

## **Optical and Magnetic properties of Cr doped PbWO<sub>4</sub> Nanostructures by Chemical method**

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### **ABSTRACT**

The consequence of Cr doping on structural, optical and magnetic properties of Lead Tungstate (PbWO<sub>4</sub>) nanostructures produced by chemical precipitation method are inspected. Powder X-Ray Diffraction (XRD) analysis reveal the tetragonal structure of pure and Cr doped PbWO<sub>4</sub> compounds. The appearance of metal oxide vibrations (Pb, W, O and Cr) is identified through Fourier Transform Infra-Red (FTIR) spectroscopy analysis. Electron microscopy images confirms the formation of double taper like shape in PbWO<sub>4</sub> and the morphological changes induced by Cr ions in the doped compounds. Magnetization studies demonstrate that paramagnetic nature of pure compound and carrier induced exchange interactions which results anti-ferromagnetic phase transition in higher concentration of Cr doped PbWO<sub>4</sub> samples. From the present investigation, tunability of magnetism with respect to the dopant concentration in PbWO<sub>4</sub> system at room temperature leads the material for fabrication of magneto-optical devices.

**Key words:** Lead Tungstate, Precipitation, Nano spindles, optical bandgap, Magnetism

## 1. Introduction

The development of nano or micro materials with controlled morphologies may open new opportunities to explore the chemical and physical properties of materials [1]. In the recent years, Metal tungstates with formula  $MWO_4$  have attracted much attention due to their interesting structural and photoluminescence properties [2]. In the  $MWO_4$  compounds, if  $M^{2+}$  has small ionic radius  $< 0.77 \text{ \AA}$  ( $Ni = 0.69$ ), it belongs to the wolframite-type monoclinic structure where the tungsten atom adopts an overall six-fold coordination [3]. However, if larger bivalent cations with ionic radius  $> 0.99 \text{ \AA}$  ( $Ba=1.35$ ), they exist in the so-called scheelite type tetragonal structure where the tungsten atom adopts tetrahedral coordination. These scheelite structured materials have found applications in scintillation counters, lasers and optical fibers [4,5,6,7]. Some of the divalent transition metal tungstates have also gained commercial interest in lasers and fluorescent lamps, while some are of special importance due to their electrical conductivity and magnetic properties [8].

Among various metal tungstates, lead tungstate ( $PbWO_4$ ) is a promising and potential material for high-energy physics because of its high density ( $8.3 \text{ g/cm}^3$ ), short decay time, high-irradiation damage resistance, intriguing luminescence and stimulated Raman scattering behavior [3]. In recent years, the metal tungstates have been focused due to their structural, optical and photocatalytic properties. From the earlier reports, the Sb doped  $PbWO_4$  nano spindles shows the enhanced luminescence properties synthesized by shape controlled sono chemical method [9]. Two dimensional dendritic  $PbWO_4$  compounds exhibits the good luminescence behavior [10].

Numerous works are dedicated to the development of tungstate compounds because of their intriguing structural properties and their potential application in various fields such as phosphors, optical fibers, and pigments [11, 12]. In general,  $PbWO_4$  compounds are synthesized by soft chemical methods, such as chemical precipitation, sol–gel, sono chemical synthesis, micro emulsion method and hydrothermal route [13- 17] these methods have been employed to control the chemical composition, homogeneity and microstructure of  $PbWO_4$  compounds. However, room temperature chemical precipitation method is more convenient, economic and eco friendly.

In the present work, pure and Cr doped  $\text{PbWO}_4$  compounds was synthesized by Chemical precipitation method without using any surfactants. The synthesized compound was characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR), Raman Spectroscopy, High Resolution Scanning electron microscopy (HRSEM), UV–Visible spectroscopy and Room temperature magnetization studies

## **2. Experimental**

### **2.1 Synthesis**

All the chemical reagents were analytical grade and used without further purification. In a typical procedure. The pure and Cr doped  $\text{PbWO}_4$  compounds were synthesized by simple chemical precipitation method. Initially, the stoichiometric solutions of Lead nitrate [ $\text{Pb}(\text{NO}_3)_2$ ], Chromium nitrate [ $\text{Cr}(\text{NO}_3)_3$ ] and Sodium Tungstate ( $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ) have been prepared by dissolving in de-ionized water separately. Then, the prepared Lead nitrate solution was added drop wise into Sodium tungstate solution under constant stirring. The solution was stirred constantly for 6h and then the precipitate was left aging for 12h. In order to remove the solvents and organic moieties such as  $\text{Na}^+$  and  $\text{NO}_3$ , the precipitate was separated by centrifugation and washed with de-ionized water, ethanol and acetone consecutively for several times and then the resultant product was dried at ambient temperature for 24h. Finally, the end product was well ground and calcined at  $500^\circ\text{C}$  to achieve high crystalline nature. Similar procedure was followed to prepare Cr (Chromium nitrate solution) doped  $\text{PbWO}_4$  compounds.

