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Synthesis and characterization of $CdWO_4$ nanocrystals

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Abstract

The $CdWO_4$ nanocrystals were successfully synthesized by simple co-precipitation method. The X-ray diffraction pattern confirms the phase purity and the single phase formation of monoclinic Wolframite structure of $CdWO_4$. The average crystallite size of 22 nm was calculated from X-ray line broadening method. The FT-IR spectra confirm the presence of stretching and bending vibrations of metal cations like Cd-O, W-O and Cd-O-W bands in the $CdWO_4$ structure. The morphological features were analyzed by TEM and HRTEM techniques. The electrical conductivity of the materials is found to increase with increasing temperature as well as frequency which enumerates the semiconducting behavior of the material.

Keywords: $CdWO_4$; Nanocrystals; X-Ray diffraction; Electrical conductivity; Impedance spectra

1. Introduction

Metal tungstate is a very important family of oxide materials that have potential applications in many fields such as photoluminescence, microwave applications, optical fibers, scintillator material, humidity sensors and catalysis [1]. Among the metal tungstates, $CdWO_4$ with a monoclinic structure is a promising scintillation material for X-ray tomography, detection of slow neutrons, dissymmetry, photochromic substances and photovoltaic cell. It has high efficiency, high chemical stability, high stopping power, and short decay line. Yong et al. has prepared $CdWO_4$ nanocrystals and nano fibers at low temperature with various aspect ratios by hydrothermal method [2] and molten salt synthesis method [3]. Similarly, Wenming et al., has prepared $CdWO_4$ nanocrystals with controlled particle size and crystallinity by hydrothermal method using citric acid as a capping agent for photocatalytic applications [4]. Urchin-like $CdWO_4$ microspheres with hollow interiors have been successfully synthesized by Ling et al. using facile template free hydrothermal treatment method [5]. Recently, Yan et al. has successfully prepared both the polymorphs of tetragonal and monoclinic $CdWO_4$ spherical particles by solvothermal method and also studied their photocatalytic properties [6].

In the present study, we have successfully prepared $CdWO_4$ nanocrystals by simple co-precipitation method without using any complexing agent and characterized their structural, morphological and electrical properties using XRD, FT-IR, TEM, HRTEM, EDAX and impedance spectra methods. To the best of our knowledge, there is no previous literature available indicating the a.c. electrical properties of $CdWO_4$ nanoparticles at elevated temperature. Hence it may be the first report of its kind.

2. Experimental method

The $CdWO_4$ particles were prepared by simple co-precipitation method. The stoichiometric quantities of $Cd(NO_3)_2.4H_2O$ (4.281 gm) and $Na_2WO_4.2H_2O$ (4.578 gm) were dissolved in 50 ml of distilled water individually for preparing 5gm of $CdWO_4$. Subsequently, the $Na_2WO_4.2H_2O$ was added drop wise in to cadmium nitrate solution. The precipitate is formed immediately at room temperature without any pH control. Then the precipitate is filtered out and washed several times with distilled water and finally ethanol in order to remove the impurities. Finally, the precipitate was dried at 100 °C for one hour to remove the water content. Then the collected samples were calcined at different temperatures like 400, 500 and 600 °C for 3 hours. The compound formation,

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phase purity and crystallinity of $CdWO_4$ are identified by XRD (PANalitical XPER Pro Diffractometer). The background corrections were made using X'Pert High Score software based on bending factor and granularity. The lattice parameter values are calculated using CELREF software. The stretching and bending vibrations of $CdWO_4$ are examined by FT-IR (Nicolet Avarter Model FT-IR spectrometer). The morphological features were examined by HRTEM (JEOL JEM 2100). The electrical properties were studied by impedance measurement using computer controlled impedance analyzer HIOKI 3532 LCR HITESTER in the frequency ranging from 50 Hz to 10 KHz at elevated temperature. For better ohmic contact in these measurements silver paste was applied to both surfaces of the pellet before being sand - witched between the two electrodes of sample holder.

