Synthesis and Structure of Pure and Dy-Doped $CoWO_4$ Nanostructure

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ABSTRACT

Nanocrystalline pure and Dysprosium (Dy) doped CoWO4 nanostructures were synthesized successfully by chemical precipitation technique. Experimental results confirmed the particles in nanometer range and homogenous dispersion of nanocrystalline Dy3+ particles in the CoWO4 matrix. The prepared sample was characterized by X-ray diffraction (XRD), High resolution scanning electron microscope (HRSEM), Energy Dispersive X-ray spectra (EDS) and Transmission Electron Microscopy (TEM). XRD pattern reveals the pure and Dy doped CoWO4 nanoparticles belongs to the monoclinic structure. Electron microscopy studies clearly evidence the formation of nanocubes and crystalline nature with an average particle size of 80-90 nm.

KEY WORDS: structure, nanomaterials, chemical precipitation, XRD.

1. INTRODUCTION

When compared to traditional binary oxides (e.g. TiO_2, ZnO and SnO_2 etc.), multi-metal oxide semiconductors possess higher tolerance to structural distortion due to their inherent lattice strain, which enables the incorporation of foreign ions into the host matrix (Wang, 2006). The multi-metal oxides show higher chemical stability and fewer electron–hole pair recombination centers, so that charge carrier separation and migration is more effective (Shi, 2011). Bimetallic compound materials belonging to the tungstate and molybdate families have a long history of practical applications and have been the object of extensive research over the past century.

Numerous interests in these compounds lie in their excellent optical properties, which form the basis of their wide use as phosphors, laser materials, and scintillation detectors (Anicete-Santos, 2006; Klassen, 2002; Danevich, 1995). Especially, metal tungstates are attractive materials and have received great research interest due to their intriguing luminescence and structural properties (Saito, 1996). As a p-type semiconductor $CoWO_4$ has been most widely studied material for various technological applications such as catalysis, sensor, displays and optoelectronics (Bharti, 1981). It is well established that the additional doping will induce the structural and magnetic changes in the host systems (Navarro, 2003). Fu-Shan Wen (2002), reported the photo luminescent properties of hydrothermally synthesized Eu^{3+} doped $ZnWO_4$. Fugui Yang (2008), study the growth and spectral analysis Ho^{3+} doped $ZnWO_4$. Recently, Naik (2010), reported the luminescent features of $CoWO_4$: Ce^{3+} nanostructure. There are no reports published elsewhere with electron or hole doped $CoWO_4$ nanocrystals. Hence it is interested to study the effect of electron doping on Co site in particular by the rare earth metal ions.

Semiconductors doped with rare earth (RE) elements such as (Ln^{3+} = Yb, Nd, Pr, Gd, Eu, Er, Tm, and Tb etc.) have been intensively pursued because of their important applications in optoelectronics as emitters at visible wavelength (Steckl, 2007; Chunxia Li, 2009) reported the Ln^{3+} doped YPO_4 nano/microstructures with tunable luminescent colors. The effect of Nd impurities on the optical and dielectric and electrical properties of $PbWO_4$ single crystals was reported by Weifeng Li (2005). The bright white up conversion luminescence from Er^{3+}-Tm^{3+}-Yb^{3+} doped $CaSnO_3$ powders has been reported by Pang (2011). Further it is reported that the Lanthanide ions possessing special 4f intra shells are recognized as excellent candidates for luminescence centers of the doped inorganic phosphor systems due to their many optical advantages (Dandan Wang, 2011).

