

Effect of Thermal Annealing on the Cd(OH)₂ and Preparation of CdO Nanocrystals

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Abstract

Nanosized β -Cd(OH)₂ were successfully synthesized via simple chemical precipitation method using cadmium nitrate as a precursor in a solution of sodium hydroxide. The CdO nanoparticles were harvested from β -Cd(OH)₂ by thermal decomposition at 400°C. The structural, optical, and magnetic properties of the as prepared and annealed products of β -Cd(OH)₂ were studied. The morphology of the CdO nanocrystals annealed at 400°C analyzed by FE-TEM exhibits pseudo spherical morphology with sizes around 60 nm.

Keywords: Nanosized β -Cd(OH)₂; Decomposition; Annealed products; Magnetic properties

Introduction

In the past two decades, new terms with prefix nano have captured ample space among the scientific community owing to the unusual physical and chemical properties of nanomaterials. Usually on the basis of size, morphology and structure applications of nanomaterials are justified. Recently, interests in the study of Transparent Conductive Oxide (TCO) nanomaterials have gained special attention due to their important applications in the current technology. Among the transparent conducting metal oxide semiconductor materials, CdO is an important n-type semiconductor material with direct band gap of 2.2-2.7 eV and indirect band gap of 1.36-1.98 eV [1]. CdO finds its potential applications in the field optoelectronics devices such as solar cells, phototransistors, photodiodes, transparent electrodes, catalysts and gas sensors [2-11]. Despite cadmium is toxic, CdO is widely used as a photo catalyst for effluent treatment [4,12,13]. Many researchers have reported the preparation of CdO nanostructures with different methods such as chemical vapour deposition, sol-gel, laser ablation, spray pyrolysis and hydrothermal methods. Nowadays, the usage of the simple chemical precipitation method in comparison with other methods increases among researchers because of its less time consuming and less expensive nature. Lof Ali, et al. have synthesized Cd(OH)₂ and CdO nanocrystals by the solvothermal method. They predicted the conversion of nanosized Cd(OH)₂ into CdO at 500°C [14]. Siraj et al. have studied the magnetic properties of Al-doped CdO thin films and reported their para and ferromagnetic behaviors [15].

Herein, we demonstrate a simple chemical precipitation method for the synthesis of nanocrystalline β -Cd(OH)₂. Nanocrystals of CdO can be obtained through the thermal decomposition using the as-prepared β -Cd(OH)₂ as precursor.

Materials and Methods

Chemicals

Cadmium nitrate hexahydrate [Cd(NO₃)₂·6H₂O], sodium hydroxide [NaOH] were purchased from Merck and were used as received since they were of analytical reagent grade with 99% purity. Ultra-pure water was used for all procedures of sample preparation and dilution.

Synthesis of CdO nanocrystals

In the preparation of CdO nanocrystals from cadmium nitrate hexahydrate (Cd(NO₃)₂·6H₂O) and sodium hydroxide (NaOH), 0.5

M of Cd(NO₃)₂·6H₂O in 50 ml of deionized water and 2 M of NaOH in 50 ml water were mixed up dropwise. The entire mixture was stirred magnetically until a white precipitate of cadmium hydroxide hexahydrate was formed. The resultant precipitate was filtered and then washed alternately with deionized water and ethanol for 3 times to remove the impurities. Further, the precipitate of cadmium hydroxide hexahydrate (Cd(OH)₂·6H₂O) was dried in hot air oven at 100°C for 4 h and cadmium hydroxide was harvested in the nanosize. The obtained product was thermally annealed at different temperatures (200, 300, 400, 600 and 800°C) for 2 h. The formation of CdO took place at 400°C upon thermal annealing.

Growth mechanism

Formation of Cd(OH)₂ in the presence of NaOH can be explained on the basis of buffer action of cadmium ions. Cadmium ions in the solution become hydrated and transformed to solid cadmium hydroxide through stepwise coordination of hydroxyl ions. However, depending upon the concentration of the base and the synthesis temperature, cadmium hydroxide is transformed into cadmium oxide through dehydration.

