EFFECT OF Cu - DOPING ON THE STRUCTURAL AND OPTICAL PROPERTIES OF ZnO NANO CRYSTALLITES PREPARED BY CHEMICAL PRECIPITATION METHOD

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ZnO and Cu doped ZnO nanoparticles have been prepared by chemical precipitation method. X-ray diffraction analysis reveals that the undoped and Cu doped ZnO nanoparticles exhibit cubic zinc blende structure and the average particle size of the nanoparticles is in the range of 26-39 nm. The SEM images shows the doped particles agglomerated on the ZnO surface. The compositional analysis result indicates that Zn, O and Cu are present in the samples. From the optical studies it is observed that the absorption edge of the prepared ZnO and Cu doped ZnO nanoparticles are shifted towards the short wavelength region (blue shift) when compared to that of bulk ZnO and this shift is due to the quantum confinement effect present in the samples. Photoluminescence studies showed blue emission with appreciable luminescence quenching with increasing Cu concentration.

1. Introduction

In recent years quantum dots of II-VI semiconductors have received immense attention due to the ease with which they can be synthesized leading to quantum confinement. Due to the decrease in particle size below the Bohr exciton radius, quantum confinement of electron-hole pair result in size dependent optical and magnetic properties and electronic properties such as blue shift of absorption edge and increased band gap due to the particle size decrease. ZnO has wide band gap of 3.68 eV is an important semiconductor, which is important in a semiconductor has wide applications such as semiconductors and lasers [1-4], solar cells, infrared windows, flat screen display. With the reduction in size of the particle to nanometer scale, the physical and chemical property of the material deviate from their bulk properties compared to bulk ZnO, nanocrystalline ZnO have wide bandgap. The optical absorption edge shift towards the lower wavelength side (blue shift) in quantum dot ZnO. With the decrease in particle size, the increase in bandgap happens due to the quantum size effect. Many workers have used various techniques such as microwave irradiation, microemulsion, chemical precipitation method, hot injection, chemical vapor deposition, hydrothermal and sol-gel spin coating method, soft chemical method [9-17]. Among them chemical precipitation is a simple and inexpensive method. In recent years, doping of ZnO with materials has gained importance.In the present study Cu (0, 0.03, 0.06, and 0.09 at %) doped ZnO nanocrystallites have been prepared by chemical precipitation method and the effect of Cu concentration and characterizes by the morphology, structure and optical properties has been discussed.

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2. Experimental

Materials

Zinc(II)nitrate hexahydrate $(Zn(NO_3)_2.6H_2O)$, copper (II) nitrate trihydrate $(Cu(NO_3)_2.3H_2O)$, sodium carbonate (Na_2CO_3) and sodium hydroxide (NaOH) are purchased from Sd. Fine chemicals (AR) grade and used without further purification.

Synthesis of undoped Cu doped ZnO nanoparticles

The high purity chemicals (>99% purity) such as Zinc (II) nitrate hexahydrate $(Zn(NO_3)_2.6H_2O)$, copper (II) nitrate trihydrate $(Cu(NO_3)_2.3H_2O)$, sodium carbonate (Na_2Co_3) and sodium hydroxide (NaOH) were used as the precursors without further purification. For the preparation of $Zn_{0.97} Cu_{0.03}O$ nanopowder were dissolved in 50ml double distilled water and kept in magnetic stirrer for 30 mins under vigorous stirring. A separate buffer solution was prepared by dissolving 4g of sodium hydroxide and 10.6g of sodium carbonate in 50 ml double distilled water. Buffer solution was then added drop wise to the initial solution under constant string for 2hrs at room temperature to produce a white gelatinous precipitate. The white precipitates were filtered and washed with distilled water for many times. The final precipitates were dried in oven at 80°C for four hours. The dried precipitates were collected and ground in an agate mortar. The same procedure was repeated for other samples preparation. The collected nanopowder was annealed at 550°C for two hours followed by furnace cooling. The use of furnace is many fold purpose such as, (i) to improve the crystallinity, i.e., order of the alignment of the atoms (ii) to enhance the conductivity and (iii) to reduce the secondary phase formation. The same procedure is repeated to the remaining samples synthesized with nominal compositions of $Zn_{1-z} Cu_zO$ with z = 0, 0.03, 0.06, and 0.09 at %.

