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Effect of Cadmium on Structure and Optical Properties of ZnO Nanopowders by Sol-Gel Method

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Abstract

Zn_{1-x}Cd_xO (x=0, 0.04, 0.06, 0.08) ternary alloys were successfully synthesized by Sol–gel method. The prepared powders were sintered at 800°C for 4hrs. The compositional, structural and optical studies were investigated by SEM equipped with EDS, XRD and UV-Visible Spectroscopy. XRD results were compared with JCPDS data and confirmed the formation of Cd doped ZnO nanoparticles with polycrystalline single phase hexagonal wurtzite structure. The crystallite size was found to decrease from 21 to 17 nm with increase in the concentration of Cd. EDS analysis revealed the existence of Cd content in ternary alloys. From Ultraviolet-visible spectral studies optical band gap vary from 3.21 eV to 3.12 eV with Cd concentration.

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Keywords: ZnO; Compound semiconductor; Sol-gel method; Nanocrystalline; EDS; Band gap.

Nomenclature

XRD	X-Ray Diffraction
SEM	Scanning Electron Microscopy
EDS	Energy Dispersion Spectra
ZnO	Zinc oxide
GaN	Gallium Nitride
CdZnO	Cadmium doped zinc oxide

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1. Introduction

Recently, preparation of II-VI compound semiconductor in nanoscale has attracted much attention owing to wide range of applications in the fields of electronics. Because of wide band gap equivalent that of GaN (3.4 eV), ZnO (3.37 eV) paid much attention from research communities [1,2]. The dopant has a strong influence on the physical behaviour of ZnO samples, and can adjust the band gap, which plays an important role in the development of ZnO based materials and their applications. Transition metals doped ZnO materials have been investigated extensively by both experimental and theoretical studies [3-5]. However, very few people are working with cadmium doped ZnO. Among ternary alloys of ZnO, particularly $Zn_{1-x}Cd_xO$ is a potential candidate prospective semiconductor material that possesses intriguing electrical and optical properties, allowing it to be used as transparent electro design solar cells and active media in light emitting sources and photovoltaic devices [6,7]. Due to the direct band gap of ZnO and possibility to tune its band gap, its absorption/emission range is large and covers virtually the entire solar spectrum [1,2]. Various methods such as pulsed laser deposition [8], chemical vapour transport [9], electro-deposition [10], co-precipitation [11] solid-state reaction [12], spray pyrolysis [13] and sol-gel [14] can be used to synthesize ZnO. Among these methods, sol-gel technique is applicable without vacuum environment; of course, this technique is cheap with high atomic level mixing of dopants and displaying comparable properties that produced by other techniques. In this article, we carried out a detailed investigation on structural and optical properties of Cd doped ZnO nanopowders of different concentrations (0, 4, 6 and 8 atomic %) synthesized by sol-gel method.

2. Experimental

Firstly, Zinc nitrate and cadmium nitrate (A.R. grade chemicals) were weighed according to stoichiometric ratio and dissolved in 100ml double distilled water. Citric acid solution was added to the metal nitrates solution as a chelating agent. The mixture solution was maintained at room temperature under vigorous stirring for 60 min. Liquid ammonia solution was used to neutralize the pH (6.5–7) of the solution and heated up to 80°C till a transparent and homogeneous gel was obtained. Ethylene glycol (EG) was added to the gel; gel burned and given ash like powders which were then sintered at 800°C for 4h. Off-white powders formed after sintering were ZnCdO nanoparticles. The flowchart for sol-gel synthesis is shown in Fig. 1. The XRD patterns of the prepared powders were recorded on a Panalytical X'pert powder X-Ray diffractometer with $CuK\alpha$ radiation ($\lambda = 1.5405\text{\AA}$) in the angular range of 20°–80°. The morphological investigation and elemental analysis of nanoparticles were obtained by a ZEISS EVO-18 Scanning Electron Microscope equipped with EDS. The optical properties of nanoparticles were examined with a PG Instruments T90+ UV-Vis double beam spectrophotometer in the range from 250 to 850 nm.

