Doping Effect an Optical Band Gap and Luminescence of Pure and Nd-Doped CoWO₄ Wolframite Nanostructure Synthesized by Chemical Precipitation

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Abstract : Wolframite type pure andNd-doped CoWO₄ were synthesized by easy and effective chemical precipitation technique. Typical monoclinic phase and crystal structure of the samples were confirmed from the XRD pattern. Well defined nanocubicalmorphology with round edges of the pure and doped samples were confirmed from the electron microscopy analysis. UV-Vis spectra for pure and Nd³⁺ doped CoWO₄ demonstrates that the excellent optical behaviour of the wolframite cobalt tungstates nanostructure. Optical energy band gap was varied with the doping as well as calcination temperature ascribes to the changes in the electronic structure. From the band gap calculation it is confirmed that the observed band gap is direct which is not belongs to the indirect. Further, the red shift in the absorption edge substantiates the formation of nanacrystalline CoWO₄ and thus evidences the incorporation of Nd into Co lattice site completely. The strong PL emission peak was centered at 455 nm region for all the samples due to the radtiative transition within the $[WO_4]^{-4}$ tetrahedral group. The relative intensity of the emission band reduced and at 5 mole% doping it is almost no emission was observed. This luminescent quenching is confirms the lower annihitaion process in doped CoWO₄ nanostructure when compared to pure wolframite. Overall, from this study tuning of an electronic structure by doping will influences on the optical band gap as well as PL emission in the CoWO₄ nanostructure.

Keywords : Chemical synthesis, Wolframite, optical band gap, luminescent quenching.

Introduction

Recently, ternary oxide semiconductors that are $M^{2+}WO_4$ with the wolframite crystal structure have been received much attention due to their technological properties such as higher values of thermal stability, refractive indexes, ferroelasticity, ionic conductivity and X-ray absorption coefficeints [1-3]. Because of its intriguing luminescence and structure properties, the metal tungstate is an attractive material for photonics and photoelectronics. In these applications it is important to study their optical band gap very accurately [4]. However, earlier reports show wide dispersion in the band gap and there was no agreement has been observed. Till date wolframite structured metal tungstates of CdWO₄, ZnWO₄, CoWO₄ and MnWO₄ are known for their wide applications in conventional catalysis, or as scintillator material, in photoluminescence, optical fibres and as materials in microwave technology [5-11]. Besides the above, themetal tungstates were used as photocatalyst for removal of various organic pollutants from the water [12]. As a p-type semiconductor, CoWO₄ has been widely investigated for optical devices and photoluminescence materials [1&2]. It is well known that optical behaviour is particle size dependent, therefore it should controlled through typical synthetic conditions. According to the earlier reports many methods have been reported including conventional ceramic method, sol-gel, hydrothermal and precipitation technique [8-11]. Among them chemical precipitation method is most widely used due to their adequate synthetic conditions and cost effective for large scale production.

Recent years, the materials with both the d and f-electrons have received more attention for optical displays. To tune their magnetic and optical property it is important to synthesis the new phosphor material with mixed (d&f) electrons [13]. Generally, rare earth metal ions can offer the f-electron which changes the optical character of the host material.Till date only few reports are available for rare earth doped metal tungstates. Mixed electron compounds such as metal doped rare earth metal tungstates are extensively studied as the white light emitting diodes. For clear understanding the comprehensive spectral studies are essential in related to the luminescent behaviour. Naik et al have reported the systematic investigations in luminescent characteristic of Ce^{3+} doped $CoWO_4$[14]. The strong luminescent enhancement was found from their report in contrast to earlier studies which show the emission quenching by doping. Further,in our earlier report it is explained the magnetic and suppressed luminescent features in Yb^{3+} doped $CoWO_4$[15]. From the earlier reports it can be understandable that, in addition to the host material, the dopant also play a vital role for luminescence efficiency. However, the energy transfer and typical electronic transition and site symmetry of the host material is still not clear and it needs further investigations.

In this present study we are interested to investigate the optical band gap and luminescent characteristic Nd^{3+} doped $CoWO_4$ nanostructure with respect to the calcination temperature. To the best of our knowledge there is no reports has been published elsewhere, the magnetic and optical response of $CoWO_4$ with Nd rare earth metal ion. Here for the first time we are reporting the variation in optical band gap for f-electron mixed $CoWO_4$ nanostructure. The origin of characteristic band gap variation and their luminescence were discussed.

Experimental Techniques

Synthesis Procedure

The simple and effective chemical precipitation techniques was used to synthesis the pure and Nd^{3+} doped $CoWO_4$ as reported earlier [8]. Briefly, special grade Cobalt II Acetate (Alfa Aaser), Neodinium III acetate were purchased from Alfa Aaser (99.9%) and used as received without further purification. The various molar concentration of Nd^{3+}cation solution (1%, 3% and 5%) was prepared with mixing the appropriate concentration of Co(CHOO)2 solution. Disodium Tungstate (Merck) was dissolved in double distilled water separately under constant stirring. As prepared Co^{2+}/Nd^{3+}mixed metal-ion solution was added dropwise to tungstate solution rapidly, the violet colored precipitates were formed immediately. 0.1 M of semisolid polyethylene glycol (PEG-mw 1000) was added to the above mixture as a surfactant. After 3 h stirring followed by 15 h aging, the end product was separated by centrifugation and washed thoroughly with deionized water, ethanol and acetone consecutively. In continuation to drying at ambient temperature for 24 h, the powder was calcined at 500 C and 600 °C for 6 h in air. For comparisiona pure $CoWO_4$ nanostructure, also synthesized using the same procedure Nd^{3+}cation solution as mentioned above.

Characterization

XRD pattern of the wolframite nanostructure was taken from the BRUKER D5 Phaser, FTIR spectra of the samples were obtained from the Perkin FTIR spectrophotometer over range of 400-4000 cm^{-1}, UV-Vis spectrophotometer (Shimadzu UV-2450) was used to see the optical absorbance of the sample. For microstructure and morphological features Scanning Electron Microscope (HRSEM) (HITACHI (Japan) SU6600-15KV) and Transmission Electron Microscope (TEM) (HITACHI (Japan) H-7650-80KV) were directly used with Energy Dispersive Spectroscopy attachment. Thermal stability of the $CoWO_4$ was studied using Thermo gravimetric Analyzer (TGA) (BRUKER SDT Q600 V8.0). X-ray fluorescence spectrometer (PL) (S4 PIONEER BRUKER) was used to analyze the luminescent characteristic of the material.