X-ray diffraction studies have been carried out using PANalytical x-ray diffractometer. Elemental composition of the prepared samples has been studied using Energy dispersive analysis of X-ray (EDAX,Thermo-Noran system Six) and scanning electron microscope (SEM) images of the prepared ZnO and Cu doped ZnO have been recorded using JEOL JEM 2010 microscope. The optical properties have been studied using absorbance spectrum recorded using spectrophotometer (JASCO V-570). Photoluminescence emission spectrum has been recorded using Cary Eclipse spectrophotometer.

3. Results and discussion

Figure 1 shows the X-ray diffraction pattern of ZnO and Cu doped ZnO nano particles. Fig 1 shows the XRD patterns of z = 0.03, 0.06 and 0.09 at % Cu doped ZnO nanopowder. The XRD patterns of Cu doped ZnO clearly shows the crystalline nature with peaks corresponding to (100), (002), (101), (102), (110), (103), (200), (112), and (201) planes. The standard diffraction peaks shows the crystal structure (space group p6$_3$ mc, 186, JCPDS date card No. 36-1451) with preferred orientation along (101) plane in all the samples. This is most stable phase of ZnO. It is evident from the XRD spectra that there is no extra peak corresponding to Cu, oxides of Cu or Cu related secondary and impurity phases. The diffraction peaks at 2θ around 28.8^o, 48.15^o and 56.85^o had planes (111), (220) and (311) corresponding to the ZnO cubic zinc blende. The lattice constant was found to be a=5.3970 A^o and is in accordance with JCPDS No. 03-0570. A small shift towards the higher 2θ was observed with Cu doped ZnO when compared to bulk ZnO. This could be due to the filling of Cu ions in Zn sites.
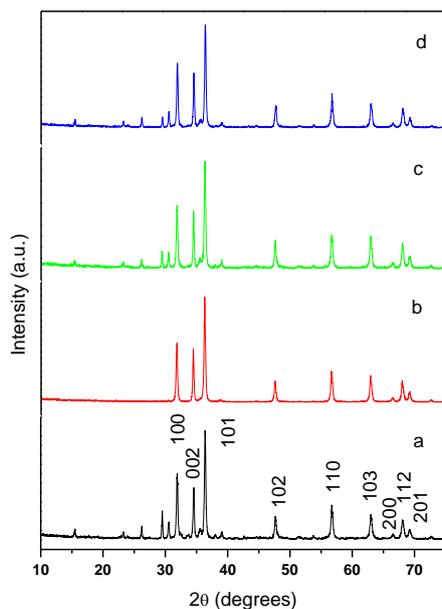
Fig. 1 X-ray diffraction pattern of a) ZnO b) $Zn_{0.97}Cu_{0.03}O$ c) $Zn_{0.94}Cu_{0.06}O$ d) $Zn_{0.91}Cu_{0.09}O$.

Cu doped ZnO exhibited zinc blende structure in the diffraction pattern. Structural phase transformation was not seen due to doping of Cu in ZnO, but lattice concentration was seen. Due to the Cu doping there is a decrease in the lattice contraction. This is due to the ionic radius of Cu being lesser than Zn. The crystallite size was found to be 26-39 nm (±0.1 nm) for the ZnO and Cu doped ZnO nanoparticles. The crystallite size increased with the increase in Cu concentration. This is due to the increase in the Cu in Zn sites.

Table 1. The Average particle Size $Zn_{1-z}Cu_zO$ Nps using X-ray diffraction spectra.

Samples	2θ values (°)	d-space values (Å)	Cell parameter (Å)			Average Crystallites size (D) nm
			a =b	c	ratio c/a	
ZnO	36.213	2.48350	3.264	5.209	1.6012	26
$Zn_{0.97}Cu_{0.03}O$	36.366	2.468	2.856	5.178	1.8130	37
$Zn_{0.94}Cu_{0.06}O$	36.347	2.469	2.864	5.205	1.8173	38
$Zn_{0.91}Cu_{0.09}O$	36.265	2.475	2.858	5.198	1.8206	39

