

Optical Behavior Of Pure And DY-DOPED CoWO₄ Nanomaterial

J Juliet Josephine Joy, Department of Physics , Adhi College of Engineering and Technology,
Kancheepuram, India. jose_joy56@yahoo.com

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 increase of Dy³⁺ doping decreased the particle growth, and enhanced “blue-shift” in the UV-Vis absorption spectra. The systematic investigation of optical studies reveals that interesting optical behavior of Dy-doped CoWO₄ nanocrystals. Measured optical energy band gap are found to be in the range of 2.6 – 3.0 eV. The shift in absorption band edge may be due to the presence of larger size Dy ion which influences on the luminescence efficiency significantly.

Keywords: optical, nanomaterials , chemical precipitation, Photo Luminescence.

I. INTRODUCTION

When compared to traditional binary oxides (e.g. TiO₂, ZnO and SnO₂ 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 (1). 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 (2). 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 (3,4,5). Especially, metal tungstates are attractive materials and have received great research interest due to their intriguing luminescence and structural properties (6). As a p-type semiconductor CoWO₄ has been most widely studied material for various technological applications such as catalysis, sensor, displays and optoelectronics (7). It is well established that the additional doping will induce the structural and magnetic changes in the host systems (8). Fu-Shan Wen et al (2002) reported the photo luminescent properties of hydrothermally synthesized Eu³⁺ doped ZnWO₄. Fugui Yang et al (2008) study the growth and spectral analysis Ho³⁺ doped ZnWO₄. Recently, Naik et al (2010) reported the luminescent features of CoWO₄:Ce³⁺ nanostructure. There are no reports published elsewhere with electron or hole doped CoWO₄ 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 (Ln³⁺ = 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 (9). Chunxia Li et al (2009) reported the Ln³⁺ doped YPO₄ nano/microstructures with tunable luminescent colors. The effect of Nd impurities on the optical and dielectric and electrical properties of PbWO₄ single crystals was reported by Weifeng Li et al (2005). The bright white up conversion luminescence from Er³⁺-Tm³⁺-Yb³⁺ doped CaSnO₃ powders has been reported by Pang et al (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 (10).

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 (11,12) and promising applications in optoelectronics (13,14). Till date several chemical synthesis processes such as sonochemical (15), hydrothermal (16), co-precipitation (17) etc., have been used for the preparation of metal tungstate especially for the wolframite nanocrystals. In this way Di Chen et al (2003) reported the low temperature synthesis of metal tungstates nanocrystallites in ethylene glycol. Similarly, Fen Zhang et al (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 CoWO₄ 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, photoluminescence (PL) and optical band gap of the Dy-doped CoWO_4 nanocrystals are studied.

II. EXPERIMENTAL TECHNIQUES

2.1 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 $\text{Co}(\text{CHOO})_2$ and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ were dissolved separately in deionized water under vigorous stirring for 30min. 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 $\text{Dy}(\text{CHOO})_3$ with the $\text{Co}(\text{CHOO})_2$ solutions using the same experimental procedure.

2.2 Characterization

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 find the optical absorbance of the sample. 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. X-ray fluorescence spectrometer (PL) (S4 PIONEER BRUKER) was used to analyze the luminescent characteristic of the material.

III. RESULTS AND DISCUSSION

3.1 FTIR Studies

FTIR measurements have been made in the wave number range 400 to 4000 cm^{-1} . The most significant bands recorded in the FT-IR of the pure and Dy-doped CoWO_4 nanocrystals calcined at 600°C is reported in Figure 1. In comparable with the pure CoWO_4 there is no much difference in the FTIR spectra for Dy-doped samples. The characteristic metal oxides band can be clearly visible at low wave number region. The band well below to the 1000 cm^{-1} may be assigned to the deformation modes of Co-O, W-O and W-O-W bridges. As a clear indication, the vibration within the WO_6 octahedral appeared at 500 cm^{-1} . Similarly, the band at 821 cm^{-1} is directly associated to the stretching vibrations of O-W-O bonds. Further, the

stretching due to the W-O bonds is located at 620 cm^{-1} . When compared to the pure CoWO_4 the