### **2.2 Characterization**

The phase and crystallinity of the samples was examined by Bruker D2 PHASER X-Ray Diffractometer. The XRD pattern was recorded with  $\text{CuK}\alpha$  ( $1.5418 \text{ \AA}$ ) radiation in  $2\theta$  range of  $10^\circ$ - $80^\circ$  and step size of  $0.02^\circ$ . FTIR spectra were recorded in the range of  $400$ -  $4000 \text{ cm}^{-1}$  by Perkin- Elmer IR instruments. Surface morphology and elemental composition of the samples was investigated by Quanta 200 FEG HRSEM empowered with EDAX facility. UV-Visible absorption spectral analysis of all the prepared compounds was carried out by Shimadzu (UV2450)

spectrophotometer in the wavelength range of 200 to 800 nm. The magnetization behaviour of all samples was analyzed by Lakeshore 7410 Vibrating Sample Magnetometer (VSM).

### 3. Results and discussion

#### 3.1. Phase analysis

The phase and crystallinity of synthesized pure and Cr doped PbWO<sub>4</sub> samples are analyzed by powder XRD and shown in Fig. 1. From the figure, all the reflection peaks correspond to the crystallographic planes of (112), (004), (200), (204), (220), (116), (312), (224), (208) and (316) tetragonal stolzite phase of PbWO<sub>4</sub> compound, which can be indexed and matched with standard data of (JCPDS card No. 19-0708, a = b = 5.462 Å and c = 12.049 Å with space group I41/a) [13]. The strong and sharp diffraction peaks indicate the good crystallinity of the prepared samples. However, the intensity of the diffraction peaks at various dopant concentration suggests that the Cr concentration influences the crystallinity of samples with the same crystalline phase of PbWO<sub>4</sub> since the observed diffraction peaks are similar.

The crystallite size was calculated using scherrer method and relation is given by:

$$D = \frac{K\lambda}{\beta \cos\theta} \text{----- (1)}$$

Where D is the crystallite size (nm), K is the shape factor (0.9);  $\lambda$  is the wavelength of CuK $\alpha$  (1.5418 Å),  $\beta$  is the Full Width Half Maximum (FWHM),  $\theta$  is the diffraction peak position (Bragg angle).

The calculated crystallite size from Scherrer's formula is around 55 nm for pure samples, and doped samples shows the peak broadening was considered as a result of reduction in crystallite size. Hence, the X-ray diffraction studies confirms the single phase formation of pure and Cr doped PbWO<sub>4</sub> compounds.

#### 3.2 FTIR Spectroscopy studies

FTIR spectra of pure and Cr doped PbWO<sub>4</sub> samples measured in the region of 400- 4000 cm<sup>-1</sup> are shown in Fig 2. The characteristic vibrations of the tetrahedral anion WO<sub>4</sub><sup>2-</sup> are at 1000–

700  $\text{cm}^{-1}$  [3]. The peak position at 1569  $\text{cm}^{-1}$  corresponds to the surface-hydroxyl group [3]. The characteristic broad absorption band around 777  $\text{cm}^{-1}$  was related to  $\nu_3$  internal modes which were assigned to O–W–O anti-symmetry stretching vibrations in  $[\text{WO}_4]$  tetrahedron. The 1124  $\text{cm}^{-1}$  and 2334  $\text{cm}^{-1}$  represents the residual of organic materials present in the sample. The peak at 3396  $\text{cm}^{-1}$  corresponds to water molecules adsorbed on the surface of the sample. From the figure, it also observed that there are small discrepancies in the metal oxide vibration as the content of Cr ions introduced in the Pb-W-O lattice.