3. Results and discussion

Fig. 1 shows the XRD pattern of $CdWO_4$ nanoparticles thermally treated at various temperatures (400, 500 and 600 °C). Some broad peaks are obtained at 400 °C, which indicates the amorphous nature of $CdWO_4$. By increasing the sintering temperature from 400 °C to 600 °C large numbers of peaks are emerged which corresponds to $CdWO_4$ phase. These peaks were intensified and become sharper at high temperatures, which depict the phase formation, increased crystallite size and crystallinity. The sharp and well defined peaks are observed that indicates the crystallinity of the synthesized materials. The observed diffraction peaks at 2θ = 23.18, 28.88, 29.46, 30.41, 35.28, 47.41, 50.16 and 51.50 corresponds to the lattice planes of (1 1 0), (−1 1 1), (1 1 1), (0 2 0), (0 0 2), (0 2 2), (−2 0 2) and (2 2 1) respectively. These diffraction peaks enumerate the formation of monoclinic structure of $CdWO_4$. There is no extra peaks are observed which infers the single phase formation of the products. The calculated lattice parameter values are a = 5.0595Å, b = 5.8668Å, c = 5.0762Å and β = 91.574° which confirm the formation of monoclinic structure of $CdWO_4$ and well agreed with the standard report (PDF No: 14-0676). The average crystallite size is calculated as 22 nm using Debye- Scherer formula. The cell volume is calculated as 150.6204 A^{o3}. When the sintering temperature is increased from 400 °C to 600 °C the crystallite size increased due to particle agglomeration. The calculated crystallite sizes are 10, 15 and 22 nm for the $CdWO_4$ at 400, 500 and 600 °C respectively. The calculated lattice density of 7.942 g/cm^3 is well agreed with the reported values of 8.005 g/cm^3 (PDF No: 14-0676).

Fig. 2 shows the FT-IR spectra of 600 °C calcined $CdWO_4$ measured in the wave number region of 400-4000 cm^{-1}. A symmetrical stretching vibrations of W-O-W bond in WO_4^{2-} group is represented by the band at 797 cm^{-1}.The observed bands at 411, 456, 572 cm^{-1} are assigned to the in-plane deformation of the WO_4^{2-} group [3]. The strong band centered at 1460 cm^{-1} is assigned to the symmetrical and asymmetrical vibrations of the carboxylate group. The bands located at 2923 cm^{-1} is due to the stretching modes of CH_2 group of CH_3CH_2OH. The broad absorption bands centered at

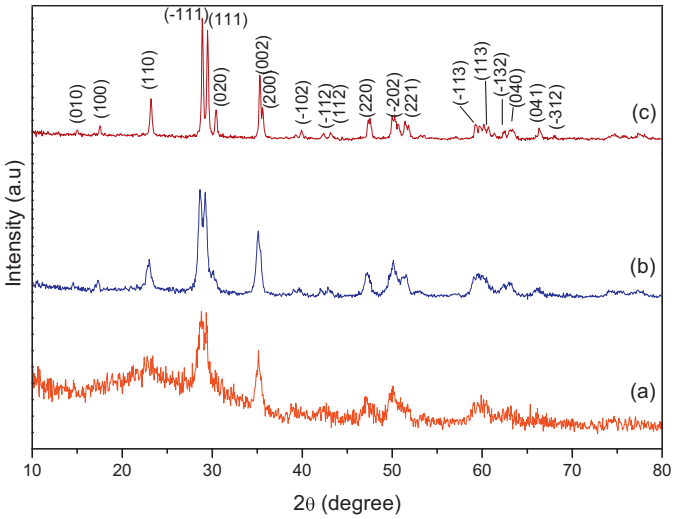

Fig. 1. XRD patterns of $CdWO_4$ calcined at (a) 400 °C, (b) 500 °C and (c) 600 °C.

3851 cm^{-1} is attributed to the vibration of H-O bonds for surface hydration layers. The bands at 3431 cm^{-1} region exhibit a strong absorption band, which is assigned to the H-stretching vibrations and the bands absorbed at 1635 cm^{-1} are assigned to the H-O-H bending vibrations [7].

