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Journal of Chemical and Pharmaceutical Research

J. Chem. Pharm. Res., 2010, 2(4):178-183

ISSN No: 0975-7384
CODEN(USA): JCPRC5

Synthesis and Characterization of Copper doped ZnO nanoparticles

Ruby Chauhan[a,b]*, Ashavani Kumar[c] and Ram Pal Chaudhary[a]

[a]*Department of Chemistry, Sant Longowal Institute of Engg. & Tech. Longowal 148 106 India*
[b]*Technology Education and Research Integrated Institutions, Kurukshetra 136 119 India*
[c]*Department of Physics, National Institute of Technology, Kurukshetra 136 119 India*

ABSTRACT

Nanocrystals of undoped and copper doped zinc oxide ($Zn_{1-x}Cu_xO$ (where x = 0.00 to 0.05) were synthesized by coprecipitation method. Crystalline phases and optical absorption of prepared samples were determined by X-ray diffraction and UV-visible spectrophotometer. The average particles size was determined from X-ray line broadening. X-ray analyses reveals that Cu doped ZnO crystallizes in hexagonal wurtzite structure. The incorporation of Cu^{+2} in the place of Zn^{2+} provoked an increase in the size of nanocrystals as compared to undoped or pure ZnO. Optical absorption measurement indicates red shift in the absorption band edge upon Cu doping. The band gap decreases from 3.15 eV to 2.92 eV with copper (5 %) doping at temperature 450 °C.

Keywords: Nanoparticles, Coprecipitation, Optical absorption, XRD, UV-vis spectrophotometer.

INTRODUCTION

Nanocrystalline materials have attracted a wide attention due to their unique properties and immense potential application in nano device fabrication [1-4]. Zinc oxide (ZnO), a direct wide bandgap (3.4 eV at Room temperature) *II-VI* compound n-type semiconductor, has a stable wurtzite structure with lattice spacing $a = 0.325$ nm and $c = 0.521$ nm and composed of a number of alternating planes with tetrahedrally-coordinated O^{2-} and Zn^{2+} ions, stacked alternately along the c-axis. It has attracted intensive research effort for its unique properties and versatile applications in transparent electronics, ultraviolet (UV) light emitters, piezoelectric devices, chemical sensors and spintronics [5-14]. It has been proposed to be a more promising UV emitting phosphor than GaN because of its larger exciton binding energy (60 meV). All these predominant properties make ZnO a great potential in the field of nanotechnology.

Nano zinc oxide is non-toxic, with wide band gap has also been identified as a promising semiconductor material for exhibiting ferromagnetism (RTFM) at room temperature when doped with most of the transition metal elements [15]. Transition metal doped nanostructure is an effective method to adjust the energy level surface states of ZnO, which can further improve by the changes in doping concentrations of doped materials and hence in its physical and especially optical properties [16].

The coprecipitation method is one of the most appropriate ways of synthesizing a nanopowder. Coprecipitation is the name given by analytical chemists to a phenomenon whereby the fractional precipitation of a specified ion in a solution results in the precipitation not only of the target ion but also of other ions existing side by side in the solution. The additional precipitation of unwanted ions is, of course, an impediment to the analytical process [17]. Some of the most commonly substances used in coprecipitation operations are hydroxides, carbonates, sulphates and oxalates.

In the present work we used the coprecipitation method to prepare undoped and copper doped nanoparticles with nearly uniform and controlled size. The high quality of $Zn_{1-x}Cu_xO$ (where x=0.00 to 0.05) nanoparticles were successfully synthesized.

EXPERIMENTAL SECTION

Synthesis of $Zn_{1-x}Cu_xO$ (where x = 0.0 to 0.05) nanoparticles were fabricated by the coprecipitation method [18]. All chemicals used are of analytical grade purity. X-Ray Diffraction (XRD) with CuK_α radiation (Mini-desktop, Rigacu) patterns was obtained to examine the phase composition of the powder samples. The optical absorption spectra were recorded on Shimadzu double beam double monochromator spectrophotometer (UV-2550), equipped with integrated sphere assembly ISR-240A in the range of 190 to 900 nm.