### 3.3 Raman Spectroscopy studies

To characterize the evolution of observed phases and try to correlate with vibration modes existing in the substances, Raman spectroscopy was used. The Raman spectra of pure and chromium doped  $\text{PbWO}_4$  compounds are shown (Fig.3). The peaks at 898, 748, 318, and 161  $\text{cm}^{-1}$  correspond to the vibration modes  $\nu_1(\text{Ag})$ ,  $\nu_3(\text{Bg})$ ,  $\nu_3(\text{Eg})$ ,  $\nu_2(\text{Bg})$ , and  $\nu_2(\text{Ag})$ , respectively, according to the spectra, which are comparable with those previously reported [3]. The high frequency bands that correspond to Raman-active vibration modes are related to strong force constants between W and O atoms, and they are mostly caused by the stretching and bending vibrations of the shorter metal–oxygen bonds within anionic groups [13].

### 3.4 Morphological Studies

The HRSEM micrographs of pure and Cr (10% & 20%) doped  $\text{PbWO}_4$  compounds are shown in Fig. 3. From the images, spindles like shape was observed for pure  $\text{PbWO}_4$  compounds whereas the dopant concentration increases the shape of the samples get altered, this may be due to the Cr ions involved in the growth mechanism. In general, the surface morphology and dimensions of particles were strongly depends on reaction conditions such as; initial concentration, molar ratio, temperature and pH of the solution. Therefore, the size or shape of compounds could be tuned easily by controlling the experimental conditions.

In this reaction process,  $\text{PbWO}_4$  nuclei were generated via the reaction between  $\text{Pb}^{2+}$  and  $\text{WO}_4^{2-}$  in the precursor solution. The formed nuclei of  $\text{PbWO}_4$  tend to grow into larger particles. It is well known that the growth rates of various faces of the nanoparticles could be kinetically

controlled by selective adsorption and desorption on the surfaces [5,6]. After continuous nucleation and growth spindle like  $\text{PbWO}_4$  particles evolved from polyhedra like  $\text{PbWO}_4$  polycrystalline samples. This phenomenon might be explained by the Ostwald ripening process in which nanoparticles are described in terms of growth of larger particles at the expense of smaller particles [13]. Reduction in surface energy is the primary driving force for nanoparticles and morphological evolution.

### 3.5 Optical studies

The UV–Vis absorption spectra of pure and Cr doped  $\text{PbWO}_4$  compounds are shown in figure 6. The absorption peak was observed around 300 nm could be related to the band transition between the occupied O2p orbital and the empty W 4f orbital [3]. According to the band theory, the lower part of conduction band (CB) is formed by 5d states of the  $\text{W}^{6+}$  ion and 6p states of the  $\text{Pb}^{2+}$  ion in  $\text{PbWO}_4$ , and the coping of valence band (VB) is formed by 6s states of the  $\text{Pb}^{2+}$  ion and 2s states of the  $\text{O}^{2-}$  ion. It has been reported that there might be  $(\text{WO}_4)^{3-}$  and  $\text{Pb}^{2+}\text{-VO}$  as the centers of electron traps in the band gap of  $\text{PbWO}_4$  [3]. The corresponding energy of  $(\text{WO}_4)^{3-}$  and  $\text{Pb}^{2+}\text{-VO}$  centers below the bottom of the conduction band is 0.05 eV and about 0.55 eV, respectively. From the optical absorption spectra, the addition of Cr in the lattice, induce optical transition between them, which is evidenced from the visible region absorption. The strong optical interaction between Cr 2p states with 4f states of tungsten.

Tauc equation is utilized to identify the energy gap ( $E_g$ ) of pure and Cr doped  $\text{PbWO}_4$  nanostructures [13]:

$$\alpha h\nu = (h\nu - E_g)^n \quad (3.2)$$

Where  $\alpha$  = absorbance,  $h$  = Planck's constant,  $\nu$  = frequency and  $E_g$  = optical band gap [19].

In the present work, the existence of high absorption coefficient discloses the direct allowed electronic transition of the prepared compounds. Plot was made between  $E_g$  against  $(\alpha h\nu)^{1/2}$  are shown in Fig. 6 (a & b), then the observed band gaps are presented in Table 2. From the table, as the concentration of Cr increases, there is an increasing trend in optical band gaps are observed, this may be due to the effect of quantum confinement. Which clearly suggested that the

impact of crystallite size, and surface morphology of the prepared nanostructures. Hence, inverse relation between the particle size and optical bandgaps were affirmed by UV-VIS analysis. The optical bandgap values are associated with development of intermediary energy levels because of the distortions on  $[\text{WO}_4]^{2-}$  tetrahedrons on synthesis process [2, 3]. Further, the dopant concentration against optical bandgap is presented graphically and shown in Fig. 3.5c. Hence, the difference in optical band gaps confirm the role of surface morphology, dopant involved growth process.