Apparatus

The prepared products were characterized by powder X-Ray Diffraction (XRD) on a X'PERT PRO diffractometer with Cu-K α radiation ($k=1.5406 \text{ \AA}$). From the line broadening, the size of the particle was estimated by the Scherrer equation. FT-IR analysis was made to characterize the functional groups of the precursor and nanosized cadmium oxide using SHIMADZU-8400 with a resolution of 4 cm⁻¹. The Photoluminescence (PL) emission spectra of the samples were recorded with a Spectrofluorometer (Jobin Yvon, FLUOROLOG-FL3-11). Vibrating Sample Magnetometer (VSM) is used to identify the nature of magnetic species in the material. To study the morphology and size of the nanocrystals FE-TEM (Model JSM 2100F JEOL, Japan) analysis was made.

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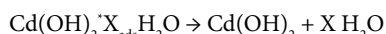
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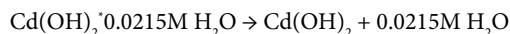
Results and Discussion

Thermal analysis

To understand the thermal behavior of β-Cd(OH)₂, TG-DTA analyses were carried out between room temperature and 1000°C with a heating rate of 20°C/min in nitrogen atmosphere. Figure 1 shows the TG and DTA traces of β-Cd(OH)₂. Five prominent weight losses were observed at the end set temperatures 157°C (2.63%), 244°C (9.61%), 398°C (2.79%), 729°C (2.58%), and 1000°C (11.39). The initial weight loss of 2.63% observed between room temperature and 157°C could be ascribed to the removal of water molecules adsorbed on the surface of the Cd(OH)₂ nanoparticles. The dehydration process involved in the first stage is given by the following chemical equation



From the initial weight loss of 2.63%, it is possible for us to estimate the amount of water exists in the as prepared Cd(OH)₂. From the weight loss, the water absorption in molar fraction has been calculated as 0.0215 M (moles of H₂O per mole of Cd(OH)₂). Therefore, the possible dehydration reaction is modified as



The second stage of weight loss occurring between 157-244°C may be ascribed to the transformation of β-Cd(OH)₂ into γ-Cd(OH)₂. The third stage of weight loss predicted between 244-398°C is due to the decomposition of γ-Cd(OH)₂ into CdO. The fourth stage of minimum weight loss of 2.58% recorded between 398-729°C indicating the improved crystallinity of the CdO. A final and fifth stage of steep weight loss of 11.39% ascribed to the transformation of CdO nanocrystals into CdO₂. The DTA curve of β-Cd(OH)₂ shows two endothermic peaks at 204°C and 354°C corresponding to the removal of adsorbed water and decomposition of Cd(OH)₂ into CdO respectively. Further, the DTA curve exhibits two exothermic peaks at 272°C and 695°C which are related to the phase transformation of Cd(OH)₂ and conversion of CdO into CdO₂ respectively. The obtained DTA results support the results of the TG curve.

XRD analysis

The XRD patterns of as-synthesized and annealed products are shown in Figure 2. As synthesized products exhibited twelve

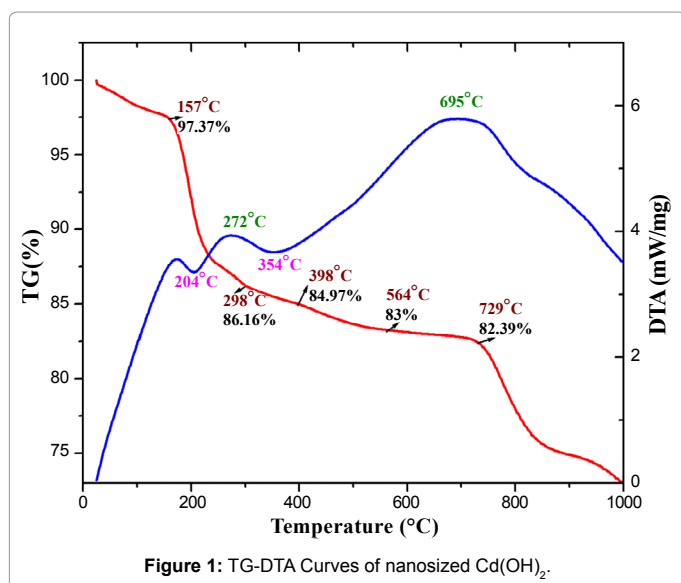


Figure 1: TG-DTA Curves of nanosized Cd(OH)₂.

