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The Comparison Synthesis of $CdWO_4$ Ceramics Generated by Solvent Free Microwave Combustion and Solvothermal Microwave Route

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Abstract: ***In the present study, we report two different methods for synthesis of cadmium tungstate ($CdWO_4$) particles under microwave assistance. One is microwave-assisted solvent free synthesis, and the other is microwave assistance solvothermal method. Metallic salts are made to paste for microwave irradiation in a solvent-free method, whereas metallic salts are dissolved in water along with the fuel for microwave irradiation in a solvothermal method. Both synthesis procedures lead to the light yellow colored $CdWO_4$ powders, and the samples are characterized by powder X-ray diffraction (PXRD), scanning electron microscopy (SEM). The optical properties are characterized by diffuse reflectance spectroscopy (DRS), photoluminescence (PL) spectroscopy and Fourier transform infrared spectroscopy (FTIR). The powder XRD analysis has confirmed the phase and chemical composition. The band gap energy was estimated as Eg = 5.6-5.2 eV from Tauc plotting.***

Keywords: $CdWO_4$, microwave assisted synthesis, characterization, photoluminescence

1. Introduction

In the recent years, nanostructure materials have gained more attention in the field of material applications because of their unique nanocrystaline properties. These crystalline properties don't just depend on their composition, but also on their size and shape [1]. Metal tungstates and molybdates, from the family of heterometalic oxides, have attracted the interest of many researchers in the world, because of their broad industrial applications like humidity sensors, scintillators, optical and photoluminescent devices, microwave and photocatalytic applications [2,3]. In these metal tungstates and molybdates, every heavy metal atom 'X' (X = W and Mo) is being surrounded by four oxygen atoms giving rise to a tetrahedral $[XO_4]^{-2}$ configuration. The divalent metal atom will share the corners with that of the oxygen atoms of $[XO_4]^{-2}$ tetrahedron [4–6]. Metal tungstates are found to deliver useful applications in the fields of laser, detector, luminescence and photovoltaic's [7]. These metal tungstates usually have the structural formula of AWO_4 type (A= divalent metal), and that can be further crystallized into two categories, such as scheelite structures ($CaWO_4$, $BaWO_4$, and $SrWO_4$) and wolframite structures ($MnWO_4$, $ZnWO_4$, $CdWO_4$ and $MgWO_4$) based on their ambient conditions like temperature and relative pressure [8].

Among these metal tungstates group, cadmium tungstate ($CdWO_4$) with a monoclinic wolframite structure has attracted lots of attention due to its unique properties such as low radiation damage, high X-ray absorption coefficient, low afterglow to luminescence and high density [9]. $CdWO_4$ is used as X-ray scintillators and X-ray detector in Computerized Tomography (CT) [10]. Apart from the uses, the $CdWO_4$ shows different band gap energies ranging from 3.8 to 5 eV [11] which is larger when compared to that of 3.2 eV of TiO_2 and hence $CdWO_4$ can be considered to be an efficient photocatalitic material. Till to date, various methods have been reported for the synthesis of $CdWO_4$ and related powder materials such as hydrothermal and solvothermal methods [12–14], co-precipitation method [15, 16], Sonochemical method [2, 17] solid-state reaction [18], spray pyrolysis [19], sol–gel method [20], microwave-assisted synthesis [21, 22].

The purpose of the present research work was to synthesize CdWO4 micro- and nanoparticles by two different methods under microwave assistance. Sample-A is synthesized by a microwave-assisted solvent-free method and sample-B is synthesized by the microwave-assisted solvothermal method. The samples are investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), diffuse reflectance spectroscopy (DRS), photoluminescence (PL) spectroscopy and Fourier transform infrared spectroscopy (FTIR). Microwave heating methods have unique effects when compared to that of the conventional heating process. The effects of microwave heating are volumetric heating, higher reaction selectivity, higher reaction rates, shorter reaction time and energy saving.

