

Effect of CuO loading on Structural Properties of ZnO

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Abstract: Copper Chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) (Hexahydrate) powder of different weight percent (1, 3, 5 and 7 wt %) were loaded in Analar Reagent grade (99.9 % pure) ZnO powder by mixing mechanochemically 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 material 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 ($\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$) (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 mechanochemically 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.

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 $\text{CuK}\alpha$ 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.

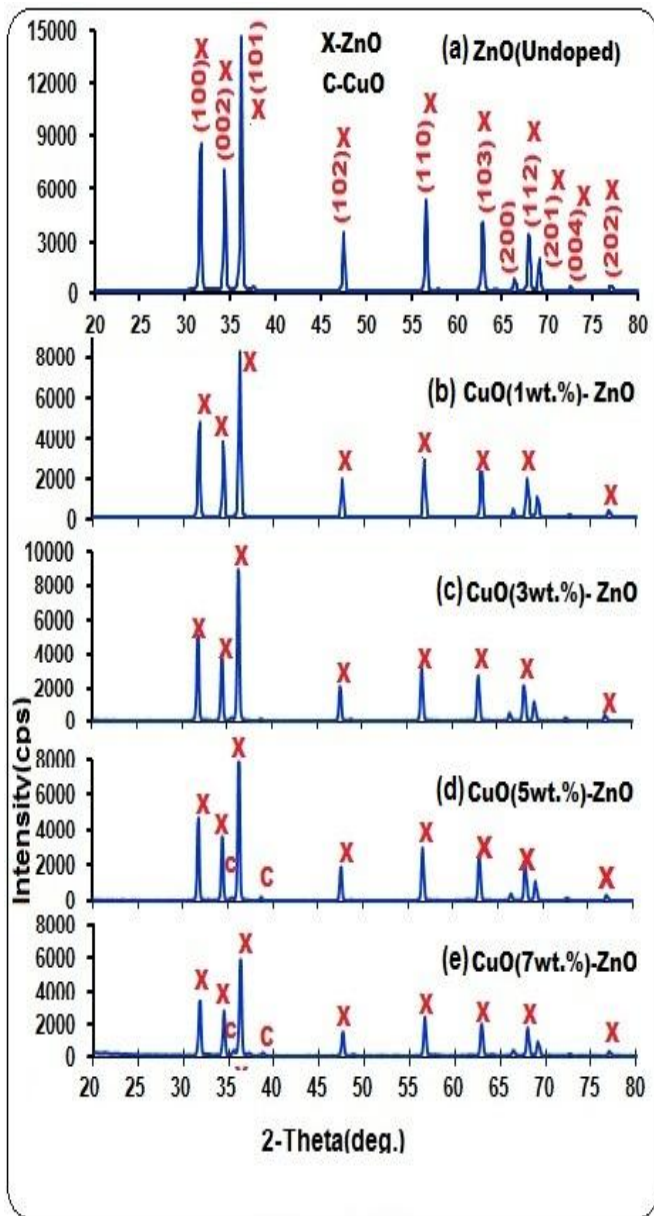


Figure 1: XRD pattern pure ZnO and CuO loaded ZnO composite material.

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

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

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

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

Where

D- is average crystallite size,

β - is the broadening of the diffraction line measured at half maximum intensity (FWHM)

λ - is wavelength of the x- ray radiation and (0.1542 nm).

θ - 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

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

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

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 the crystallite size. Slightly broadening of diffraction lines may be attributed to small crystalline effects or chemical heterogeneity of the samples. For planes (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]

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

Where „d“ is interplanar distance,

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

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

Table 2: Lattice constants of pure and CuO loaded ZnO

Phase	hkl-Plane	2θ	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

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 [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 ($a = 3.25 \text{ \AA}$, $c = 5.207 \text{ \AA}$) 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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