Results and Discussion

Thermal Analysis

Typical temperature versus mass change of the pure and Nd doped $CoWO_4$ are shown in Figure 1. The stepwise crystallization with respect to temperature is as follows; initial weight loss in the TGA curve at around 200 °C is associated to decomposition of metal acetate and solvent evaporation. In continuous, the major weight loss was observed in between 200 °C to 400 °C is mainly attributed to crystallization process takes place. Further, very small and gradual weight loss followed by the plateau region in the TGA curve beyond 400 C. By adding the Nd into Co site the crystallization temperature reduces significantly as shown in fig 1 (b-d). To

maintain the nanocrystalline nature we have fixed the calcination temperature as 500 °C and 600 °C which is in good agreement with earlier reports [8].
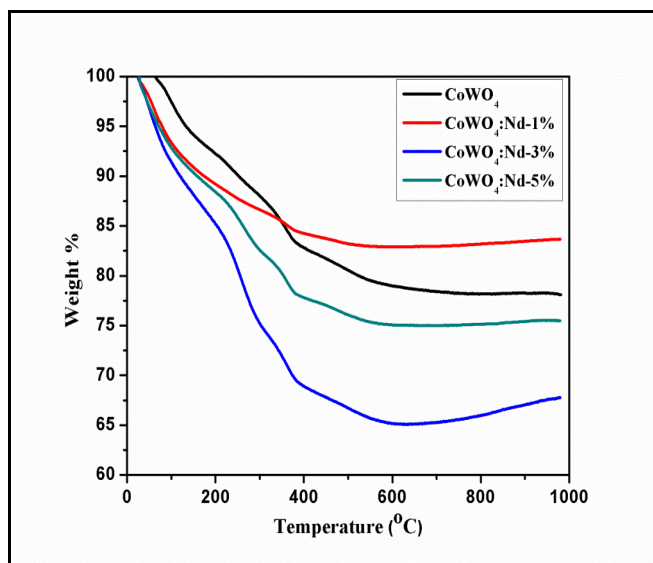

Figure 1. TGA curves of pure and Nd-doped CoWO$_4$ nanostructure.
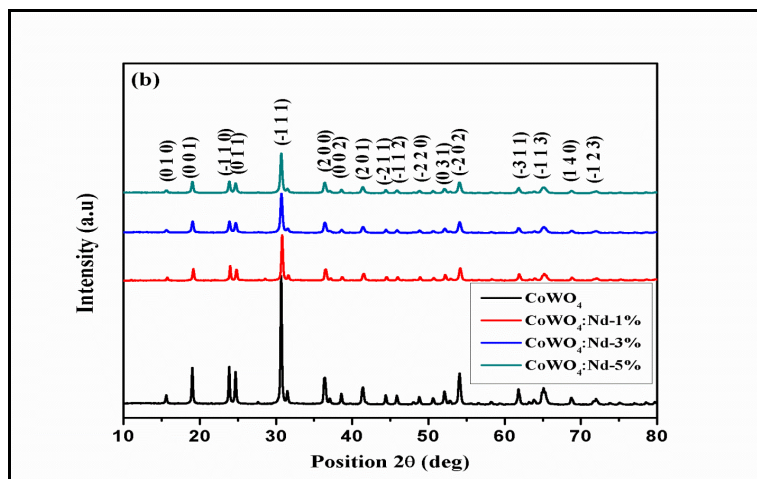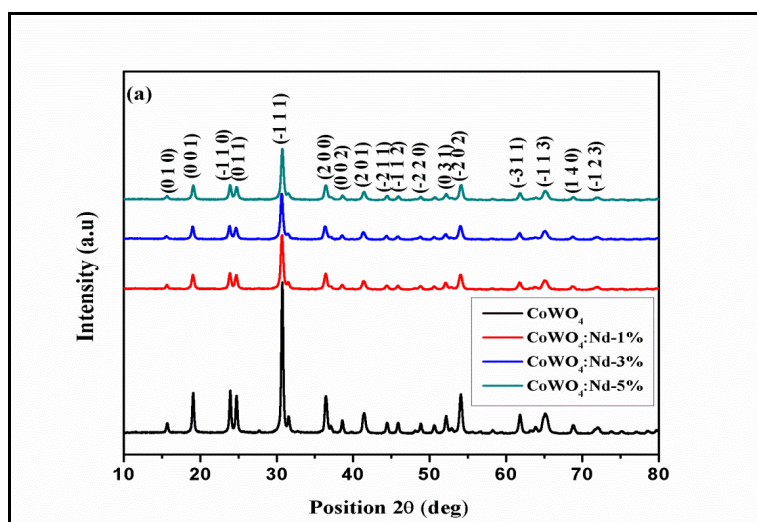
Phase Analysis

Figure 2.XRD Pattern of CoWO4 nanostructure with Nd doping for two calcination temperature (a) 500 °C and (b) 600 °C

The phase and crystal structure of the chemically precipitated pure and Nd doped $CoWO_4$calcined at 500 °C and 600 ºC are shown in Fig. 2 (a&b). The diffraction peaks are assigned well to the monoclinic $CoWO_4$ nanostructure with the space group of P_2/c (13). Further,addition of Nd does not affect the crystalline structure which indicates that complete incorporation of Nd into Co lattice site. There is no additional peaks were found in the XRD pattern due to ternary oxide phasessuch as WO_4 and Co_3O_4. For both the temperature the similar XRD pattern were observed it reveals that the high thermal stability of the compound. The corresponding peak position and their relative intensity were indexed with standard spectrum of [JCPDS # 72-0479] wolframite $CoWO_4$ monoclinic phase. The lattice parameters of the $CoWO_4$ nanostructures were calculated using Unit Cell software and the values are found to $a = 4.949 \text{ Å}, b = 5.680 \text{ Å}, c = 4.696 \text{ Å} \text{ and } \beta = 90.0°$. These values are having good agreement with the previous reports [4, 9&10]. Interestingly, absence of Nd_2WO_6 phase even at higher concentration of Nd (5 mol%) concludes that dopant ion may be substituted in Co site completely. Only the changes observed in the XRD pattern due to the rare earth ion doping is the decrease of relative intensity of the peak with respect to the Nd doping concentration. This ascribes to the addition of Nd^{3+} into Co^{2+} site reduces the crystalline size of $CoWO_4$ considerably. The average crystallite size was estimated from the XRD peaks using Scherer Equation [11].