Coprecipitation method

The starting materials, $ZnSO_4.7H_2O$, Na_2CO_3, NaOH, $CuSO_4.5H_2O$ were used without further purification. In a typical synthesis of undoped ZnO, 0.1 M $ZnSO_4.7H_2O$ was dissolved in distilled water. Separately, a buffer solution (pH = 4.6) was prepared by dissolving appropriate amounts of sodium hydroxide and sodium carbonate in distilled water. The pH of buffer solution was selected so as to cause precipitation of basic zinc carbonate. Buffer solution was then added drop wise to the vigorously stirred zinc sulphate solution to produce a white, gelatinous zinc basic carbonate precipitate. The reactions for obtaining basic zinc carbonate are written as:
Sodium hydroxide precipitates; the white, gelatinous zinc hydroxide:

$$(Zn^{2+} + SO_4^{2-}) + 2(Na^+ + OH^-) \rightarrow Zn(OH)_2 + (2Na^+ + SO_4^{2-})$$

The precipitate is soluble in sodium hydroxide reagent, resulting zincates, which behave like a weak acid:

$$Zn(OH)_2 + 2(Na^+ + OH^-) \rightarrow (2Na^+ + ZnO_2^{2-}) + H_2O$$

Sodium carbonate precipitates with zinc salts the white basic carbonate with variable composition:

$$4\,(Zn^{2+} + SO_4^{2-}) + 4(Na^+ + CO_3^{2-}) + HOH \rightarrow Zn_4(CO_3)_3(OH)_2 + CO_2 + 4(Na^{2+} + SO_4^{2-})$$

After addition of buffer solution the mixture was stirred for two hours at room temperature. The precipitates were filtered and washed with distilled water. The precipitates were dried in oven at 110°C for two hours and calcinated at 450 and 800 ^{o}C in muffle furnace. The basic zinc carbonate precipitate was decomposed in zinc oxide; a nano white powder. Decomposition reaction of basic zinc carbonate (hydrozincite) in zinc oxide is written as:

$$Zn_4(CO_3)_3(OH)_2 \rightarrow 4ZnO + H_2O + 3CO_2$$

For the synthesis of ZnO doped with transition metal (Copper) a solid mixture of 1 -5% CuSO4.5H_2O in $ZnSO_4.7H_2O$ was dissolved separately in 50 ml distilled water and then mixed with buffer solution of sodium carbonate and sodium hydroxide, followed by the same procedure as for undoped ZnO. Sodium hydroxide precipitates the Copper oxide. Sodium carbonate precipitates the copper carbonate, which decomposes in Copper oxide. The reactions are written as:

$$(Cu^{2+} + 2\,NO_3^-) + 2(Na^+ + OH^-) \rightarrow CuO + 2(Na^+ + NO_3^-)$$
$$(Cu^{2+} + 2\,NO_3^-) + (2Na^+ + CO_3^{2-}) \rightarrow CuCO_3 + 2(Na^+ + NO_3^-)$$
$$CuCO_3 \rightarrow CuO + CO_2$$

RESULTS AND DISCUSSION

X-ray diffraction studies: All the samples analyzed; pure and copper doped ZnO nano powders; presented are hexagonal wurtzite structure. Figure-1 shows the XRD diffraction patterns of $Zn_{1-x}Cu_xO$ (x =0.0 to 0.05) powder samples at 800^{o}C temperature. Undoped and copper doped ZnO samples were calcined at 800 ^{o}C in muffle furnace to ascertain the formation of different nanocrystalline phases. The diffraction patterns of samples can be indexed to the hexagonal wurtzite structure of ZnO. No other peaks corresponding to Cu related secondary or impurity phase was found in copper doped sample, which may be attributed to the incorporation of Cu ion into the Zn lattice site rather than interstitial ones. The mean crystalline size was calculated from the full-width at half-maximum (FWHM) of XRD lines by using the Debye-Scherrer formula:

