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Synthesis and Characterization of Cr Doped ZnO Nanocrystals

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ABSTRACT

Samples of chromium doped ZnO were synthesized using co-precipitation technique at room temperature. Structural and optical properties of Cr doped ZnO samples were investigated by X-ray diffraction technique (XRD and UV-Visible spectroscopy (UV-Vis) respectively. X-ray diffraction (XRD) patterns confirm that the samples have hexagonal (wurtzite) structure with no additional peak which suggests that Cr ions go to the regular Zn sites in the ZnO crystal structure. The lattice constants were calculated using X-ray diffraction data and it is found that lattice parameters decrease with increasing Cr content. The average grain size was calculated using Scherrer's formula for pure and Cr doped ZnO samples and it is observed that grain size is in the range 11 to 17 nm. Band gap of $Zn_{1-x}Cr_xO$ samples has been evaluated using UV-Vis spectrometer. It is found that the band gap decreases as Cr increases; it is attributed to the s-d and p interactions and the smaller average grain size. It indicates that incorporation of Cr ions into the ZnO matrix. The chemical species of the grown crystals were identified by Fourier transform infrared spectroscopy (FTIR). From FTIR spectra it is observed that IR peaks corresponding to the Zn-O bands. Such results are presented in this paper quantitatively and qualitatively.

Keywords: Wurtzite Structure; Average Grain Size; Scherrer's Formula; FTIR Spectra

1. Introduction

In recent years, much attention has been paid to Diluted Magnetic Semiconductors (DMSs) formed by the partial replacement of cations in a non-magnetic semiconductor by magnetic transition metal ions for spintronic applications. Spintronics is a field which investigates the applications of carrier spins transport as well as charge transport in a new generation of devices such as spin-valve transistors [1], spin light-emitting diodes [2] and logic devices [3]. To realize these devices it is necessary to develop semiconducting materials that show ferromagnetic behavior at room temperature. Among the different types of wide-band-gap semiconductors ZnO, with a direct band gap of 3.37 eV and a large exciton binding energy of 60 meV, has become one of the most important functional semiconducting materials for electro-optical devices like UV light emitters [4], piezoelectric transducers [5] and gas sensors [6]. Since then, many systems of TM-doped ZnO (TM = Co, Mn, Ni, etc.) have been studied by different methods [7-10]. However, the reported experimental results on the studies of Cr-doped ZnO have been very conflicting. Some studies reveal that the magnetic behavior of Cr-doped ZnO appears to be very sensitive to the deposition method. For example, Ueda *et al*. [11] did not observe any ferromagnetic behavior for Cr-doped ZnO film grown by pulse laser deposition, whereas Roberts *et al*. [12] prepared Cr-doped ZnO via magnetron sputtering and obtained ferromagnetic ordering at 9.5 at% doping concentration. Furthermore, the results of Jin *et al*. [13] showed no ferromagnetic behavior for Cr-doped ZnO film at low temperatures even down to 3 K. Lee *et al*. [14] did not find ferromagnetism in solgel synthesized $Zn_{1-x}Cr_xO$ thin films; however, ferromagnetism appeared when the same films were co-doped with Li. We report a detail study on the structural and optical properties of $Zn_{1-x}Cr_xO$ nanocrystals synthesized by co-precipitation technique at room temperature.

2. Experimental

2.1. Sample Preparation

Samples with compositional formula of $Zn_{1-x}Cr_xO$, with x = 0.00 and 0.10 were prepared by co-precipitation route in an alcoholic medium (methanol). In this procedure, to prepare pure ZnO, Zinc acetate dihydrate (with 99+%

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purity, kemphasol make, A. R. Grade) was dissolved in methanol (100 ml) and KOH (purity 99+%, sd FiNE-CHEM Limited make, A. R. Grade) was dissolved in methanol (100 ml). Both the solutions were mixed by constant magnetic stirring by heating at 52˚C for 2 h. The precipitate separated from the solution by filtration, washed several times with distilled water and ethanol then dried in air at 127˚C to obtain ZnO nanocrystals. For the synthesis of Cr doped ZnO nanocrystals, Zinc acetate dihydrate and Chromium acetate tetrahydrate (with 99% purity, kemphasol make, A. R. Grade) were dissolved in methanol (100 ml) and KOH was dissolved in methanol (100 ml). Both the solutions were mixed by constant magnetic stirring by heating at 52˚C for 2 h. The precipitate separated from the solution by filtration, washed several times with distilled water and ethanol then dried in air at 127˚C to obtain Cr doped ZnO nanocrystals.