Dy-doped sample have shown the broad vibrational band at around 450 cm^{-1} which corresponds to the Co-O and ascribes the incorporation of Dy into Co lattice. While increasing the Dy concentration there is no visible band due to the Dy-O-Co or Dy-O is seen which confirms the homogenous dispersion of Dy within the CoWO_4 matrix. In addition to the above, the O-H stretching and bending vibrations bands also can be visible at 3300 cm^{-1} and 1635 cm^{-1} respectively. This mainly arises from the internally bonded water molecules or physically adsorbed water molecules. From the FTIR spectra the formation of CoWO_4 nano crystals is confirmed.

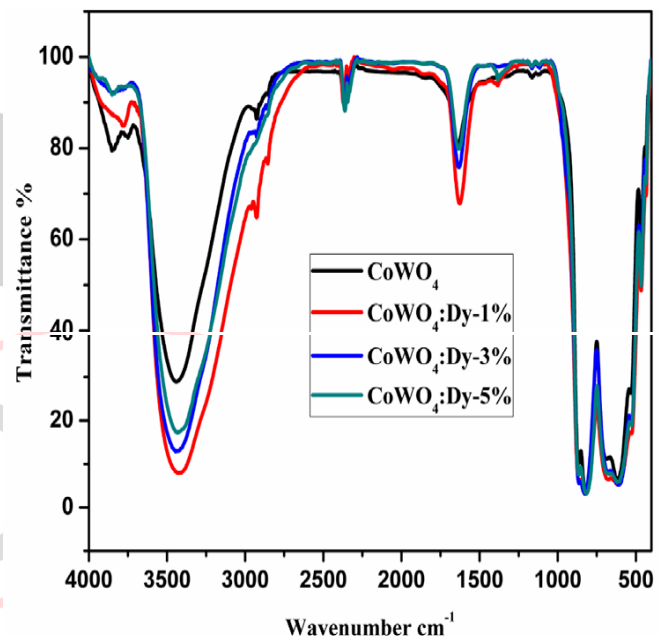


Figure 1 FTIR spectra of pure and Dy doped CoWO_4 nanomaterial heat treated at 600°C for 6 h

3.2 UV-Vis Absorption Analysis

The optical properties of the prepared samples were analyzed by UV-Visible absorption technique. UV-Vis absorption spectra were observed to investigate the optical features of the CoWO_4 nano crystals. Figure 2 (a&b) illustrates the UV-visible absorption spectra of pure and Dy-doped CoWO_4 nano crystals calcined at different temperatures. The samples were found to exhibit a sharp absorption edge in the UV region, which gets shifted slightly to lower wavelengths (blue shift) with Dy doping. The characteristic absorption edge associated to metal to ligand charge

transfer was observed at ~270 nm for all the samples. There is no band due to the Dy was observed even at higher concentration which further support the homogenous dispersion of Dy within the CoWO_4 host matrix. CoWO_4 is a typical semiconductor exhibits both direct and indirect band gap. The clear investigation on optical band gap was not yet concluded in this CoWO_4 . Therefore it is important

to investigate the band gap with the experimental studies. It is well known that the UV-Vis spectral analysis is most widely accepted experimental technique to understand the

energy band gap of the metal oxide semiconductors. In this study, UV-Vis absorption method has been used to estimate the band gap energy of the Dy-doped CoWO₄nanocrystals.

