# Effect of CuO loading on Structural Properties of ZnO

#### M. K. Deore

Material Research Laboratory, Department of Physics, M. V. P. Samaj's, Arts, Science and Commerce College, Ozar (Mig) 422206, India

Abstract: Copper Chloride (CulCl<sub>2</sub>.  $2H_2O$ ) (Hexahydrate) powder of different weight percent (1 3, 5 and 7 wt %) where loaded in Analar Reagent grade (99.9 % pure) ZnO powder by mixing mechnochemically in acetone medium. The prepared materials were sintered at 1000°C for 12h in air ambience and ball milled to ensure sufficiently fine particle size. The structural properties of the powder materials were investigated by X-ray diffraction analysis. The observed powder materials show the polycrystalline nature and the crystallite size found to be in the range of 23 to 35 nm. The lattice parameters of all powder samples were determined.

Keywords: ZnO, CuO, XRD, Crystallite size, d-spacing, Lattice constants

### 1. Introduction

A composite material is a material made from two or more constituent materials with significantly different physical or chemical properties that, when combined, produce a material with characteristics different from the individual components. More recently, researchers have also begun to actively include sensing, actuation, computation and communication into composites, [1]. CuO-ZnO Composite structures having Optoelectronics, Sensing and Catalytic Applications.

ZnO is a II–VI group compound semiconductor with a hexagonal wurtzite crystal structure. It has a wide and direct band gap of 3.37 eV at 300 K and a large free exciton binding energy of 60 meV. It has unique physical and chemical properties, low-dimensional volume, high aspect ratio, light-matter interaction, cost-effectiveness and can be synthesized by various chemical and physical methods ZnO has become one of the most popular materials for electrical and optical applications over the time. It is promising material for many optoelectronic applications such as ultraviolet lasers, light-emitting diodes, p–n junction devices, thin-film transistor, solar cells, acoustic devices, chemical and biological sensors, areas like SAW devices, varistors, transparent electrodes, gas sensors[2-15].

On the other hand, cupric oxide (CuO) is p-type semiconductors having band gap energy of 1.21 to 1.51 eV. CuO is an attractive material for photovoltaic applications since it has advantages of a relatively high absorption coefficient in the visible region, low cost production, and is non-toxic. CuO has been established as a number of applications like in various fields such as dye sensitized solar cells, gas sensors, bio-sensors, nanofluid, photo detectors, energetic materials (EMs), field emissions, super capacitors, removal of inorganic pollutants, photo catalysis and magnetic storage media, gas sensors, solar photovoltaic, lithium ion electrode etc[16-27].

In order to obtain better crystallization quality and better optical and electrical properties, researchers have performed doping in metal oxides. Doping of the base martial was carried out by adding the additives in the base material. Zinc is an important transition metal element and  $Zn^{2+}$  has close ionic radius parameter to that of  $Cu^{2+}$ , which means that Zn can easily penetrate into CuO crystal lattice or substitute Cu position in the crystal [28, 29].

#### 2. Experimental Procedure and Results

#### 2.1 Synthesis of composite material

CuO - ZnO composite material were obtained by adding the Copper chloride (CuCl<sub>3</sub> •6H<sub>2</sub>O) (Hexahydrate) powder of different weight percent (0.5, 1 3, 5 and 7 wt %) with Analar Reagent grade (99.9 % pure) ZnO powder by mixing mechnochemically in acetone medium. The prepared materials were sintered at 1000oC for 12h in air ambience and ball milled to ensure sufficiently fine particle size.

#### 3. Physical Characterization

#### **3.1 Structural analysis**

In order to understand the structural properties of pure ZnO and CuO loaded ZnO powder materials at different doping concentration, X-ray diffraction analysis of these sintered powders were carried out using Cuka radiation

Fig. 1 (a- e) shows the XRD pattern of unloaded- ZnO and CuO loaded ZnO composite material with different doping concentration concentrations. The observed diffraction peaks correspond to the hexagonal wurtzite structure of ZnO (JCPDS 76-0704) and monoclinic phase of CuO (JCPDS 22-1107). The observed ZnO phase has preferred orientation in (101). The sharp peaks of XRD are corresponds to ZnO and CuO materials and are observed to be polycrystalline in nature. The higher peak intensities of an XRD pattern are due to the better crystallinity.



