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Structural and Optical Study of Zn doped CuO Nano Particles Synthesized by Sol Gel Method

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ABSTRACT: In this work we have determined structural and optical properties of Zn-Doped CuO nanoparticles [$Zn_xCu_{1-x}O$ where = 0.1, 0.3, 0.5, 0.7 and 0.9] prepared by sol gel method. Different samples were prepared by changing the concentration of zinc. Prepared samples were studied using X-ray diffraction and analysis shows that particles size increases with increase in zinc concentration from 24.2nm to 49.9nm. UV-VIS spectroscopy shows that band gap increase with increase in zinc concentration from 2.15 eV to 2.53 eV.

Keywords: Nanomaterials, XRD, UV-VIS, Band gap, Doped metal oxide

I. INTRODUCTION

Zn-doped copper oxide nanoparticles or copper–zinc–oxide nanocomposites have been intensively studied due to its major potential for applying to wide range of applications, such as optical coatings, light-emitting diodes, laser diodes and catalysts. Recently, the unique properties demonstrated in Cu-doped zinc oxide nanoparticles have gained great interest for developing a wide range of advanced applications including field effect transistors [1,2], field emission arrays, ultraviolet lasers, light emitting diode [3], sensors, biosensors [4, 5], catalyst [6, 7], energy storage and solar cell [8]. The advanced functional properties of nanostructure materials are due to several factors such as high surface mass ratio, selective control surface terminal, different local structure from bulk, magnetic property and also electronic structure. Various techniques have been used to synthesize Zn-doped copper oxide nanoparticles and copper–zinc–oxide nanocomposites by many researches such as hydrothermal, co-precipitation, sono-chemical and ball milling. But here in the present study we have synthesized zinc doped copper oxide nanoparticles by sol-gel method. Five samples were prepared by taking different concentration of starting materials.

II. METHOD AND MATERIALS

All the reagents used for the preparation of samples [$Zn_xCu_{1-x}O$ where =0.1, 0.3, 0.5, 0.7 and 0.9] are of analytical grade. Zinc Nitrate $Zn(NO_3)_2$. $6H_2O$, Copper Nitrate $Cu(No_3)_2.3H_2O$ and Ethanol (CH_3CH_2OH) were used as raw Materials and poly vinyl alcohol(PVA) as the sol-gel forming solvent. For synthesis of $Zn_{0.1}Cu_{0.9}O$, we took 2.9748 g of $Zn(NO_3)_2$ .6 H_2O and 21.744 g of $Cu(No_3)_2$.$3H_2O$. We have mixed 50 ml of ethanol in 50 ml of distilled water. Then we added these two nitrates($Zn(NO_3)_2$. $6H_2O$ and Copper Nitrate $Cu(No_3)_2.3H_2O$) in this solution with continuous stirring. Further we have added 5g of PVA in this mixture. Final mixed solution was heated at 80°C and continuous stirring has been carried out during this heat treatment. After about one hour of heating a gel, starts to appear. The solution is heated till whole solution is converted into gel. Then this gel is dried for 24 hrs and then crushed and calcinated at 400°C. Similarly we have prepared other samples by increasing the concentration of zinc nitrate and decreasing the concentration of copper nitrate [$Zn_xCu_{1-x}O$ where x = 0.1, 0.3, 0.5, 0.7 and 0.9]. The final powder is taken out for characterization [9].

III. RESULT AND DISCUSSION

A. XRD Analysis

The typical XRD pattern of nanoparticles of $Zn_{0.1}Cu_{0.9}O$, $Zn_{0.3}Cu_{0.7}O$, $Zn_{0.5}Cu_{0.5}O$, $Zn_{0.7}Cu_{0.3}O$ and $Zn_{0.9}Cu_{0.1}O$ annealed at 400°C are shown in Figure 1. It gives a single-phase with a monoclinic structure. In the diffraction pattern, all peaks are well indexed to the monoclinic phase of copper oxide (CuO confirmed from JCPDS card No. 05-0661.

The main peaks at 2θ = 35.62 and 38.73 corresponding to (002) and (111) planes are the characteristics peaks for monoclinic phase of pure CuO nanoparticle. Furthermore, the sharpness of the peaks in the diffraction pattern indicates the formation of highly crystalline single phase Zn doped CuO nanoparticles. These finding indicate that the crystal structure of the base CuO matrix was not distorted by the substitution of Cu^{+2} ions by Zn^{+2} ions in the CuO system.