2. Experimental Details

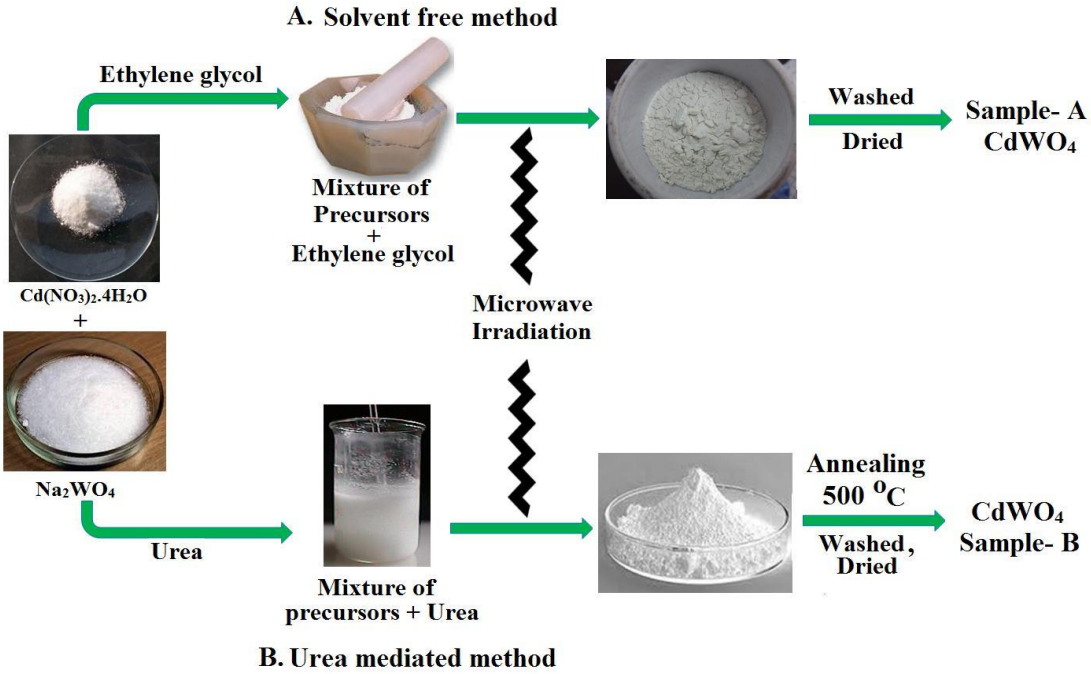
The $CdWO_4$ micro- and nanoparticles are prepared by green chemical routes under microwave assistance. High purity cadmium nitrate and sodium tungstate were purchased from Bros scientific, Tirupathi and they were used as received in the synthesis of cadmium tungstate ($CdWO_4$). The stoichiometric ratios of (1:1) cadmium nitrate and sodium tungstate salts are taken in both methods for the synthesis. In a solvent-free process, metallic salts are made to paste by adding two drops of ethylene glycol in a quartz boat, and this quartz boat is kept under microwave irradiation for 30 s. Hence, we get a light yellow fluffy mass, which is washed with distilled water and ethanol several times and dried to produce the powdered sample-A. In a solvothermal method, metallic salts are dissolved in water along with urea as a fuel, and this mixed solution is stirred for 30 min to get a

homogenous mixture. This solution is kept under microwave irradiation for about 5 min with a break at every 60 s to avoid the solution spilling. Finally, a yellow colored residue is obtained and it is washed with distilled water and ethanol several times and annealed at 500 ^{o}C to get the powdered sample-B. Thus obtained powder samples are characterized by XRD, SEM for morphological properties and analyzed with FTIR, PL and UV-VIS spectroscopy for its optical properties.

The reaction mechanism can be described as follows

$$Cd(NO_3)_2 + Na_2WO_4 \rightarrow CdWO_4 + 2\,NaNO_3$$
$$4\,NaNO_3 + 2H_2O \rightarrow 4\,NaOH + 4NO_2 + O_2$$

A schematic representation of synthesis method is illustrated below.



Scheme.1: Stepwise synthesis procedure

3. Results and Discussion

3.1. Powder X-ray diffraction

To examine the crystallization process and distinguish different phases the powder X-ray diffraction (PXRD) analysis was performed on the $CdWO_4$ samples. The XRD patterns of 'sample-A' and 'sample-B' are shown in Figure. 1(a) and 1(b). The characteristic 2θ X-ray diffraction peaks of $CdWO_4$ samples are identical to that of the standard JCPDS No. 14-0676. All the diffraction peaks can be exclusively indexed to the monoclinic $CdWO_4$ with unit cell parameters a = 5.029, b = 5.859, c = 5.074 ^{o}A and space group P2/c. Some unknown phases of impurities are seen in 'sample-A' synthesized under solvent free method, whereas 'sample-B' of solvothermal synthesis has pure and crystallized particles and are formed without impurities. The diffraction peaks for sample-A are observed in 2θ value at 16.79°, 23.29°, 28.97°, 29.55°, 30.47°, 35.35°, 39.96°, 43.16°, 47.36°, 50.06°, 51.47°, 59.30° and 63.08° that are associated with the (100), (110), (-111), (111), (020), (002), (121), (112), (022), (130), (202), (-113) and (132) planes, respectively. The diffraction peaks for sample-B are indexed at 2θ = 17.58°, 23.24°, 28.92°, 29.50°, 30.44°, 35.30°, 39.94°, 43.14°, 47.34°, 50.04°, 51.44°, 59.20° and 63.08° and are corresponds to the (100), (110), (-111), (111), (020), (002), (121), (112), (022), (130), (202), (-113) and (132) planes, respectively. The peak positions and intensities obtained for the synthesized powders are identical to that of standards and that indicates the complete formation of $CdWO_4$ phase under the experimental condition.