Recently, Dy as one element belongs to the Lanthanide family doped phosphors have been the focus of numerous investigations because of their unique optical properties (Zeng, 2007; Mehta, 2003) and promising applications in optoelectronics (Chen, 2007; Wang, 2007). Till date several chemical synthesis processes such as sonochemical (Anukorn Phuruangrat, 2010), hydrothermal (Zhao, 2009), co-precipitation (Zhang Qing, 2011) etc., have been used for the preparation of metal tungstate especially for the wolframite nanocrystals. In this way Di Chen, (2003) reported the low temperature synthesis of metal tungstates nanocrystallites in ethylene glycol. Similarly, Fen Zhang, (2008) proposed the room temperature synthesis and properties of multifunctional doped Tungstate nanorods. Among various synthesis techniques chemical precipitation method has gained more interest due to their easy and cost-effective synthesis for large scale production. However, the synthesis of Dy-doped $CoWO_4$ nanocrystals and the effects of the dopant on the structures, and optical properties were not yet reported.

In this work, it is reported that a facile and cost effective chemical precipitation route for fabricating Dy-doped $CoWO_4$ nanocrystals and study the effects of Dy doping on the structures of nanocrystals. In future we have to study the photoluminescence (PL) and optical band gap of the Dy-doped $CoWO_4$ nanocrystals.

2. EXPERIMENTAL TECHNIQUES

Materials & Method: All the chemicals were purchased from Alfa Asar and used as received without further purification. Typical synthesis process are as follows; initially equal mole of Co $(CHOO)_2$ and $Na_2WO_4.2H_2O$ were

dissolved separately in deionized water under vigorous stirring for 30 min. Two solutions were mixed together and continued stirring until the complete precipitation. Subsequently, 1 g polyethylene glycol was added followed by the 3 h continuous stirring and ageing for 15 h. As obtained precipitate was separated out by centrifugation and repeatedly washed with deionised water, Ethanol and acetone. The end product was dried at room temperature for 24 h and calcined at the choice of temperature 500 and 600°C for 6 h under air. Similarly, the 1%, 3% and 5% Dy doped $CoWO_4$ were synthesized by adding the appropriate amount of $Dy(CHOO)_3$ with the $Co(CHOO)_2$ solutions using the same experimental procedure.

Characterization: XRD pattern of the wolframite nanostructure was taken from the BRUKER D5 Phaser, For microstructure and morphological features Scanning Electron Microscope (HRSEM) (HITACHI) (Japan) SU6600-15 KV) and Transmission Electron Microscope (TEM) (HITACHI (Japan) H-7650-80KV) were directly used with Energy Dispersive Spectroscopy attachment.

3. RESULTS AND DISCUSSION

XRD Analysis: To determine the phase and crystal structure of Dy^{3+} doped $CoWO_4$ nanocrystals calcined at two different temperatures. Powder XRD analysis was carried out as shown in Figure.1. The results show that, there are the diffraction peaks representing the characteristic of monoclinic phase. As obtained XRD pattern indicates that the structure of $CoWO_4$ is not affected by doping of Dy^{3+}. All the nanocrystals give similar patterns without any peak due to the doping of Dy^{3+} doping, which may be attributed to the well dispersion of Dy^{3+} in the $CoWO_4$ matrix. Thus, the addition of Dy^{3+} to $CoWO_4$ makes the decrement of diffraction peaks intensity due to the reduction of the average crystallite size and an increase in the lattice strain, generally referred to as a loss of crystallinity in the mixed oxides. Associated diffraction line broadening may be due to a fine nature of crystallites. The average grain sizes of the samples were determined by employing the Scherrer's formula. The calculated mean crystallite diameters of Dy^{3+} doped $CoWO_4$ nanocrystals are found to be ~82 and 91 nm for the sample heat treated at 500°C and 600°C respectively.

