

2. MATERIALS AND METHODS

We provide, in this chapter, the details of materials used and various experimental and other methods followed in the present study.

2.1. Materials Used

The precursor materials used for the preparation of ZnO, CdO, $Zn_xCd_{1-x}O$ and $Zn_xCd_{1-x}O:Mn$ nanocrystals are listed below:

- (1) Zinc acetate dihydrate (Analytical Reagent grade) $C_4H_6ZnO_4 \cdot 2H_2O$
- (2) Cadmium acetate dihydrate (Analytical Reagent grade)
 $C_4H_6CdO_4 \cdot 2H_2O$
- (3) Manganese acetate tetrahydrate (Analytical Reagent grade)
 $C_4H_6MnO_4 \cdot 4H_2O$

- (4) Urea (Analytical Reagent grade)
$$\begin{array}{c} O \\ | | \\ H_2N-C-NH_2 \end{array}$$

Solvent used for the synthesis is ethylene glycol ($C_2H_6O_2$). For all the washing purposes double distilled water was used. Acetone, $(CH_3)_2CO$ was used to remove any unwanted organic substances present in the compounds and composites prepared as such.

2.2. Preparation of Oxide Nanocrystals

Analytical reagent (AR) grade zinc acetate, cadmium acetate, manganese acetate and urea along with ethylene glycol were used for the preparation of $Zn_xCd_{1-x}O$ and $Zn_xCd_{1-x}O:Mn$ nanocrystals. Zinc acetate and cadmium acetate taken together in the required composition and urea in 1:3 molecular ratio were mixed and dissolved in 100ml ethylene glycol and kept in a domestic microwave oven (operated with frequency 2.45GHz and power 800W).. The amounts of precursor materials taken are given in Table1.

Microwave irradiation was carried out till the solvent was evaporated completely. The colloidal precipitate obtained was cooled and washed several times with water and then with acetone to remove the organic impurities present, if any. The sample was then dried and collected as the yield. 1 mole % manganese acetate was added to zinc and cadmium acetates in the case of $Zn_xCd_{1-x}O:Mn$ nanocrystals.

A total of twelve (6 without and 6 with adding Mn) samples were prepared with x varying from 0.0(pure CdO) to 1.0(pure ZnO) in steps of 0.2. In order to improve the ordering annealing of samples was done. $Zn_{0.4}Cd_{0.6}O$ was used as a test sample and annealed at different temperatures, viz 200, 450 and 600°C for 30 minutes in each case.

Table 1: The amounts of precursor materials used

System (with composition expected)	Amount (g) of			
	Zinc acetate	Cadmium acetate	Urea	Manganese acetate
ZnO	21.950	---	18.018	---
Zn _{0.8} Cd _{0.2} O	17.560	5.330	18.018	---
Zn _{0.6} Cd _{0.4} O	13.170	10.660	18.018	---
Zn _{0.4} Cd _{0.6} O	8.780	15.990	18.018	---
Zn _{0.2} Cd _{0.8} O	4.390	21.322	18.018	---
CdO	----	26.620	18.018	---
ZnO:Mn	21.950	---	18.018	0.1225
Zn _{0.8} Cd _{0.2} O:Mn	17.560	5.330	18.018	0.1225
Zn _{0.6} Cd _{0.4} O:Mn	13.170	10.660	18.018	0.1225
Zn _{0.4} Cd _{0.6} O:Mn	8.780	15.990	18.018	0.1225
Zn _{0.2} Cd _{0.8} O:Mn	4.390	21.322	18.018	0.1225
CdO:Mn	----	26.620	18.018	0.1225

X-ray powder diffraction patterns were obtained using an automated X-ray powder diffractometer with monochromated CuK_α radiation ($\lambda=1.540598$ AU) and scintillation counter for the unannealed, annealed at 200, 450 and 600°C samples. The patterns (see Figure 1) indicated that it was necessary to anneal the samples upto 450°C to have a good ordering.