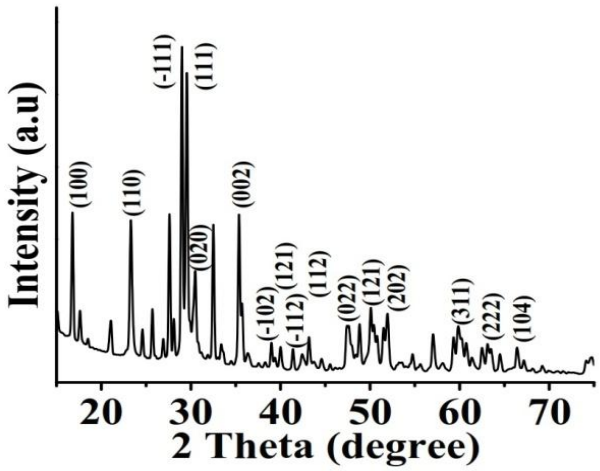


Figure 1(a): XRD of $CdWO_4$ particles synthesized by solvent-free method (sample-A)

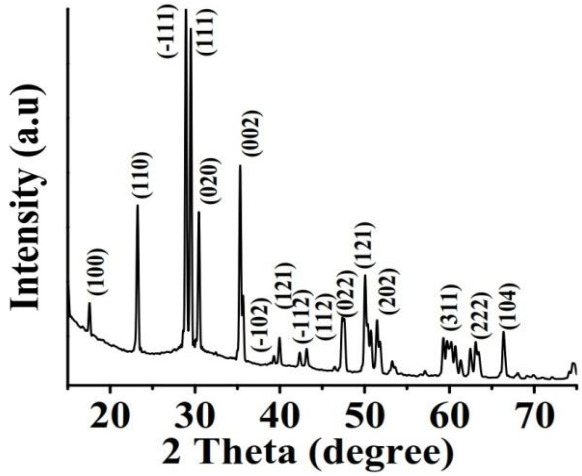


Figure 1(b): XRD of $CdWO_4$ particles synthesized by solvothermal method (sample-B)

The average crystallite size in the samples was calculated from diffraction pattern using Scherrer formula:

$$L = \frac{0.94\lambda}{\beta_{1/2}\cos\theta}$$

Where L is the average crystallite size (A^o), λ is the X-ray wavelength (0.154 nm), θ is the diffraction angle, and β the peak position and the FWHM (full-width at half maximum). The average crystallite size values 108 ± 2 nm and 99 ± 2 nm are found for sample-A and sample-B, respectively. 81 % and 73 % yields are reported for sample-A and sample-B respectively in the present work.

3.2 Scanning electron microscopy (SEM) studies

The typical surface morphologies of $CdWO_4$ particles are examined by scanning electron microscopy (SEM). The SEM images of sample-A and sample-B are shown in Figure 2 and 3 respectively. The SEM patterns reveal the presence of small particulate matter and large agglomerates. The agglomeration of $CdWO_4$ particles can be excused by solid state welding of $CdWO_4$ micro- and nanoparticles. The particle size values are in the range of 0.2 - 0.6 µm. Besides, large agglomerates of more than 1 µm in size can be seen in SEM images. The sample-B shows more uniform and less agglomerated structures than that of a sample-A.

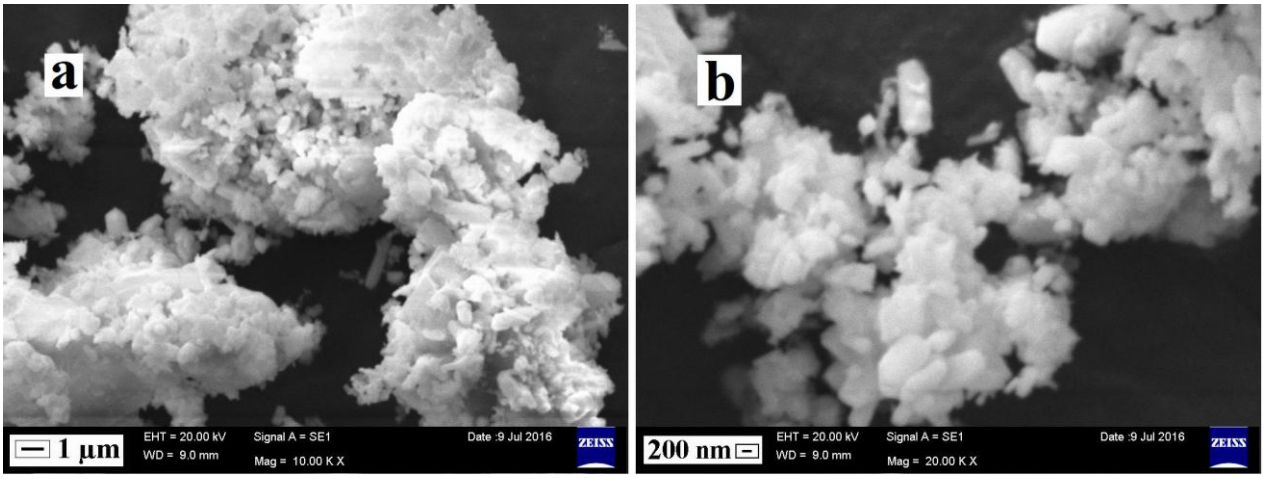


Figure 2: SEM image of $CdWO_4$ micro and nanoparticles synthesized by the solvent-free method.