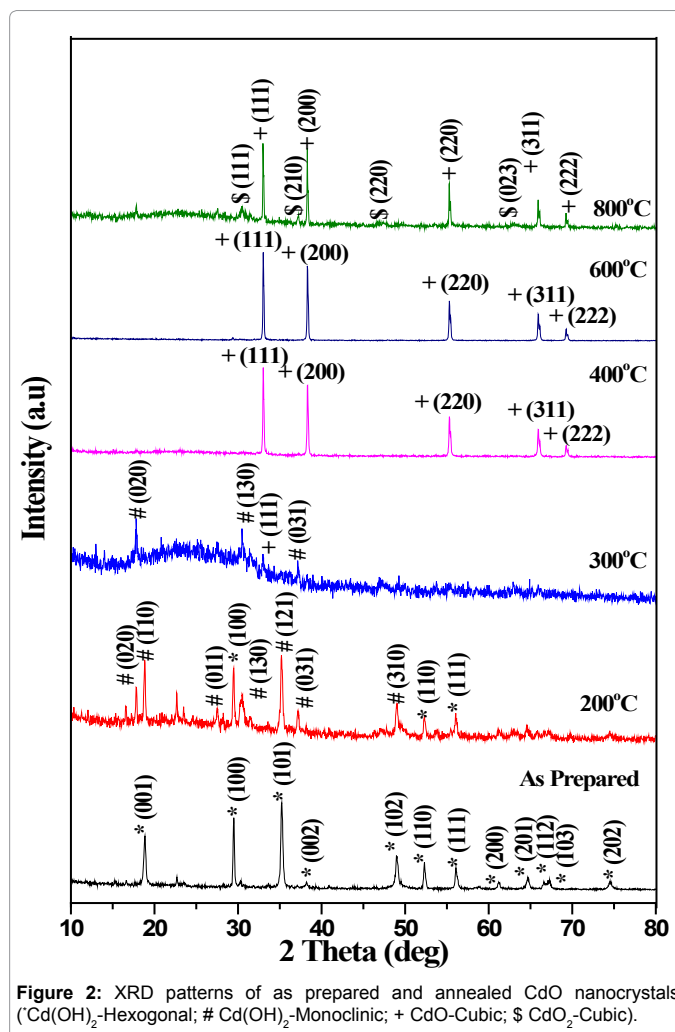


Figure 2: XRD patterns of as prepared and annealed CdO nanocrystals (Cd(OH)₂-Hexagonal; # Cd(OH)₂-Monoclinic; + CdO-Cubic; \$ CdO₂-Cubic).

diffraction peaks corresponding to the (001), (100), (101), (002), (102), (110), (111), (200), (201), (112), (103) and (202) planes of hexagonal β-Cd(OH)₂ nanoparticles. The XRD patterns of the products annealed at 200°C show the presence of hexagonal as well as monoclinic (JCPDS: 20-0179) phases of γ-Cd(OH)₂. Further, on annealing at 300°C, in addition to the (020), (130) and (031) planes of monoclinic phase of γ-Cd(OH)₂, a dominating cubic (111) peak of CdO is also seen. After annealing at high temperatures of 400 and 600°C, the diffraction peaks could be indexed as (111), (200), (220), (311) and (222) planes of cubic CdO (JCPDS: 05-0640). The XRD patterns of the sample annealed at 400°C show the formation of pure cubic phase of CdO. However, the sample annealed at 600°C shows sharp diffraction peaks with reduced peak width as a result of improved crystallinity. Further annealing of the sample at 800°C leads to the formation of both cubic CdO and CdO₂.

The average grain size was calculated from the XRD patterns using the Debye Scherrer's formula [16] for the as prepared and annealed products. The crystal structure, lattice parameters, and particle size of the as prepared and annealed products are given in Table 1. As can be seen from the table, the grain size increases with annealing temperature and thus the crystallization of the products is improved. The lattice constants calculated for all the products almost identical to the JCPDS values, especially the lattice parameters of the products annealed after 400 and 600°C exactly match the JCPDS values.

