Influence of Dopant Concentration on Structural and Optical Properties of Cu Doped ZnO Nanoparticles

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Abstract

Cu doped ZnO nano particles were prepared by solvothermal method. The prepared samples were annealed at different temperatures. X-ray powder diffraction (XRD) shows that the Cu doped ZnO nanocrystals exhibit hexagonal wurtzite structure and the particle size was found to be within the range between 25 and 45 nm by transmission electron microscope. The functional group is analysed by using FT-IR. The intensity of PL spectrum increases with the increasing in Cu concentration. UV–vis absorption spectrum Cu-doped ZnO displayed a band gap absorption peak at about 365 nm.

Key words: Effect of dopant Solvothermal method, nanoparticles, XRD, TEM, FT-IR, photoluminescence**.**

Introduction

The synthesis, characterisation and processing of nanostructure materials are parts of an emerging and rapidly growing research work in recent times [1, 2]. Zinc oxide is a versatile material. Zinc oxide is well known to have a direct band gap of 3.37 eV at room temperature and has distinguished performance in electronics, optics and photonics [3, 4, 5].

Recently, nano structured materials have been a great deal of interest due to their unique properties and potential applications [6-11]. Among the oxides of transition metals, Copper oxide nanoparticles are of special interest because of their efficiency as nano fluids in heat transfer applications. For example it has been reported that 4% addition of CuO improves the thermal conductivity of water by 20 % [12].

One of the effective approaches to tailor the electrical, optical and magnetic properties of this material for various practical applications is the doping with selective elements [13, 14]. Very recently K.Das et.al prepared Cu doped ZnO films by sol-gel technique of Zinc acetate and Copper acetate using 2- Propanol as a solvent [15]. They observed that the orientation of the plane with increasing molar % of copper in the films. Inthe present work, we have attempted to prepare, for the first time; Cu doped ZnO nanoparticles by using some simple solvothermal methods and characterizes the prepared samples. The results are reported and discussed.

Experimental

Materials

All chemicals used in the experiment are analytic reagent grade. Zinc acetate dihydrate, Copper acetate monohydrate, Urea, Ethylene glycol, and acetone were purchased from HPLC, India. De ionized water was used throughout the experiment.

Preparation of Cu doped ZnO Nano particles by solvothermal method.

Analar grade Zinc acetate, Copper acetate, and urea, along with ethylene glycol, were used for the preparation of $Zn_xCu_{1-x}O$ nanocrystals. Zinc acetate and Copper acetate taken together in the required composition and urea in 1:3 molecular ratios were mixed and dissolved in 50ml of ethylene glycol and kept in a microwave oven. 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. We have prepared the following ratios $Zn_{0.4}Cu_{o.6}O$, $Zn_{0.6}Cu_{o.4}O$, $Zn_{0.1}Cu_{o.9}O$ and $Zn_{0.9}Cu_{o.1}O$. All the samples were annealed at different temperatures, 200^0C and 600^0C.

Table1.
Crystalline size of Copper doped Zinc Oxide for various concentration

Name of the samples	2 θ	FWHM	h k l	Crystalline Size
$Zn_{0.0.4}Cu_{0.6}O$ A 600^0 C	32^0	0.0181	1 0 0	79
	36^0 5^0	0.207	0 0 2	70
	47^0 5^0	0.28	1 0 1	54
	56^0 5^0	0.485	1 1 0	32
$Zn_{0.6}Cu_{0.4}O$ A 600^0 C	32^0 5^0	0.306	1 1 0	31
	34^0 5^0	0.395	0 0 2	36
	38^0 5^0	0.524	1 1 1	37
	56^0 5^0	0.426	0 2 1	37
	67^050^0	0.092	1 1 3	18
$Zn_{0.1}Cu_{0.9}$ O A 200^0 C	29^0 5^0	0.028	1 1 0	51
	36^0 5^0	1.367	0 0 2	11
	38^0 5^0	0.925	1 1 1	16
	57^0 5^0	0.308	2 0 2	51
$Zn_{0.9}Cu_{0.1}$ O A 600^0 C	31^0 50^0	1.3	1 0 0	11
	34^0 50^0	1.024	0 0 2	12
	36^0 50^0	0.839	1 0 1	17
	56^0 50^0	2.08	1 1 0	34

