J. Mountain Res. P-ISSN: 0974-3030, E-ISSN: 2582-5011 DOI: https://doi.org/10.51220/jmr.v16i2.15
Vol. 16(2) Special Issue ICRAMS-2021, (2021), 111-119

Effect of Divalent Metal Ions on Thermal Evolution and Band Gap Energy of Cadmium Oxide (CdO) Nanocrystallites: Comparetive Study

Chitra Bhukkal[1]* • Rachna Ahlawat[2] • Surender Ahlawat[3]

[1]*Physics Department, Government College, Adampur, Hisar, Haryana-125052, INDIA*
[2]*Department of Physics, Chaudhary Devi Lal University, Sirsa-125055, INDIA*
[3]Department of Economics, *Chaudhary Devi Lal University, Sirsa-125055, INDIA*

* Corresponding Author Email: chitrabhukal@gmail.com

Received: 28.8.2021; Revised: 16.9.2021; Accepted: 20.10.2021

Abstract: In this study, pure and divalent metal ions doped cadmium oxide samples are synthesized by cost effective co-precipitation method at the nanoscale dimensions. Here, we have represented a comprehensive study which conclude that how structural and optical behavior of undoped cadmium oxide has been modified with single doping of Cu, Mn and their co-doping (Cu-Mn) also. The prepared nanopowder is being investigated using different complementary techniques like TG-DTA and UV-Vis spectroscopy to explore their bandgap energy and thermal behavior. A strong and broad optical absorption band is obtained at 262, 250, (312 and 475), (250-350) nm for respectively samples. The optical band gap values are calculated using Tauc's plot as 4.45, 3.86, 2.39 and 2.44 eV for undoped CdO, Cu doped CdO, Mn doped CdO and Cu-Mn co-doped CdO respectively. UV-Vis spectra revealed that the prepared samples are having high absorbance and extended sufficiently into visible region. Therefore, it is suggested that the co-doping efficiently alter the band gap of the CdO and make it suitable for optoelectronics and other applications like gas sensing, photo catalyst etc.

Keywords: Band gap Energy, co-doping, Cu, Cu-Mn doped CdO, Mn, TG-DTA analysis

Introduction

Nanocrystals of II-VI compound semiconductors are widely attracted due to their enhanced structural and optical characteristics in the field of nanoscience and nanotechnology. From II-VI series of elements, Cadmium Oxide (CdO) is found to be the most versatile transparent conducting oxide (Rajput et al., 2017). Pure cadmium oxide generally has its place to the set of TCOs (transparent conducting oxides) holds n-type of conductivity (10^2-10^4 S/cm), possesses high transparency in the NIR region and narrow forbidden gap (Rajput et al., 2017). Recently, doped CdO are also investigated due to its large applicability in flat display devices, photonic diodes and thin film electroluminescence (Mohanraj et al., 2018, Purohit et al.,2017). The process of doping would modify its chemical and physical properties up to large extent. In literature, many fabrication processes are reported by researchers for undoped and doped CdO nanomaterials. Likewise, Gupta et. al have

reported thin films of CdO doped with tin and investigated effect of concentration and growth temperature (Gupta et al.,2008). Ziabani et. al have reported the Al doped CdO film synthesized with dip coating sol-gel rout. They have investigated the relationship of surface morphology and optoelectronic properties (Ziabari et al., 2012). Siva Kumar et. al have prepared undoped and Silver doped CdO nanoparticles by the wet chemical procedure (Sivakumar et al., 2015). Also, Usha Rani et. al were represented Mg doped CdO and elaborated the physical and optoelectronic behavior (Usha Rani et. al). From these studies, it came into known that researchers have focused more on morphological and electronic properties of pure and doped CdO as compare to other properties. Hence in this paper, it is proposed that thermal and absorbance of CdO could be tuned by suitable doping of divalent metal ion and therefore considered as the thrust topic of investigation. In this way, we have selected two divalent metal ions (Cu, Mn) as dopant and discussed the changes in thermal behavior and bandgap engineering. Besides, some interesting results are also highlighted owing to single (Cu, Mn) and double doping (Cu-Mn) in CdO.