The grain size in each case, was determined by using the Debye-Scherrer formula[193], $D = K\lambda/\beta\cos\theta$ where D is the mean size(diameter) of the grain, K (=0.96) is the size factor, β is the full width at half maximum (in radians), λ is the wavelength of the X-radiation used and 2θ is the angle at which maximum intensity was observed. Two to three different peaks were chosen whenever possible and consistency in the grain sizes obtained from using their widths was confirmed. The grain sizes obtained are given in Table 2. The grain size increased by 200% (i.e. from 27.02 to 54.52 nm) when the temperature of annealing was increased from 450 - 600°C. So, all the twelve samples prepared were annealed at 450°C for about 30 minutes and cooled naturally and used for further characterization.

From Figure 1, it is evident that before annealing, i.e., at room temperature the XRD pattern shows amorphous nature of the sample. It can be understood that after annealing the sample at 200, 450, and 600°C, the sample becomes ordered having the minimum orderded crystallite size at 450°C.

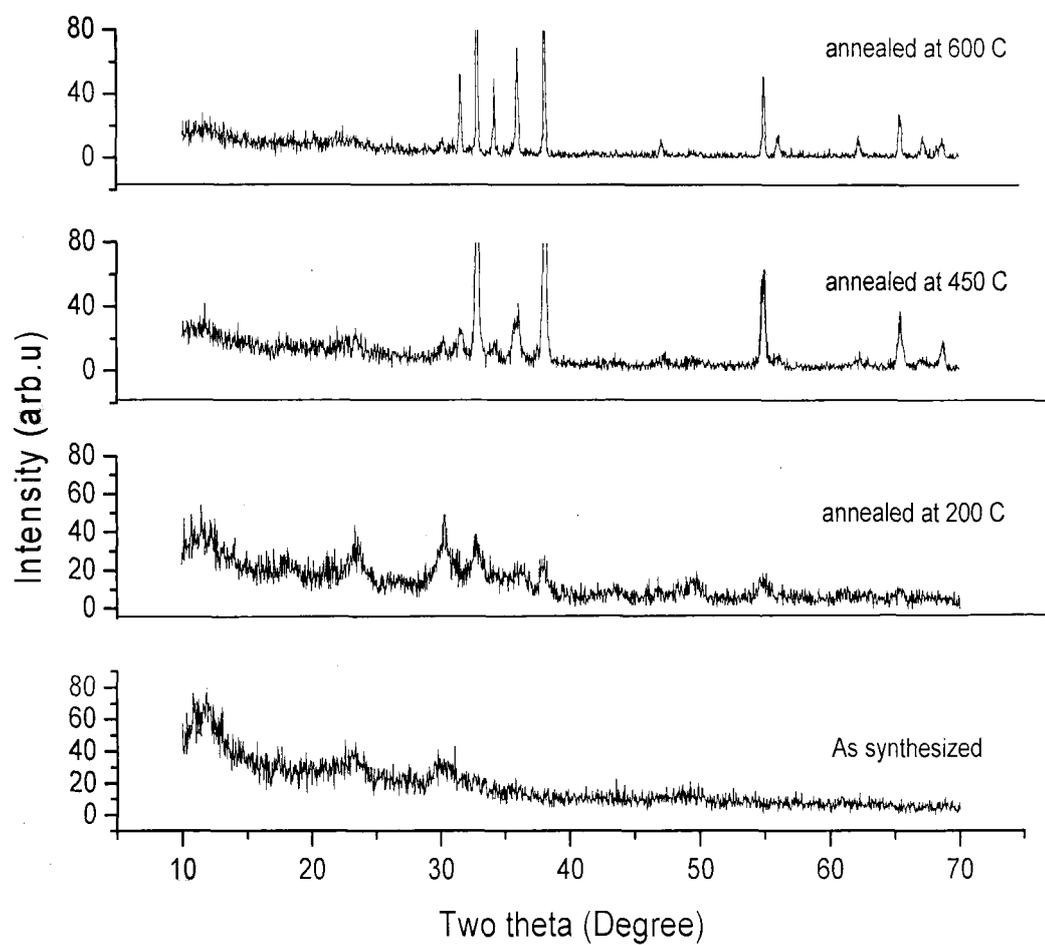


Figure1: Powder XRD patterns of $Zn_{0.4}Cd_{0.6}O$ composite annealed at different temperatures

2.3. Estimation of Composition

In order to characterize the samples prepared chemically, it is necessary to determine accurately the metal atom (Zn, Cd and Mn) contents. As these samples are not soluble in water, atomic absorption spectroscopic(AAS) technique cannot be used for this. However, other techniques like energy dispersive X-ray analysis(EDAX) can very well be utilized. Also, scanning electron microscope(SEM) can be used to understand the surface features.