$$d = {k\lambda}/{\beta cos\theta} \qquad (1)$$

whereβ is the full width half-maximum value of the high intensity peak, k is the so-called shape factor, and λ is the wavelength of the X-ray source used in the XRD. The measured$d$ values are about in the range of 57-85 nm. These values are fairly agreed with the FESEM and TEM observation.
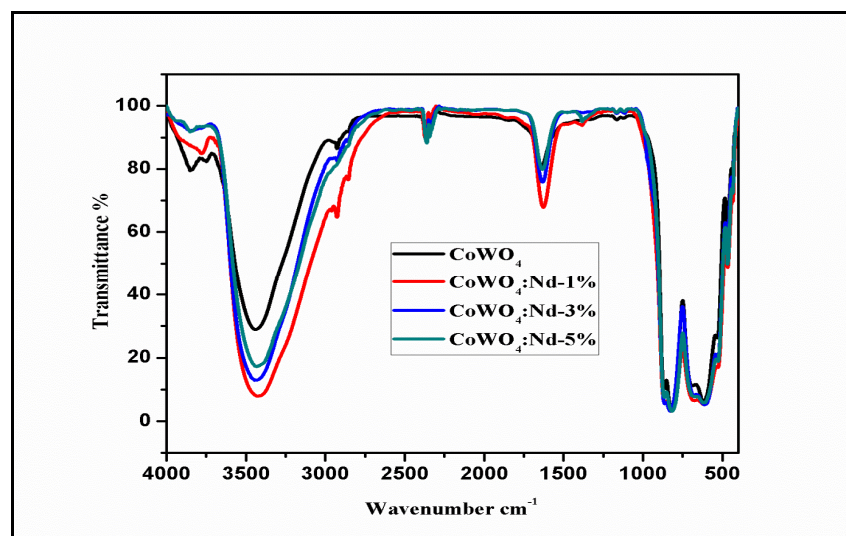
Ftir Studies

Figure 3. FTIR spectra of pure and Nd doped $CoWO_4$ nanostructure heat-treated at 600 °C for 4 h.

Fig. 3 represents the FTIR spectra of pristine and Nd^{3+} doped $CoWO_4$ nanoparticles. All the spectra are shows the similar IR active modes. It can be seen that the characteristic deformation modes fo Co-O, W-O and W-O-W bridges are appeared at low frequency region which around 400-100 cm^{-1}[12]. The strong band at around 500 cm^{-1} corresponds to W-O bonds within the WO_6octahedra. The bands due to O-W-O and W-O bond stretching vibrations are present at 820 cm^{-1} and 621 cm^{-1} respectively. The region around 3000-3800 cm^{-1} corresponds to OH stretching vibration of surface absorbed or internally bonded water molecules [15]. The bending mode of H-O-H is located at about 1640 cm^{-1}. In addition to the above peaks the small peak positioned at 2400 cm^{-1} is associated to the absorption of carbonate pieces by the sample during annealing process [21].

Electron Microscopy Analysis

The surface morphology and particle size of the pure and Nd^{3+} doped $CoWO_4$ nanostructure was analysed using HRSEM. Captured HRSEM images of the samples calcined at 500 °C and 600 °C for 6 h are shown in Fig. 4(a-h). It can be seen that the particles are in present in the shape of round edged cubical morphology with uniform distribution. Further it shows the doped samples are also exhibit similar images like

the pristine one with significant agglomeration thus confirms the formation well defined nanocrystals. Observed particle sizesare in the range of 40-55 and 50-79 nm for the doped samples at two different calcination temperatures. This concludes the doping of rare earth metal ion does not affect the crystal morphology which confirms the incorporation of Nd on to Co lattice site. The doping concentration increases the particle size was considerably reduced and emerges with larger aggregation. In order to confirm the particle size and morphology further TEM observation was taken for pure and 3% Nd doped $CoWO_4$as shown in Fig. 5(a-e). Observed TEM metaphors are directly evidences the formation of well-defined cubical $CoWO_4$ nanoparticles with round edges [9]. No the changes in the morphology was observed by the addition of Nd (3%) even at calcinations. To increase the doping concentration more uniform and smaller particle size was observed. However, increasing the calcination temperature the considerable grain growth can be seen at TEM images. This leads to the formation of well distributed particles and were polycrystalline in nature. From the EDS spectra the primary elemental composition of the compounds was studied and is illustrated in Fig. 6. It evidences the presence of all the elements such as Co, W, O and Ndand appropriate atomic scale stoichiometry without any impurities.
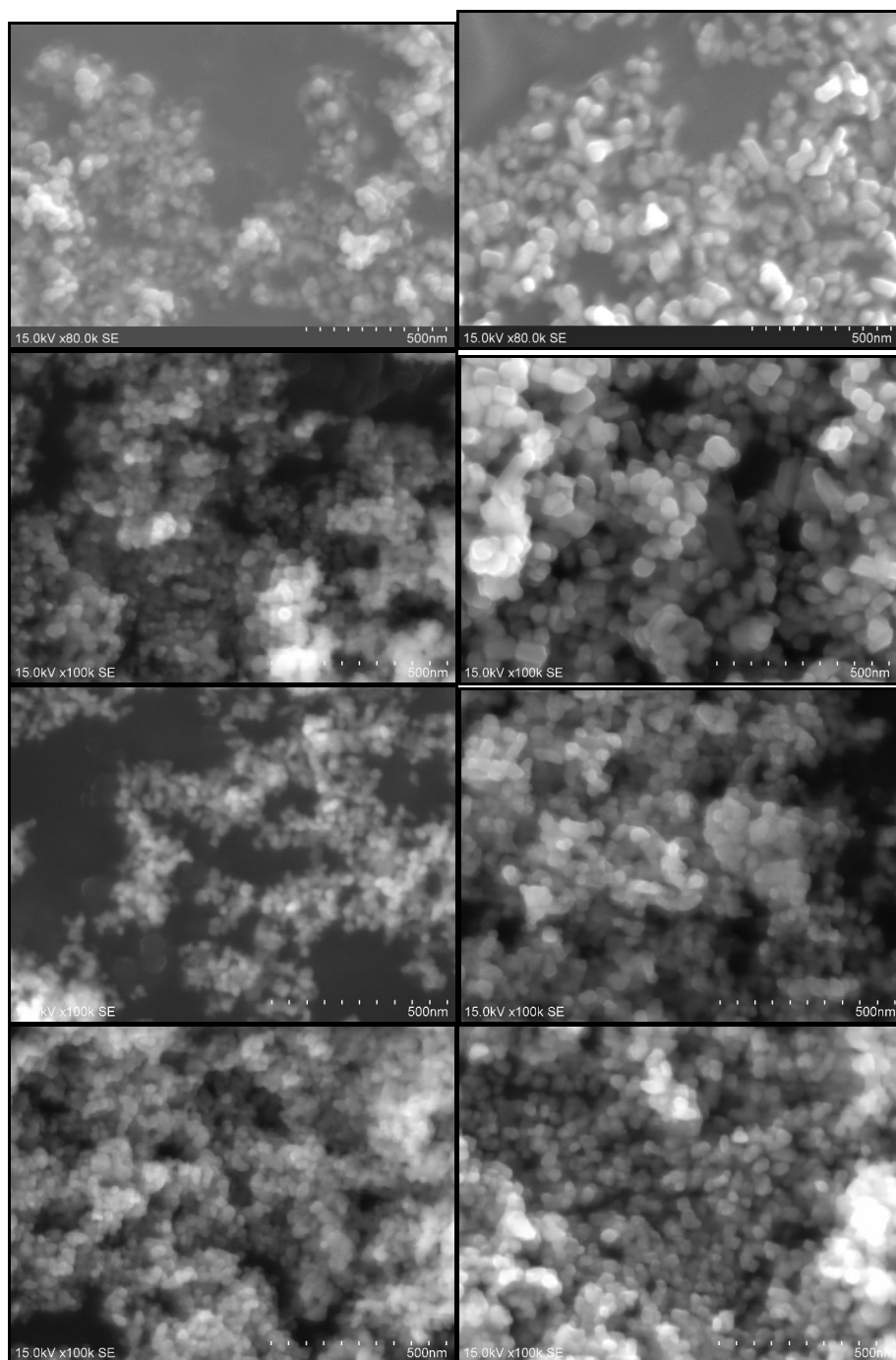