Figure 1: XRD pattern pure ZnO and CuO loaded ZnO composite material.

Fig. 1(b, c) shows that the in the XRD pattern of CuO loaded ZnO composite materials (1 and 3 wt. %) there was no prominent peaks of CuO are observed. It is due to low concentration of dopant as compared to base material (ZnO). Also it implies that copper atoms replace zinc in the hexagonal lattice and/or copper segregate to the non-crystalline region in the grain boundary [30].

Fig. 1 (d, e) shows that the in the XRD pattern of CuO loaded ZnO composite materials (5 and 7 wt. %) the some traces of CuO are present in it. It may indicate that the solid solubility of Cu in ZnO has been exceeded. CuO peaks of corresponding to the planes (002) and (111) are observed.

The average crystallite size was calculated from XRD data based on Debye Scherer's formula equation (5.1) [31, 32].

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$
(1)

Where

D- is average crystallite size,

 $\beta$  - is the broadening of the diffraction line measured at half maximum intensity(FWHM)

- $\lambda$  -is wavelength of the x- ray radiation and (0.1542 nm).
- $\theta$  is the Bragg angle

The d-spacing of the planes corresponding to the different observed peaks, FWHM, crystallite size and hkl-planes of the pure ZnO and CuO –loaded ZnO materials are listed in Table 1

| rr                  |            |                      |                               |       |                              |                 |  |  |  |  |
|---------------------|------------|----------------------|-------------------------------|-------|------------------------------|-----------------|--|--|--|--|
| Doping<br>level     | Sr.<br>No. | 2 <i>θ</i><br>(deg.) | Observed<br>d- Spacing<br>(Å) | FWHM  | Crystallite<br>Size<br>D(nm) | Planes<br>(hkl) |  |  |  |  |
| Pure ZnO            | 1          | 31.70                | 2.82                          | 0.265 | 35                           | Z-100           |  |  |  |  |
|                     | 2          | 76.90                | 1.22                          | 0.422 | 27                           | Z-202           |  |  |  |  |
| 1wt% CuO<br>loading | 1          | 31.70                | 2.82                          | 0.267 | 34                           | Z-100           |  |  |  |  |
|                     | 2          | 76.90                | 1.24                          | 0.436 | 26                           | Z-202           |  |  |  |  |
| 3wt% CuO<br>loading | 1          | 31.70                | 2.82                          | 0.276 | 33                           | Z-100           |  |  |  |  |
|                     | 2          | 76.90                | 1.24                          | 0.413 | 27                           | Z-202           |  |  |  |  |
| 5wt% CuO<br>loading | 1          | 31.80                | 2.81                          | 0.259 | 35                           | Z-100           |  |  |  |  |
|                     | 2          | 76.90                | 1.23                          | 0.423 | 27                           | Z-202           |  |  |  |  |
| 7wt% CuO<br>loading | 1          | 31.70                | 2.81                          | 0.299 | 31                           | Z-100           |  |  |  |  |
|                     | 2          | 76.90                | 1.23                          | 0.496 | 23                           | Z-201           |  |  |  |  |

 Table 1: XRD data of pure ZnO and CuO loaded ZnO composite materials

Table 1 shows the variation of crystallite size of pure ZnO and CuO loaded ZnO composite material with different concentration of dopant. It has been observed that the increased dopant concentration decreases in crystallite size. Slightly broadening of diffraction lines may be attributed to small crystalline effects or chemical heterogeneity of the samples. For planes and (202) the crystallite size decreases.