2.3.1. SEM

In many fields of material science, chemistry, geology and biology, detailed knowledge of the physical nature and chemical composition of the surfaces of the solids on a submicrometer scale is becoming more and more important, such vital information can be obtained using a Scanning Electron Microscope (SEM). With an X-ray spectrometer attached to the instrument, one can perform elemental analysis of almost all elements. To select an area for investigation, the sample is mounted on a special stage which allows translation, tilt and rotation of the sample. This stage can be controlled from outside the vacuum chamber. To vary the magnification, the size of the scanned area of the sample is varied while the scanning width on viewing screen is kept constant: scanning of a small area, therefore, corresponds to high magnification. Usually a separate screen is used for taking micrographs. The most striking feature of a SEM image is its depth of view about as large as its field of view, giving a good topographical impression of the sample. The maximum useful magnification

(M) is determined by the minimum diameter of the electron beam in the microscope and hence its resolution. Resolution down to 10 nm is obtainable. The magnification (M) achievable in the SEM image is given by,

$$M = W/w$$

where W is the width of the CRT display and w is the width of a single line scan across the sample. Because W is a constant, increased magnification is achieved by decreasing w. The inverse relationship between magnification and the width of the scan across the sample implies that a beam of electrons that has been focused to an infinitely small point could provide infinite magnification. A variety of other factors, however, are there to limit the magnification.

2.3.2. EDAX

Energy dispersive X-ray analysis was used to estimate the composition of the materials. When an element is bombarded with a particle beam (in this case, an electron beam), the specimen will release some of the absorbed energy as the result of changes in the speed of an electron, which is random; however, when this interaction removes an electron from a specimen's atom, frequently an electron from an outer shell (or orbital) occupies a vacancy, it must lose a specific amount of energy to occupy the closer shell. This amount is readily predicted by the laws of Quantum Mechanics and usually much of the energy is emitted in the form of X-rays. Two methods are used to determine the X-rays that are produced: (1) the energy dispersive analysis separates and detects X-rays of specific energy and displays them as histograms and (2) wavelength

dispersive analysis uses the reflection of X-rays off of a crystal at a characteristic angle to detect X-rays of specific wavelength. The advantages of X-ray sampling is non-destructive, natural heterogeneity is retained, analysis can be conducted on microgram quantities, adjacent structures can be directly compared and it has excellent probe size (20 - 200 nm). Elements in an EDAX spectrum are identified based on the energy content of the X-rays emitted by their electrons as these electrons transfer from a higher energy shell to a lower energy.

2.4. Crystallite Size Determination

The crystallite sizes were calculated using the powder X-ray diffraction method, atomic force microscope and transmission electron microscope.

2.4.1. PXRD method

Powder X-ray diffraction(PXRD) patterns were recorded for all the twelve samples prepared in the present study on a RICH SEIFERT Model JSO-Debye Flex 2002 X-ray diffractometer equipped with graphite monochromated CuK_α radiation ($\lambda=1.540598$ AU). The angle(2θ) range is in between 0 and 70°. Debye-Scherrer formula (see section 2.2) was used to calculate the crystallite sizes from the PXRD patterns.

2.4.2. AFM method

Atomic force microscope(AFM) is a device used to get the image of the materials at the atomic level. LASER was used as the source to pick up the

deflections. Sample was dispersed in EtOH and sonicated. A drop of this solution was spotted on a freshly cleaved mica substrate and dried in ambience (4 hours). This was then loaded on the stage for performing contact mode AFM measurements. The top surface of the cantilever was coated with highly reflective material like Al. Beam deflection laser fell on the cantilever and it was reduced to a photodiode.