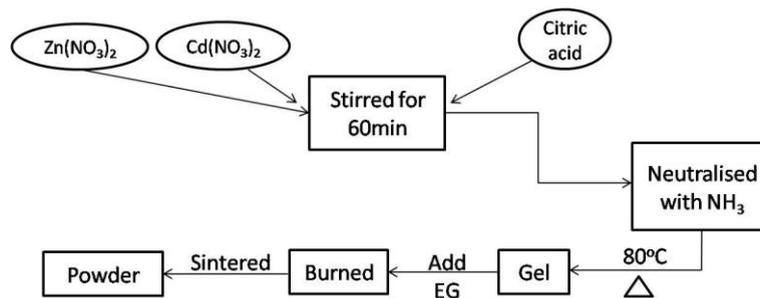


Fig. 1. Flow chart of sol-gel process for the preparation of $Zn_{1-x}Cd_xO$ compounds.

3. Results and Discussion

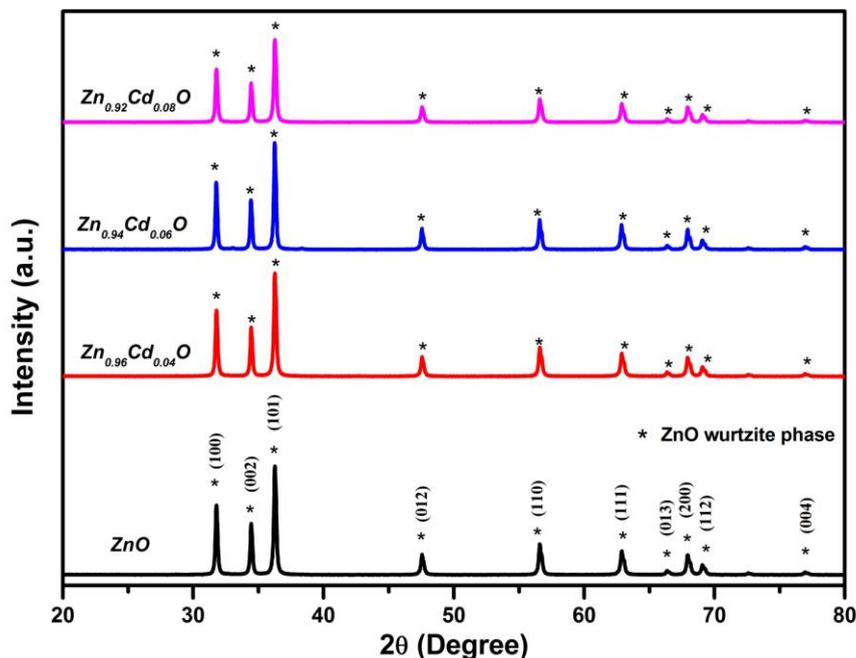


Fig. 2. X-ray diffractograms of ZnO and Cd doped ZnO nanopowders.

Fig. 2 shows the X-ray diffraction patterns of the ZnO and ZnCdO nanoparticles sintered at 800°C for 4h. These diffractograms are in accord with diffractograms of standard samples, signifying the synthesis of ZnO and ZnCdO nanoparticles with high crystallinity. No impurity peak was found in these diffractograms. The observed diffraction peaks at $2\theta = 31.4^\circ, 34.2^\circ, 35.9^\circ, 47.3^\circ, 56.2^\circ, 62.6^\circ, 66.1^\circ, 67.7^\circ, 68.8^\circ$ and 76.7° are connected to (100), (002), (101), (102), (110), (111), (103), (200), (112) and (004) planes, respectively. All the diffraction peaks for ZnO and ZnCdO nanoparticles are attributed to hexagonal phase of ZnO [2, 8-14]. The average crystallite size of ZnO and ZnCdO nanoparticles was calculated (shown in Table 2.) by Debye–Scherrer formula,

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where,

D is the average crystallite size,

λ is the wavelength of X-ray,

β is the FWHM and

θ is the Bragg's angle.

