extending from 200 nm to 240 nm and the tail extends towards higher wavelengths. The intensity variation of these spectra is in accordance with the intensity variation of the



upconversion spectra. Similar results were observed for PL spectra with 220 nm excitation [11]. The extension of the excitation spectra tail towards the higher wavelength side suggests of the formation of intermediate levels in the band gap of the material.

Fig. 6(a) shows W 4f XPS spectrum collected for 3% Ce<sup>3+</sup> doped CoWO<sub>4</sub> compound sintered at 600 °C. The doublet is observed around BE=37 eV and 35 eV corresponding to W 4f<sub>5/2</sub> and W 4f<sub>7/2</sub> states, respectively. For W<sup>6+</sup> ions the W 4f<sub>5/2</sub> and W 4f<sub>7/2</sub> characteristic peaks were observed around BE=38 eV and 36 eV respectively for pure WO<sub>3</sub> [13]. The shift in peaks toward lower BE by ~1 eV for our sample compared to that for the pure wolframite oxide indicates the presence of W<sup>5+</sup> ions [13,14]. Fig. 6(b) shows Co 2p XPS spectrum collected for 3% Ce<sup>3+</sup> doped CoWO<sub>4</sub> compound sintered at 600 °C. The two peaks around BE=780 eV and 797 eV are due to Co<sup>3+</sup> ions and the satellite peaks around BE=786 eV and 805 eV are due to Co<sup>2+</sup> ions. The signals at BE=780 eV and 786 eV are the characteristic peaks of Co 2p<sub>3/2</sub> state, whereas those at BE=797 eV and 805 eV belong to the characteristic peaks of Co 2p<sub>1/2</sub> state [15,16]. Also there is a

report of intermediate levels formed inside the band gap of CoWO<sub>4</sub> host material due to Co<sup>3+</sup> and W<sup>5+</sup> defects which are formed due to partial oxidation of Co<sup>2+</sup> ions and the charge compensation by the reduction of W<sup>6+</sup> to W<sup>5+</sup> [10].

The upconverted intrinsic luminescence emission in the nano-samples can be explained by the anti-Stokes multi photon theory involving the capture of electrons in the intermediate levels due to d–d transition of Co<sup>2+</sup> ions. Upconversion process generally occurs due to two possible mechanisms: excited state absorption (ESA) and energy transfer upconversion (ETU) [17]. In the first mechanism a single ion is involved whereas two ions are involved in the second one [18]. In the ETU process the two ions excited in an intermediate state in close proximity are coupled by a nonradiative process in which one ion returns to the ground state while the other ion is promoted to the upper level. In most cases, these cross-relaxation processes are based on electric dipole–dipole interaction [19]. In our samples the Co<sup>2+</sup> ions absorb energy through d–d transition and transfer it to the [WO<sub>6</sub>]<sup>6-</sup> ions for intrinsic emission. Therefore the upconverted intrinsic luminescence observed in the undoped and Ce<sup>3+</sup> doped nanosamples sintered at 600 °C is due to the ETU process. Similar mechanisms are reported for Pr<sup>3+</sup> doped PbWO<sub>4</sub> samples [18] and Er<sup>3+</sup> doped PbWO<sub>4</sub> samples [20].

Upconversion luminescence was not observed for bulk samples excited with 600 nm. Earlier [11] it was found that the PL intensity observed for the bulk samples sintered at 1000 °C and excited at 220 nm were 40 times less than that for the nanosamples sintered at 600 °C. Also the spectral intensity did not vary with different Ce<sup>3+</sup> concentrations for bulk samples. The cause for the weak intrinsic PL emission and no upconversion emission for the bulk samples sintered at 1000 °C is due to the overlapping of the absorption maxima at 425 nm, 475 nm, 525 nm and 600 nm with the intrinsic emission region (400 nm–570 nm). Overall absorption intensity is quite low compared to that of nanosamples; the absorption intensity of the broad band centred around 600 nm is greater than that of the band between 200 nm and 450 nm and imbalance in the amount of [WO<sub>4</sub>]<sup>2-</sup> and [WO<sub>6</sub>]<sup>6-</sup> clusters [11].