The photodiode uses a ceramic or semiconductor tip one atom wide positioned at the end of a cantilever bar. As the tip is moved over the material, it either continuously touches or periodically taps the surface and bends as it is repelled or attracted to the structure. A laser picks up the deflections. AFM can be used to image non-conductive materials. With the data provided in micrometer both in x-axis and y-axis the size of a particle is drawn as a graph (Figure 2) and the lower and upper tips are marked. Horizontal lines intercepting the y-axis are drawn. They are marked as y_1 and y_2 . The difference gives the actual size of the particle.

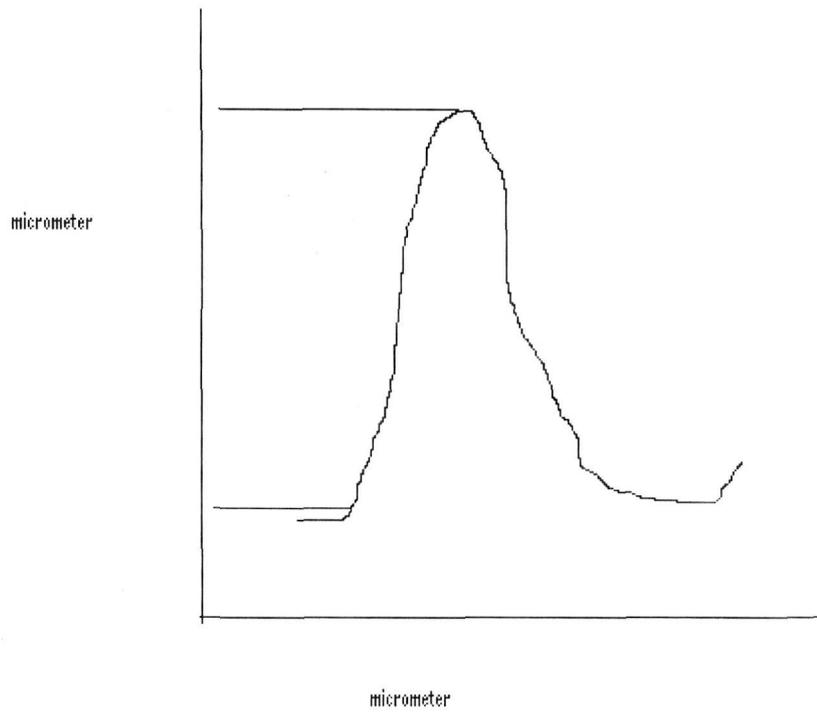


Figure 2: Model graph for particle size calculation using AFM

Table(2): Grain sizes obtained for $Zn_{0.4}Cd_{0.6}O$ annealed at different temperatures

Temperature(°C) at which annealed	Particle Size (nm)
32	---
200	24
450	27.02
600	54.52

2.4.3. TEM method

Transmission electron microscope(TEM) images were recorded in the present study.

TEM is an imaging technique whereby a beam of electrons are focused onto a specimen causing an enlarged version to appear on a fluorescent screen or layer of photographic film or can be detected by a camera. The magnification effect would be very clear. TEM is used heavily in both material science/metallurgy and biological sciences. In both the cases the specimens must be very thin and should be able to withstand the high vacuum present inside the instrument. A crystalline material interacts with the electron beam mostly by diffraction rather than absorption. A length calculated bar is provided already inside the TEM picture. Using that scale one can estimate the size of the particle. Sample is dispersed in EtOH and sonicated for 5 minutes. The dispersion is dispersed on a Cu TEM grid and allowed to dry overnight in ambience. This is then analysed in TEM.

2.5. UV-Vis Spectral Analysis

Ultraviolet-Visible (UV-Vis) absorption spectra were recorded for all the nanocrystalline samples prepared in the present study using a CARY-5E model instrument.