The morphological features of 600 °C calcined $CdWO_4$ nanoparticles were analyzed using transmission electron microscope techniques and are given in Fig. 3. Fig. 3 (a & b) shows that the synthesized particles are in rod like morphology with the aspect ratio of ∼2-3. The nanocrystals identified by the TEM image are more or less uniformly distributed without any particle agglomeration. The corresponding SAED pattern (inset of Fig. 3a) indicates the dot pattern that attribute to the single crystalline nature of the particles. In order to further confirm the phase purity and crystallinity the $CdWO_4$ samples were subjected to HRTEM analysis and given in Fig. 3c. It shows that the well defined lattice fringes reveal the high crystalline nature of $CdWO_4$. The calculated inter-planar spacing,'d' is 5.03 Å corresponding to the (100) plane which further confirms the formation of single

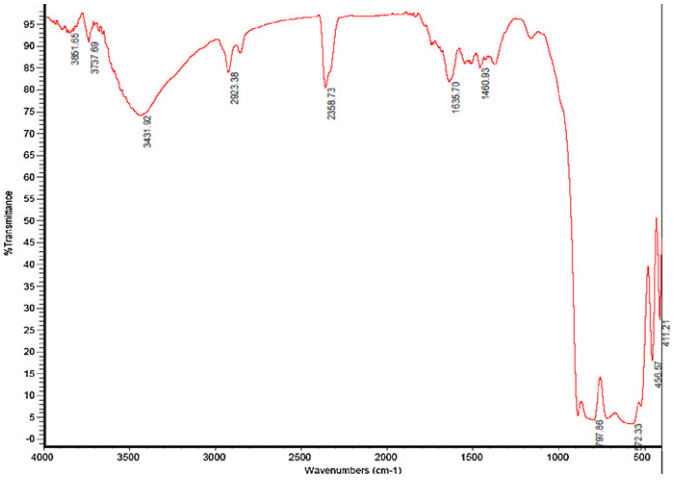

Fig. 2. FT-IR spectra of 600 °C calcined $CdWO_4$.