Characterization techniques

FTIR spectrum of $Zn_xCu_{1-x}O$ nano particles were done in the range 4000 to 400cm^{-1} using thermo Nicolet V-200 FTIR Spectrometer by KBr pellet technique. The UV-visible spectra of $Zn_xCu_{1-x}O$ nano particles were recorded employing Jasco V-530 dual beam spectrometer. The PL property of $Zn_xCu_{1-x}O$ wasstudied by using FP-6500 Spectro fluro meter- 67 at room temperature.TEM images were taken using Hitachi 600 transmission electron microscopy $Zn_xCu_{1-x}O$ nano particles.X-ray diffraction patterns of

$Zn_xCu_{1-x}O$ nano particles were obtained usingadvance diffractometer (for 2θ range from 10 º to 80 º) with monochromatic CuKα radiation(λ=1.54Å) to identify crystalline nature of the samples.

Result and Discussion

Structural properties

Fig. 1a-d shows the XRD patterns of the Cu doped ZnO nanorods deposited at 95 ◦C. The intense diffraction peaks of the Cu doped ZnO appear at 31.68, 34.43, 36.08, 47.28, 56.32 and 62.48, which correspond to the (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0) and (1 0 3) planes, respectively. All Bragg peaks with miller indices are associated with the hexagonal wurtzite structure of ZnO is in good agreement with JCPDS DATA (36-1451). The (0 0 2) peak positions 2Θ of the doped sample were shifted to a higher value for the higher dopant concentrations respectively. The shift in the (0 0 2) peak for Cu-doped ZnO might be due to the substitution of Zn by Cu in the hexagonal lattice. These shifts agree with previous reports [16–18].No extra peak in the pattern shows the formation of single phase. This indicates that Cu2+ ion successfully occupy the lattice site rather than interstitial one. This is due to the fact that ionic radius of Cu2+(0.73Å) is very close to that of Zn2+(0.74Å),due to which Cu can easily penetrate into ZnO crystal lattice. [19].

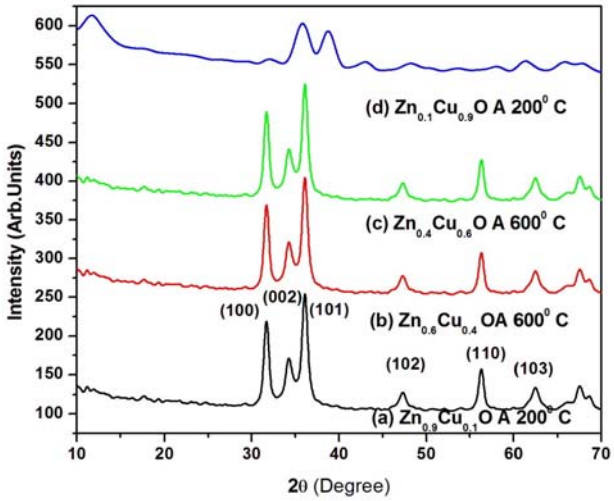

Fig. 1 X-ray diffraction patterns of Cu doped ZnO nano particles

The intensity of the peaks increases with temperature. The estimated values of particle sizes are given in table 2.All the four samples were tested for their structures using XRD. Particle sizes were calculated using Debye- Scherer's formula.

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

Where λ is wave length of X-ray (0.1541 nm), β is FWHM (full width half maximum) and θ is diffraction angle [20]. From table1, we observed that as the concentration of the dopant is increased the product of the yield is decreased. From table 2, we find that the sample $Zn_{0.4}$ $Cu_{0.6}$ O A 600 ^{0} C, the particle size is increases with increasing temperature around 45– 50 nm. The sample $Zn_{0.1}$ $Cu_{0.9}$ O A 200 ^{0} C, the particle size is decreases with decreasing temperature around 10 - 20 nm. The annealed temperature and dopant concentration affects the crystalline size.