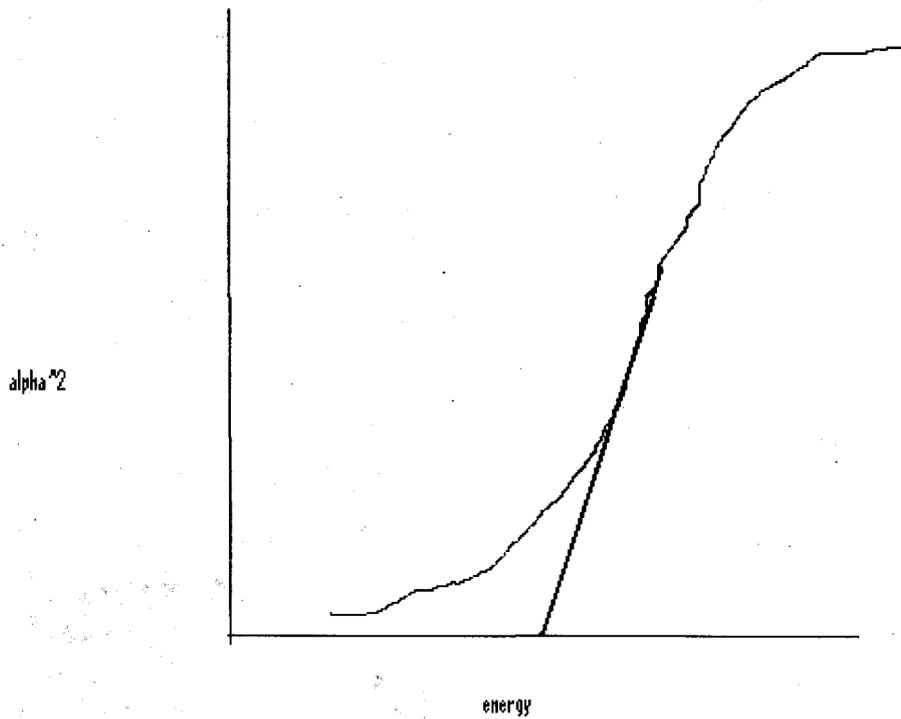


Figure 3: Model graph for bandgap energy calculations

Absorption against wavelength values were used to determine the bandgap energy. The absorption coefficient α was determined using the relation $\alpha = 2.303 \log (\text{abs})/\text{size of the sample}$. α^2 values were plotted against the corresponding $h\nu$ values (see the model curve shown in Figure 3). The bandgap energy was calculated by determining the $h\nu$ value corresponding to the linear portion of the curve extrapolated to $h\nu$ axis[194].

2.6. Photoluminescence Measurements

In all photoluminescence(PL) studies there is a host material which is generally semiconducting. When its bandgap is excited it exhibits fluorescence particularly from the lowest as well as the highest levels of the conduction band. As a result the fluorescence emission always gives a broad band. In order to have a sharp and intense band it is customary to use nano sized materials which possess fewer number of levels in conduction band. PL spectra of all the twelve samples prepared in the present study were recorded using a Perkin Elmer LS 55 model luminescence spectrometer.

2.7. Photoacoustic Measurements

Photoacoustic(PA) technique is currently used to determine accurately the thermal conductivity of nanomaterials. In order to understand the thermal transport behaviour of the nanomaterials considered in the present study, we have carried out the PA measurements for three samples (as an illustration), viz, ZnO, $Zn_{0.4}Cd_{0.6}O$ and CdO.

For measuring the thermal diffusivity and hence the thermal conductivity of the sample the variation of the photoacoustic signal was observed for different chopping frequencies. The sample was placed in the PA cell and the mike was placed very near the sample. 400W Xe lamp (Jobin Yuon) was used as the light

source. The PA signal from the sample was fed to a lock in amplifier (Model Perkin Elmer 7225 DSP). Light was allowed to fall on the sample through a monochromator (Model Triax 180, Jobin Yuon) [195].

If f_c is the characteristic frequency of the sample of thickness 'l' then the thermal diffusivity can be calculated from $D = f_c l^2 \text{ m}^2/\text{sec}$.

