

Structural, Morphological, and Optical Properties of Pure and Copper doped Zinc Oxide Nanoparticles prepared by Co-precipitation Technique

S. S. Dange, S. N. Dange

Abstract— Pure and Copper-doped Zinc Oxide (ZnO) nanoparticles were synthesized using a microwave-assisted co-precipitation method. The copper doping concentration was varied to 5 wt% and 10 wt%, while the pH of the bath solution was kept constant. The structural, morphological, and optical properties of the synthesized nanoparticles were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-visible spectroscopy, and photoluminescence (PL) spectroscopy. The XRD analysis confirmed that both pure and Cu-doped ZnO nanoparticles exhibit a hexagonal wurtzite structure, with a shift in the XRD peak positions for the Cu-doped samples. SEM images revealed irregular morphology for pure ZnO and 10 wt% Cu-doped ZnO nanoparticles, whereas 5 wt% Cu-doped ZnO nanoparticles displayed a spherical morphology with an average particle size ranging between 50-100 nm. The optical band gap decreased for 5 wt% Cu doping concentration. PL spectroscopy indicated a reduction in the intensity of the near-band-edge emission with increasing Cu content.

Keywords: ZnO, Nanoparticles, Cu doping, Co-precipitation method

I. INTRODUCTION

Zinc oxide (ZnO) is an II-VI direct wide-bandgap semiconductor known for its exceptional properties, making it suitable for diverse applications such as gas sensors, transparent conductors, and piezoelectric devices [1,2]. It has a relatively large bandgap of 3.37 eV and a high exciton binding energy of 60 meV at room temperature [3]. Additionally, ZnO exhibits various morphologies, including nanorods, nanosheets, nanobelts, and microalmonds [4-8].

The structural and morphological properties of ZnO can be modified by doping with transition metals [9]. Among these metals, Copper (Cu) is a commonly used dopant as it introduces both an electron donor state (Cu^{2+}) and an acceptor.

State (Cu^+ , $3d^{10}$) within ZnO's bandgap [10,11]. Several synthesis techniques, such as sol-gel, spray pyrolysis, ultrasonic, chemical vapor deposition, and co-precipitation have been employed to produce ZnO nanoparticles [12-17]. Among these, the co-precipitation method is particularly popular due to its simplicity, low cost, and controllability [18].

In the present work, pure and copper doped zinc oxide nanoparticles were synthesized by the co-precipitation method assisted by microwave irradiation. The microwave oven was used for uniform and fast heating.

II. MATERIALS AND METHOD

A. Synthesis of pure and Copper doped zinc oxide nanoparticles:

The chemicals used in this work were analytic reagent grade (SDFCL) and used as received without further purification. For the synthesis of pure ZnO nanoparticles, 0.1M zinc nitrate solution was prepared in double distilled water. Aqueous ammonia solution (sp.gr. 0.91) was added drop wise to the above solution till the pH of the bath solution became 8. The obtained milky solution was irradiated in microwave oven (SAMSUNG 900W) for 15 minutes. After that, the precipitate was washed with double distilled water and ethanol several times and further annealed at 300°C for 2 hours. For the synthesis of 5wt% and 10wt% copper doped zinc oxide nanoparticles, the above process was repeated by mixing zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) with copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) in a proportional ratio by weight.

The structural properties of the prepared samples were studied from an X-ray diffraction pattern recorded using an X-ray diffractometer (Miniflex-II) of Cu-K α radiation of wavelength $\lambda = 0.1541$ nm. The morphology of the samples was investigated by using a scanning electron microscope SEM-EDAX (ZIESS Ultra55 FESEM) and the optical absorption spectra were recorded using a UV-VIS spectrophotometer (SHIMADZU UV-1800). The photoluminescence (PL) spectra of the samples were recorded using a fluorescence spectrometer (PerkinElmer LS 55) with a xenon lamp as an excitation source.

III. RESULTS AND DISCUSSION

A. XRD Analysis

Figure 1 (a) shows the XRD pattern of pure and Copper doped Zinc Oxide nanoparticles. The peak positions of the

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XRD pattern are in good agreement with the standard JCPDS card no.36-14519.