The crystalline size was calculated using the Scherer formula [10]

$$D = 0.9\,\lambda/\,\beta\cos\theta \qquad \ldots(1)$$

where λ is the wavelength of X-ray radiation, β is the full width at half maximum (FWHM) of the peaks at the diffracting angle θ. Crystallite size calculated by the Scherer formula of each sample was shown in table. The average crystallite size of Zn-doped CuO nanoparticles is found to be 25-60 nm using Scherrer formula.

The increase in crystallite size can be explained by the lattice distortion induced by Zn doping, which can be attributed in terms of Vegard's law which states that the change in crystallite size may be due to the difference between ionic radii of replacing and replaced ions [10]. In the present system, the increase in crystallite size is because of the greater ionic radii of Zn^{+2} (0.74 Å) ions compared to that of Cu^{+2} (0.73 Å). Therefore, this observation could be possible from Zn^{+2} replacement of Cu^{+2} in the CuO lattice structure [11]. Fig. 1 shows the XRD graph of all five samples. Table 1 shows two intense peak of each sample from their respective graph.

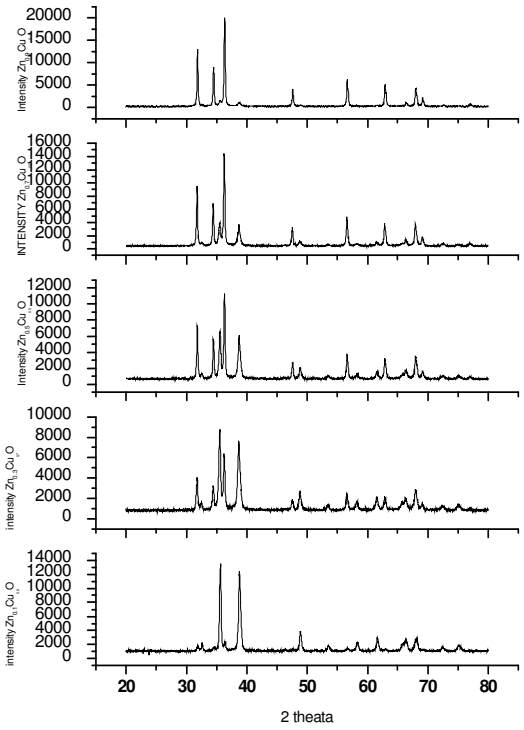

Fig. 1. Comparative analysis of XRD of all five samples.

Table 1.

Name of sample	2θ	D(nm)	FWHM	Relative intensity	Particle size(nm)
$Zn_{0.1}Cu_{0.9}O$	38.73	2.3230	0.364	100.00%	24.2
	35.620	2.5184	0.281	84%	31
$Zn_{.3}Cu_{0.7}O$	38.619	2.3294	0.472	100%	18.6
	35.521	2.5252	0.338	91.43%	25.8
$Zn_{.5}Cu_{0.5}O$	36.300	2.4728	0.213	100%	41
	38.647	2.3278	0.396	84.72%	22.2
$Zn_{0.7}Cu_{0.3}O$	36.247	2.4763	0.205	100%	42
	31.759	2.8152	0.186	61.22%	47.1
$Zn_{0.9}Cu_{0.1}O$	36.332	2.4709	0.191	100%	45.8
	31.845	2.8078	0.173	58.35%	49.9

B. UV -VIS Analysis

UV-visible absorption spectra of synthesized Zn doped CuO nanoparticles have been recorded by UV- visible spectrophotometer in the range of wavelength between 200 nm to 800 nm at room temperature. The optical energy band gap was calculated using Tauc relation

$$(\alpha h\nu)^2 = \mathrm{A}(h\nu - \mathrm{E}g) \qquad \ldots(2)$$

Where *A* is a constant that depends on the transition probability, *Eg* is the optical band gap energy, *h* is the Plank constant and *v* is the frequency. Assuming that the transition probability was 1, the equation could be simplified as listed below.