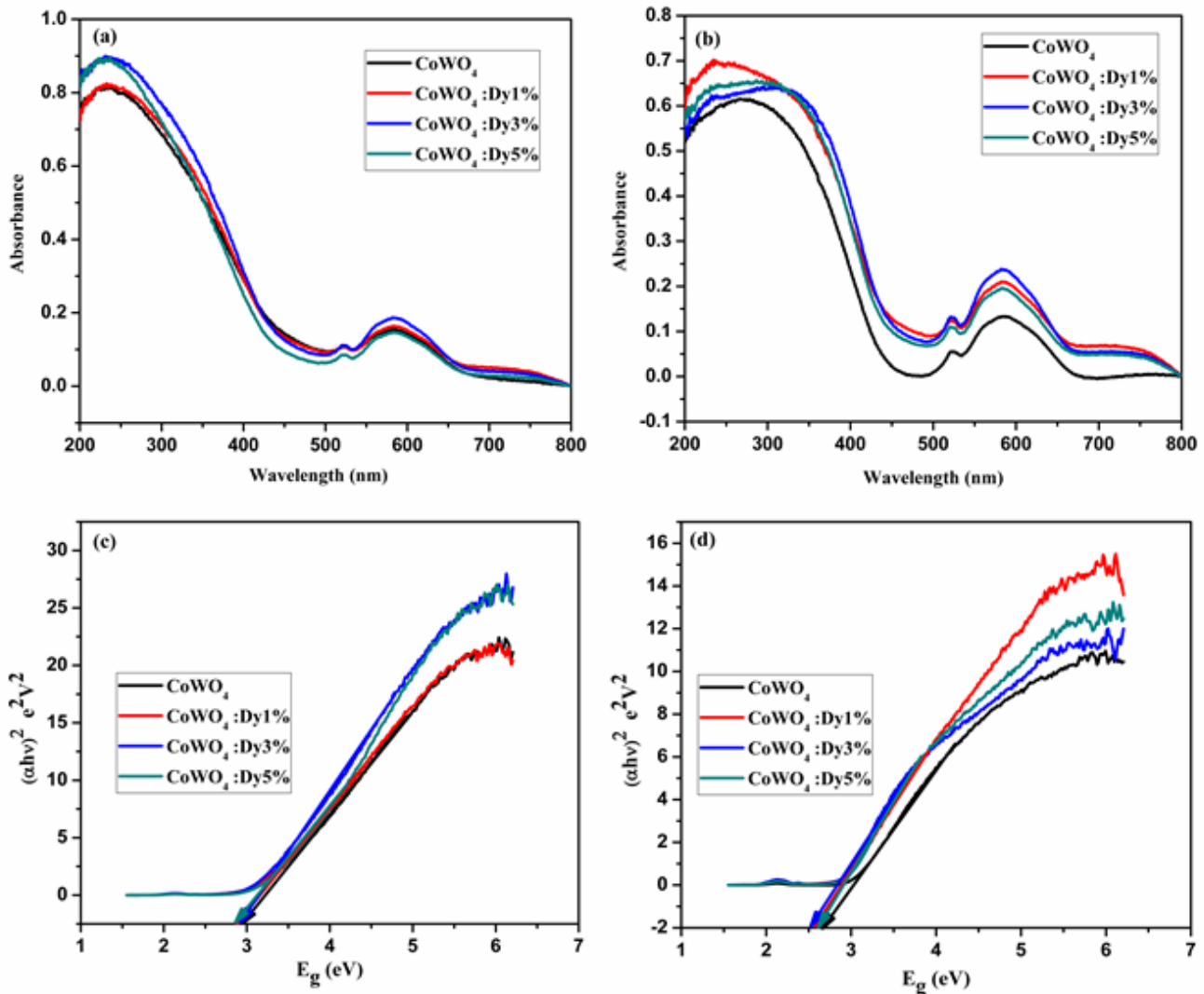


Figure 2 UV-Vis absorption spectra of pure and Dy-doped CoWO₄ nanostructure with different calcination temperature of 500°C (a) and 600°C (b), the corresponding Taucs plot for 500°C (c) & 600°C (d)