Figure 4. SEM micrographs of pure CoWO₄ (a&b) with various concentration of Nd-1% (c&d), Nd-3% (e&f) and Nd-5% (g&h)
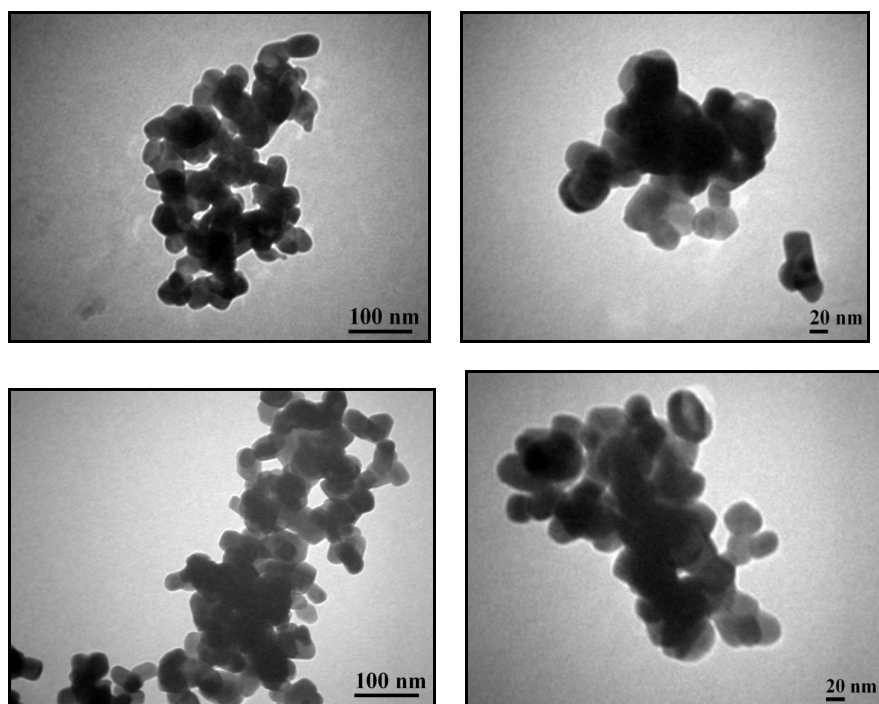
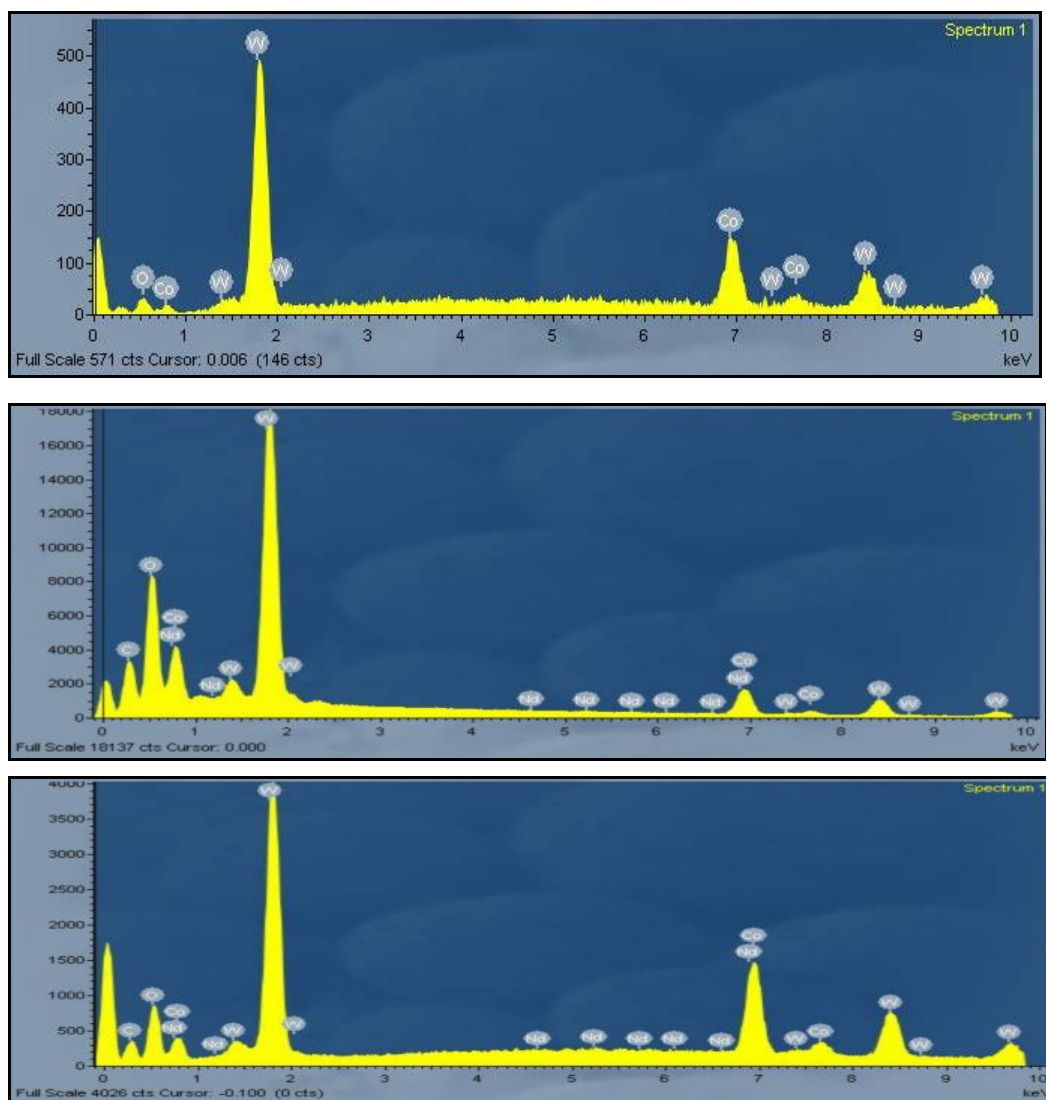**Figure 5. TEM Images of Pure (a&b) and 3 mole% Nd-doped (c&d) CoWO₄ nanostructure**