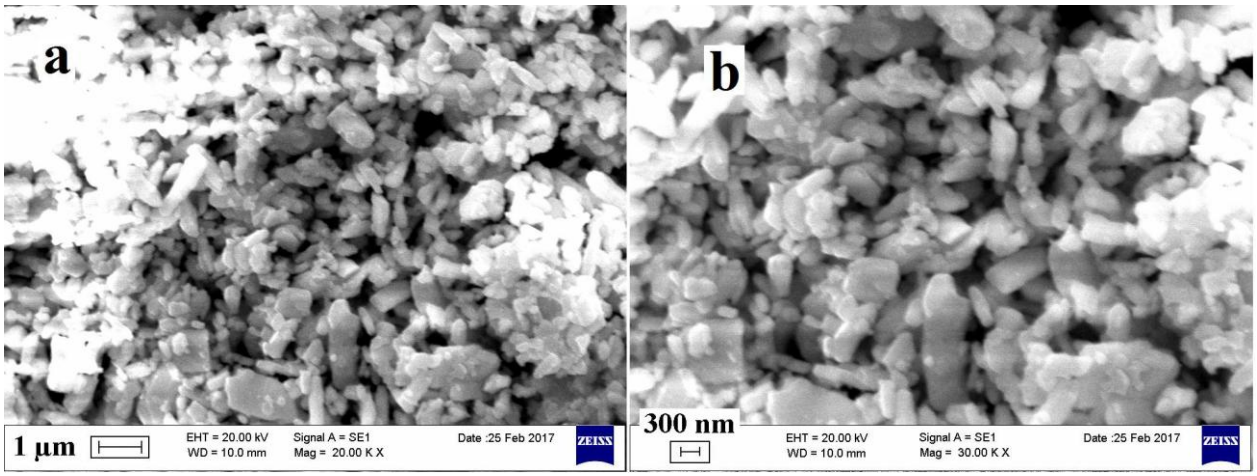


Figure-3: SEM image of $CdWO_4$ micro and nanoparticles synthesized by solvothermal method

In the solvent-free route, the precursor reaction mixture holds just two drops of ethylene glycol along with metal salts made to paste and no surfactants are used. From the SEM images, it is found that the $CdWO_4$ particle morphologies of sample-A and sample-B obtained are better when compared to that of the $CdWO_4$ particles synthesized by Chang Sung Lim [21, 22]. Chang Sung Lim, synthesized the $CdWO_4$ particles by microwave assistance method where the microwave irradiation is about 40 minutes with a working cycle of 60 s on and 30 s off [21] and for about 10 minutes continuously [22]. In the present work, the precursor mixtures were irradiated for 30 seconds in solvent-free method and 5 minutes in solvothermal methods under microwave assistance.

3.3. Fourier Transform Infrared (FT-IR) Spectroscopy Analysis

Infrared studies were performed aiming to identify the metal oxygen bond vibrations. The FT-IR spectra of $CdWO_4$ particles are recorded in the frequency range 400 – 4000 cm^{-1} and they are shown in Figures. 4. Sample-A exhibited a broadband near 3441 cm^{-1} and a peak at 1641 cm^{-1}, which can be attributed to the –OH stretching and bending vibrations. The -OH group may be from ethylene glycol used as fuel and presented in trace amounts as in the sample even after washing. The sample-B exhibited a sharp and less intense peak near 1737 cm^{-1}, which can be anticipated due to –OH group of water molecules due to moisture absorption from the atmosphere. The absorption band at 1383 cm^{-1}in the spectra (a) is from the CH_3^- ion which may be due to the slight presence of ethylene glycol inside the sample-A. The spectra showed the metal–oxygen stretching frequencies in the range of 500–1000 cm^{-1} associated with the vibrations of Cd–O, and W–O bonds. Sample-A exhibits two sharp bands centred at 834 and 600 cm^{-1}. Similarly, FT-IR spectrum of the sample-B shows two active bands centred at 804 and 551 cm^{-1} and they can be attributed to the Cd–O–W and W–O bond vibrations respectively. Chang Sung Lim [21] reported the similar IR spectra of $CdWO_4$ with bands observed at 838 and 621 cm^{-1} for $CdWO_4$.