From the UV-Vis absorption spectra as shown in Figure 2 (a&b) the energy band gap was calculated using the following relation as reported earlier,

$$\alpha h\nu = A(h\nu - E_g)^n, (1)$$

where h is Planck's constant, ν is the frequency of the incident photon and A is a constant which depends on the electron-hole mobility. In order to determine the optical band gap, $(\alpha h\nu)^2$ against $h\nu$ graph was plotted Figure 2 (c&d). The optical band gap was determined from this plot for all the pure and doped samples by the linear fit in the straight portion of the graph. Band gap of un-doped sample was 2.79 eV. This decreased slightly with doping concentration and became 2.94 eV for 5% Dy doped sample. The observed red shift indicates the formation of electronic state impurity band into the band gap of CoWO₄ by Dy (4f) electron localized states, which are located closer to the lower edge of the conduction band to form the new lowest unoccupied molecular orbital. The merging of

this electronic state with the bottom of the conduction band could be reasoned for the reduction in bandgap.

3.3 Luminescent Studies

Figure 3 shows the PL spectra of pure CoWO₄ calcined at 500°C and 600°C. Dy doped CoWO₄ with different Dy doping concentrations as well as two different calcination temperature of 500°C and 600°C are shown in Figure 4 (a) & (b) respectively. The characteristic luminescent band of CoWO₄ usually appeared at violet-blue region associated to the radiative recombination of free excitons through an exciton-exciton collision process. In comparison to the undoped sample, the Dy doped CoWO₄ exhibit a blue shift to lower wavelength region in the emission band, with decrease in the intensity. The shift in emission band to lower wavelength might be related to the nature of variation of band gap. It is noticeable in the PL spectra the sudden drop in the intensity at higher Dy concentration

demonstrates that the large amount of Dy acts as the luminescent killer in the CoWO₄ matrix.

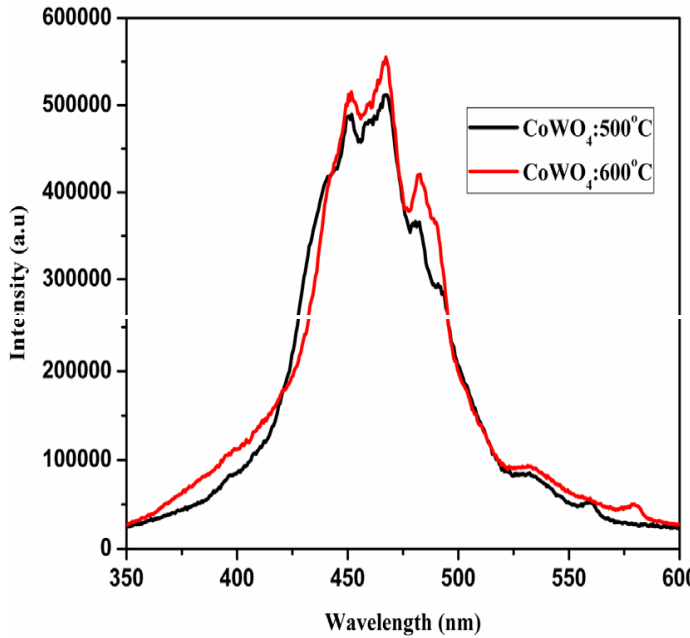


Figure 3 PL spectra of wolframite pure CoWO₄ nanostructure with two calcinations temperature of 500°C (Black) and 600°C (Red)