Typical SEM micrographs for ZnO and Cd doped ZnO (4%, 6%, 8%) powders are shown in Fig. 3. From these images, there is evidence for uniform size nanoparticles formed in the prepared powders. The change in the surface morphology with the increase in Cd concentration can clearly be seen. From above results both crystallite size and surface morphology are affected significantly with the Cd concentration. Table 1 shows the EDS analysis of ZnCdO nanoparticles and also confirms the composition of cadmium increment. It is observed that all the elements in the compounds are present according to stoichiometric ratio.

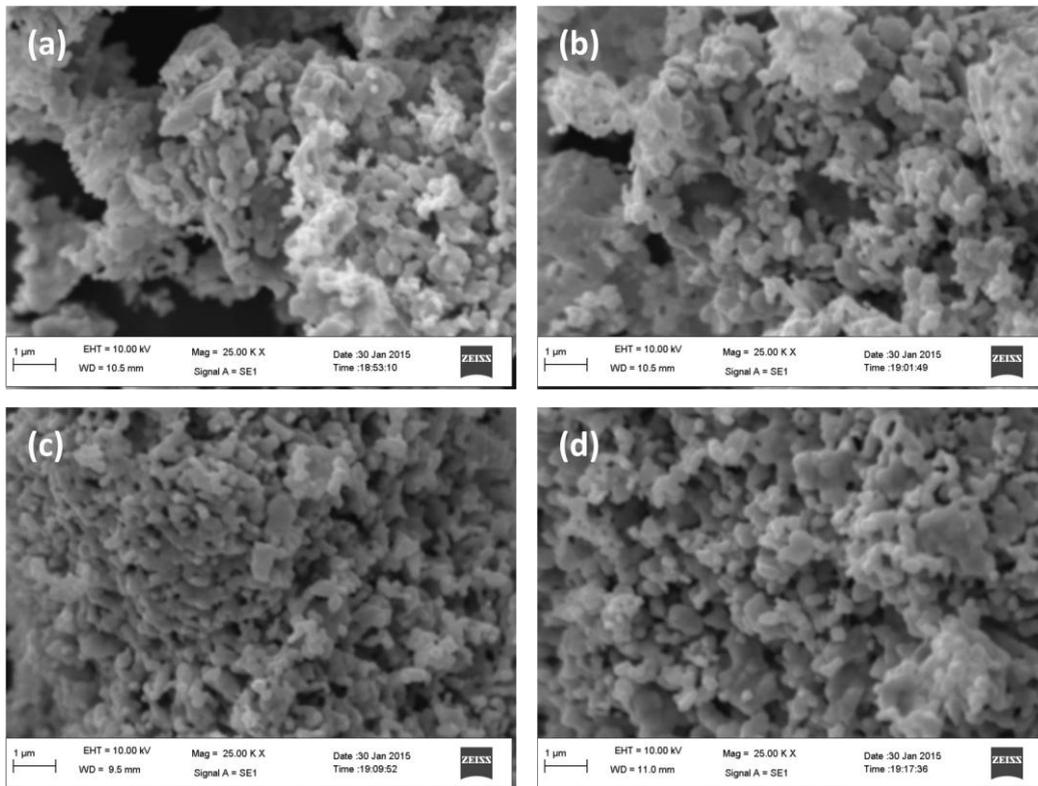


Fig. 3. Scanning Electron Microscope (SEM) images of Zn_{1-x}Cd_xO (a) x=0 (b) x=0.04 (c) x=0.06 and (d) x=0.08 nanopowders respectively.