2.2. Characterization

The crystalline structure, phase purity and size of the nanoparticles were determined by X-ray diffraction (XRD) using X-ray diffractometer (Model: PW-3710) employing CuKα radiation. Fourier Transform Infrared (FTIR) spectra of the samples were recorded using JASCO FI-IR 460 spectrometer in the range 400 - 4000 cm^{-1} by KBr pellet technique. Absorption spectra of the samples in the UV-visible spectral region were recorded using UV-VIS-NIR (JASCO V 570) spectrophotometer.

3. Results and Discussion

3.1. X-ray Diffraction Study

Figure 1 shows XRD patterns with distinct diffraction peaks, corresponded to the (100), (002), (101), (102), (110), (103), (200), (112) and (201) lattice planes, reveal that as prepared nanocrystals have a wurtzite (hexagonal) structure. It is seen from the XRD patterns that the peaks of ZnO shift towards higher angles with increasing Cr concentration of ZnO samples. Such shifts of the XRD peaks reveal a lattice expansion due to the Cr substitution for Zn in the ZnO crystal lattice. It shows the small reduction in the lattice constant as Cr concentration increases. **Table 1** shows the lattice constant of Cr doped ZnO was slightly decreased with increasing Cr concentration. It may be due to the larger ionic radius of Zn as compared to Cr ions. The volume of the unit cell was also decreased with increasing Cr concentration. It indicates that Cr ions go to Zn site in ZnO structure.

The broadening of XRD peaks attributed nano-sized formation of Cr doped ZnO samples. The average grain size of Cr doped ZnO nanocrystals are estimated using Debye Scherer's formula. It is found that the average grain size is in the range of 11 - 17 nm. The average

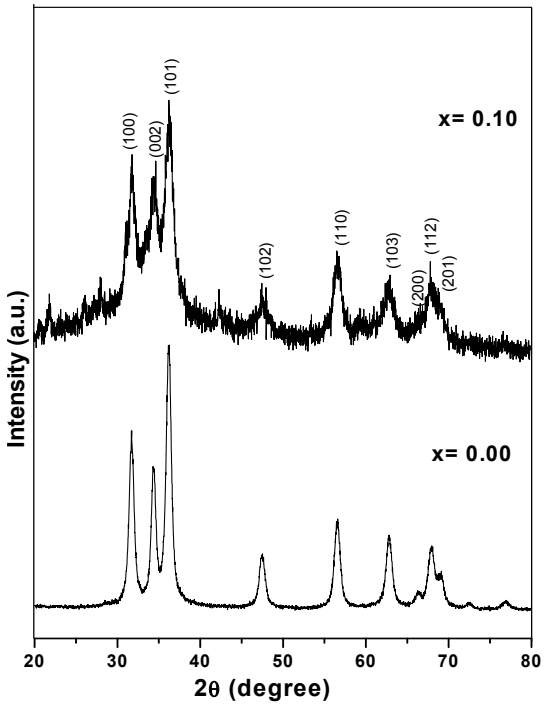

Figure 1. X-ray diffraction patterns of Cr doped ZnO at room temperature.

Table 1. Lattice parameters, grain size, volume cell and band gap at room temperature for $Zn_{1-x}Cr_xO$ system.

Sample	a(Å)	c(Å)	Grain size (nm)	Volume $(Å)^3$	Band gap (eV)
0.00	3.2606	5.2186	16.70	48.0494	3.06
0.10	3.2406	5.2068	11.09	47.3555	2.50

grain size, lattice parameter and absence of impurity phases with increasing Cr concentration for all samples could be attributed to the ionic radii of Zn and Cr ions. This is mainly because of the nucleation and subsequent growth rate with increasing Cr due to the difference of ionic radii of Zn and Cr ions.

3.2. Fourier Transform Infrared (FTIR) Analysis

FTIR spectra of pure and Cr doped ZnO nanoparticles are shown in the **Figure 2**. The broad peak in higher energy in the region at 3400 - 3600 cm^{-1} is due to OH stretching or it may be due to the M-OH-M. The peak in the range 1400 - 1757 cm^{-1} is due to OH bending of adsorbed moisture in the sample and all other peaks are attributed to the characteristic of the material. The bands appeared near at 2000 - 2200 cm^{-1} indicates the CO adsorption on the surface of oxide. Similarly the bands at 780 - 980 cm^{-1} might be due to the peroxide formation (M-O-O-M) and peak in the range of 900 - 1200 cm^{-1} is