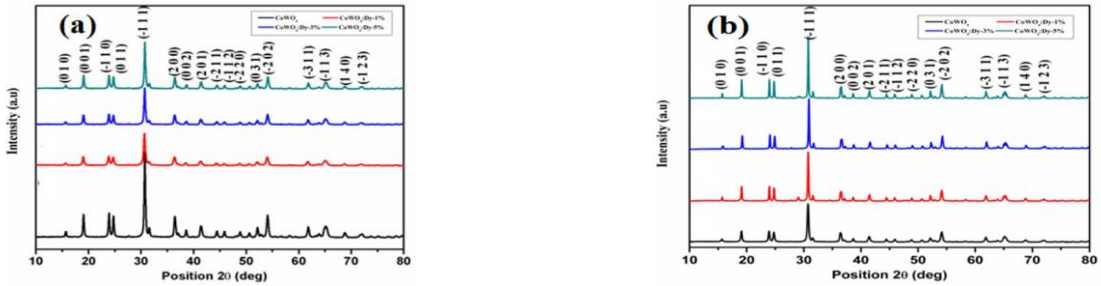

Figure.1. XRD Pattern of $CoWO_4$ nanostructure with Dy doping for two calcination temperature (a) 500°C and (b) 600°C

Table.1. Average particle size and atomic concentration of Dy doped CoWO4 nanoparticles

Compound	Average Particle size (nm)		Elements	Atomic %		
	500 °C	600 °C		Dy-0%	Dy-3%	Dy-5%
CoWO4	86 ±2	89 ±2	Co	25.69	23.97	20.04
CoWO4:Dy-1%	84 ±2	86 ±2	W	25.15	24.11	24.52
CoWO4:Dy-3%	79 ±2	85 ±2	O	50.05	49.82	49.06
CoWO4:Dy-5%	75 ±2	79 ±2	Dy	--	0.99	4.98

SEM Analysis: To investigate the surface morphology and the grain size variation of CoWO4with respect to Dysprosium content SEM analysis was taken and represented in Figure 2 (a-e). From the SEM images it can be seen the more information on the grains and nature of the samples. Typical SEM micrograph shows that the samples are highly homogeneous and cubical in shape. It is clearly seen that the particles are highly aggregated emerged in well crystalline in nature. All the samples show identical surface morphology. This confirms the presence of Dy does not alter the crystalline structure as well as morphology. It can be seen that there is significant reduction in crystalline size by adding Dy ions to CoWO4 host. However to increase the calcination temperature the crystalline size increases as expected due to the grain growth. Further this result is in consistent with the XRD analysis.

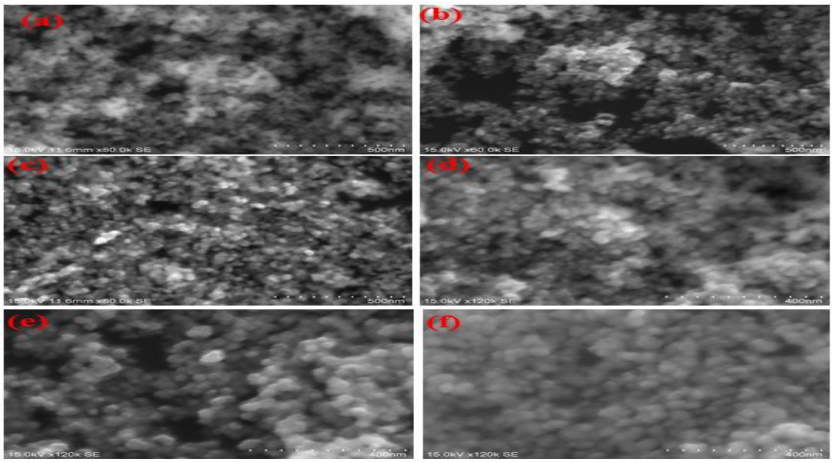

Figure.2. SEM micrographs pure $CoWO_4$ (a&b) and various concentrations of Dy-1% (c&d), and Dy-5% (e&f)

EDAX: The quantitative elemental analysis was performed using EDAX directly attached with the SEM analysis. The observed EDAX spectra of pure and 3 mol% Dy-doped CoWO4 are shown in Figure.3 (a & b). The atomic concentration of the primary elements present in the pure and Dy doped CoWO4 nanoparticles are given in Table.1. EDAX spectra obviously designate the presence of functional elements of Co, Dy, W, and O with appropriate concentration without any impurities which confirms the stochiometric concentration of the elements.

