Structural Characterization of Cu-doped ZnO (Zn$_{1-x}$Cu$_x$O) Using Solid State Reaction Method.

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Abstract: Cu-doped Zinc oxide was successfully synthesized by solid-state reaction method. Five compositions of Zn$_{1-x}$Cu$_x$O with x = 0.01, 0.03, 0.10, 0.20 and 0.30 were prepared at calcination & sintering temperature 500°C using the starting materials Zn(CH$_3$COO)$_2$ and Cu(CH$_3$COO)$_2$. In this paper the structural property has been characterized using powder X-ray diffraction (XRD). To study structural property it has been used two composition of Zn$_{1-x}$Cu$_x$O with x = 0.01, 0.10 (Zn$_{0.99}$Cu$_{0.01}$O & Zn$_{0.90}$Cu$_{0.10}$O). In this case, in order to getting homogeneous and fine sample powder, it has been used mortar & pestle to grind and muffle furnace for annealing. Repeating the process until the homogeneous powder sample is prepared. From the XRD analysis it is found that the prepared samples are of single phase with hexagonal structure. The lattice parameters of the hexagonal phase calculated in this study by Hess-Lipson method are consistent with the published values. From XRD analyses the XRD pattern shows the crystalline structure of the Zn$_{1-x}$Cu$_x$O samples. The peaks were identified as (100), (002) and (101) comparing with the standard JCPDS card no 80-00075 (Grant Aid report in 1987).

Keywords: ZnO, Cu-doped, Solid-state reaction, structural property, single phase

I. INTRODUCTION

Diluted magnetic semiconductor (DMS) materials have a great deal of attention in the recent years as an outstanding material where the transition metal atoms replace a stoichiometric fraction of the constituent atoms [1]. Cu-doped ZnO has been a promising candidate for dilute magnetic semiconductor (DMS). Many researchers are investigating this system to study and further manipulate the magnetic semiconductor properties, the material Cu-doped ZnO which has received widespread interest since it was discovered to be ferromagnetic at room temperature by R. Elilarassi. G. Chandrasekaran [2]. Recently, wide band gap diluted magnetic semiconductors have been widely studied with the aim of identifying doped semiconducting materials with large magnetic moments M and with a high Curie temperature $T_c$ [3-6]. Among the semiconducting metal oxides, ZnO is one of the best candidates with wide band gap (3.4 eV) possessing hexagonal wurtzite structure with exciting optoelectronic device applications such as light-emitting diodes (LEDs), efficient laser diodes [7-9]. Lee et al. [10] reported that Cu-doped ZnO powder samples exhibits ferromagnetic hysteresis loops, but Cu-doped ZnO films were nonmagnetic. In the present work, we have prepared copper doped samples using solid-state reaction method. The reason for choosing Cu and ZnO in this research is because Cu is a well-known magnetic element while the ZnO has been extensively studied for several decades since it has many technologically important properties. Zinc oxide is an inorganic compound. It is insoluble in water. It melts at 1,975 °C. It has wide band gap and magnetic susceptibility. With all these properties and a doping with Cu magnetic ions, it would be able to control its optical, magnetic, structural and semiconductor characters for suitable applications. Therefore, it is interesting to investigate the structural properties of Cu-doped ZnO fine powder. In previous work many researchers have been investigated this property but the exceptional part of this current paper is that we have used different sample composition (Zn$_{0.99}$Cu$_{0.01}$O & Zn$_{0.90}$Cu$_{0.10}$O) and different calcination & sintering temperature than the previous work and comparing the results with standard values.
II. EXPERIMENTAL PROCESS

The polycrystalline samples $\text{Zn}_{0.99}\text{Cu}_{0.01}\text{O}$ and $\text{Zn}_{0.90}\text{Cu}_{0.10}\text{O}$ were prepared by the standard solid-state reaction processes. Sample preparation has been completed by two steps-

2.1 Grinding and calcinations

At first, the component which has been used in this section such as mortar, pestle and crucible were cleaned with distilled water and then Chromic Acid ($\text{H}_2\text{CrO}_4$). The stoichiometric amount of working materials highly pure reagent grade such as $\text{Zn(CH}_3\text{OO)}_2$, $\text{Cu(CH}_3\text{OO)}_2$ were kept in a dirt free mortar. Using pestle these samples were grounded about three hours for homogeneous mixture. The powder thus obtained was placed in an alumina crucible. The crucible containing the grounded powder was then placed in the furnace and heated at 500°C for 12 hours and then furnace cool. Slow cooling is essential for crystalline sample. When the furnace cool down at room temperature, the crucible was taken out and the powder was grounded until it become to a fine powder. The sample process was repeated to obtain fine sample powder.