The thermal conductivity can then be calculated using the relation,

$$K = D\rho C_p \text{ W/m-K.}$$

where ρ is the density and C_p is the specific heat capacity of the sample [196].

2.8. Impedance Measurements

The method of complex impedance analysis (CIA) or Impedance Spectroscopy has emerged as a very powerful tool [197-201]. The availability of high quality Impedance Analysers working over extended frequency regions has made Impedance Spectroscopy an extremely popular field in the last few years and an increasing trend is being witnessed for its widespread applications in various areas. In this method experimentally measured values of complex impedance are plotted as a function of frequency or on complex plane (i.e., Z'' versus Z'). These plots show special features depending upon the relative contributions from the grain, grain boundaries and electronic polarization processes [202]. For the case when these processes have widely separated time constants distinct semi-

circular arcs are obtained and when they have time constants close to each other depressed looking semi-circular arcs or distorted arcs are obtained.

The resultant powder material prepared in the present study was compacted into disc shaped pellets of dimensions 8 mm in diameter. The pelletised samples were heated in air at about 100°C to achieve densification. After the sintering process, both surfaces of the sample were coated with silver paste to have good conductive surface layers.

The ZnO and ZnO:Mn samples prepared in the present study were pelletised (8 mm in diameter and 2 mm in thickness) and impedance measurements were carried out on these pellets. The impedance spectra were recorded using a SOLATRON 1260 GAIN/PHASE ANALYSER frequency range 1-10 MHz and at various temperatures ranging from room temperature to 327°C. The temperature was controlled to an accuracy of $\pm 0.05^\circ\text{C}$.

2.9. EPR Spectral Analysis

Electron Paramagnetic Resonance(EPR) deals with the interaction of electromagnetic radiation with magnetic moments; the magnetic moments arise from electrons rather than nuclei. In almost all cases encountered in EPR spectroscopy, the electron magnetic dipole arises from spin angular momentum with only a small contribution from orbital motion[203]. Resonant absorption of electromagnetic radiation by such systems is

variously called “paramagnetic resonance”, “electron spin resonance”, or “electron paramagnetic resonance”. The term “resonance” is appropriate, since the well-defined separation of energy levels is matched to the energy of a quantum of incident monochromatic radiation. The term electron paramagnetic resonance was introduced as a designation taking into account contributions from electron orbital as well as spin angular momentum. The term electron spin resonance (ESR) has also been widely used because in most cases the absorption is linked primarily to the electron-spin angular momentum. Electron magnetic resonance (EMR) is an alternative.

The frequency of radiant energy used in the majority of EPR spectrometers is approximately 9.5GHz, in the medium-frequency microwave region. This frequency corresponds to a wavelength of about 32mm. The microwave source is usually a klystron. In the present study the microwave frequency was kept constant at 9.2GHz while the magnetic field was varied between 2300 and 4300G. EPR spectra for ZnO:Mn, CdO:Mn and $Zn_{0.4}Cd_{0.6}O:Mn$ were recorded at two different temperatures one at room temperature (35°C) and the other at liquid nitrogen temperature(-196°C) with Varian E-112 spectrometer at the X-band (9.2GHz) frequency. The formula used to calculate the g-factor is

$$gBH = hv,$$

where

h is the Planck’s constant,

v is the frequency of radiation used,

g is the splitting factor,

B is the Electronic Bohr Magnetron, and
H is the strength of applied magnetic field.

2.10. VSM Measurements

When a sample is placed in a uniform magnetic field, the dipole moment is induced in the sample which is directly proportional to the sample susceptibility and magnetic field. If the sample is made to undergo vertical motion an electrical signal is induced in pick up. This signal is proportional to the magnetic moment. The maximum magnetic field is 7.5 kOe, bipolar power supply is 36 amp, temperature range is in between -196 and 727°C. Small amounts of ZnO:Mn, Zn_{0.4}Cd_{0.6}O:Mn and CdO:Mn were loaded into very thin tube of about 2mm diameter and 6mm length. The magnetic behaviour of Mn doped ZnO, CdO and ZnCdO were studied using the EG&G Princeton Applied research Model: 4500.