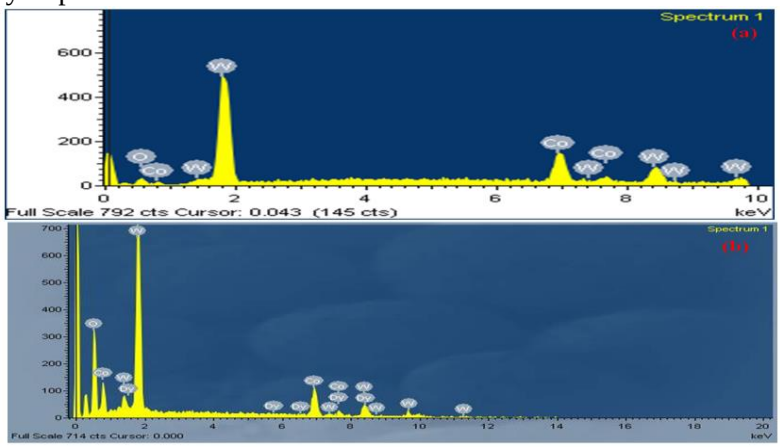

Figure.3. EDS spectra of pure $CoWO_4$ (a) and Dy-3% doped $CoWO_4$ nanostructure

Transmission Electron Microscoscope (TEM): The transmission electron microscopic (TEM) images of 3 mol % Dy^{3+} doped $CoWO_4$ are shown in Figure.4(a-d). The particles are roughly cubical in shape with narrow size distribution. The presence of aggregation between nanocrystals is clearly seen. Hence dysprosium may be spread over the entire solid matrix as discussed in XRD. Also, there is a possibility for the Dy^{3+} to be incorporated into the interstitial positions of the $CoWO_4$ matrix. Based on the scale provided, the mean size of the particles is found to be around 82 nm. The particle size of the samples estimated from the TEM micrographs corresponded well to the crystallite size calculated from the XRD line broadening.

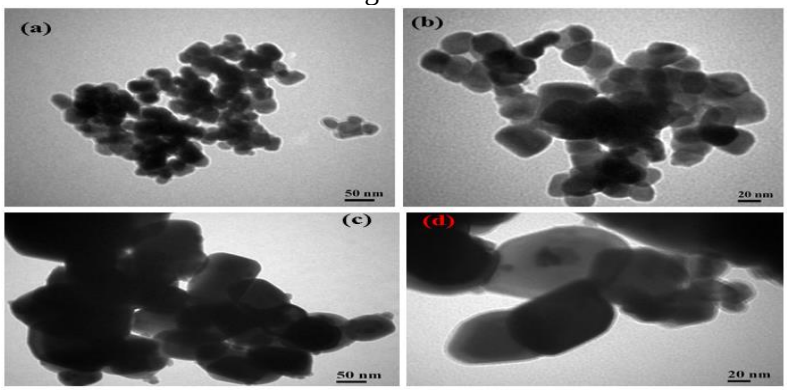

Figure 4 TEM Images of Pure (a & b) and 3 mole% Dy-doped (c & d) $CoWO_4$ nanostructures

4. CONCLUSIONS

In this present investigation, we adopt the single step solution based chemical precipitation technique to synthesis the pure and Dy doped CoWO4 nanostructure. Experimental results confirmed the particles in nanometer range and homogenous dispersion of nanocrystalline Dy3+ particles in the CoWO4 matrix. From the XRD pattern it

is confirmed that the DY3+ ion was incorporated into the lattice and interstices of CoWO4nanocrystals. XRD pattern reveals the pure and Dy doped CoWO4 nanoparticles belongs to the monoclinic structure and mean crystalline diameters of are found to be ~82 and 91 nm. High resolution scanning electron microscope (SEM) and transmission electron microscopy (TEM) analysis showed that the formation nanocubes crystalline nature with an average particle size of ~ 80-90 nm.Interestingly, the Dy doped $CoWO_4$ have shown the unusual structural features when compared to other rare earth ions. Yet further studies has to be carried out to analyse the optical properties of the materials which may lead to device fabrication.

5. ACKNOWLEDGMENT

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