Figure 6.EDAX spectra of pure CoWO₄ (a) Nd-1% doped CoWO₄ (b), and Nd-5% doped CoWO₄ (c)
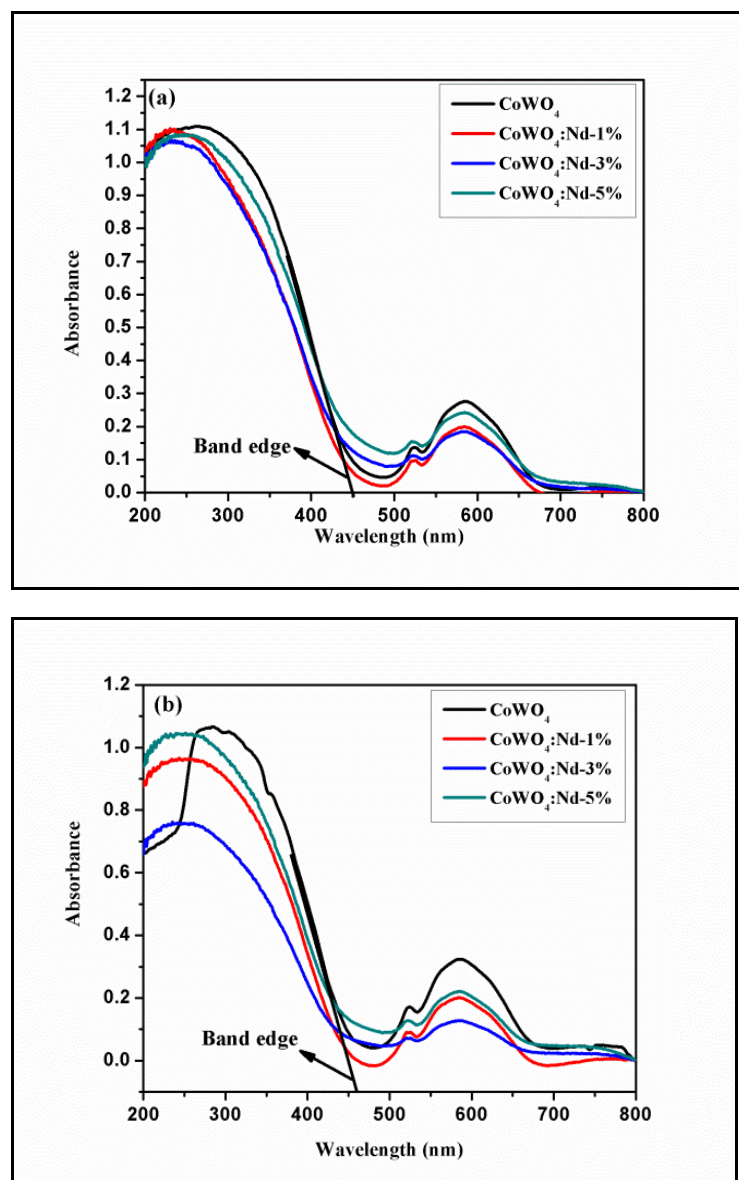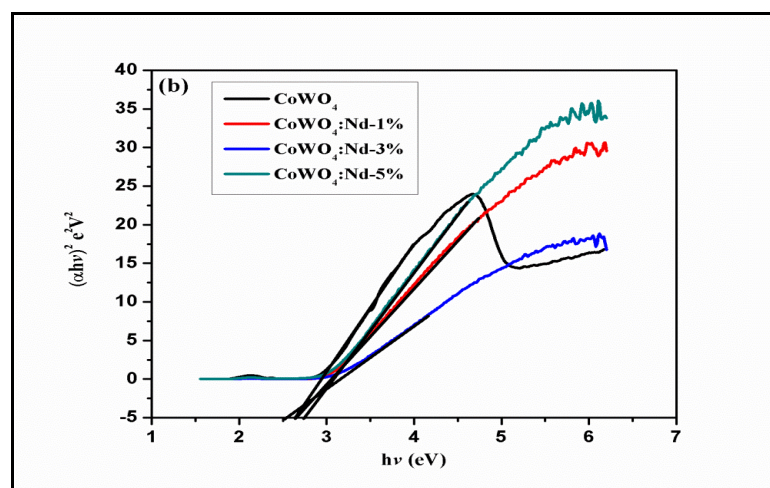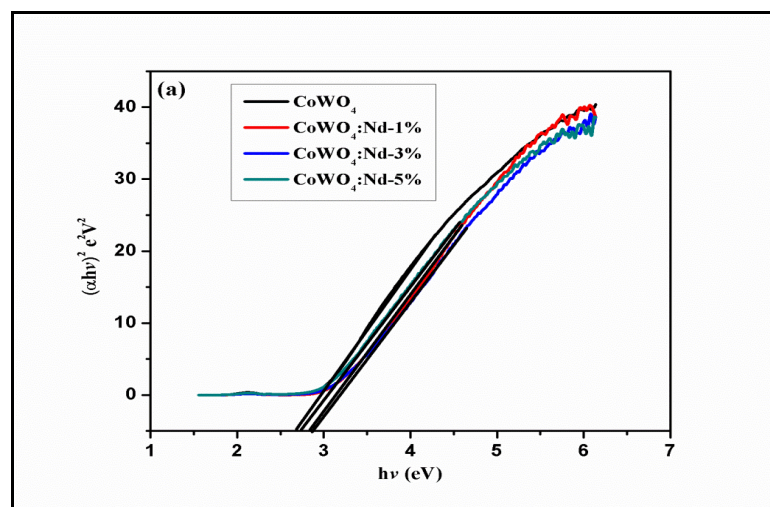
Uv-Visible Spectral Studies