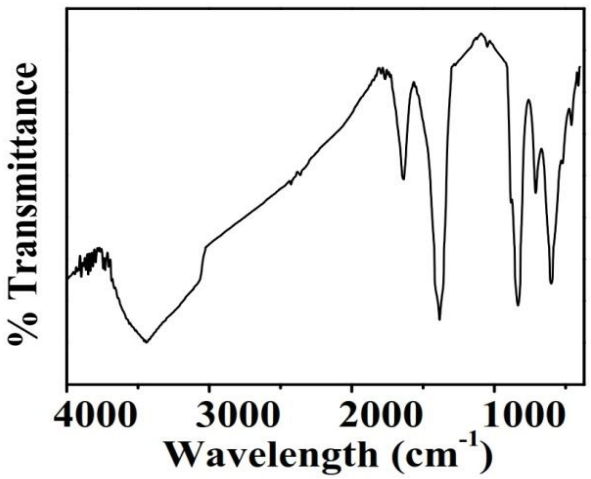


Figure-4(a): FTIR of $CdWO_4$ particles synthesized by solvent-free method

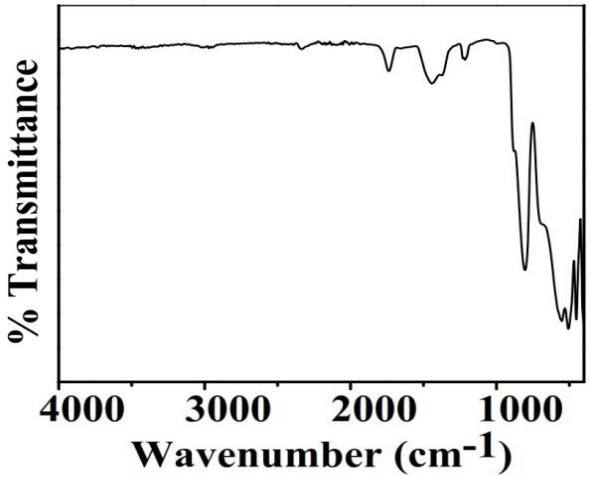


Figure-4(b): FTIR of $CdWO_4$ particles synthesized by solvothermal method

3.4. Optical properties

CdWO4 nanoparticles are intensively utilized in the area of photo-electronic devices due to their large band gap energy. The optical study of $CdWO_4$ nanoparticles is performed with a Jasco UV-670 spectrophotometer, UV-VIS-NIR diffuse reflectance spectrophotometer and the DRS spectra low-intensity at room temperature. $CdWO_4$ is a colorless crystalline powder, though cadmium is a transition metal it has filled outer d – orbitals and, hence, its oxides are white in color. The absorption and reflectance spectra of sample-A and sample-B are shown in figure 5 and 6, respectively. From figure 5(a), the typical UV–Vis absorbance spectrum of sample-A shows UV-absorption bands peaked at 335 nm. The absorption peaks at 220 and 250 nm may be due to organic impurities formed from ethylene glycol under microwave combustion. As seen from figure 6(a), the absorbance spectrum of sample-B shows UV-absorption bands peaked at 320 nm and is similar to that of sample-A. N. Tian et. al.[23] states that the pure $CdWO_4$ nanoparticles show the absorption only in UV region (i.e. $\lambda \leq 378$nm). Hence, the $CdWO_4$ samples synthesized in the present work showed the similar peaks that are compatible with the literature.

The UV–Vis reflectance spectra i.e. the diffuse reflectance spectra (DRS) are recorded for the estimation of optical band gap energy of $CdWO_4$ nanoparticles and the curves are shown in Figure-5(b) and Figure-6(b). The optical band gap of a semiconductor can be estimated by applying the following equation:

$$\alpha(v) = A(\hbar v/2 - E_g)^{m/2},$$

The band gap is determined by relating diffuse reflectance (R) of the samples with the Kubelka–Munk function F(R) in the equation $F(R) = (1-R)^2/2R$. The energy intercept plot of $(F(R)*h\nu)^2$ versus $h\nu$ is plotted which yields the $E_{g,\,dir}$ for a direct allowed transition, when the linear regions are extrapolated to the zero ordinate, one can get the band gap of the sample. By this method, the band gap energy calculated for $CdWO_4$ samples are found to be 5.6 and 5.2 eV respectively, as shown in Figure 7. According to the effect of quantum confinement, we could state that the band gap

energy increase apparently by a decrease in nanoparticles size, but as evident from XRD and SEM it is clean that the particle size is big enough to exclude this cause. Hence, the larger band gap energy of 5.6 and 5.2 eV for $CdWO_4$ samples can be justified by the diamagnetic nature of the cadmium.

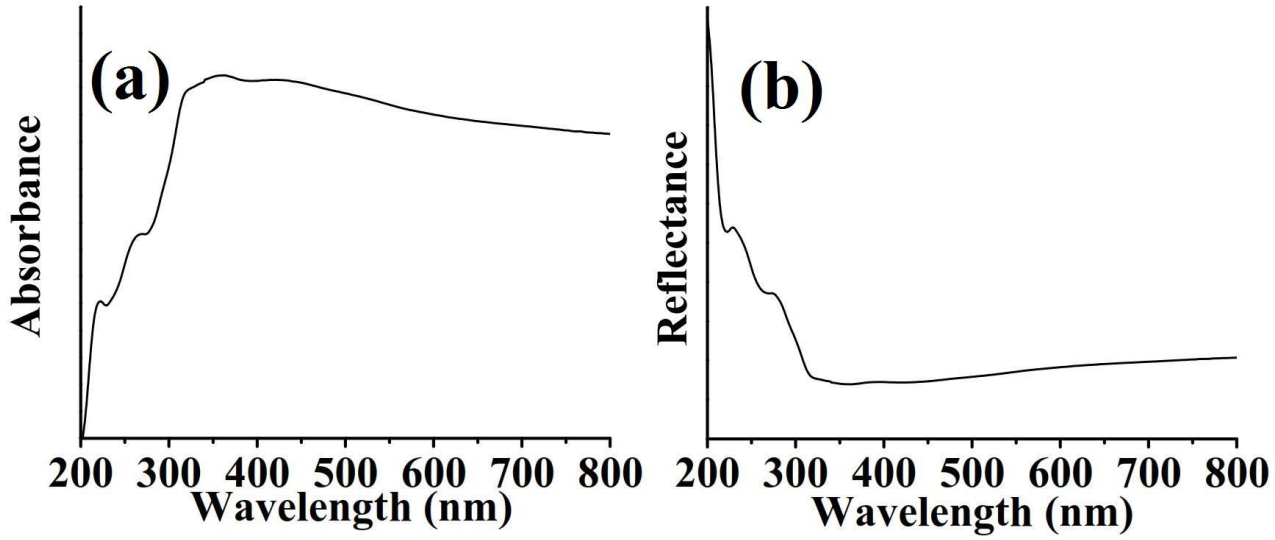


Figure 5: UV-Vis absorbance spectrum (a) and UV-Vis reflectance spectrum (b) of $CdWO_4$ particles (sample-A) synthesized by the solvent free method