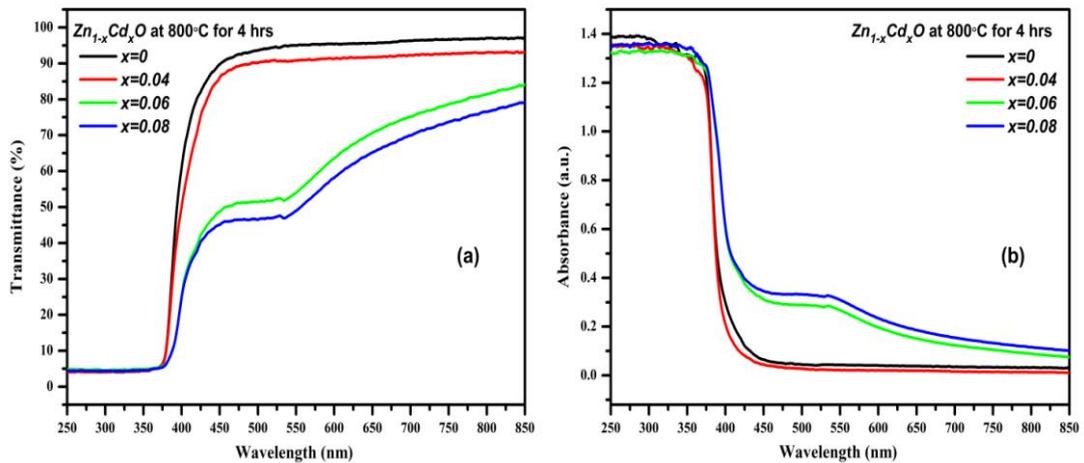


Fig. 4. (a) Transmittance spectra and (b) Absorbance spectra of Zn_{1-x}Cd_xO Compound.

Table 1. EDS analysis of Zn_{1-x}Cd_xO compound.

Cd _x Zn _{1-x} O	x = 0	x = 0.04	x = 0.06	x = 0.08
Element	At%	At%	At%	At%
Oxygen	49.95	49.02	53.73	51.49
Zinc	50.32	50.92	45.59	46.32
Cadmium	-0.27	0.05	0.68	2.13
Total	100.00	100.00	100.00	100.00

The optical properties of $Zn_{1-x}Cd_xO$ ternary compounds are shown in Fig. 4. The effects of Cd doping into the ZnO lattice are clearly observed in the optical transmittance and absorbance spectra. The increase of Cd concentration in the ZnO structure decreases the optical transmittance and increase the absorbance. The first derivative of transmittance with respect to wavelength ($dT/d\lambda$), determines the band gap energy for the ZnO and ZnCdO nanopowders [15,16]. According to our optical data analysis, the band gap energies are calculated and found that 3.21, 3.20, 3.17 and 3.12 eV for the ZnO and $Zn_{1-x}Cd_xO$ ($x=0.04, 0.06, 0.08$) nanopowders respectively. The observed peak position and energy gap values are tabulated in Table. 2, which clearly shows the concentrations effect on size and band gap of prepared samples.

Table 2. Average crystallite size, peak position of $dT/d\lambda$, and optical band gap (E_g) of $Zn_{1-x}Cd_xO$ compound semiconductors.

$Zn_{1-x}Cd_xO$	Size D (nm)	Peak position λ_g (nm)	Band gap E_g (eV)
x=0 (ZnO)	21	386	3.21
x=0.04	19	389	3.19
x=0.06	18	393	3.15
x=0.08	17	397	3.12

4. Conclusions

This study presents data on preparation and characterization of ZnO and ZnCdO nanopowders with different amount of cadmium (0, 4, 6, 8 at. %). The influence of cadmium doping on structure and optical properties of the synthesized ZnO samples have been investigated using various analytical techniques. According to XRD analysis, the crystalline structure of the synthesized ZnO and ZnCdO powders is hexagonal wurtzite. The SEM images show spherical shape in all samples. The EDS analysis indicated that the cadmium doped ZnO powders contain all the constituent elements of compound on their surfaces. Optical properties of the ternary compounds were investigated under UV-Visible region. It was also found that the band gap of ZnCdO compound decreased by doping cadmium.

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