Synthesis and Characterizations

For sample preparation of CdO doped with different divalent metals (TM) ions, an easy and cheap co-precipitation method is chosen. The full explanation of synthesis method has been discussed in our previous publication (Bhukkal et al., 2020). After synthesis, all samples are calcined at similar 750°C (3h). To investigate the characteristic weight loss behavior of the prepared nanopowder, thermal analysis has been carried out from 25- 900°C per 5°C/min rate of heating. For this, Perkin Elmer STA 6000 thermal analyzer is being used to conduct the DSC and TGA measurements. Absorbance is analyzed in the UV-Vis range (200-900 nm) from Perkin Elmer Lambda 750 spectrophotometer.

Results and Discussion

Thermal Analysis by DSC

The physio-chemical nature of prepared samples is examined by Differential Scanning Colorimetric which generally establishes the thermal change either scanning mode (as a function of temperature) or isothermal mode (as a function of time). Fig. 1 shows the DSC traces for undoped and doped CdO samples which are obtained after centrifugation and drying the precipitates in oven.DSC curve emphasized prominent peaks at the temperatures: 45°C, 195°C, 296°and 730°C as exposed in Fig. 1(a). The initial decay at 50°C could be credited to the discharge of water available on the top layer of sample. Major endothermic peak at 195°C insured that sample absorbs heat to decompose the organic at the particular temperature with enthalpy 237.85 J/g and also due to the change of hydroxide precursors into CdO (Bhukkal et

al., 2020). However, few endothermic peaks are seemed at 296°C and 730°C which support the crystalline phase of cubic CdO nanocrystallite. At last, beyond 750°C, negligible mass loss is found that indicate the development of pure CdO at this temperature.

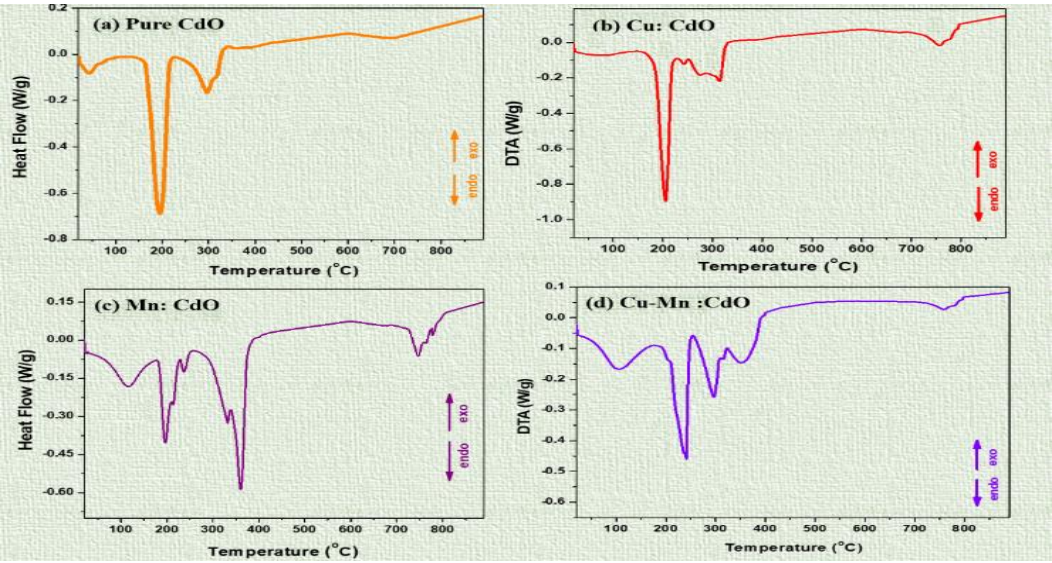

Figure 1: Differential Scanning Colorimetric curve for (a) Pure CdO (b) Cu doped CdO (c) Mn doped CdO (d) Cu-Mn doped CdO

DSC curve obtained for Cu doped CdO sample is depicted in Fig. 1(b). In this sample, major main peak is observed at 205°C that is endothermic and has enthalpy = 194.60 J/g. It is ascribed to burning of precursors specially citrates, organics and residual alkoxy groups (Bhukkal et al., 2020).Phase identification in cadmium oxides is confirmed by other two peaks noticed at 312°C and 738°C. Moreover, two medium peaks are also found at temperature 240°C and 280°C with small enthalpy values as 3.45 and 7.01J/g. All these peaks are emphasized the endothermic chemical reactions between precursors. Few impurities phases are also evolved on account of the peak at 312°C in DSC curve with 13.23 J/g enthalpy. The significant peak in this sample is formed at 738°C and has enthalpy 9.4J/g owing to crystallization of the cubic CdO.