$$D_{h,k,l} = 0.9\lambda / (\beta_{h,k,l}\cos\theta)$$

where D is the average crystalline diameter, λ is the wave-length in angstrom, β is the line width at half – maximum and θ is the Bragg angle. We used the most intense peak (101) in the XRD patterns to calculate the average crystalline size. It can be seen that the average size of nanoparticles decreased as the doping percentage of copper metal is increased. The calculated values of particles size are presented in Table- 1 for undoped and Cu doped (1-5%) ZnO at 800 °C. The particles size are in the range of 28 to 40 nm at 800°C corresponding to the $Zn_{1-x}Cu_xO$ (x = 0.0 to 0.05) nanoparticles respectively.

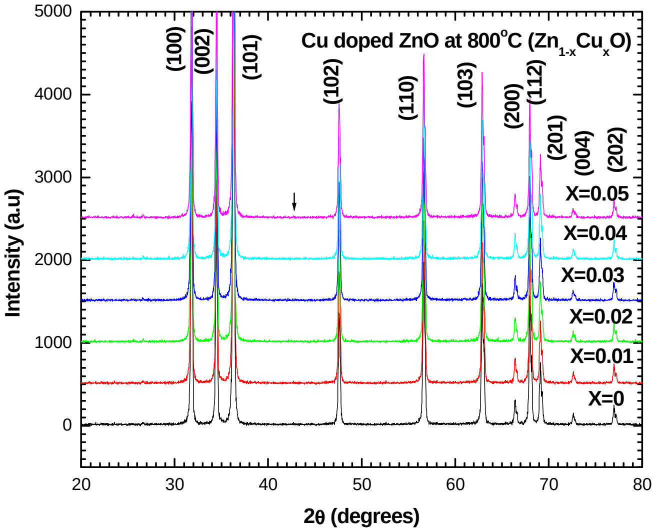


Fig. 1 XRD patterns of pure ZnO and $Zn_{1-x}Cu_xO$ nanoparticles at 800°C

Table 1. Variation of size with temperature of undoped and copper doped ZnO nanoparticles

% of doping of Cu	**Average size of particles for sample annealed at temperature 800°C**
0 %	27.8
1 %	39.8
2 %	39.0
3 %	38.8
4 %	38.2
5 %	38.0

Optical studies: The optical absorption spectra of $Zn_{1-x}Cu_xO$ (x=0.00, 0.05) samples by using UV-vis spectrophotometer in the range of 200 to 800 nm. Absorption edges values of as prepared undoped and copper doped samples at 450 °C are 393 nm and 424 nm respectively as in figure-2(a) & (b).

The energy band gap is determined by using the relationship:

$$\alpha = A\,(h\nu - E_g)^n$$

where hν= Photon energy, α= Absorption coefficient (α = 4πk/λ; k is the absorption index or absorbance, λ is wavelength in nm), E_g =Energy band gap, A=constant , n=1/2 for allowed direct band gap. Exponent n depends on the type of transition and it may have values1/2, 2, 3/2 and 3 corresponding to the allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively [19]. The value of band gap at temperature 450 °C is determined by extrapolating the straight line portion of $(\alpha\, h\nu)^2 = 0$ axis; as shown in figure 3 (a) & (b). The band gap decreases from 3.15 eV to 2.92 eV with copper (5 %) doping at temperature 450 °C.