The surface morphology of the undoped and Cu doped ZnO nanoparticles is shown in Figure 2 (a-d). The SEM pictures clearly shows that spherical particles. When increasing dopant concentration, the surface spherically agglomerated. From the EDAX spectrum, we confirmed that the elements Zn, O and Cu in the sample.
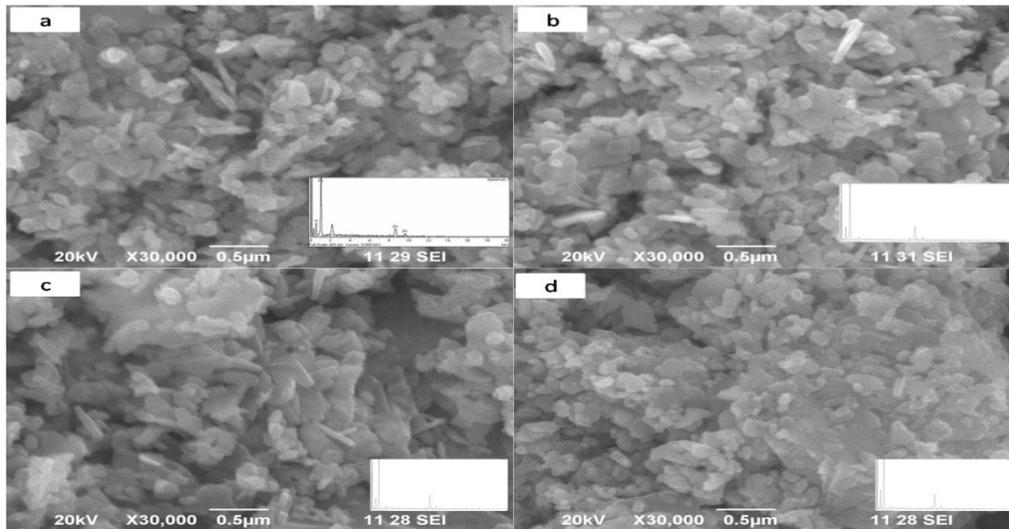
Fig. 2 SEM/EDS micrograph of a) ZnO b) $Zn_{0.97}Cu_{0.03}O$
c) $Zn_{0.94}Cu_{0.06}O$ d) $Zn_{0.91}Cu_{0.09}O$.

The synthesized ZnO nanoparticles have band around 45 nm corresponding to emission band. Self-activated luminescence related to interstitial sulfur ion of undoped particles is attributed to the blue emission. Reports on blue emission for ZnO nanoparticles have been reported by many research groups.
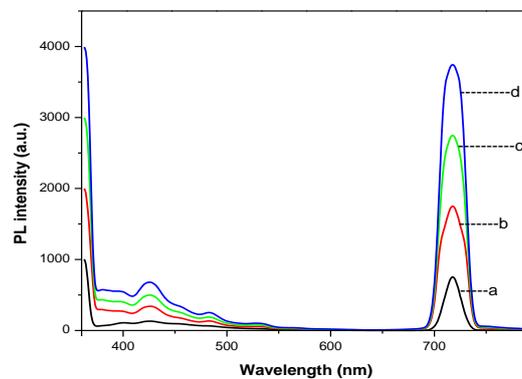
Fig. 3 Photoluminescence spectra of a) ZnO b) $Zn_{0.97}Cu_{0.03}O$ c) $Zn_{0.94}Cu_{0.06}O$ d) $Zn_{0.91}Cu_{0.09}O$.

Cu concentration increases the luminescence intensity in the PL spectra. The decrease in this property is attributed to deep center formation inhibiting the exciting of electron (holes) leading to nonradioactive enhancement. Also it can be seen that red shift of Cu doped sample increased with increase in Cu doping. This leads to the change in nanoparticle's particle size.

Optical absorption spectra of undoped and Cu doped ZnO nanoparticles are shown in Fig 4. It is well known that the position of absorption edge is related to the size of the nanoparticles. The absorption edge of the ZnO nanoparticles shows a blue shift and is located at 300 nm when compared to the value 337nm of bulk ZnO. This blue shift is due to quantum confinement effect which is due to decrease in particle size [18-20]. Absorption spectra of Cu doped ZnO nanoparticles shows that the absorption edge is slightly shifted towards the longer wavelength (red shift) when compared to undoped ZnO. The shift of the absorption edge to the longer wavelength is due to the small increase of particle size with increasing Cu concentration. The fundamental absorption, which corresponds to the electron excitation from the valance band to the conduction

band, can be used to determine the nature and value of the optical band gap. The absorption maxima for undoped and Cu doped ZnO nanoparticles lie at 225 nm to 230 nm, respectively. The band gap of all the samples was calculated using a simple wave energy equation [21].