For Mn doped CdO sample, DSC curve has been depicted in Fig. 1(c) which shows major endothermic peaks at 355°C along with three minor peaks at 110, 190 and 750°C. It is calculated from inbuilt software of DSC that major peak at 355°C that has enthalpy value ~ 91.45 J/g. The particular peaks at 110°C corresponds to deletion of adsorbed water has 86 J/g of enthalpy. Also, two endo-thermic peaks are noticed at 190°C with 35.75 J/g enthalpy and at 740°C with 12 J/g of enthalpy. Major endothermic peak has been occurred at 240°C similar to other samples [12].Peaks at 300 and

350°C are developed from the reaction of various chemicals while peak at 740°C is devoted to complete crystallization of cubic CdO. For Cu-Mn doped CdO, major peak is evolved at 240°C with enthalpy 95.31 J/g as shown in Fig. 1(d). The other relevant peaks exist at 100°C, 300°C and 750°Cin DSC curve owing to enthalpies 473.54, 3.07 and 3.54 J/g, respectively (Bhukkal et al., 2020).

Thermal Analysis (TGA)

The potential of TGA to produce elemental quantitative data has led to its wide spread use in nanoscience and nanomaterials.For pure sample (a),TG- curve emphasized prominent weight losses of 15%, 35%, 12%and 3%which are in full support of the DSC curve of corresponding sample. The initial decay noticed from room temperature to 90°C which could be credited to the evaporation of water. The second stage of 35% weight loss occurred between 160-220°C which may be assigned to the phase transformation from precursor to cubic cadmium oxide and removal of acetates, carbonates etc (Singh et al.,2009). The third stage of weight loss 12% between 250-350°C predicted the improved crystallinity of the prepared nanocomposite. Further, a minimum weight loss of)~3 %(observed in final stage between 700-750°C, indicated complete appearance of cubic phase CdO nanocrystallites as well as removal of impurity phases. For Cu doped sample, entire weight loss ~ 44 % is detected in the entire 25° - 750°C range and after that no weight loss occurred for Cu doped CdO nanocrystallites. As depicted in Fig. 2(b), starting weight loss ~11 % is called 1st step of TG analysis curve. The prominent peak in temperature range 186-218°C called as 2nd step (~25 % weight loss) while negligible weight loss (8 %) is presented as 3rd step in corresponding TGA curve (Bhukkal et al., 2020).

Further, the DSC graph of Mn doped CdO emphasized initial decay of 5% noticed from 25-110°C which is mainly due to the evaporation of water available on top facet of the sample. The next step of 7 % loss of weight occurred between 180-200°C which may be attributed to the removal of acetates, carbonates etc (Singh et al., 2009). The next stage of weight loss ~8 % in the range 250-350°C predicted the improved crystallinity of the sample. Further, a small weight loss of)~5%(observed in final stage between 700-750°C signifies crystalline structure of cubic phase CdO nanocrystallites.