FT-IR analysis

FT-IR analysis was used to study the β -Cd(OH)₂ powder during heating. The heated samples were ground with KBr and pressed into pellets. IR spectra were recorded on samples after heat treatment at 200, 300, 400, 600 and 800°C. As shown in Figure 3 the IR spectra of the as-prepared sample annealed at 100°C show a sharp and intense band at 3605 cm⁻¹ arising from the stretching vibrations of structural OH groups confirming they are β -Cd(OH)₂ [11,17]. Usually β -Cd(OH)₂ can show a band at around 3605 cm⁻¹, whereas γ -Cd(OH)₂ may provide absorption bands at around 3588 and 3531 cm⁻¹. Absorption bands observed around 3447 and 1640 cm⁻¹ are respectively assigned to the stretching and bending vibrations of H₂O molecules. Further, on heating at 200°C, the sharpness of the band at 3603 cm⁻¹ decreases and a new band at 3522 cm⁻¹ emerges. This indicates the conversion of β -Cd(OH)₂ into γ -Cd(OH)₂. Upon heating at 300°C, the absorption band at 3603 cm⁻¹ completely disappeared. Since the absorption bands of γ -Cd(OH)₂ are predicted at 3524 and 3584 cm⁻¹, the observation

Temperature (°C)	Product	Crystal structure	Lattice parameters (Å)		Particle size (nm)
			Standard values	Calculated values	
100	Cd(OH) ₂	Hexagonal	a=3.494 c=4.710	a=3.4973 c=4.791	41.29
200	Cd(OH) ₂	Hexagonal		a=3.5002 c=4.8132	38.96
	Cd(OH) ₂	Monoclinic	a=5.63 b=10.18 c=3.4127	a=5.0231 b=9.9507 c=3.4127	34.52
300	Cd(OH) ₂	Monoclinic		a=5.0131 b=9.9317 c=3.4012	99.82
	CdO	Cubic	a=4.695	4.7004	19.15
400	CdO	Cubic		4.6963	64.63
600	CdO	Cubic		4.6960	86.46
800	CdO	Cubic	a=4.695	4.6984	98.61
	CdO ₂	Cubic	a=5.313	5.0789	17.20

Table 1: Crystal structure, lattice parameters, and particle size of the as prepared and annealed products.

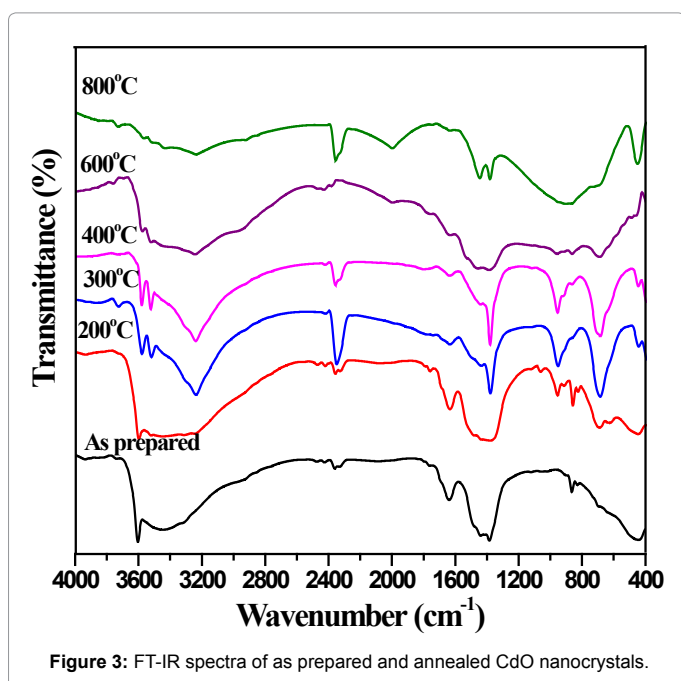


Figure 3: FT-IR spectra of as prepared and annealed CdO nanocrystals.

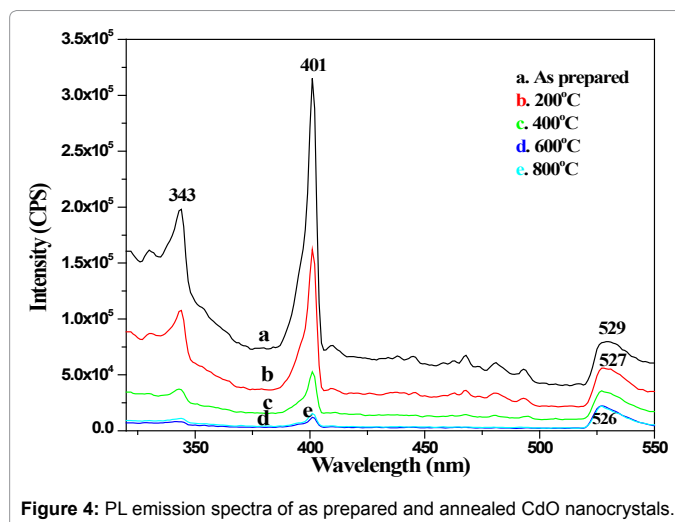


Figure 4: PL emission spectra of as prepared and annealed CdO nanocrystals.

