International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.8, No.12 pp 522-529, 2015

Structural and optical properties of $Zn_xCd_{1-x}O$ nanoparticles

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Abstract: $Zn_xCd_{1-x}O$ is a promising optical material to enhance the luminescence property for possible applications in luminescent devices. They have unique optical, thermal and structural properties. Zinc and Cadmiun nanoparticles and Cd substituted ZnO nano particles with different concentration were prepared by microwave assisted method. The effect of Cd substituted ZnO concentrations on the crystal structure, morphology and optical properties of the nanoparticles was also investigated. Temperature is deemed as a key parameter for the formation of different morphologies of $Zn_xCd_{1-x}O$ nanostructures. In this paper, we reported the synthesis of $Zn_xCd_{1-x}O$ nanoparticles successfully with the diameter of 20nm. By using scanning electron microscope (SEM) the surface morphology of synthesized material was investigated. The structure and phases of $Zn_xCd_{1-x}O$ were analyzed by powder X-ray diffraction (XRD) method and the optical properties were measured by using UV visible spectrophotometer and photoluminescence spectroscopy. The results suggest the applicability of these nano materials as transparent conductors in various solid state devices.
Keywords: *$Zn_xCd_{1-x}O$*; microwave method, XRD, SEM,PL and Photoconductivity.

1. Introduction

The fabrication of complex nanosystems arises due to the progress of nanotechnology for the recent years. Enhanced impetus is being given to the development of multi-functional and size-dependent materials. Recent trends and developments in nanotechnology and nanoscience have brought potential building blocks for a nanoscale electronic, optoelectronics, luminescent devices, medicines and solar cells [1-4]. The material dimension decreases to nano-order as the surface/volume ratio increases. Hence the high surface/volume ratio of nanomaterials has significant implications with respect to energy storage density.

Over the last few years nanomaterials, especially metal oxides have received a considerable attention in various fields due to their distinguished performance and potential applications. Among these oxides, ZnO exhibits the most diverse and abundant configurations of nanostructures [5-7]. ZnO considered and reported to be one of the best metal oxides that can be used at a nanoscale level. ZnO has a hexagonal or wurtzite structure and it is an n-type II–VI semiconductor with a wide direct band-gap of about 3.37 eV and a large exciton binding energy of 60 meV [8]. They have large applications in catalysis, electronics, optoelectronics, transducers, solar cells, electrical & acoustical devices, luminescent, chemical sensor, gas sensor devices and biomedical devices [9,10]. Enormal applications have made the ZnO as treasure material for material scientists and the usage of ZnO in different application is also increasing. Hence, its production ever increases and trial on suitable method for preparing ZnO possessing less operating cost, working at ambient temperature, less time with narrow size range and better properties is a challenge task for researchers [11]. One of the well-known II – VI semiconductor with a direct band gap of 2.39 eV (563.6 nm) is Cadmium oxide (CdO) and it has found its use in various applications such as in solar cells, photodiodes [12], phototransistors[13] and

sensors[14]. There are several researches reported the preparation of CdO particles, but most of these methods describe only the thin film formation of CdO [15]. There is very rarely little available literature on the synthesis of the particles as a free-standing powder.

For the fabrication of optoelectronic devices, knowledge about the properties of impurities like donors, acceptor and isoelectronic impurities, is of essential interest. An overview of theoretical models describing the binding of excitons to isoelectronic impurities has been given by Zhang [16]. The replacement of host atom on cation site has been reported in many journals. Preparation and characterization of alloys like (Zn- Cd)O are considered to be very important for creating a new combinations to form a substance of modified optical properties. It was reported that the electrical conduction has been found to increase for higher concentration of Cd in ZnO [17,18, 19]. Covalent radii of Zn and Cd are 122 and 144 pm respectively. Similarly ionic radii of Zn and Cd are 88 and 109 pm respectively [20]. Cd having larger radii can set in place of Zn in ZnO lattice structure with few deformations[20]. ZnO and CdO both are used as transparent conducting oxides [21], their alloys will have modified properties. Especially the

UV luminescence intensity increases[22] by doping with the group II element (Cd) may modulate the value of the band gap.