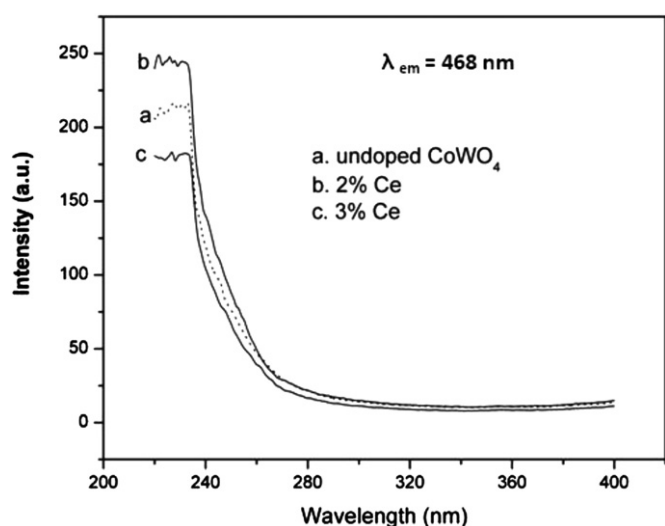


Fig. 5. Excitation spectra of PL emission at 468 nm for nano-CoWO<sub>4</sub>:Ce<sup>3+</sup> sintered at 600 °C.

#### 4. Conclusions

Undoped and Ce<sup>3+</sup> doped CoWO<sub>4</sub> nanopowder samples prepared by the co-precipitation method show bluish green upconversion

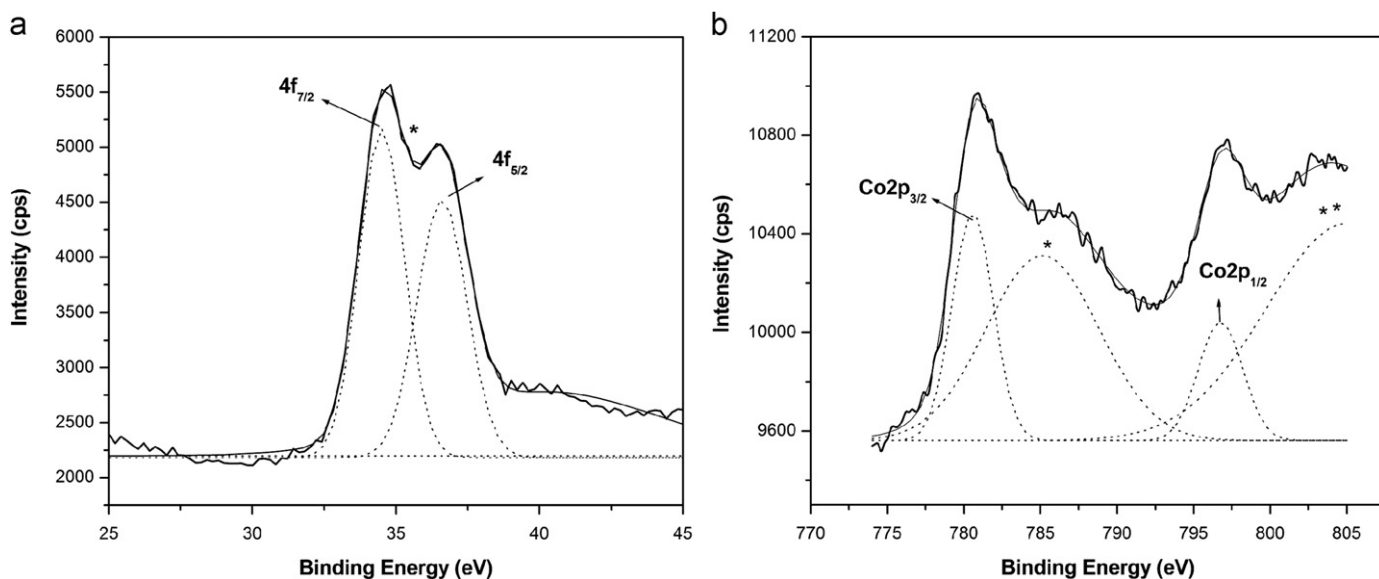


Fig. 6. (a) W 4f XPS spectrum collected for 3% Ce<sup>3+</sup> doped CoWO<sub>4</sub> compound sintered at 600 °C. (b) Co 2p XPS spectrum collected for 3% Ce<sup>3+</sup> doped CoWO<sub>4</sub> compound sintered at 600 °C.

intrinsic luminescence by excitation with 600 nm Xe lamp. The intensity of the upconversion luminescence is one third that of the PL emission due to 220 nm excitation. This upconversion emission is attributed to ETU process involving  $\text{Co}^{2+}$  ions and  $[\text{WO}_6]^{6-}$  ions. Bulk samples of undoped and  $\text{Ce}^{3+}$  doped  $\text{CoWO}_4$  sintered at 1000 °C did not show any upconversion luminescence.

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