TEM

Figure 2a and b show the TEM images of Cu doped ZnO nanoparticles for different annealing temperatures at 600^0C and 200^0 C. the TEM images exhibit particle size of Cu doped ZnO powder which are in the range 45 and 25 nm. The size of the particles observed in the TEM image is in the range of 25–45 nm in table 2. This is in good agreement with that estimated by Debye's Scherer formula from the XRD pattern.

FT-IR

FITR spectrum of the Cu doped ZnO nanoparticles powders are shown in the fig.3a-d.Abroad peak observed at 3400 cm^{-1} has been attributed to–OH group of H_2O, which indicates the existence of water adsorbed on the surface of nanocrystalline powder. A broad band has been observed at around 490 cm^{-1} for the pure ZnO corresponding to the formation of Zn–O bond [21].The broad band in the coupled Cu-ZnO at 694 cm^{-1} is assigned to the characteristic stretching mode of Cu-O, while other absorption bands found around 1036, 1423, and 1570 cm^{-1} are mainly due C=C, C-H and C=O stretching.[22]. The peaks at 2924, 2914 cm^{-1}asymmetry is assigned to CH_2 vibrations of Ethylene glycol adsorbed on the ZnO surface. This alcohol was used during the preparation of ZnO.

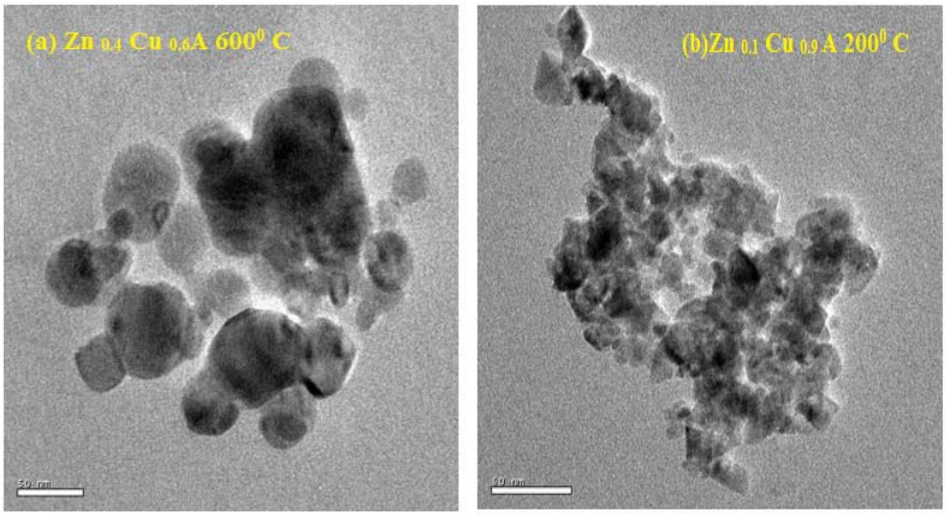

Fig. 2 TEM images of Cu doped ZnO nano particles

UV

The UV-vis absorption spectrum of Cu-doped ZnO nano particles are shown in Fig. 4a–d.From Fig.4a–d, the excitonic absorption peak at the wavelength of about 365 nm can be found in the absorption spectra of Cu-doped ZnO nanoparticles.

PL

PL spectrum of Cu doped ZnO nanoparticles are shown in the fig.5a-d. Pure ZnO exhibits band at 394 nm and a broad yellow emission at 600 nm [23].The UV emission of 390nm for the samples may be a result of the electron transfer from a shallow donor state of Cu^{2+} to the valence band [24].In addition, yellow luminescence are commonly reported in ZnO nanostructures, and represent common features in samples prepared from aqueous solutions of zinc nitrate hydrate [25].These emissions are typically attributed to oxygen interstitials or zinc vacancies [26].The intensity of NBE emission depends strongly on Cu concentration. When doped with 0.9 ratios of Cu atoms, the Cu doped ZnO exhibit more intense

NBE emission than undoped ZnO nanoparticles, and the intensity of NBE emission increases quickly with further increase of Cu dopant.[27], which can also result in the quenching of NBE emission.