2. Objective of Research

Many results have been reported on doping ZnO with dopant such as Cadmium (Vijaylaxmi et al., 2008: Tabet-Derraz et al., 2002: Vinodkumar et al., 2010) [17,18,19] but to the best our knowledge no work is reported so far on substitution of ZnO with Cadmium from 0.25 %, 0.50% and 0.75 % by microwave method and to study its electrical analysis, photoconductive and photoluminescence properties. We put our effort to find certain proportion of dopant (Cd) in ZnO nanopowder which will increase the conducting behavior substantially of ZnO and enhance other properties.

3. Experimental

3.1 Synthesis

$Zn_xCd_{1-x}O$ nanoparticles were synthesized by employing microwave irradiation heating method. This method has some special relevance in the preparation of $Zn_xCd_{1-x}O$ nanocrystals. For the microwave decomposition of a material in a mixture the different absorption of microwave energy can be used to advantage. A precursor material can be chosen such that it has a high value of ε'r and decomposes by preferential microwave absorption to yield the desired materials. Thus, if a metal organic or an inorganic complex salt, of reasonably high value of dielectric constant that yields the desired material upon decomposition is dissolved in a suitable liquid medium of low dielectric constant and irradiated with microwaves, we can expect the formation of the material. The material generally forms as a suspension in the chosen liquid.

Mixture of $CdCl_2$, $ZnCl_2$ and urea were taken in 1: 3 molar ratio. At first the mixture of $CdCl_2$ and $ZnCl_2$ were dissolved in 100 ml of double distilled water. The mixer solution was stirred well and kept at 60°C for about an hour. Similarly the urea was dissolved in 100 ml of double distilled water and stirred well and maintained with 60°C for about an hour separately. Now the urea solution was slowly added into the mixture solution of $CdCl_2$-$ZnCl_2$. All the mixed solution was continuously stirring about an hour by using magnetic stirrer. During this process the temperature was maintained as 60 ºC.

The above prepared mixture was kept in microwave oven. Microwave irradiation was carried out with power 50% until the solvent gets evaporated. The colloidal precipitate obtained was cooled to room temperature naturally and washed 20 times with doubly distilled water and then 10 times with acetone to remove the organic impurities and unreacted compound present, if any. The collected samples are centrifuged and kept in hot air oven at 70 ºC for about 48 hrs. The percentage of Cd can be expressed as $Z_xCd_{1-x}O$, where x = 1, 0.25, 0.50, 0.75, and 0S. The dried samples were collected as yield and the prepared samples are annealed at 600 ºC for 1 hour.

Table 3.1 Sample details of the synthesized samples

Sample Name	Chemical Formula	Percentage ratio of Zn & Cd
MM1	Zn_1Cd_0O	100:0
MM2	$Zn_{0.75}Cd_{0.25}O$	0.75:0.25
MM3	$Zn_{0.50}Cd_{0.50}O$	0.50:0.50
MM4	$Zn_{0.25}Cd_{0.75}O$	0.25:0.75
MM5	Zn_1Cd_0O	100:0

3.2 Characterization

The absorption characteristics of as-prepared and annealed (600 °C) zinc oxides were studied using a spectrophotometer (model UV-1700, Shimadzu, Japan). The $Zn_xCd_{1-x}O$ was coated (around middle portion) on the inside surface of one of the sides of the cuvette and a small amount of solution (about 2 ml) was placed at the bottom of the cuvette to produce a vapour. The coating did not make a contact with the solution. Another similar cuvette with the same amount of solution was taken without any coating for reference. The open ends of the cuvettes were closed with teflon lids and the solutions were allowed to vaporize for 10 min. The powder X-ray diffraction studies on the synthesized $Zn_xCd_{1-x}O$ nanoparticles were performed with automated X-ray powder diffractometer(PAN alytical) in the 2 theta range of 20-70˚ using CuKa (1.54 A˚) radiation with a scan rate of 0.02o S-1. A beam voltage of 40 kV and a beam current 30 mA were used.

The surface morphology and elemental analysis of the prepared nanoparticles was analyzed by scanning electron microscope (SEM) fitted with an energy dispersive X-ray spectroscopy (EDAX) (JEOL JSM-840A). The sample was coated with gold using low voltage sputtering and then analyzed under SEM operating at a voltage of 20 kV. The photoluminescence spectroscopy (Perkin Elmer Spectrometer LS-55) was used to measure the emission characteristics of doped and undoped ZnO nanoparticles. The PL spectra were investigated at room temperature using Xenon lamp (325 nm) with the slit size of 100 μ and D2 filter.