From the XRD pattern, the lattice constants of hexagonal ZnO phase in all doping concentrations can be calculated using the equation [31, 32]

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

Where 'd' is interplanar distance,

$$\frac{c}{a} = \sqrt{\frac{8}{3}}$$
(3)

'a' and 'c' are lattice constants.)(Being hexagonal structure).

**Table 2:** Lattice constants of pure and CuO loaded ZnO

| Phase         | hkl-<br>Plane | 20    | d (Å)  | a (Å) | c (Å) |  |  |  |  |
|---------------|---------------|-------|--------|-------|-------|--|--|--|--|
| ZnO(Pure)     | 202           | 76.90 | 1.2237 | 3.199 | 5.224 |  |  |  |  |
| ZnO-CuO(1wt%) | 202           | 76.90 | 1.2388 | 3.238 | 5.288 |  |  |  |  |
| ZnO-CuO(3wt%) | 202           | 76.90 | 1.2393 | 3.240 | 5.290 |  |  |  |  |
| ZnO-CuO(5wt%) | 202           | 76.90 | 1.2372 | 3.234 | 5.281 |  |  |  |  |
| ZnO-CuO(7wt%) | 202           | 76.90 | 1.2379 | 3.236 | 5.284 |  |  |  |  |

The calculated values of lattice constants are given in Table 2, From the Table 2, it has been observed that there is variation of lattice constants from JCPDS value (a = 3.25 Å, c = 5.207 Å) of ZnO. The slight increase in lattice parameter

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revealed that the ionic size of tetrahedrally coordinated  $Cu^{2+}$  is larger than  $Zn^{2+}$ . The reason of increment may be due to the nonuniform substitution of Cu ion into the Zn site as the radius of Cu2+ ion is smaller than the  $Zn^{2+}$  ion [33, 34].

# 4. Summary and Conclusions

From the results obtained, following conclusions can be made;

- i) It shows that the CuO –ZnO functional material can be obtained by mechanochemical method.
- ii) The XRD analysis shows that the observed powder materials show the polycrystalline nature and the variation in the crystallite size due to doping. The crystallite size was found to be in the range of 23 to 35 nm.
- iii) It has been observed that there is variation of lattice constants from JCPDS value (a = 3.25 Å, c = 5.207 Å) of ZnO. The slight increase in lattice parameter revealed that the ionic size of tetrahedrally coordinated  $Cu^{2+}$  is larger than  $Zn^{2+}$ . The reason of increment may be due to the nonuniform substitution of Cu ion into the Zn site as the radius of  $Cu^{2+}$  ion is smaller than the  $Zn^{2+}$  ion
- iv) CuO loaded ZnO functional material would be used for the preparation of thick films and thick films would be use full for gas sensing application.

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### **Author Profile**



M. K. Deore (India) is currently an Associate Professor of Physics at M. V. Samaj's, Arts, Science and Commerce, College, Ozar(Mig), India. He received his M. Sc. degree in Physics and Ph. D. degree from the Savitribai Phule Pune University,

Pune, India. He has 27 years of teaching experience. He is recognized guide for M. Phil of Savitribai Phule Pune University. His areas of interest are nanomaterial and metal oxide semiconductor gas sensor. He has published 24 research articles extensively on the above topics in various refereed International Journals and book chapters. He has reviewed the research papers for International Journals Sensor Review, Sensor Letters, Journal of Advanced Physics, Material Science. He has presented 22 research articles in International, National and state level conferences held at Stony Brook University, Long Island, New York State, USA (2015), Palmerston North New Zealand (2011), Tainan (Taiwan),

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Shilong (Meghalaya), Kolkata(W.B.), Bhopal(U.P.), Amritsar (Panjab, ), Chennai(Tamilnadu, ), Mumbai(M.S.), He has organized one State level and one National level conference at A. S. C. College, Ozar (Mig)(India). He has received best paper presentation award in Indian Science Congress held at Shilong(Meghalaya) in 2009 and 2<sup>nd</sup> best paper presentation award in National Conference on Development of Electronic Materials and Their Applications held at Shivaji University, Kolhapur, 6-8, 1995.