Figure 7. UV-Vis absorption spectra of pure and Nd-doped CoWO$_4$ nanostructure with different calcination temperature of 500 °C (a)and 600 °C (b)

Optical activity of the CoWO$_4$wolframite nanostructure synthesized by chemical precipitation process were analysed through UV-Vis spectrophotometer. The optical absorption spectra of Nd doped wolframite heat treated at 500 °C and 600 °C are illustrated in Fig. 7(a&b). BroadUV absorption maximum at around 270-300 nm, were observed for all the samples which confirms the unique optical behaviour of the material and it is associated to thedirect charge transfer between ligand and metal within the (WO$_4^{2-}$) groupsand not related to the dopant ion [24]. Further,addition of Nd does not change the host CoWO$_4$ matrix andwhich suggests that this absorption may be related to the formation of [WO$_6$]$^{6-}$ complex within the wolframite structure [25].It can be seen that the strong UV absorption edge with extended tail to higher wavelength in the UV-Vis spectra represents the presence of localized energy bands within the band gap of CoWO$_4$. The absorption band shifted towards lower energy by adding the rare earth metal ion for both the temperatures. This is mainly due to the quantum confinement effect which arises by the interaction of divalent metal ion and trivalent rare earth ions. With the strong UV absorption generally localized inter-atomic excitation was observed at visible region and which is mainly due to d-d transition on Co^{2+} or f-f transition of Nd^{3+}. In our case there is the absorption band appeared at above 500 nm belongs to the d-d transition of octahedrally coordinated Co^{2+} ions in the CoWO$_4$ nanostructure.

Generally, the energy band gap is directly related to the crystallnity, particle size and morphology. Only limited studies have been reported earlier with the band gap energy of metal tungstates. Especially, wolframite structured metal tungstates there is no reports to conclude the exact band gap energy. Few authors have studied but still it is controversial. According to their reports it is concluded that optical band gap energy strongly depends on the structural disorder and surface defects which change their optical behaviour [12]. When compared to pure tungsten oxide (WO_3) transition metal tungstates having different electronic structure with M^{2+} and W5f hybridized valence and conduction band. Therefore it is very difficult to calculate the actual energy band gap of the metal tungstates. However, these materials exhibit both the direct and indirect band gap as reported earlier . We believe that foreign impurities also play a vital role in the optical behaviour by changing their electronic structure. To the best of our knowledge there is no reports has been published elsewhere on the optical band gap for rare earth doped $CoWO_4$. In this study by adding the Nd into Co site the significant variation was observed in the optical energy band gap (Eg). Also we followed the same way as reported by Paolo Fornasiero et al to understand the band gap energy and its structural relation in the pure and Nd doped $CoWO_4$ nanostructure.For better understanding we have calculated the band gap using absorption band as well as reflectance spectrafrom the following equations.

Table 1: Measured Band Gap Values of Pure and Nd-doped CoWO4 nanostructure

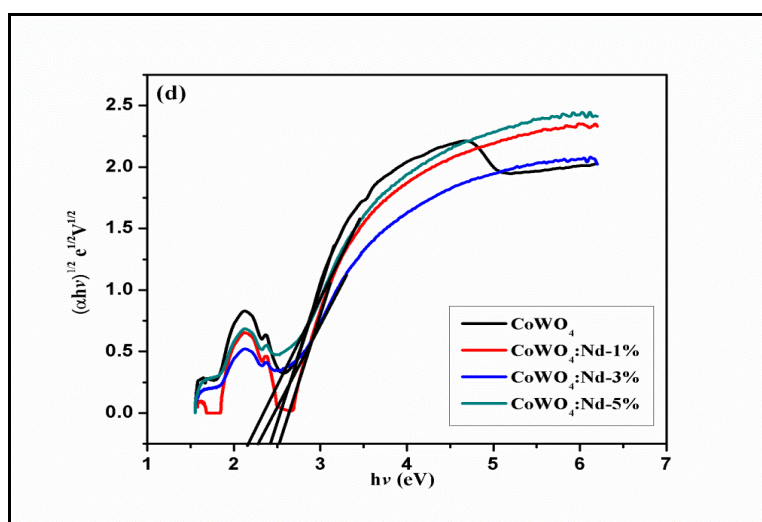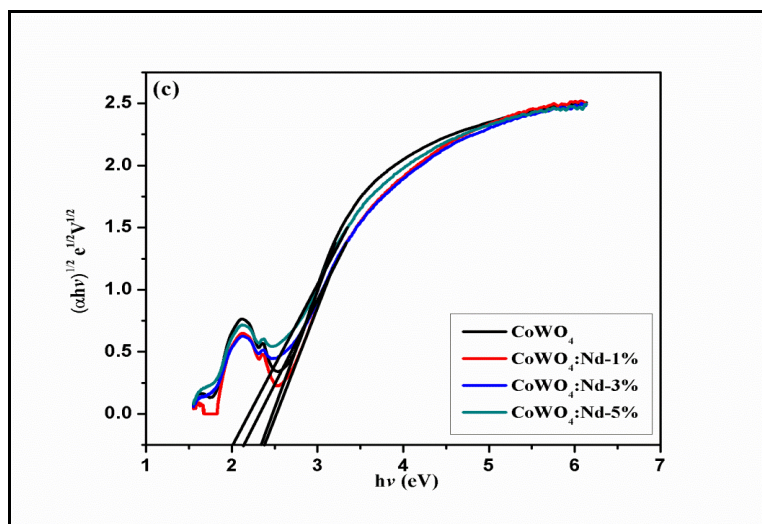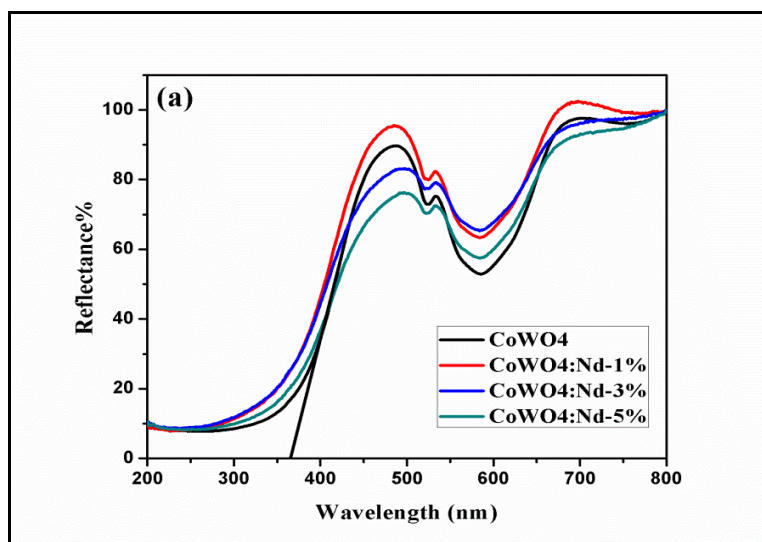| Compound	Direct Band Gap in eV		Indirect Band Gap in eV		Band gap from reflectance spectraeV	
	500 °C	600 °C	500 °C	600 °C	500 °C	600 °C
$CoWO_4$	2.67	2.61	2.15	2.41	2.05	2.09
$CoWO_4$:Nd-1%	2.83	2.66	2.40	2.50	2.12	2.11
$CoWO_4$:Nd-3%	2.87	2.51	2.33	2.28	2.24	2.22
$CoWO_4$:Nd-5%	2.73	2.73	2.02	2.16	2.19	2.16