4. Results and Discussions

4.1 XRD analysis

Fig. 1 shows the XRD pattern of $Zn_xCd_{1-x}O$. That is Cd substituded ZnO with different Cd concentration(0.25,0.50,0.75) and annealed at 600° C for 2 hours. Fig. 1a illustrates a typical XRD spectrum of $Zn_xCd_{1-x}O$ nanoparticles prepared by the microwave method. Five major diffraction peaks were seen at 32.5, 38, 55.2, 65.6, and 68.5, which can be assigned to the diffractions from (111), (200), (220), (311) and (222) planes respectively, according to the data base in JCPDS card (No-78-0653) with the lattice parameters: a=b=c=4.725A°. The result reveales that the resultant nanoparticles were pure CdO with cubic structure. X-ray diffraction pattern of bulk ZnO shows eight major diffraction peaks at 31.7, 34.6, 36.2, 47.6, 56.5, 62.9, 66 and 68.5 which can be assigned to the diffractions of (100), (002), (101), (102), (110), (103), (200) and (112) planes respectively, according to the data base in JCPDS card (No-79-0208) with the lattice parameters:a=b=3.2648 A°, c=5.2194 A°. This reveales that the resultant nanoparticles were pure ZnO with a hexagonal structure.

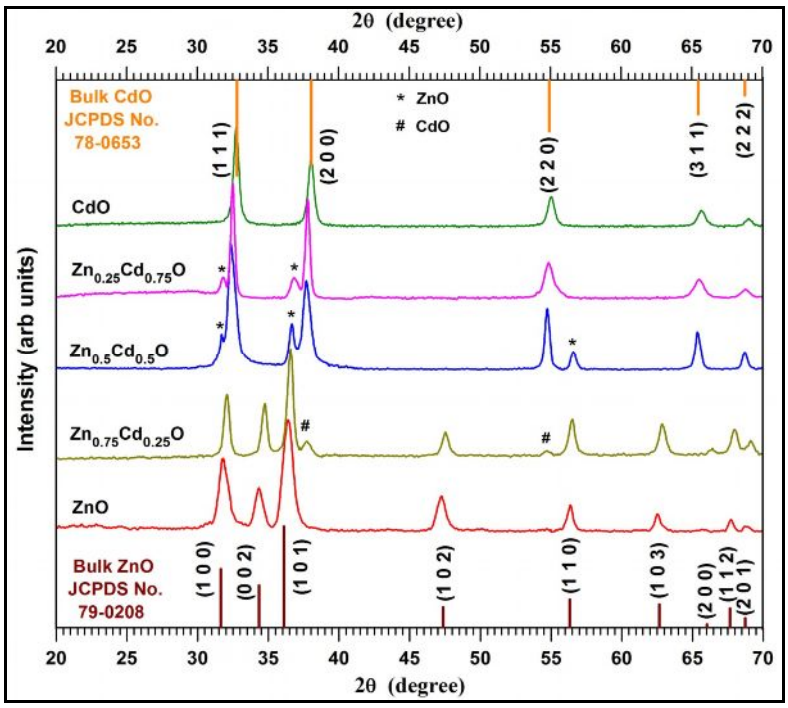

Fig. 1 XRD pattern of CdO , $Zn_{0.25}Cd_{0.75}O$, $Zn_{0.50}Cd_{0.50}O$, $Zn_{0.75}Cd_{0.25}O$, ZnO nanoparticles calcined at 600^0C.

The impurities are not detected in this pattern, which implies hexagonal phase ZnO nanoparticles and cubic phase CdO nanoparticles could be obtained under the current synthetic route. The presence of asymmetry in crystallite shape was seen from the narrow peaks in the XRD pattern.

The crystallite size was determined by using the Debye-Scherrer formula[23],

$$D = \frac{0.9\ \lambda}{\beta \cos\theta},$$

Where
D is the crystallite size,
β is the full width at half maximum of intensity (in radians),
λ is the wavelength of the X- ray radiation used (1.540598 A°), and
θ is half the angle at which maximum intensity was observed.