$$E = h \gamma = \frac{hc}{\lambda} \quad -------- (2)$$

The band gap has been calculated and is found to be 2.82 to 2.59 eV for undoped ZnO and 0.03, 0.06 and 0.09 at % Cu doped ZnO respectively.
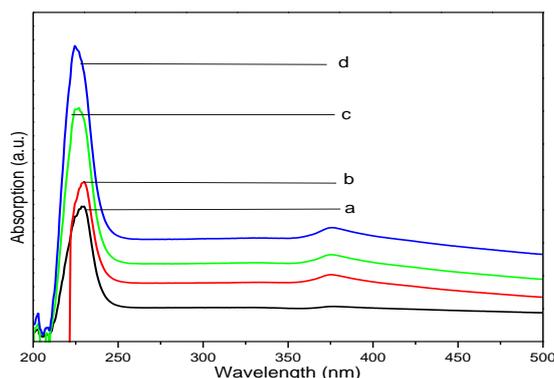
Figure-- 4. Ultra Violet spectra of a) ZnO b) $Zn_{0.97}Cu_{0.03}O$ c) $Zn_{0.94}Cu_{0.06}O$ d) $Zn_{0.91}Cu_{0.09}O$.

In a bulk semiconductor a bound electron – hole pair, called an exciton, can be produced by a photon having an energy greater than that of the band gap of the material. The band gap is the energy separation between the top filled energy level of valance band and nearest unfilled level in the conduction band above it. The photon excites an electron from the filled band to the unfilled band above. The result is a hole in the otherwise filled valance band, which corresponds to an electron with an effective positive charge. Because of the Coulomb attraction between the positive hole and the negative electron, a bound pair, called an exciton, is formed that can move through the lattice. The existence of the exciton has a strong influence on the electronic properties of the semiconductor and its optical absorption. It is particularly interesting to see what happens when the size of the nanoparticles becomes smaller than or comparable to the radius of the orbit of the electron – hole pair. There are two situations, called the weak confinement and the strong confinement regimes. In the weak regime the particles radius is larger than the radius of the electron – hole pair, but the range of motion of the exciton is limited, which causes a blue shift of the absorption spectrum. When the radius of the particle is smaller than the orbital radius of electron – hole pair, the motion of the electron and hole become independent and the exciton does not exist. The hole and electron have their own set of energy levels. Here also there is a blue shift [22]. Quantum size effects become dominating when the size of the nano crystallites is less than bulk exciton Bohr radius and it affects the electronic energy bands of the semiconductors. Coulomb interaction between the hole and the electron plays a crucial role in nano crystalline materials. The quantum confinement of charge carriers modifies the valence and conduction bands of the semiconductors. The blue shift in the band gap of nanoparticles due to quantum confinement is of the quantitative form [23]

$$E_g^{nano} = E_g^{bulk} + \frac{\hbar^2 \pi^2}{2\mu R^2} - \frac{1.8e^2}{\varepsilon R}$$

(1)

where E_g^{nano} and E_g^{bulk} are the band gap values of the nanoparticles and the bulk material respectively, $\mu = m_e m_h / (m_e + m_h)$ is the reduced mass and m_e and m_h are effective masses of electron (0.19 m for ZnO) in conduction band and holes (0.80 m for ZnO) in valance band respectively, e is the electron charge, ε is the relative permittivity of the semiconductor, R is the

radius of the particle and the second term is the columbic term and is generally neglected. The particle size has been calculated using Equ.3. The particle size of ZnO and Cu doped ZnO is found to lie in the range of 39-26 nm.

4. Conclusions

ZnO and Cu doped ZnO nanoparticles have been prepared by chemical precipitation method.   X-ray diffraction results reveal that ZnO and Cu doped ZnO nanoparticles exhibit cubic zinc blende structure. The average particle size of the nanoparticles is found to be in the range of 26-39 nm. The PL spectra of undoped and Cu doped ZnO samples shows blue emission and a rapid luminescence quenching was observed with increasing Cu concentration. The absorption edge of Cu doped ZnO nanoparticles is found to be shifted towards longer wavelength side when compared to that of undoped ZnO and the band gap is observed to lie in the range of 4.18 – 4.23 eV. The nanoparticles with lower Cu concentration exhibited strong ferromagnetism, whereas in samples with higher Cu concentrations the ferromagnetism was found to be suppressed.

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