Figure 8(a-d).UV-Vis absorption spectra Tauc Plots of the pure and Nd-doped CoWO₄ nanostructure.
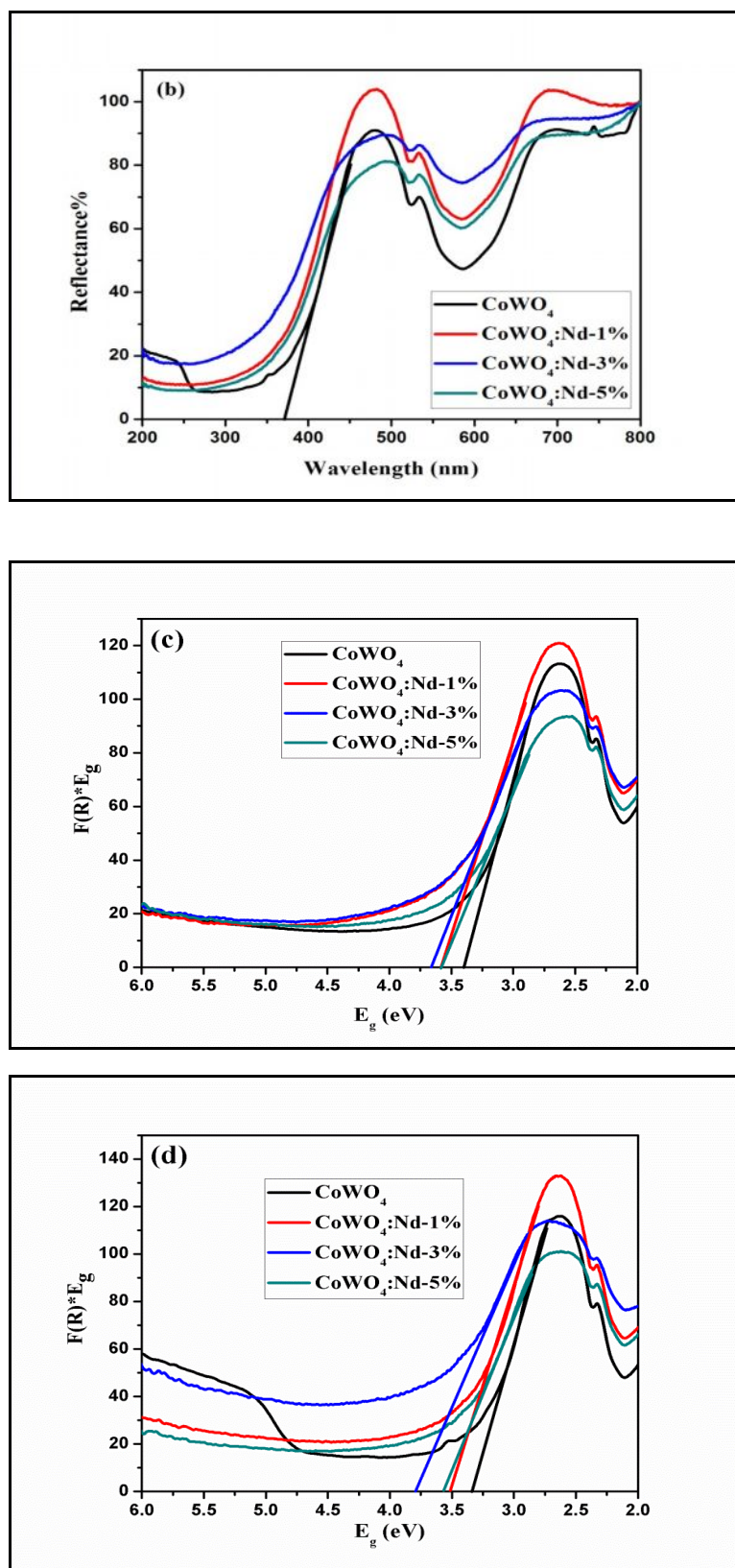
Figure 9. UV-DRS spectra of wolframite CoWO₄ nanostructure with Ndcalcined at 500 °C (a) and 600 °C (b) and (c&d) its corresponding Tauc Plots

$$\alpha h\nu = A(h\nu - E_g)^n \qquad (2)$$

$$F(R) = (1-R)^2/2R \qquad (3)$$

Where in equation (1) α is the absorption coefficient, h is the Plank's constant, ν is the photon energy, B is a constant, E_g is the band gap energy and n is a transition coefficient which is 1/2 and 2 for allowed direct