Table 1: Calculated Crystallite size

Sl. No.	Sample Name	Crystallite size nm
1	ZnO	5.28±0.14
2	$Zn_{0.75}Cd_{0.25}O$	6.35±0.23
3	$Zn_{0.5}Cd_{0.5}O$	7.06±0.37
4	$Zn_{0.25}Cd_{0.75}O$	8.74±0.34
5	CdO	10.48±0.46

4.2 SEM analysis:

The surface morphological properties of the nanoparticles were analyzed by using FESEM. Fig. 3a shows the scanning electron microscope pattern of ZnO nanoparticle and Fig 3b, 3c and 3d shows the SEM pattern of Cd substituded ZnO with the different concentrations of Cd (0.25, 0.50 and 0.75 M) Fig.3e shows the SEM pattern of CdO nanoparticles. The shape of ZnO nanoparticle is granular and well dispersed. Sometimes

the surface properties of ZnO are influenced from the incorporation of dopant. Especially the amount and kind of dopant can play an important role on the surface properties. The Cd substituded ZnO nanoparticles are flake like structures and inhomogeneous in nature. This may be due to the defects created by Cd doping. As the substitution concentration increases from 0.25 to 0.75 M the agglomeration of particles takes place.

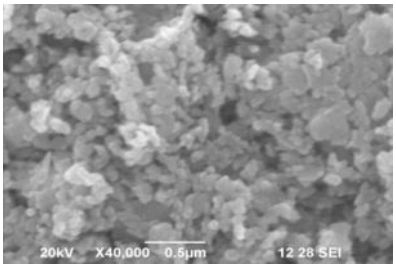

Fig.3(a)

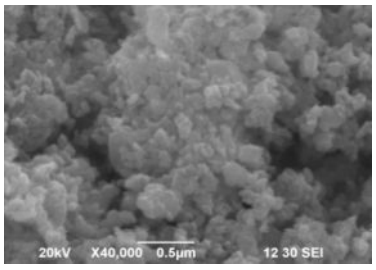

Fig.3(b)

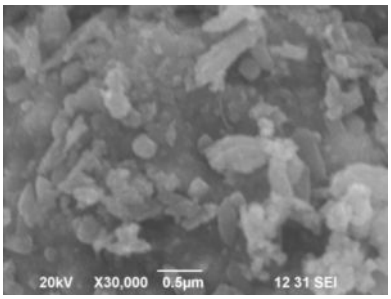

Fig.3(c)

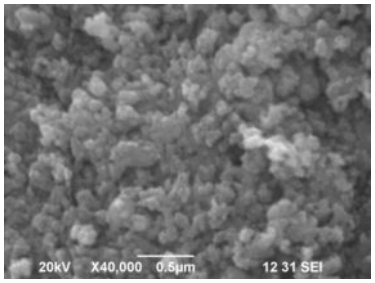

Fig.3(d)

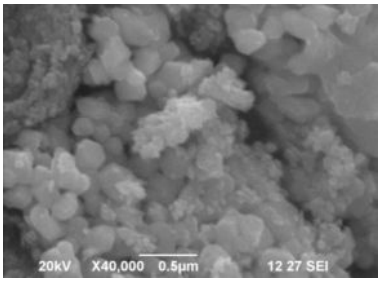

Fig.3(e)

Fig. 3 SEM image of (a)ZnO (b) $Zn_{0.75}Cd_{0.25}O$(c) $Zn_{0.50}Cd_{0.50}O$ (d) $Zn_{0.25}Cd_{0.75}O$ (e)CdO nanoparticles calcined at 600^0C.

4.3 UV-Vis spectroscopy analysis:

Fig. 4 shows the UV-Vis spectra of CdO/ZnO and Cd substituded ZnO nanoparticle obtained by microwave method. ZnO shows the absorption peak at -296 nm (4a) and the Cd assisted ZnO nanoparticles with different concentrations of Cd (0.25, 0.5 and 0.75 m) shows the absorption peaks at 326nm (4b), 351nm (4c) and 390nm (4d) and for CdO is410nm respectively. The small shift in the absorption band is attributed to the doping of Cd into ZnO. The band gaps (Eg) of CdO/ZnO and Cd substituded ZnO were calculated by using the formula $E = hc/\lambda$, where h is plank's constant, c is the velocity of light and λ is the wavelength. The band gap of ZnO was found to be 3.58 eV and Cd substituded ZnO for different concentrations of Cd (0.25, 0.50 and 0.75 M) were found to be 3.14, 2.99 and 2.69 eV.The band gap of pure CdO was also found to be 2.60eV respectively. With increase of Cd concentration, the optical absorption edge slightly shifts towards the longer wavelength region which may be attributed to the increase of the grain size.