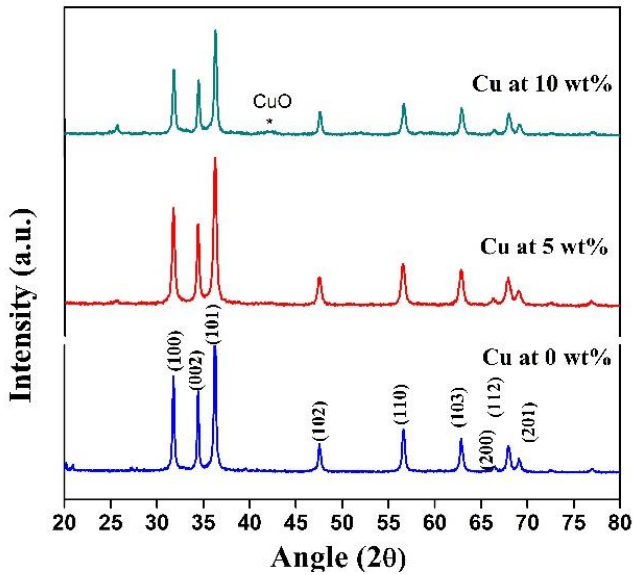


Figure: 1 (a) XRD pattern of pure and Cu doped ZnO nanoparticles.

The samples with Cu doping at 5wt% are in a single phase and no peak corresponding to Cu related phase or any other impurity phase is seen indicating that Cu ions have been added to the ZnO lattice. The samples with Cu doping at 10wt% show a small trace of CuO near 42° indicating a small mixture of CuO secondary phase with ZnO. The shift in XRD peaks can be seen in Figure 1 (b) suggesting that there are structural changes due to the substitution of Zn by Cu ions in the ZnO.

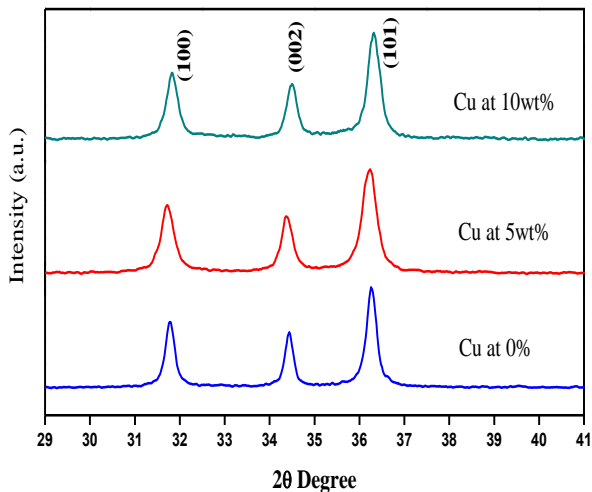


Fig. 1 (b) magnified XRD pattern.

The lattice constants of the crystals shown in Table (1) are calculated from the following equation.

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

The average crystallite size (D) is determined from the most intense diffraction peak (101) using Debye-Scherrer's equation,

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

The strain (ϵ) of the crystallites is calculated from the most intense peak (101) using the equation :

$$\epsilon = \frac{\beta \cos\theta}{4}$$

Table 1: Crystallite size, lattice parameter, and micro-strain of ZnO nanoparticles

Cu doping	Size (nm)	Lattice constant (Å)		Microstrain (ϵ)
		a=b	c	
0wt%	30.43	3.252	5.210	1140
5wt%	20.51	3.258	5.220	1691
10wt%	23.78	3.247	5.201	1459

Table 1 shows that the average crystallite size is in the range of 20-30nm and the addition of Cu leads to a decrease in crystallite size. The value of lattice parameters increases for Cu doping at 5wt% and decreases for Cu at 10wt%. The strain of the crystallites observed is in the range of 1100-1700 micron.

B. SEM Analysis

Fig. 2 (a,b,c), shows the SEM images of pure and copper doped ZnO nanoparticles. Fig. 2(a) shows that the pure ZnO nanoparticles have asymmetric and irregular morphology. Fig. 2(b) shows that at Cu 5wt% doping the morphology becomes uniform and distinct spherical like. Fig 2(c) shows that at Cu 10% doping the particle structure becomes comparably more distorted. The average particle size seen from the images of pure and Cu doped samples is about 50-100nm.