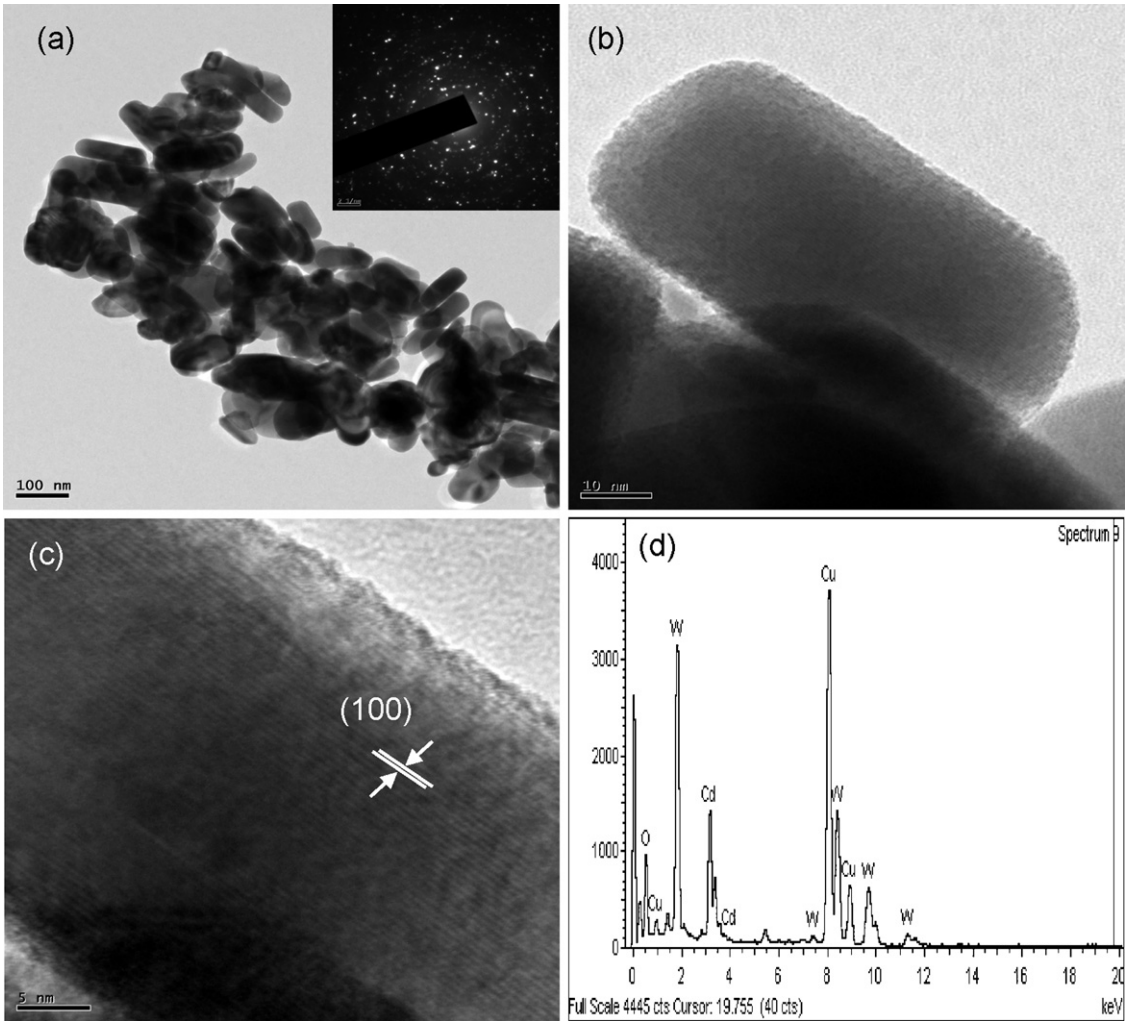

Fig. 3. TEM (a), HRTEM (b and c) and EDAX (d) patterns of 600 °C calcined $CdWO_4$ nanorods (inset: SAED pattern).

phase $CdWO_4$. The EDX pattern (Fig. 3d) elucidates that the elements present in the $CdWO_4$ sample as well as the calculated atomic ratio of Cd/W is 0.98, which is very close to the stochiometric ratio of $CdWO_4$.

Complex impedance spectrum of 600 °C calcined $CdWO_4$ is shown in Fig. 4a at two different temperatures. At high frequency it exhibits a semicircle with a centre under the real axis. The high frequency semicircles are due to parallel combination of bulk resistance R_b and bulk capacitance C_b. The associated capacitance values for all the temperatures has been calculated at the maximum frequency using the relation $2\pi\gamma_{max}RC = 1$. The capacitance value has been found to be in the order of pF which reveals that the conduction process is through the bulk of the material. The calculated capacitance values are 27 and 25 pF for 520 and 540 °C respectively. It has been found that with increase in temperature, the radius of the semi circle decreases. It indicates the reduction of bulk resistance with respect to temperature which elucidates the semiconducting behavior of the materials. The bulk resistance is calculated from the intercept of high frequency semicircle on the x-axis. It is seen that the conductivity increases with increase in temperature and is due to the increase in the thermally activated drift mobility of the charge carriers according to the hopping conduction mechanism [8]. The maximum conductivity has been found to be 3.76×10^{-8} S cm^{-1} at 540 °C.