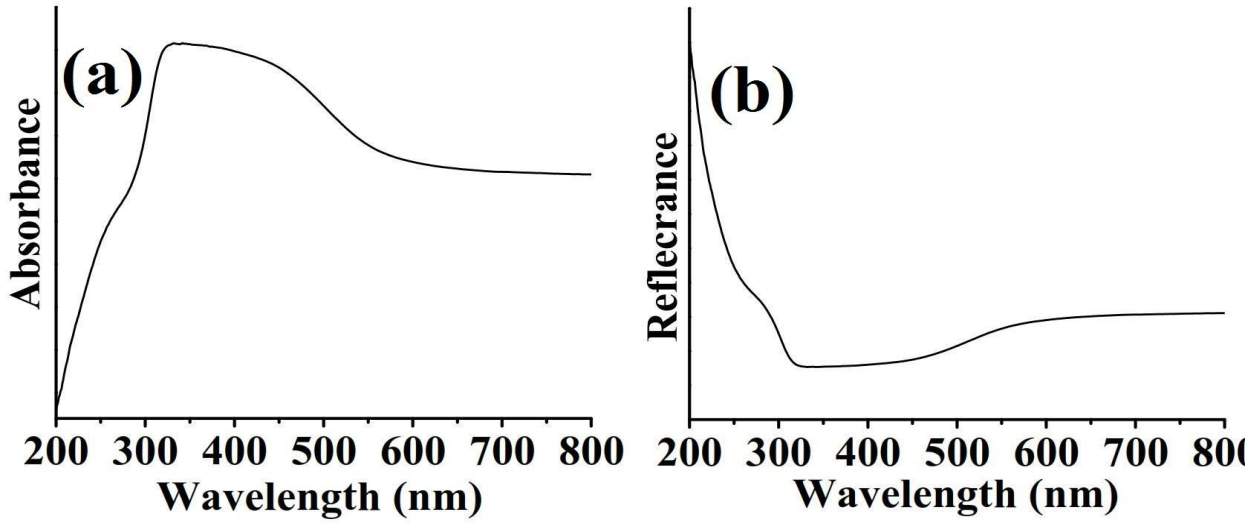


Figure 6: UV-Vis absorbance spectrum (a) and UV-Vis reflectance spectrum (b) of $CdWO_4$ particles (sample-B) synthesized by solvothermal method

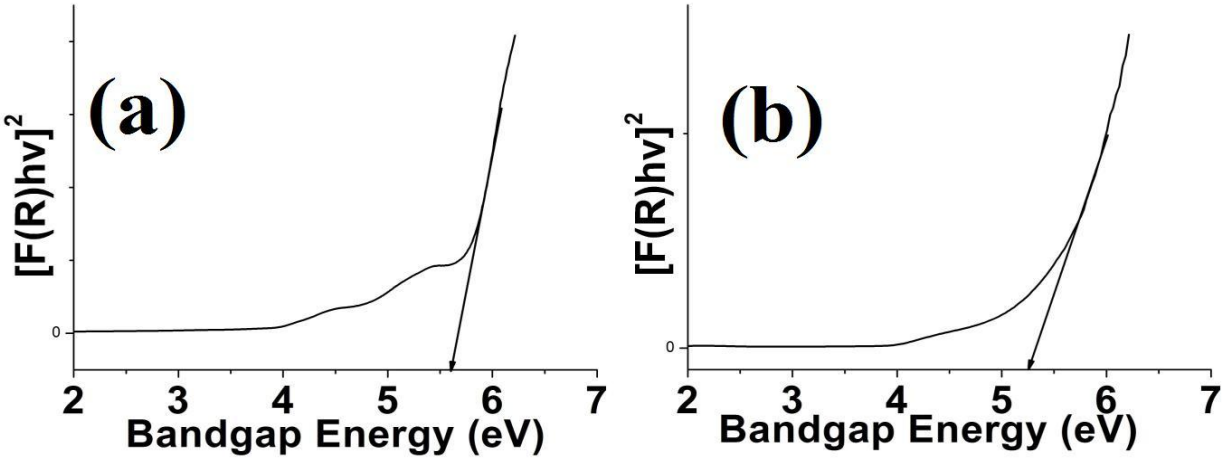


Figure 7: Bandgap energy values for $CdWO_4$ particles fabricated by solvent-free method (a), solvothermal method (b)