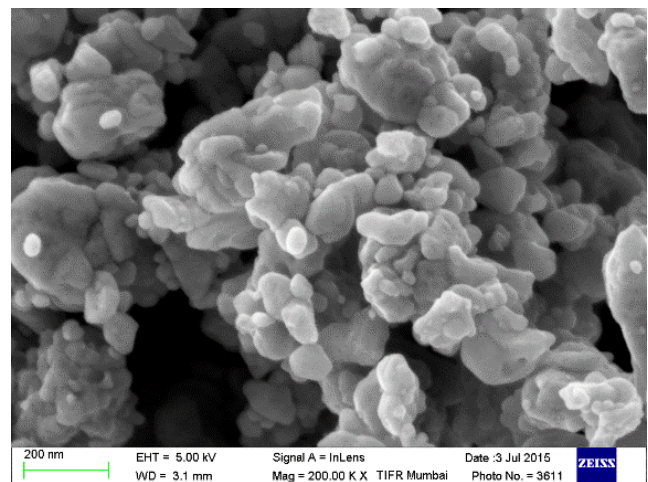


Fig. 2 (a) SEM of Pure ZnO nanoparticles

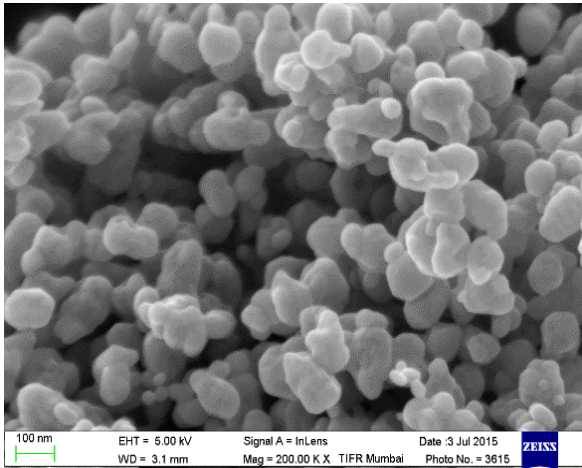


Fig. 2(b) SEM of 5wt% Cu-doped ZnO nanoparticles

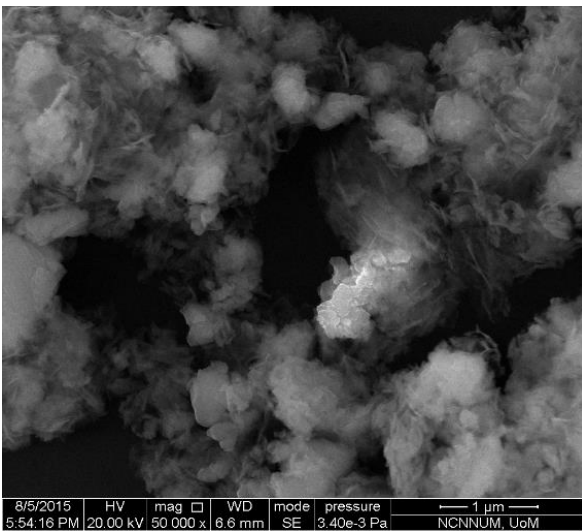


Fig. 2(c) SEM of 10wt% Cu-doped ZnO nanoparticles

C. UV-vis Analysis

The UV-visible optical absorption spectra of pure and Cu doped ZnO nanoparticles were obtained at room temperature from 350 to 600 nm.

The band gap energy for the samples has been calculated using the Tauc's relation.

$$(\alpha h\nu)^{\frac{1}{n}} = A(h\nu - E_g)$$

Where, 'A' is a constant, 'E_g' is the optical band gap energy of the material and the exponent 'n' depends upon the kind of electronic transition causing the absorption. The values of n are selected as 1/2 or 2 depending upon direct or indirect transition, respectively [18]. The graphs of (αhν)² versus hν (Tauc Plot) of pure and Cu doped ZnO are shown in Fig. 3(a, b, c).

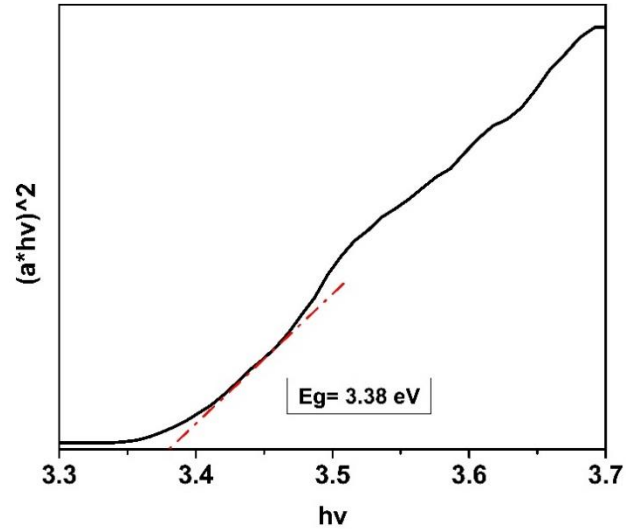


Fig 3 (a): The graph of (αhν)² versus hν of pure ZnO

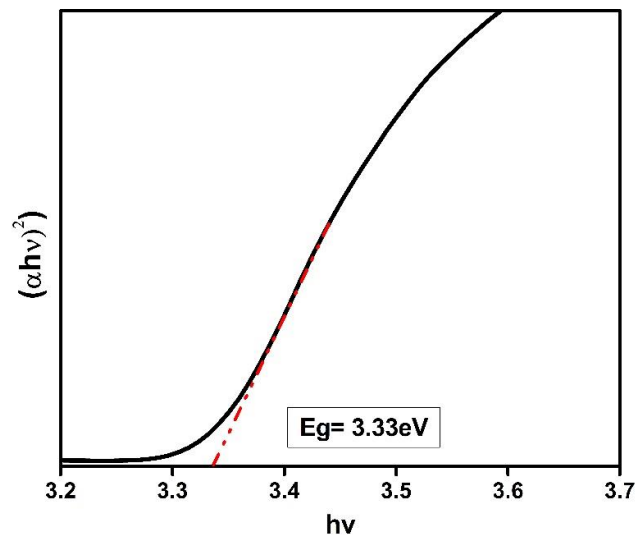


Fig 3 (b): The graph of (αhν)² versus hν of 5 wt% Cu doped ZnO.