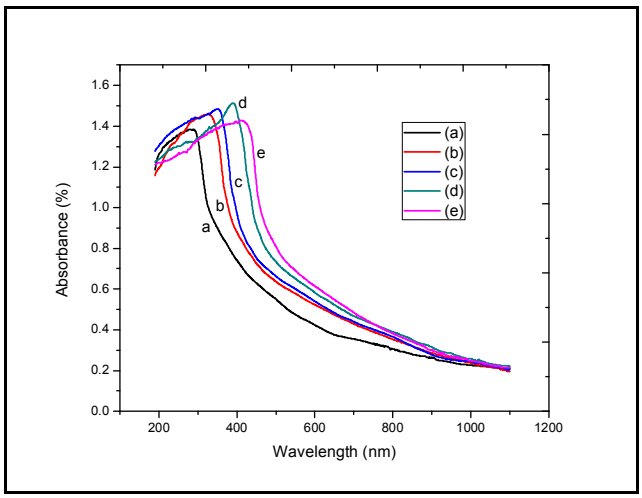

Fig. 4 UV-Vis spectra of (a)CdO (b) $Zn_{0.25}Cd_{0.75}O$(c) $Zn_{0.50}Cd_{0.50}O$ (d) $Zn_{0.75}Cd_{0.25}O$ (e)ZnO nanoparticles calcined at 600^0C.

4.4 PL Spectral analysis:

Fig. 2A shows the room temperature photoluminescence spectra (PL) of Cd substituded ZnO nanoparticle. The sample were exited with different excitation wavelength.The ZnO spectrum includes a broad visible emission and strong UV emission, corresponding to the near-band–edge (NBE) and the deep-level defects emission in ZnO structures [24, 25]. The NBE peak from CdO has a small FWHM value at 400 nm. The spectra of Cd substituded ZnO (2B) has an emission peak at 275nm, 280nm, 300nm, 350 nm. (Since the Zn doping decreased the band gap (E_g) and alternated the carrier concentration, the UV emission has a slight red-shift comparing with the emission peak of pure ZnO. In addition, it shows a broad green emission peak centered around 549 nm which is usually observed for ZnO. The green emission peak is attributed to the defects present in ZnO crystals, such as vacancies and interstitials of zinc and oxygen. Compared with the pure ZnO, weaker green light emission at 552 nm and a small hump at 635 nm in Cd-doped structures might be related to lower oxygen vacancies in the samples. Cd substituded ZnO structures have changed the optical properties significantly.

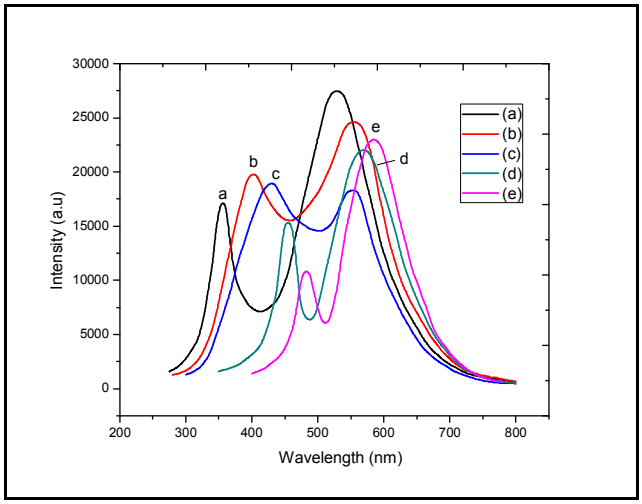

Fig. 2 PL spectra of (a)CdO (b) $Zn_{0.25}Cd_{0.75}O$(c) $Zn_{0.50}Cd_{0.50}O$ (d) $Zn_{0.75}Cd_{0.25}O$ (e)ZnO nanoparticles calcined at 600^0C.

5. Conclusion:

In the present work, $Zn_xCd_{1-x}O$ nanoparticles were prepared from different concentration of Cd substituded ZnO by simple microwave assisting method. The Cd substituded ZnO nanoparticles have got the

particle size in the range 20 nm. As the Cd concentration increases the agglomeration takes place and absorption edge slightly shifts towards the longer wavelength region which may be attributed to the decrease in band gap. The UV visible shows the band gap is altered by adding cadmium content depending on the amount of cadmium concentration. Also, from the surface morphology it is seen that hexagonal nanorods of $Zn_xCd_{1-x}O$ were formed.The Cd substituded ZnO nanoparticles have changed the optical properties effectively which was confirmed by PL spectroscopy.

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