Fig. 4b shows the conductance spectra of $CdWO_4$ measured at two different temperatures. The frequency independent region at low frequency plateau corresponds to the dc conductivity of the bulk material and the dispersive region (frequency dependent) at high frequency corresponds to the a.c. conductivity. The switch over from the frequency independent region to the frequency dependent region denotes the onset of conductivity relaxation, which shifts towards the high frequencies as temperature increases. In high frequency region the conductivity increases which indicates that the ions possess forward and backward hopping motions. The low frequency plateau is found to increase with increase in temperature. At high temperatures, there is a depression at the lower frequencies which is due to the grain boundary effect. Using non linear fitting, the dc conductivity σ_{dc}, hoping frequency (ω_p), carrier concentration (N) and mobility (μ) is calculated from the conductance spectra based on Jonsher Power law [9] and are given in Table 1. The obtained σ_{dc} values are

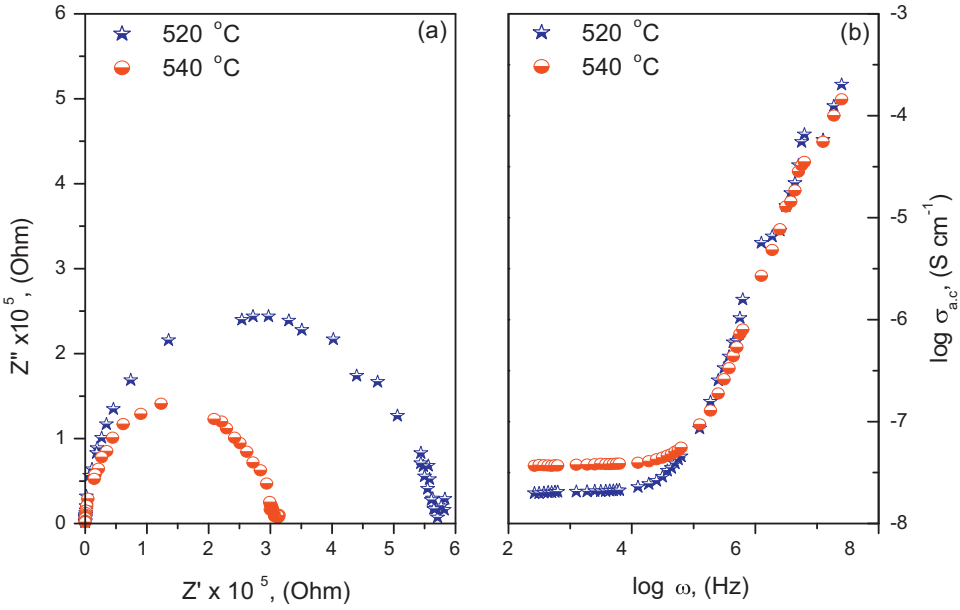

Fig. 4. Impedance (a) and conductance (b) spectra of $CdWO_4$.

Table 1
Electrical Conductivity Parameters.

Temp. °C	σ_{dc} (S cm^{-1})	N (S cm^{-1}KHz^{-1})	μ (cm^2/V s)	ω_p (Hz)
520 °C	2.10×10^{-8}	2.0×10^{-7}	06.56×10^{17}	08314
540 °C	3.86×10^{-8}	1.9×10^{-7}	12.69×10^{17}	16494

2.1×10^{-8} S cm^{-1} and 3.86×10^{-8} S cm^{-1} for 520 and 540 °C respectively which are in well agreement with the dc conductivity obtained from impedance spectra (Fig. 4a). Similarly, the hopping frequency (ω_p) and mobility increases with increase in temperature. At the same time the carrier concentration remains constant for both the temperatures, which indicates that the conductivity is mainly due to the thermally activated charge carriers by hopping mechanism [10].

4. Conclusion

The $CdWO_4$ nanocrystals have been successfully synthesized by simple co-precipitation method. XRD pattern confirms the single phase formation of $CdWO_4$. The calculated lattice parameters confirmed the monoclinic structure. The functional groups of $CdWO_4$ have been confirmed by FT-IR spectroscopy. The formation of nanocrystals and the high crystallinity of $CdWO_4$ were evident from TEM and HRTEM images respectively. The electrical conductivity shows the normal behavior of semiconducting materials. The impedance spectrum confirms the origin of conducting mechanism. The maximum electrical conductivity has been found to be 3.86×10^{-7} S cm^{-1} at 540 °C.

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