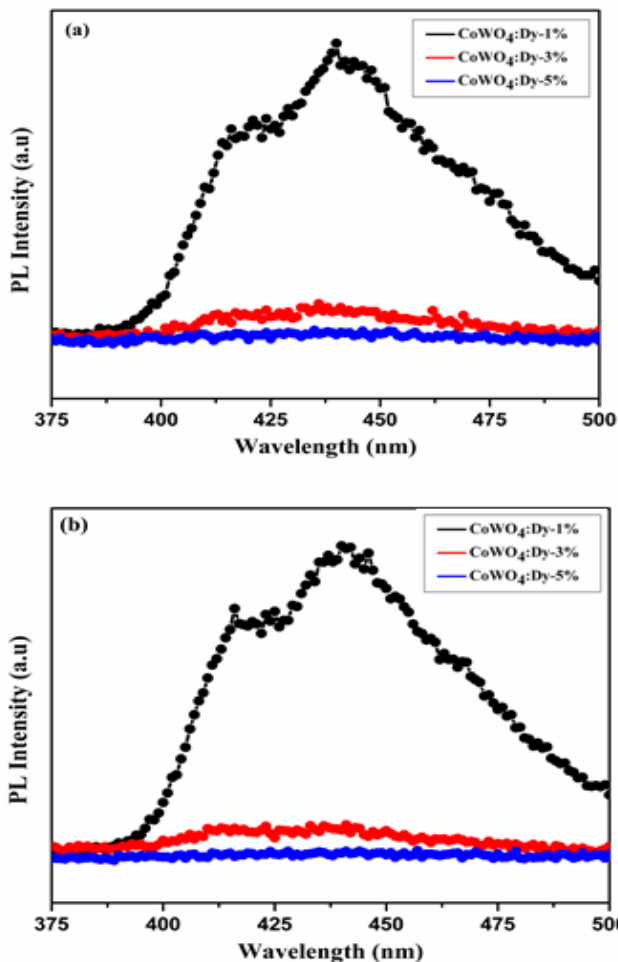


Figure 4 PL spectra of Dy-doped CoWO₄ nanostructure with twocalcination temperature (a) 500°C and (b) 600°C

Thus severe luminescent quenching was observed both lower and higher calcinations temperatures. Similar luminescent quenching was reported by et al (18). As can be seen from the figure, there is no other bands related to the Dy has been observed even at high concentration further confirms the complete incorporation of Dy into Co lattices. Similarly, when the calcinations temperature increases to 600°C from 500°C the emission band intensity increases significantly for both pure and doped samples which ascribes to the high crystallinity of the materials. Absence of deep level visible emission in the PL spectra confirms the defect free crystalline nature of the samples.

IV. CONCLUSION

In this present investigation, we adopt the single step solution based chemical precipitation technique to synthesis the pure and Dy doped CoWO₄ nanostructure. The increase of Dy³⁺ doping decreased the particle growth, and enhanced “blue-shift” in the UV-Vis absorption spectra. The systematic investigation of optical studies reveals that interesting optical behavior of Dy-doped CoWO₄ nanocrystals. Measured optical energy band gap are found to be in the range of 2.6 – 3.0 eV. The shift in absorption band edge may be due to the presence of larger size Dy ion which influences on the luminescence efficiency significantly. Interestingly, the Dy doped CoWO₄ have shown the optical features when compared to other rare earth ions such as increasing particle size, decreasing energy band gap and luminescent quenching. From these investigations the sample used is in thin film form, making it useful for many optical device applications. Further it reveals that the dopant ion and crystallization temperatures play important roles in the optical properties of the host materials by changing their electronic structure.

ACKNOWLEDGMENTS

Authors greatly acknowledged to the Sophisticated Analytical Instrumentation Facility (SAIF), Indian Institute of Technology Madras (IITM), India, for provide the analytical instruments to carry out the analysis for our materials.

REFERENCES

- [1]Wang, DF, Ye, JH, Kako, T & Kimura, T 2006, ‘Photophysical and Photocatalytic properties on SrTiO₃ doped with Cr cations on different sites’, Journal of Physical Chemistry B, vol.110, p.15824-15830.
- [2]Shi, HF, Li, ZS, Kou, JH, Ye, JH & Zou, ZG 2011, ‘Facile synthesis of single crystalline Ag₂V₄O₁₁ nanotube material as a novel visible-light-sensitive photocatalyst’, Journal of Physical Chemistry C, vol.115, pp.145-151.
- [3]Anicete-Santos, M, Picon, FC, Escote, MT, Leite, ER, Pizani, PS, Varela, JA & Longo, E 2006, ‘Room temperature photoluminescence in structurally disordered

SrWO₄', Applied Physics Letters, vol.88, pp.211913 (3 pages).