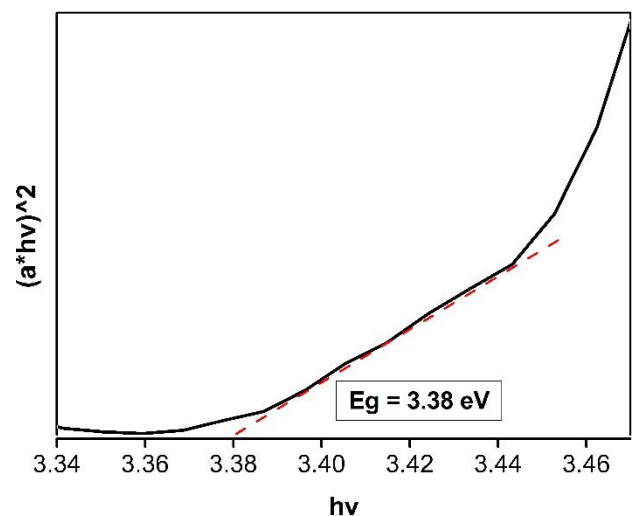


Fig 3 (c): The graph of (αhν)² versus hν of 10 wt% Cu doped ZnO.

The optical band gap energy for pure ZnO nanoparticles is found to be 3.38 eV. It is seen that the band gap energy decreases to 3.33 eV due to 5 wt % of Cu doping in ZnO and it increases again to 3.38 for 10 wt% of Cu doping. The impact of Cu doping in ZnO on the band gap was also observed in a similar manner by Muthukumar et al [19].

D. PL Analysis

The photoluminescence spectra of all the samples at room temperature are shown in Fig. 4.

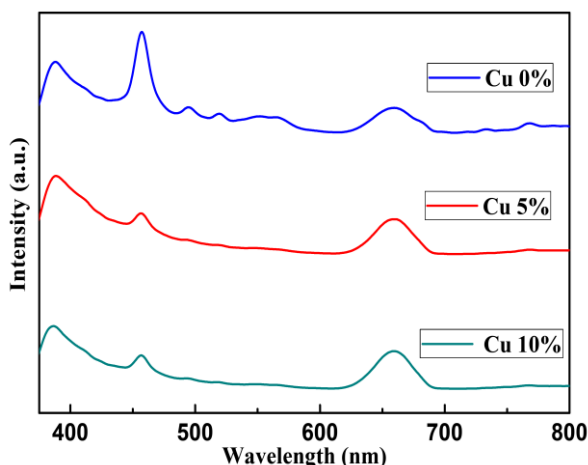


Fig 4. PL spectra of ZnO nanoparticles

The first peak, centered around 387nm, is assigned to the near-band edge (NBE) or free exciton emission. No considerable change in the position of this peak is observed due to Cu doping. The peak centered at 457nm is considered to be the result of the formation of a shallow acceptor level. The intensity of this peak is observed to be reduced due to Cu doping of ZnO with no change in peak position. This might be due to the scattering of the excitation radiation by surface-adsorbed dopant atoms [10]. Also, Cu impurity may introduce a non-radiative recombination process that reduces the PL emission [18].

IV. CONCLUSION

Pure and Copper doped ZnO nanoparticles have been synthesized by microwave assisted co-precipitation method. The microwave oven is used for uniform and fast heating. The effects of copper dopant on the structural, morphology, and optical properties have been studied through XRD, SEM, UV-vis, and PL spectroscopy. XRD pattern shows that the crystals have a hexagonal wurtzite structure. The XRD results revealed that slight changes in the lattice parameters have occurred due to the substitution of Cu. The Size of the particles is around 50-100 nm. The optical bandgap energy decreases for 5wt% Cu doped ZnO to 3.33eV. PL spectroscopy indicated a reduction in the intensity of the near-band-edge emission with increasing Cu content. Cu-doped ZnO nanoparticles hold future potential in optoelectronic devices, photo catalysis, and energy storage due to their properties like tunable bandgap and improved conductivity. They also show promise in gas sensing, solar cells, and spintronic devices, with challenges in optimizing synthesis, stability, and doping levels for advanced applications.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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