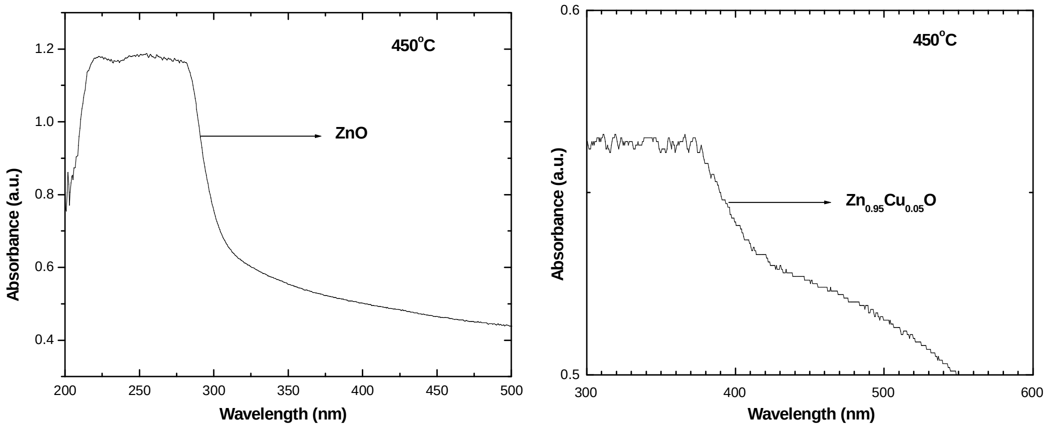
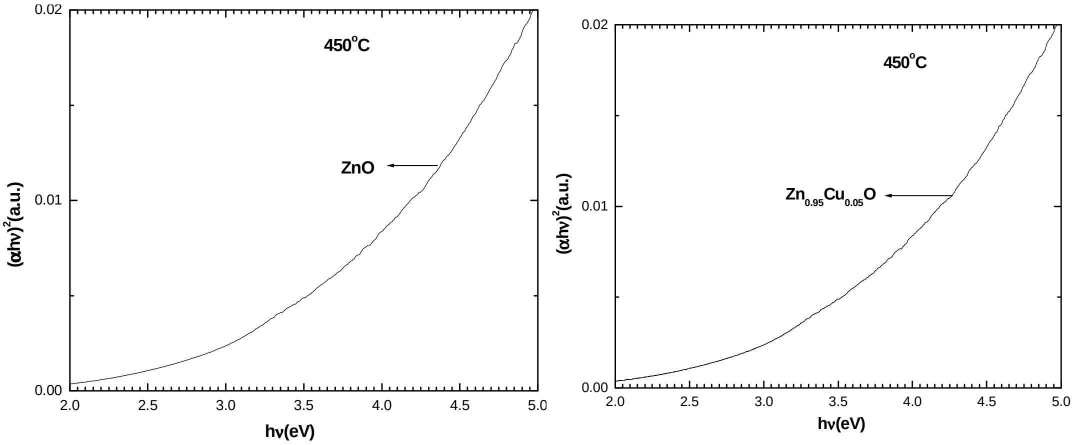


Fig.2 Optical absorption spectra of (a) undoped ZnO nanoparticles and (b) copper doped ZnO nanoparticles at 450°C.



(a) (b)

Fig. 3 $(\alpha h\nu)^2$ vs. photon energy (hν) of (a) undoped ZnO nanoparticles and (b) copper doped ZnO nanoparticles at 450°C.

CONCLUSIONS

Nanocrystals of undoped and copper doped ZnO were successfully synthesized by using a chemical coprecipitation method. The crystalline structure, optical properties and band gap were determined by XRD and UV-visible spectra. XRD analysis shows the samples prepared in hexagonal phase. The average size of nanoparticle decreased as the doping percentage of copper metal is increased. The band gap values of prepared undoped and copper doped samples are found to decrease from 3.15 to 2.92 eV. Optical absorption measurements indicate red shift in the absorption band edge upon copper doping.

Acknowledgements
Authors are thankful to Dr. Sanjeev Aggrawal and Nidhi Sekhawat, Kurukshetra University, Kurukshetra for technical support for getting UV-VIS spectra. We are also thankful to the Director, NIT, Kurukshetra for XRD facilities in physics department.

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