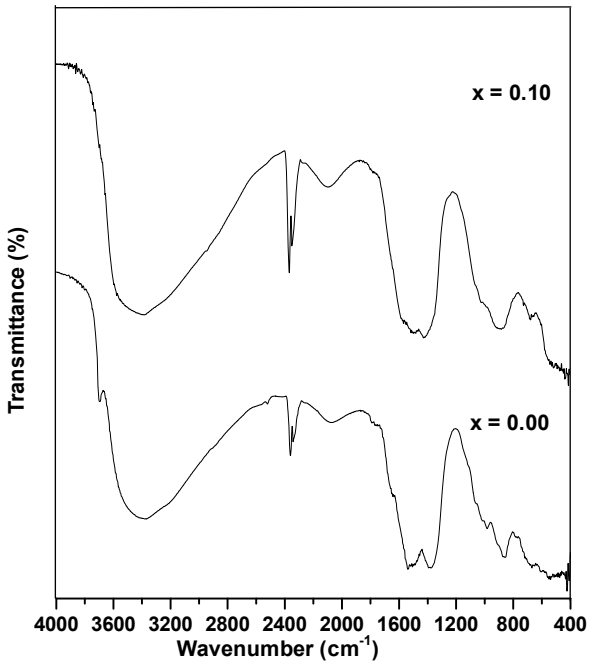

Figure 2. FTIR spectra of $Zn_{1-x}Cr_xO$ samples.

due to the M-O-M bonding. The FTIR spectrum of the main absorption band is due to Zn-O stretching of ZnO in the range of 600 - 400 cm^{-1}. FTIR spectra of pure sample of the present investigation are similar to that of Cr doped ZnO samples and are in good agreement with the reported values [15-19].

3.3. Optical Absorption and Optical Band Gap

The room temperature UV-Vis spectra of undoped and Cr doped ZnO samples are shown in **Figure 3**. The maximum absorption for all samples is observed, which indicates red shift from the bulk ZnO samples. This red shift absorption edge is due to the small size of the particles. The band gap was calculated by plotting the- absorption plot (Energy, E) versus $(\alpha h\nu)^2$. It is found that the band gaps of Cr doped ZnO samples are 2.50 - 3.06 eV. **Figure 4** shows the α-absorption is shifted slightly towards low energy as Cr content increases. The band gap is found to decrease with increasing Cr concentration. These values are tabulated in **Table 1**. The decrement in E_g with increasing Cr content is attributed to the s-d and p interactions and smaller average grain size.

4. Conclusion

Chromium doped ZnO nanocrystals were synthesized by co-precipitation method. Lattice parameters were determined using X-ray diffraction data and it is found that they show the wurtzite structure. The volume of unit cell decreases with increasing Cr concentration, it may be due to the smaller ionic radius of Cr ions as compared to Zn

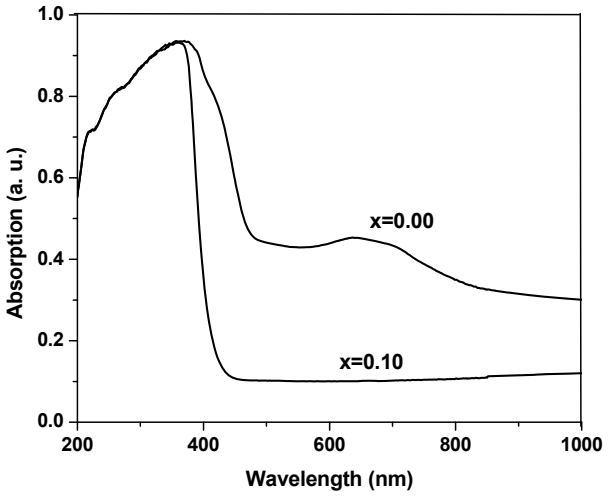

Figure 3. Absorption vs wavelength of $Zn_{1-x}Cr_xO$ samples.

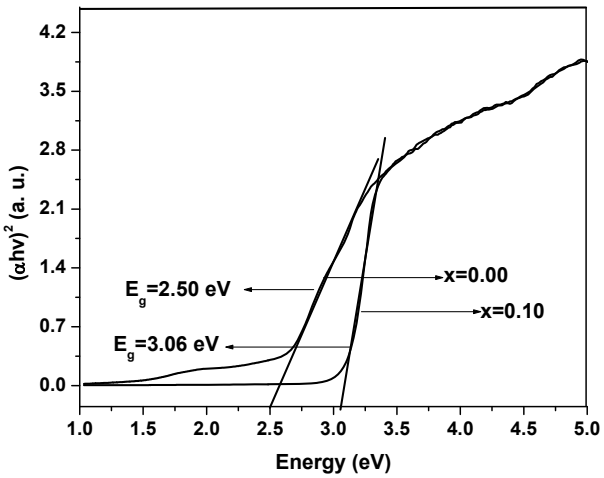

Figure 4. Energy vs $(\alpha h\nu)^2$ of $Zn_{1-x}Cr_xO$ samples.

ions. The grain size was calculated using Scherrer's formula. It is found that the average grain size is in the range 11 - 17 nm. The chemical groups of the samples have been identified by FTIR spectra. The absorption peak is shifted towards low energy side as Cr content increases. It may be owing to the s-d and p interactions and smaller average grain size of Cr doped ZnO samples.

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