3.5. Photoluminescence (PL) spectra

The Photoluminescence (PL) spectra of $CdWO_4$ particles are shown in figure 7. In general, it is presumed that in metal tungstates, the emission spectra measurements are associated with the charge transfer transitions inside the $[WO_4]^{2-}$ complex. Both the $CdWO_4$ samples are excited at 300 nm and a broad photoluminescence emission band over 400 - 600 nm is observed in both the spectra. The emission band for both the samples are centered in the blue-green wavelength region of 480-520 nm and this is compatible with that obtained earlier [24]. In general, it is considered that in semiconductors the process of recombination of excited electrons and holes is responsible for its photoluminescence emission. It is also well known that all $CdWO_4$ samples exhibit the similar emission peak in PL spectra, which is centered at ~548 nm [25]. In the present work, the PL spectra peaks are centred at 510 and 518 nm for sample-A and sample-B respectively. From the literature, we know that the $(WO_4)^{2-}$ ions are responsible for the low-intensity PL emission in the blue region, but the presence of cadmium combined with tungstate group (WO_4) enhanced the peak intensity and is spread from violet to green region [26]. The PL spectra obtained in the present work are in reasonable compatibility with the literature; hence, that indicates the appropriate quality of the sample.

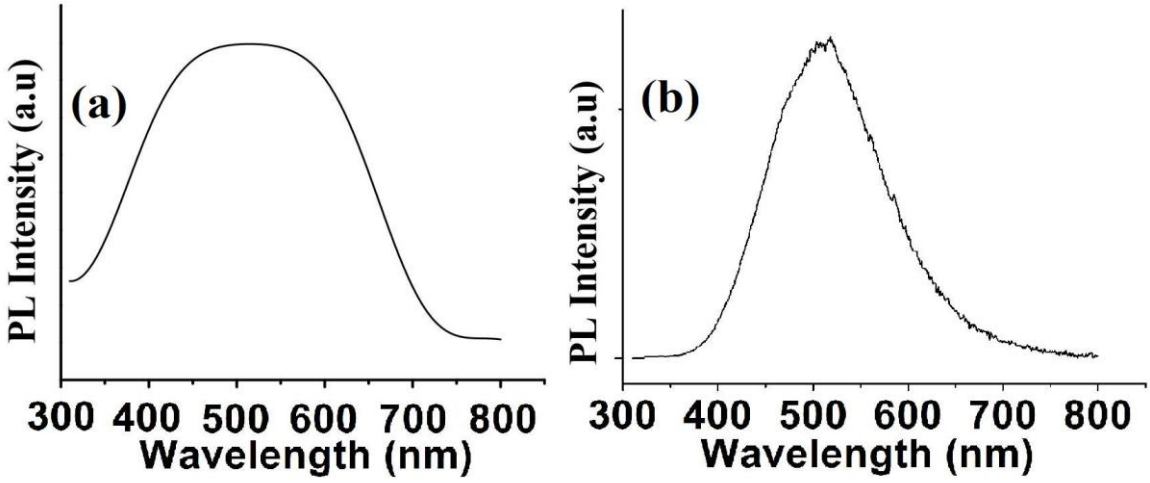


Figure 5: PL spectra of $CdWO_4$ spinels synthesized by solvent-free method (a), solvothermal method (b)

4. Conclusions

In this work, the $CdWO_4$ micro- and nanoparticles are synthesized under microwave assistance by two different methods, one solvent free and another solvothermal method. In the solvent-free process, ethylene glycol is used to create the precursor paste and that results in the organic impurities at trace amounts in sample-A. The efficiency of a solvent-free method can be increased by replacing the ethylene glycol with another fuel type so that the impurities can be reduced. In the solvothermal method, urea is used as a fuel and it is dissolved in water along with the precursors and is microwave irradiated till to the formation of sample-B. From PXRD and SEM it is observed that sample-B has preferable morphology and lower particle size when compared to that of sample-A. Sample-B has shown better results in PXRD, SEM, FT-IR and UV-VIS-NIR diffuse reflectance spectroscopy, as compared to sample-A, and this indicates the purity and excellent crystallinity of the sample-B.

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References

[1] M Vosoughifar, Influence of capping agents additives on morphology of cadmium tungstate nanoparticles and study of their photocatalitic properties, *J Mater Sci: Mater Electron* (2017), doi:10.1007/s10854-017-6377-9.

[2] S S H Mashkani, S S H Mashkani, A S Nasab, synthesis and characterisation of rod like $CaMoO_4$ nanostructure via free surfactant Sonochemical route and its photocatalitic application, *J Mater Sci: Mater Electron* (2016), 27, 4351 – 4355. doi:10.1007/s10854-016-4303-1.

[3] M Mosleh, Controllable synthesis of gadolinium tungstate nanoparticles with different surfactants by precipitation route, *J Mater Sci: Mater Electron* (2017), doi:10.1007/s10854-017-6571-9.

[4] A S Nasab M Sadeghi, Preparation and characterization of calcium tungstate nanoparticles with the aid of amino acids and investigation its photocatalytic application, *J Mater Sci: Mater Electron* (2016), 27, 7933–7938. DOI 10.1007/s10854-016-4785-x.

[5] A. Phuruangrat, T. Thongtem, S. Thongtem, Cyclic microwave assisted synthesis and characterisation of

nanocrystalline alkaline earth metal tungstates, J. *Ceram. Soc. Jpn*. (2008), 116, 605-609.