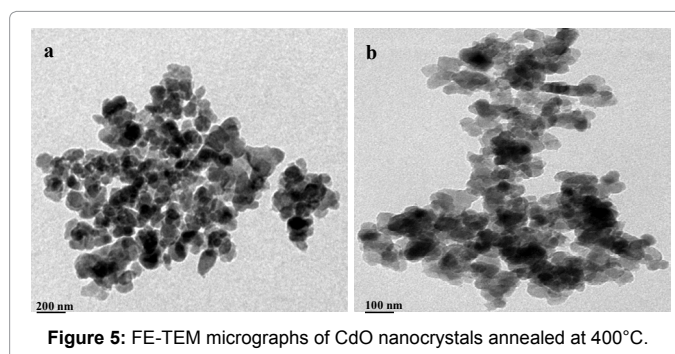


Figure 5: FE-TEM micrographs of CdO nanocrystals annealed at 400°C.

confirms a complete transformation from β -Cd(OH)₂ to γ -Cd(OH)₂ [18]. According to the literature, the bands in between 800-1400 cm⁻¹ belong to the Cd-O vibration [19]. In addition, peaks around 685 and 447 cm⁻¹ could be ascribed to the Cd-O stretching mode [14]. After being at 400°C, the formation of CdO is characterized by the sharp bands positioned at 1383, 686 and 447 cm⁻¹. On further annealing (600 and 800°C) the characteristic peaks of Cd-O are broadened as a result of increased particle size.

Photoluminescence

The room temperature Photoluminescence (PL) spectra of as prepared and annealed products with 250 nm excitation are shown in Figure 4. All the products show three emission peaks positioned at 343, 401 and 527 nm. The peak appearing at 343 and 401 nm are assigned to the near band edge emission of CdO originating from excitonic transitions between the electrons in the conduction bands and the holes in the valence bands. The emission peak at 527 nm may be ascribed to structural defects such as vacancies and surface traps [20,21]. With such visible emission, the CdO nanocrystals can be utilized in the industry of high-quality monochromatic laser.

As a general behavior, the PL spectra of the CdO nanomaterials showed a relatively broad less intense UV and visible emission bands as the annealing temperature is raised. This is due to the fact that the oxygen vacancy concentration decreases after annealing at high temperatures. However, the position of the emission bands are not majorly changed as the annealing temperature is raised from 200-800°C. This suggests that these emission bands are weakly associated with the band gap properties.