[4] Klassen, N, Shmurak, S, Redkin, B, Ille, B, Lebeau, B, Lecoq, P & Schneegans, M 2002, 'Correlation between structural and scintillation characteristics of lead and cadmium tungstates', Nuclear Instruments and Methods in Physics Research A, vol.486, pp.431-436.

[5] Danevich, FA, Sh, A. Georgadze, Kobychhev, VV, Kropyvnyansky, BN, Kuts, VN, Nikolaiko, AS, Tretyak, VI & Yu, Zdesenko 1995, 'The research of 2β decay of 116Cd with enriched 116CdWO₄ crystal scintillators', Physics Letters B, vol.344, pp.72-78.

[6] Saito, N, Sonoyama, N & Sakata, T 1996, 'Analysis of the excitation and emission spectra of tungstates and molybdate', Bulletin Chemical Society of Japan, vol.69, pp.2191-2194.

[7] Bharti, R, Singh, RA & Wanklyn, BM 1981, 'On electrical transport in CoWO₄ single crystals', Journal of Material Science, vol.16, pp.775-779.

[8] Navarro, J, Nogues, J, Munoz, JS & Fontcuberta, J 2003, 'Antisites and electron doping effects on the magnetic transition of Sr₂FeMoO₆', Physical Review B, vol.67, pp.174416.

[9] Steckl, J, Park, JH & Zavada, JM 2007, 'Prospects for rare earth doped GaN lasers on Si', Materials Today, vol.10, pp.20-27.

[10] Dandan Wang, Guozhong Xing, Ming Gao, Lili Yang, Jinghai Yang & Tom Wu 2011, 'Defects-mediated energy transfer in red-light-emitting Eu-doped ZnO nanowire arrays', Journal of Physical Chemistry C, vol.115, pp.22729-22735.

[11] Zeng, XY, Yuan, JL, Wang, ZY & Zhang, LD 2007, 'Nanosheet based microspheres of Eu³⁺-doped ZnO with efficient energy transfer from ZnO to Eu³⁺ at room temperature', Advanced Materials, vol.19, pp.4510.

[12] Mehta, A, Thundat, T, Barnes, MD, Chhabra, V, Bhargava, R, Bartko, AP & Dickson, RM 2003, 'Size correlated spectroscopy and imaging of rare-earth doped nanocrystals', Applied Optics, vol.42, pp.2132-2139.

[13] Chen, PL, Ma, XY & Yang, DR 2007, 'ZnO:Eu thin films: Sol-gel derivation and strong photoluminescence from 5D₀, 7F₀ transition of Eu³⁺ ions', Journal of Alloys Compound, vol.431, pp.317-320.

[14] Wang, X, Kong, XG, Yu, Y, Sun, YJ & Zhang, H 2007, 'Effect of annealing on upconversion luminescence of ZnO:Eu³⁺ nanocrystals and high thermal sensitivity', Journal of Physical Chemistry C, vol.111, pp.15119-15124.

[15] Anukorn Phuruangrat, Titipun Thongtem & Somchai Thongtem 2010, 'Analysis of lead molybdate and lead

tungstate synthesized by a sonochemical method', Current Applied Physics, vol.10, pp.342-345.

[16] Zhao, W, Song, X, Chen, G, Tian, G, Sun, S 2009, 'Hydrothermal synthesis of PbWO₄ uniform hierarchical microspheres', Material Letters, vol.63, pp.285-288.

[17] Zhang Qing, Meng Qingyu, Tian Yue, Feng Xiaohui, Sun Jiangting, Lu Shuchen 2011, 'Luminescent properties of Eu³⁺ doped Gd₂WO₆ & Gd₂(WO₄)₃ nanophosphors prepared via co-precipitation method', Journal of Rare Earths, vol.29, no.9, pp.815-821.

[18] Ejima, T et al 2006, 'Microscopic optical and photoelectron measurements of MWO₄ (M = Mn, Fe and Ni)', Journal of Luminescence, vol.119-120, pp. 59-63.