### 3.6 Magnetization studies

The room temperature magnetization studies of pure and Cr doped  $\text{PbWO}_4$  samples are shown in Fig. 9. From the figure, it is found that pure  $\text{PbWO}_4$  compound shows paramagnetic ordering, further, the higher concentration of Cr doped  $\text{PbWO}_4$  samples demonstrate the anti-ferromagnetic behavior. Generally, the metal tungstates exhibit paramagnetic behavior and the origin of ferromagnetism was possibly due to oxygen vacancies which can induces the exchange interaction between spins of unpaired electrons at the surface of nanoparticles. These oxygen vacancies create an additional electron and form  $\text{W}^{6+}$  ions at the surface which results in a distortion process of  $[\text{WO}_4]$  tetrahedron groups and favoring the formation of intermediary energy levels within the band gap of tungstate [16]. These energy levels are composed between oxygen  $2p$  states (near the valence band) and tungsten  $5d$  states (below the conduction band). While doping Cr ions in  $\text{PbWO}_4$ , the magnetic interaction increases depends on the unpaired electrons induced by dopants.

It is to be pointed out that the surface defects created by the synthesis process may induce surface spin disorder and alteration in coordination of surface atoms in that compound [17,18]. Due to broken exchange bonds and Cr –Cr interaction render the surface spin disorder results the anti-ferromagnetic in 20% Cr doped samples. According to RKKY interaction theory, it is to be noted that the change in magnetic interaction depends on the relation between Fermi wavenumber of conduction carriers and the distance between neighboring magnetic moments [19,20]. Hence, in the present work, the enhanced ferromagnetic behavior of Cr doped compounds may be due to the exchange interaction between local spin polarized electrons of Cr ions and conduction electrons

of  $\text{PbWO}_4$  compounds. These conduction electrons are considered as a medium to interact among Cr ions [14]. Hence, from the magnetization analysis the oxygen vacancy associated with free charge carrier play important role on magnetism behavior of Cr doped  $\text{PbWO}_4$  compounds.

#### **4. Conclusion**

In the present work, pure and Cr doped  $\text{PbWO}_4$  nanostructured compounds synthesized by co-precipitation method has been investigated. Powder XRD studies reveal the formation of szolite type tetragonal structure. Metal oxides vibrations of pure and Cr doped compounds were analyzed through FTIR spectra. From surface morphology analysis, it was found that the pure compound exhibits particles with spindles like shapes, whereas Cr doped  $\text{PbWO}_4$  samples shows high degree of agglomeration and dissolved the shape of pure compounds. The UV–Vis absorption spectral analysis of pure and Cr doped  $\text{PbWO}_4$  shows intense absorption at 260 nm and confirms the excellent optical behavior of all the compounds. The wavelength shift towards higher region for the doped compounds addresses the interaction of Cr ion with Pb-W-O lattice. Magnetization study reveals the para to anti-ferromagnetic phase transition in Cr doped  $\text{PbWO}_4$  compounds. From the present investigation, it was identified that the dopant mediated carrier injection influences surface morphology and oxygen vacancy of the compounds which enables the magnetic transition in Cr doped samples. Hence, the possible tuning optical and magnetic property of  $\text{PbWO}_4$  compounds based wide band gap semiconductors will leads to a hopeful candidature for magneto electronic applications.

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**Figure captions**

1. Figure. 1: XRD patterns of pure and Cr doped  $\text{PbWO}_4$  compounds
2. Figure. 2: FTIR Spectra of pure and Cr doped  $\text{PbWO}_4$  compounds
3. Figure. 3: SEM images of pure, 10% and 20 % Cr doped  $\text{PbWO}_4$  compounds
4. Figure. 4: UV-VIS Spectra of pure and Cr doped  $\text{PbWO}_4$  compounds
5. Figure 5a: Tauc plot of pure and Cr doped  $\text{PbWO}_4$  samples
6. Figure 5b: Optical band gap variation with respect to dopant concentration of pure and Cr doped  $\text{PbWO}_4$  samples
7. Figure. 6: Magnetization studies on pure and Cr doped  $\text{PbWO}_4$  compounds.