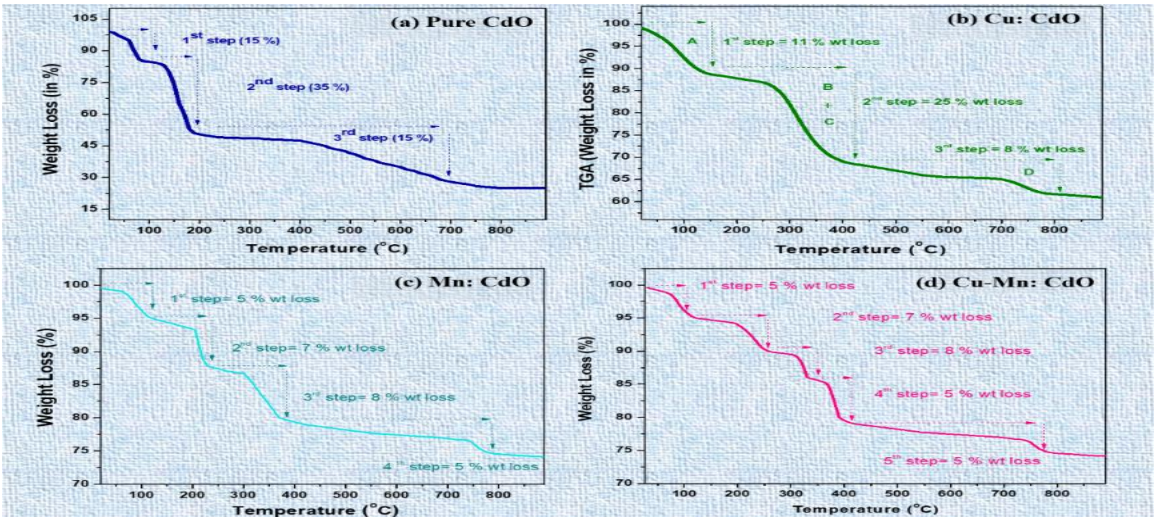

Figure 2: Thermo Gravimetric Analysis curve for (a) Pure CdO (b) Cu doped CdO (c) Mn doped CdO (d) Cu-Mn doped CdO.

For Cu-Mn doped CdO sample, the TGA graph depicted the performance of entire weight loss ~ 30 % in the temperature range 25°C-800°C mainly due to the decomposition and modification of precursors in different phases. Every step is attributed to the chemical decomposition owing to distinct reaction of chemicals (Bhukkal et al., 2020). After 750°C, there is no loss of weight; means crystallization is completed up to this temperature. The 3rd and 4th step with subsequent weight loss ~ 8 and 5% has also been displayed in Fig. 2(d). The latter is ascribed to cubic crystalline phase of CdO that exist as the fundamental phase in doped samples. It is concluded that the weight loss observed in TGA graph of pure and doped CdO demonstrated multistep degradation processes.

Uv-Vis Spectroscopy

Fig. 3 (i) presents the disparity of incident photon wavelength and optical absorption in the UV-Vis-NIR region (200-800 nm) for pure and doped CdO. Each powder sample with a fixed amount was dissolved in ethanol solvent using ultrasonic machine and observed significant absorbance mainly in UV-region (Eskizeybek et al., 2011). A sharp and strong absorption peak near 214 nm is noticed in pure CdO with clear excitonic feature owing to the nanometer size of the prepared crystallites. In Cu doped CdO sample, one may observe a strong absorption peak positioned at 240 nm accompanied by a small lump in the 325-450 nmwavelength portion. Absorbance at 240 nm is due to excitonic features that is well matched with literature (Bhukkal et al., 2019,2020). In this sample, broad hump recognized about 400 nm could be credited to the doping of divalent metal i.e. copper ions.

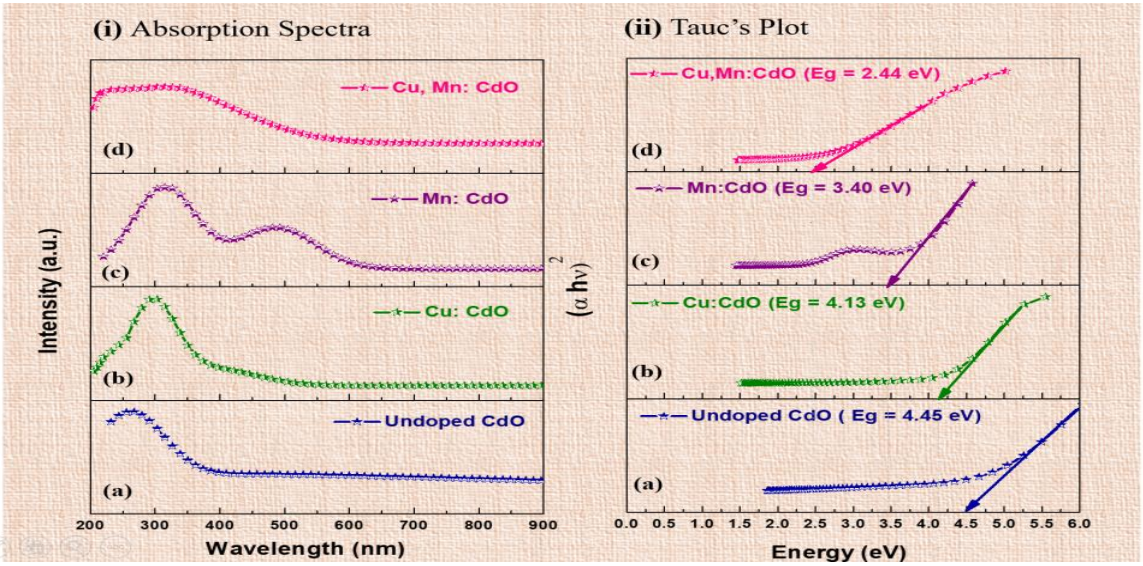

Figure 3(i): UV-Vis spectra and **(ii)** Band gap energy for (a) Pure CdO (b) Cu doped CdO (c) Mn doped CdO (d) Cu-Mn doped CdO.