$$(\alpha h\nu)^2 = h\nu - \mathrm{E}g \qquad \ldots(3)$$

$$h\nu = hC/\lambda = 1240/\,\lambda \qquad \ldots(4)$$

Using equation(4) the equation (3) could be translated into the equation (5) listed below.

$$(\alpha 1240/\lambda)^2 = 1240/\lambda - Eg \quad \ldots(5)$$

In the equation (4), α is the absorption value in the UV-VIS spectrum that could be detected by UV-VIS spectrophotometer, while λ is the detection wavelength. Figure (2) shows the UV-VIS spectrum of all samples. According to the equation (4), figure (3) was achieved by treating $(\alpha h\nu)^2$ as Y axis and hν as X axis. The Eg(eV) could be estimated by extrapolating a straight line to the $(\alpha h\nu)^2 = 0$ axis in the plots of the $(\alpha h\nu)^2$ versus optical band gap energy [12].

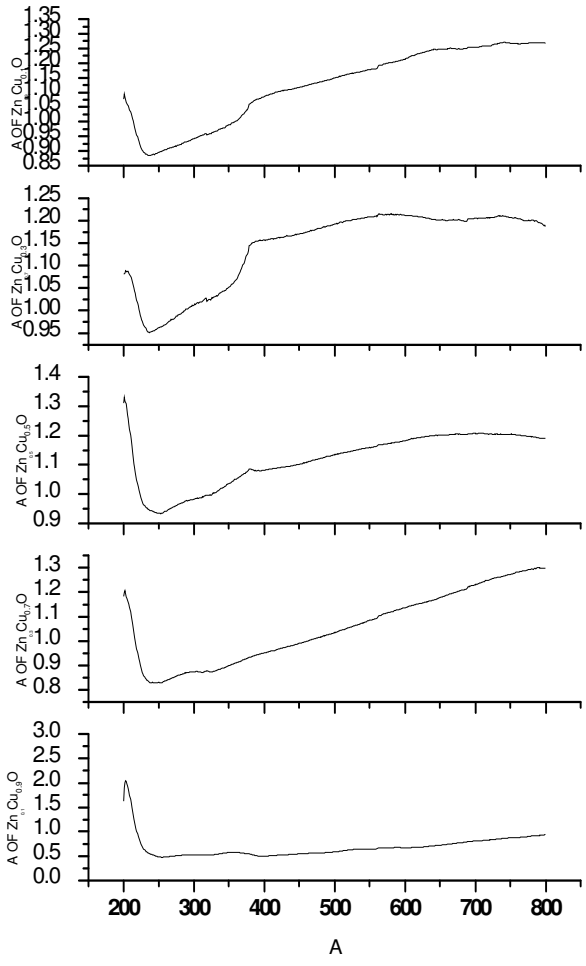

Fig. 2

The energy band gap of Zn doped CuO nanoparticles $Zn_{0.1}Cu_{0.9}O$, $Zn_{0.3}Cu_{0.7}O$, $Zn_{0.5}Cu_{0.5}O$, $Zn_{0.7}Cu_{0.3}O$ and $Zn_{0.9}Cu_{0.1}O$ is calculated to be 2.15, 2.31, 2.40, 2.47 and 2.53eV respectively.

It is evident from the Fig. (5) that with increasing Zn content, the energy band gap was slightly increasing. This increase in the band gap can be attributed to the well-known quantum size effect of semiconductors. In general, when the light is absorbed by a material, the electron jumps to the conduction band by leaving a hole in the valance band. But, if the particle size is small, it behaves like a quantum well and the energy difference between the position of conduction band and a free electron leads to the quantization of their energy levels. The fig. 2 depicts the optical absorption spectrum of of $Zn_{0.1}Cu_{0.9}O$, $Zn_{0.3}Cu_{0.7}O$, $Zn_{0.5}Cu_{0.5}O$, $Zn_{0.7}Cu_{0.3}O$ and $Zn_{0.9}Cu_{0.1}O$.