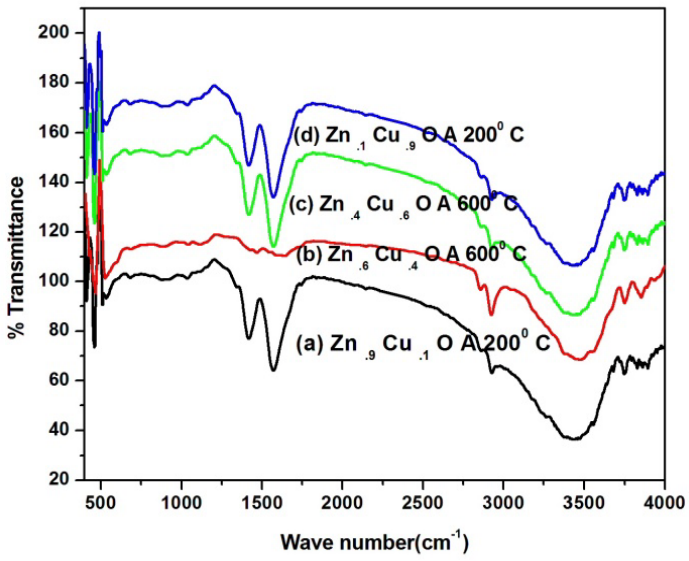

Fig. 3 FT-IR spectrum of Cu doped ZnO nano particles

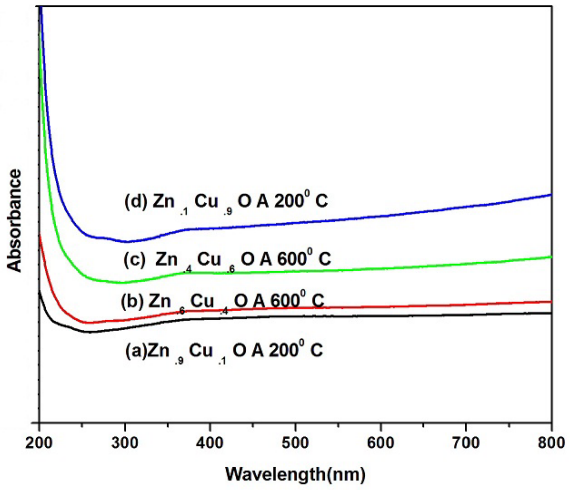

Fig. 4 UV –vis absorption spectrum of Cu doped ZnO nano particles

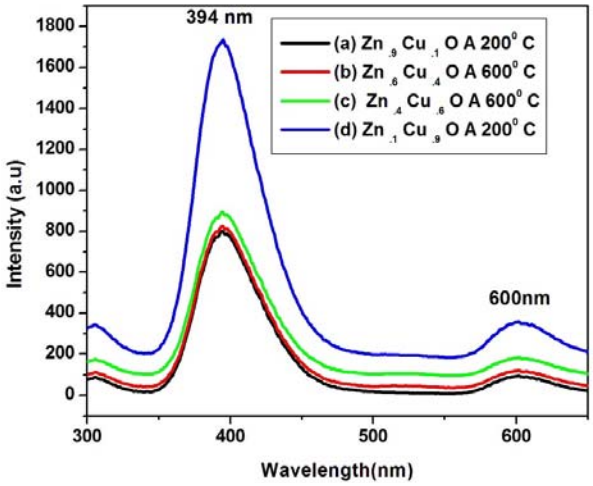

Fig. 5 PL spectrum of Cu doped ZnO nano particles

Conclusion

Cu doped ZnO nanocrystals were prepared by simple solvothermal method. The XRD results confirmed that the crystal structure of Cu doped ZnO nano particles is hexagonal structure. The size of the particles observed in the TEM image is in the range of 25– 45 nm. This is good agreement with that estimated by Debye's Scherer formula from the XRD pattern. FT -IR study confirms the presence of dopant in the ZnO structure. A PL spectrum shows a near band gap emission around at 380 nm and yellow emission at 600 nm. The intensity of PL spectrum increases with increasing the Cu concentration. The absorption peak at the wavelength of about 365 nm can be found in the absorption spectra of Cu-doped ZnO nanoparticles.

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