The prepared Cu doped CdO nanopowder revealed in significant absorbance in the optical region, therefore may be utilized in solar cells (Thovhogi et al., 2016). For Mn doped CdO, the absorption edge is transferred towards the high energy as compare to pure CdO as shown in 'c' part of Fig. 3(i). Here, two intense and broad optical absorption bands are obtained centered at 320 nm and 460 nm. First peak is attributed to CdO while second peak may be originated from Mn^{2+} ions (Kumar et al., 2015). However, in Cu-Mn doped CdO sample, a wide band is appeared in the region 220-380 nm while the band-edge approaches to the solar region (Bhukkal et al., 2020). In this investigation, the coefficient of absorbance is shifted a little towards higher wavelength range due to appropriate doping of divalent metal ions. Such a red shift happened in doped nanopowder stimulated the uses of such materials in modern optoelectronic devices.

Bandgap Energy by Tauc's Plot

The main difference in band gap of pure and doped sample is generated from non-stoichiometric composition and strongly depends on adopted synthesis rout (Rajput et al., 2017, Gupta et al., 2008). In general, band gap energy of the prepared samples is considered from the absorption spectra, wherever enrichment in the absorbance is observed possibly due to sharp band-to-band conversion. From absorption data,band gap energy (E_g) gas been calculated for all prepared samples with the help of Tauc's relation as follows:

$$(\alpha h\nu)^{1/m} = A(h\nu - E_g) \quad (1)$$

In this equation, α is known as absorption coefficient, 'm' is considered as integer that

depends on transition probability. Fig 3(b) exhibits the plot of $(\alpha h\nu)^2$ vs optical photon energy ($h\nu$) that is linear at advanced energy values (>2.5) specifies optical direct transition (Bhukkal et al., 2020). When we put energy axis x = 0, one may notice that band gap energy E_g can easily be inferred by extrapolating the straight region of the graph. The band gap energy (E_g) of undoped sample of CdO = 4.04 eV while Cu doped sample has the band gap energy (E_g) = 3.86 eV. Further, for Mn doped sample, one can see the bangap energy (E_g) = 3.07 eV that is lower than the earlier calculated values of undoped and Cu doped sample. Moreover, the band gap energy (E_g) of Cu-Mn doped sample is attained as 2.14 eV that is quite lesser than the literature bandgap of pure CdO (2.54 eV) (Purohit et al., 2017). This red shift is observed due to the occurrence of large energy levels allotted to few defect phases (Ziabari et al., 2012). Because due to doping of divalent metal ions, there is improvement of charge carriers in the conduction band that causes shift in the Fermi level leads to an increment of the bandgap energy of cubic CdO. The alteration of optical band gap towards higher energy side observed in divalent metal ion doped CdO samples could be assigned to Burstein-Moss (BM) effect (Usharani et al., 2015). According to this effect, the deliberately doped ions reinforced the free charge carriers in the C.B. and modified the Fermi level in the forbidden gap. It is suggested that using optimum doping and most efficient co-doping, the band gap is significantly altered. Many super ficial faults and existence of impurity phase is also responsible for such observations. It is suggested that nanocrystallites size, defect states, imperfections at the grain boundaries and oxygen deficiency are the key aspects which significantly stimulus the optical absorption and hence bandgap.

Conclusions

In this paper, we have synthesized pure and Cu, Mn, Cu-Mn doped CdO nanocrystallites are perfectly synthesized using the most viable co-precipitation technique. DSC curve analyzed that reaction between different precursors has been started approximately at 200°C and crystallization has been started at350°C. Further, negligible mass loss was detected after 750°C indicates the establishment of CdO nanopowder with no impurity phase even in doped samples. Multistep degradation of weight loss curve has been observed for all samples corresponding to endo/exothermic peaks of DSC graph. Strong optical absorbance is observed in UV-region (200-250 nm) attributed to excitonic band edge absorption. While, the visible portion mainly contributed by doped divalent metal ions i.e. Cu, Mn.