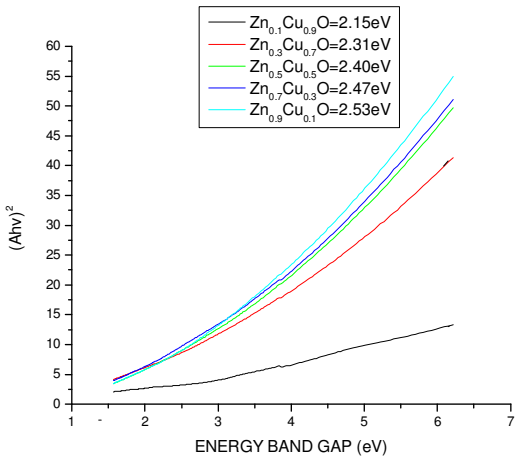

Fig. 3.

And the the Fig. 4 shows the comparative value of band gap energy of all samples. Table 2 gives the value of band gap of each sample as found by above method.

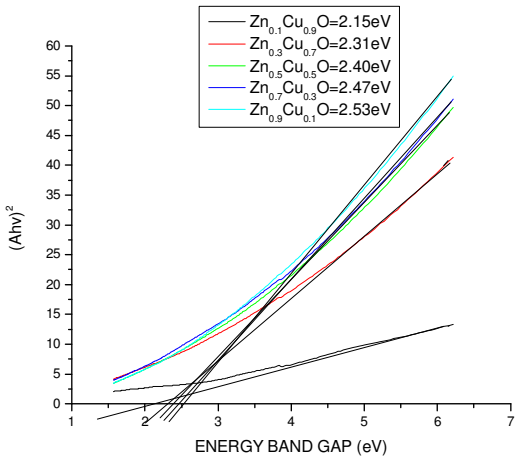

Fig. 4.

Table 2.

S.N.	Name of Sample	Band Gap Energy (eV)
1.	$Zn_{0.1}Cu_{0.9}O$	2.15
2.	$Zn_{0.3}Cu_{0.7}O$	2.31
3.	$Zn_{0.5}Cu_{0.5}O$	2.40
4.	$Zn_{0.7}Cu_{0.3}O$	2.47
5.	$Zn_{0.9}Cu_{0.1}O$	2.53

So from UV-VIS analysis we see that as we increase the concentration of zinc ,band gap increases. Fig (5) depicts it in graphical way

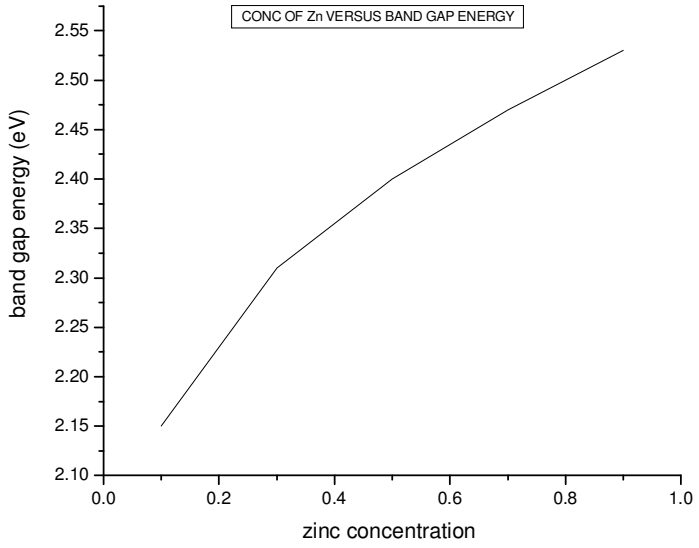

Fig. 5.

IV. CONCLUSION

Zn doped CuO nanoparticles have been synthesized by sol gel method.. We have seen the effect of Zn doping on the structural and optical properties of CuO nanoparticles. The formation of monoclinic phase of Zn doped CuO were confirmed from the XRD patterns where Zn^{+2} ions substituted Cu^{+2} ions. The crystallite size ranged from 25 nm to 60 nm. It was observed that there was a increase in the crystallite size with increasing Zn concentration due to large radius of Zn ion as compared to Cu ion. All of the doped samples showed a blue shift in the optical band gap, which can be assigned to the quantum confinement effects. There was a slight increase in the energy band gap of Zn doped CuO nanoparticles from 2.15 eV to 2.53 eV with increasing Zn content . We also conclude that sol gel method is a very nice and simple method to prepare these nanoparticles which are all crystalline in nature as obvious from XRD samples.

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