[6] L.S. Cavalcante, J.C. Sczancoski, J.W.M. Espinosa, J.A. Varela, P.S. Pizani, E. Longo, Photoluminescent behavior of $BaWO_4$ powders processed in microwave-hydrothermal, *J. Alloys. Compd.* (2009), 474, 195-200.

[7] M Babamoradi, M R Liyai, R Azimirad, H Salehi, Electronic structure and optical properties of the single crystal and two dimensional structure of $CdWO_4$ from first principles, *Physica B* (2017), 511, 103–108.

[8] Baochun Guo And Peng Liu, Microwave Dielectric Properties of $CdWO_4$ Ceramics Prepared by Using High-energy Ball-milling Method, *Ferroelectrics* (2015), 474: 105–112.

[9] J Yan, Y Shen, R Cao, T Li, $CdWO_4$ nanorods: Ultrafast synthesis via a PEG-1000 polymer-assisted enhanced microwave synthesis route and their photoluminescence property, *Ceramics International* (2014), 40, 8081–8085.

[10] V.A. Pustovarov, A.L. Krymov, B.V. Shulgin, E.I. Zinin, Some peculiarities of the luminescence of inorganic scintillators under excitation by high intensity synchrotron radiation, *Rev. Sci. Instrum.* (1992), 63, 3521-3522.

[11] R. Laasner, G_0W_0 band structure of $CdWO_4$, *J. Phys. Condens. Matter* (2014), 26, 125503.

[12] X.C. Chu, Y.N. Xu, L.T. Li, Hydrothermal synthesis and effects of pH values on properties of $CdWO_4$ powders, *J. Mater. Sci.: Mater. Electron.* (2014), 25, 2601-2604.

[13] M. Hojamberdiev, R. Kanakala, O. Ruzimuradov, Y. Yan, G. Zhu, Y. Xu, Besom-like $CdWO_4$ structures composed of single-crystalline nanorods grown under a simple hydrothermal process in ultra-wide pH range, *Opt. Mater*. (2012), 34, 1954-1957.

[14] P. Yang, G.Q. Yao, J.H. Lin, Photoluminescence and combustion synthesis of $CaMoO_4$ doped with Pb^{+2}, *Inorg. Chem. Commun*. (2004), 7, 389-391.

[15] S.M. Hosseinpour-Mashkani, M. Maddahfar, A. Sobhani-Nasab, Precipitation Synthesis, Characterization, Morphological Control, and Photocatalyst Application of $ZnWO_4$ Nanoparticles, *J. Electron. Mater*. (2016), 45, 3612-3620.

[16] T. Thongtem, S. Kungwankunakorn, B. Kuntalue, A. Phuruangrat, S. Thongtem, Luminescence and absorbance of highly crystalline $CaMoO_4$, $SrMoO_4$, $CaWO_4$ and $SrWO_4$ nanoparticles synthesized by co-precipitation method at room temperature, *J. Alloys Compd.* (2010), 506, 475-481.

[17] S.M. H Mashkani, A. S Nasab, Simple synthesis and characterization of copper tungstate nanoparticles: investigation of surfactant effect and its photocatalyst application, *J. Mater. Sci. Mater Electron.* (2016), 27, 7548-7553.

[18] S. M. V. Novais, R. S. Da Silva, and Z. S. Macedo, Thermally stimulated luminescence of polycrystalline $CdWO_4$ at low temperatures. *J. Lumin.* (2011), 131, 1283–1287.

[19] S. Thongtem, S. Wannapop, T. Thongtem, Characterization of $MnWO_4$ with flower-like clusters produced using spray pyrolysis, *Trans. Nonferr. China* (2009), 19, s100-s104.

[20] K. Lennstrom, S. J. Limmer, and G. Cao, Synthesis of cadmium tungstate films via sol–gel processing, *Thin Solid Films* (2003), 434, 55–61.

[21] C S Lim, Microwave-Assisted Synthesis and Photoluminescence of $CdWO_4$ by A Solid-State Metathetic Route, *Asian J. Chem.* (2012), 24, 4166-4170.

[22] C S Lim, Microwave Synthesis of Ag-$CdWO_4$/Zeolite Composites Assisted by A Solid-State Metathetic Route, *Asian J. Chem.* (2013), 25, 67-70.

[23] Na Tian, H Huang, Y Zhang, Mixed-calcination synthesis of $CdWO_4$/g-C_3N_4 heterojunction with enhanced visible-light-driven photocatalytic activity, *Applied Surface Science* (2015), 358, 343–349.

[24] C S Lim, Microwave-assisted synthesis of $CdWO_4$ by solid-state metathetic reaction, *Materials Chemistry and Physics* (2012), 131, 714– 718.

[25] L Hou, L Lian, L Zhang, T Wu and C Yuan, Microwave-assisted interfacial hydrothermal fabrication of hydrophobic $CdWO_4$ microspheres as a high-performance photocatalyst, *RSC Adv.* (2014), 4, 2374–2381.

[26] D Modi, M Srinivas, D Tawde, K V R Murthy, V Verma and N Patel, Hydrothermal synthesis and photoluminescence properties of cerium-doped cadmium tungstate nanophosphor, *J. Exp. Nanosci.* (2015), 10, 777–786