REFERENCES

Bhukkal C, Ahlawat R (2019). Plate like $Cd(OH)_2$-CdO nanocomposite: A study

on surface morphology and band gap energy. AIP conference proceedings 2142: 140017.

Bhukkal C, Ahlawat R (2020). Cu2+–Mn2+-Co-doped CdO nanocrystallites: comprehensive research on phase, morphology and optoelectronic properties. Research on Chemical Intermediates 46: 4211–4232.

Bhukkal C, Ahlawat R, Chauhan M (2020). Study of crystallographic modification in cadmium oxide (CdO) nanocrystallites due to doped transition metal (TM) ions. Physica B: Condensed Matters 582: 411973.

Bhukkal C, Vats R, Goswami B, Rani N, Ahlawat R (2020). Synthesis of Cu doped Cd(OH)2- CdO layered nanostructures and investigation of its different intermediate phases, optical and dc-electrical properties**.** Materials Today Communications 25: 101608.

Bhukkal C, Vats R, Goswami B, Rani N, R. Ahlawat R (2020). Synthesis of Cu doped Cd(OH)2- CdO layered nanostructures and investigation of its different intermediate phases, optical and dc-electrical properties. Materials Today Communications 25: 101608.

Eskizeybek V, Demir O, Avei A, Chhowalla M (2011). Green synthesis of zinc oxide nanoparticles using flower extract of *Nyctanthes arbor-tristis* and their antifungal activity. J Nanopart Res 13: 4673-4680.

Gupta R K, Ghosh K, Patel R, Mishra S R, Kahol P K (2008). Highly conducting and transparent tin-doped CdO thin films for optoelectronic applications. Materials Letters 62: 4103– 4105.

Kumar S, Layek S, Yashpal M, Ojha A K (2015). Room temperature ferromagnetism in undoped and Mn doped CdO nanostructures. J Magnet and Mag Mat 393: 555–561.

Kumar S, Layek S, Yashpal M, Ojha A K (2015). Room temperature ferromagnetism in undoped and Mn doped CdO nanostructures**.** J Magnet and Mag Mat **393**: 555–561.

Mohanraj K, Balasubramanian D (2017). Microstructural, Optical, Morphological, Luminescence and Electrical Properties of a CdO Nanocomposite Synthesized by a Chemical Route Assisted Microwave Irradiation Technique. Silicon DOI 10.1007/s12633-017-9579-0.

Purohit A, Chander S, Patel S L, Rangra K J, Dhaka M S (2017). Substrate dependent physical properties of evaporated CdO thin films for optoelectronic applications. Physics Letters A 318: 1910-1914.

Rajput J K, Pathak T K, Kumar V, Kumar M, Purohit L P (2017). Study of crystallographic modification in cadmium oxide (CdO) nanocrystallites due to doped transition metal (TM) ions. Surfaces and Interfaces 6: 11-17.

Rajput J K, Pathak Y K, Kumar V, Purohit L P (2017). Tailoring and optimization of hybrid ZnO:TiO2:CdO nanomaterials for advance oxidation process under visible light. Appl Surf Sci 40: 8-16.

Singh S C, Swarnkar R K, Gopal R (2009). Effect of oxygen injection on the size and compositional evolution of ZnO/Zn(OH)2 nanocomposite synthesized by pulsed laser ablation in distilled water. J Nanopart Res 11: 1831-1838.

Sivakumar S, Venkatesan A, Soundhirarajan P, Khatiwada C P (2015). Spectroscopic studies and antibacterial activities of pure and various levels of Cu-doped $BaSO_4$ nanoparticles. Spectrochim Acta A 15: 760–772.

Thovhogi N, Park E, Manikandan E, Maaza M, Gurib-Fakim A (2016). Physical properties of CdO nanoparticles synthesized by green chemistry via *Hibiscus Sabdariffa* flower extract. Journal of Alloys and Compounds 655: 314-320.

Usharani K, Balu A R, Nagarethinam V S, Suganya M (2015). Study of crystallographic modification in cadmium oxide (CdO) nanocrystallites due to doped transition metal (TM) ions. Progress in National Science: Material International 25: 251–257.

Ziabari A, Ghodsi F E, Kiriakidis G (2012). Influence of Al-doping on microstructure and optical properties of sol-gel derived CdO thin films Surf Coat 213: 15–20.