transitions and indirect transitions respectively. In equation (2) F(R) is Kubelka–Munk function and R reflectance [22].Figure 9(a&b) represents the UV-DRS spectra of pure and Nd doped $CoWO_4$ nanostructure. Further Figure 8(a-d) and Figure 9 (c&d)band gap spectra of pure and Nd-doped $CoWO_4$ nanostructure estimated from both the absorption and reflectance spectra respectively. The linear extrapolation of the plot at $\alpha=0$ corresponds to the energy band gaps of the samples.Interestingly, optical energy gaps are varied with respect to doping as well as calcination temperature confirms the well quality crystalline features of the material. The estimatedEg values both direct and indirect assumption and was obtained from the reflectance spectra are given in table (1).The band gap energies are gradually increased with Nd concentration which describes the quantum confinement effect of the nanosystems. There is no significant difference in the Band gap values which is observed from absorption spectra and reflectance spectra. In contrast, there is much difference was obtained for the direct and indirect assumption. It should be noticeable to assign the band gap of the $CoWO_4$ whether it is direct or indirect. In this study we suggest that the linear variation in the absorption band edge against the band energy is confirm the direct band gap of the $CoWO_4$ nanostructure [24].
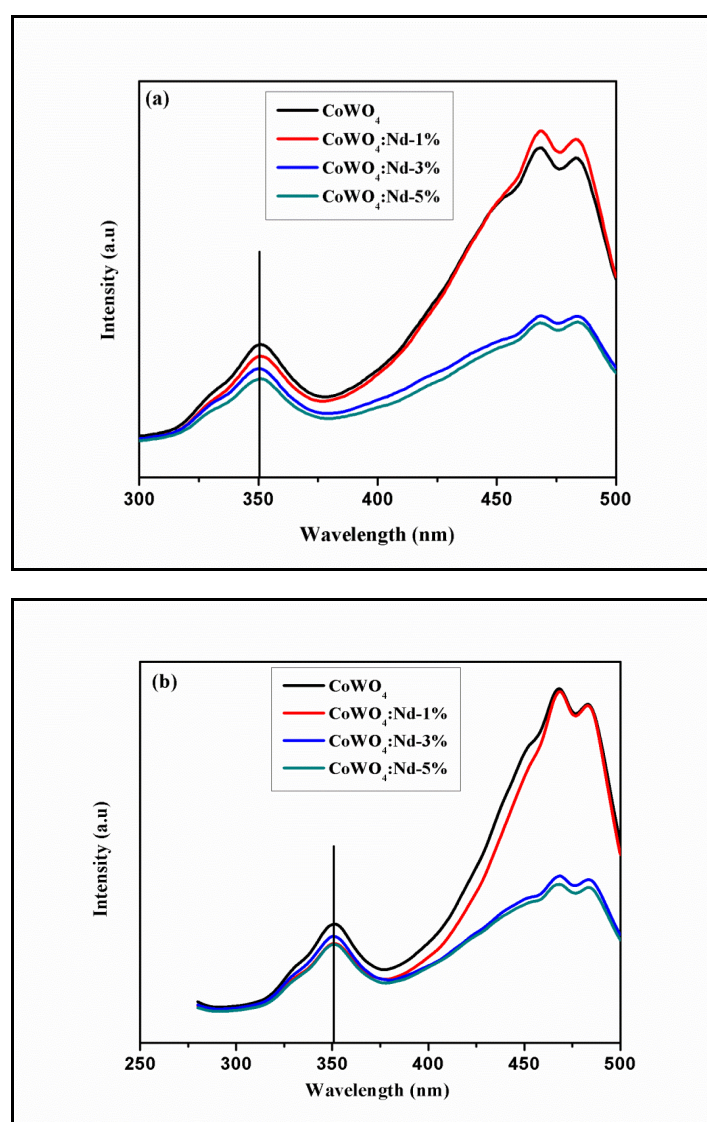
Photoluminescence Studies

Figure 10 (a&b). PL spectra of wolframite pure and Nd-doped $CoWO_4$ nanostructure with two calicination temperature (a) 500 °C and (b) 600 °C.

Figure 10 (a&b) shows the PL spectra of pure and Nd doped $CoWO_4$nanostructureannealed at 500 °C and 600 °C for excitation of 240 nm at room temperature.The broad blue emission was observed at around 455 nm without any hump or shoulder. This is corresponds to the radiative transition of $[WO_4]^{2-}$ tetrahedrons through charge transfer transition between the O2p and the empty d orbitals of W ion [25]. Although, there is no change in the emission band position due to the doping. Further, the emission band due to Nd was not

observed in the PL spectra but it decreases the PL intensity. In general, the synthetic conditions, crystallinity and morphology of the materials are strongly influences on the luminescence [8,9, 16, 18-20]. Therefore it is important to control the particle size as well as morphology in order to increase the luminescent efficiency.At 500 °C calcination there is low intense emission was observed due to the less crystalline and aggregated surface morphology. To increase the calcination temperature to 600 °C the emission intensity increases significantly. This is associated to the formation of good quality crystalline $CoWO_4$with well-defined nanocubical morphology with less aggregation. Thus enhance the PL intensity of the $CoWO_4$nanostructure. When compared to the pure one the Nd doped $CoWO_4$ shows the suppression in the PL intensity which is in good agreement with earlier reports .The observed PL quenching is still not clear for the doped samples. In our previous report on Yb^{3+} doped $CoWO_4$ have shown the lower PL intensity upto 3% and further increased for 5 mol% Yb concentration. However it is lower than the pristine $CoWO_4$nanocubes. In contrast, Naik et al. have reported that the enhancement in the PL insensityupto 2% and further it decreases for higher concentration [8]. This is due to the low annihilation within the $[WO_6]^{6-}$phase thus reduces the intrinsic luminescent features of the $CoWO_4$. We suggest that the change in electronic structure may be changing the optical features in this system. The comprehensive investigations with this factor are needed to understand the luminescent quenching as well as desired optical features of the $CoWO_4$ nanostructure.

Conclusions

In summary, well crystalline Nd-doped $CoWO_4$were synthesized using single step solution based chemical precipitation technique.Polycrystalline natures with monoclinc phase of the samples were confirmed from the XRD pattern. By doping there is no found any other possible secondary phases in the XRD pattern. Clear morphology of nanocubeswith round edges crystalswasobtained and which is confirmed from the electron microscopy analysis.The strong UV-absorption with extended tail in the UV-Vis spectra for pure and Nd^{3+} doped $CoWO_4$ demonstrates the excellent optical behaviour of the wolframite cobalt tungstates nanostructure. The variation in absorption band and optical band gap was observed with respect to annealing temperature as well as doping concentration. There is the significant change in the band gap value for the doped samples when compared to pristine. This suggest that the incorporation of Nd into Co site change their electronic band structureby introducing the inter energy bands.Further, the red shift in the absorption edge substantiates the formation of nanacrystalline $CoWO_4$ and thus evidences the incorporation of Nd into Co lattice site completely. At 240 nm excitation wavelength, the strong PL emission peak was centred at 455 nm region for all the samples. In addition of Nd the relative intensity of the emission band reduced and at 5 mole% doping it is almost no emission was observed. This luminescent quenching is in comparable with similar earlier reports but the luminescent suppression due to the doping in wolframite metal tungstates is still controversial.In this present investigations we have suggest that the tuning of an electronic structure by doping will influences on the optical band gap as well as PL emission in the $CoWO_4$ nanostructure. However, it needs further investigations with the desired optical features could be the better choice of materials for optoelectronic devices.

Acknowledgement

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