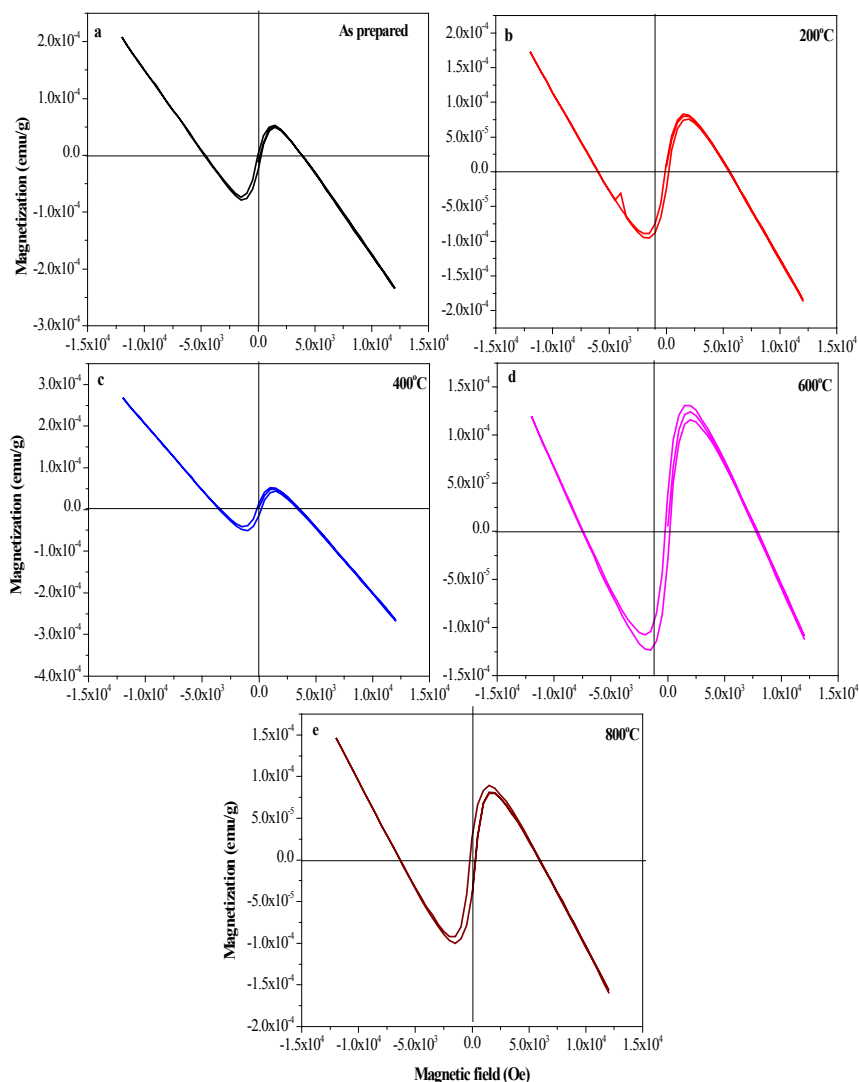


Figure 6: M-H loops of as prepared and annealed CdO nanocrystals.

Field emission-transmitting electron microscope analysis

FE-TEM analysis was used to evaluate the shape and size of the CdO nanoparticles. FE-TEM micrographs of CdO annealed at 400°C are shown in Figure 5a and b. The annealed sample is constituted of pseudo spherical 60 nm sized particles. The entire observed particles have almost same diameter. The value of crystallite size obtained from the FE-TEM analysis is in good agreement with the value obtained from the Scherrer's formula.

Magnetic characterization

The magnetic behavior of CdO nanoparticles has not been much investigated so far. Vibrating sample magnetometer was used to study the magnetic properties of CdO nanocrystals at different growth temperatures. Figure 6 a-e shows the hysteresis loops for as prepared and annealed CdO nanocrystals. It can be observed that both as-prepared and annealed formulations reveal typical paramagnetic behavior. The paramagnetism of the products is clearly shown by coercivity (H_c) saturation magnetization (M_s) and remnant magnetization (M_r) listed in Table 2. The saturation magnetization is the maximum induced magnetic moment that can be obtained in a magnetic field, beyond

Temperature (°C)	Coercivity (H_c)	Magnetization $\times 10^{-6}$ emu	Retentivity $\times 10^{-6}$
As prepared	1921.4	220.90	12.540
200	2839.7	179.67	16.317
400	1895.3	268.10	13.453
600	4078.5	127.14	31.729
800	3095.1	152.68	32.833

Table 2: The paramagnetism of the products is clearly shown by coercivity (H_c) saturation magnetization (M_s) and remnant magnetization (M_r) listed.

this field no further increase in magnetization occurs. As shown in Figure 6c and Table 2, the effect of 400°C of annealing resulted in an increase of the saturation magnetization by almost 20%. Coercivity is the reverse magnetic field required to reduce the net magnetization to zero. For magnetic materials, it is necessary to reduce the coercivity as a way to control the energy losses. As shown in second column in Table 2, as prepared and annealed at 400°C CdO nanocrystals have relatively lower coercivity compared with that of other annealed products. Simply, remnant magnetization (M_r) can be defined as the remaining magnetic momentum after realizing the magnetic field. Low remnant magnetization materials are classified as magnetically clean materials.

In some distinct fields, low remnant magnetization is highly desirable for instance in data storage applications. As shown in the last column in Table 2, both as prepared Cd(OH)₂ and CdO annealed at 400°C have low remnant magnetization.

Conclusion

In conclusion, nanometer sized particles of CdO have been successfully synthesized by thermal decomposition of β-Cd(OH)₂ at 400°C. The results of XRD and FT-IR analyses confirmed the formation of CdO phase. Thermal annealing on CdO has a considerable effect of increasing the particle size. The prepared CdO showed visible emission at 527 nm that can be used in the preparation of gas sensors. FE-TEM analysis of CdO shows the pseudo spherical particles with diameter around 60 nm. The CdO nanocrystals annealed at 400°C show low values of coercivity and remnant magnetization suggesting potential usage in data storage applications.

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