2.2 Pellet formation and sintering

Using binder the small amount of calcined powder about 0.70 gm put into a dice and pressed into pellets under a force of 15 KN held for about few minutes using Hydraulic pressure gauge. The prepared pellets were then placed in an alumina crucible and this was inserted into the furnace for sintering at 600°C for 8 hours. The sintering had been done to obtain the crystalline phase of the composition.

Fig.2.1: Powder sample of Cu doped ZnO calcined at 500°C for 12 hours.

Fig.2.2: Disk shaped pellet of Cu doped ZnO sample sintered at 600°C for 8 hours.

The crystalline nature and the phase purity of the powder sample were examined by X-ray powder diffraction analysis (XRD) with D2 PHASE (BRUKER) using voltage 30 kV and current 10 mA located at Rajshahi University of Engineering and Technology, Bangladesh.

X-ray diffraction patterns of the samples were taken using an X-ray diffractometer from Rajshahi University of Engineering and Technology, Bangladesh (RUET). X-ray diffraction pattern provides information about the
samples homogeneity, phase and orientation of the different crystallographic planes. Cu Kα radiation (λ=1.54184 Å) was used for the XRD diffraction. The scanning drive axis is taken as two-theta and the scan was recorded in between 15 to 70° of 2Ө values for samples of Zn$_{1-x}$Cu$_x$O system. The values of miller indices (hkl) were identified by adopting several indexing procedure and the lattice parameters were determined by Hess-Lipson method.

2.3 Indexing of (hkl) by Hess-Lipson technique

The interplanar spacing $d_{hkl}$ for the hexagonal system with diffraction angle Θ is given as

$$\frac{1}{d_{hkl}} = \left[\frac{4}{3}(h^2 + hk + k^2)/a^2 + \frac{l^2}{c^2}\right]^{1/2} \quad \text{(2.1)}$$

Where $d_{hkl}$, the interplanar spacing is related with the diffraction angle Θ by the relation

$$\frac{1}{d_{hkl}} = \frac{2\sin \Theta_{hkl}}{\lambda} \quad \text{……………… (2.2)}$$

Here the wavelength, $\lambda$ of X-ray of CuKα line was used 1.54184 Å. Combining relations (2.1) and (2.2) we get

$$4\sin^2 \Theta_{hkl}/\lambda^2 = \frac{4}{3}(h^2 + hk + k^2)/a^2 + \frac{l^2}{c^2}$$

Or, $\sin^2 \Theta_{hkl} = \frac{1}{3}(h^2 + hk + k^2)/a^2 + \frac{l^2}{c^2}$

Therefore,

$$\sin^2 \Theta_{hkl} = XA + l^2C \quad \text{……………… (2.3)}$$

Where, $X = h^2 + hk + k^2$

$A = \frac{\lambda^2}{3a^2}$

$C = \frac{\lambda^2}{4c^2}$

And

$\sin^2 \Theta_{100} = A$ \quad $\sin^2 \Theta_{010} = A$ \quad $\sin^2 \Theta_{001} = C$

$\sin^2 \Theta_{200} = 4A$ \quad $\sin^2 \Theta_{020} = 4A$ \quad $\sin^2 \Theta_{002} = 4C$

$\sin^2 \Theta_{300} = 9A$ \quad $\sin^2 \Theta_{030} = 9A$ \quad $\sin^2 \Theta_{003} = 9C$ \quad \text{(2.4)}$

and so on.

From these relations it is possible to make different combinations as for example:

$\sin^2 \Theta_{110} = 3A$ \quad $\sin^2 \Theta_{220} = 12A$ \quad $\sin^2 \Theta_{330} = 27A$ and so on.

If the lattice parameter ‘a’ and ‘c’ are known then A, C and their multiples can be calculated from which different combinations of $\sin^2 \Theta_{hkl}$ (depending on hkl) can be determined. The values of lattice parameter obtained in this way give the calculated value. From the X-ray diffractometer we can find $\sin^2 \Theta$ from the values of two-theta position and which these values are closely match with the calculated values obtained here.

2.4 Lattice parameter calculation by the Hess-Lipson method

In this work ZnO is the basic compound and we just substitute a fraction of zinc by copper to obtain our desired system ZnCuO. To calculate the lattice parameter ‘a’ and ‘c’ of this hexagonal system, we need a reference value of this parameter. The reference value of lattice parameters ‘a’ and ‘c’ are from JCPDS card No. 36-1451 [11], are

$$a = 3.249 \text{ Å} \quad \text{and} \quad c = 5.206 \text{ Å}$$

Now from eqn. (4.3)

$$\sin^2 \Theta_{hkl} = XA + l^2C$$

Where,

$$X = h^2 + hk + k^2$$

$A = \frac{\lambda^2}{3a^2}$

$C = \frac{\lambda^2}{4c^2}$

Putting the reported values of a and c we get,

$A = 0.07506$ and $C = 0.02192$

Therefore, putting the values of A and C we can get the different values of $\sin^2 \Theta_{hkl}$ for different combination of (hkl).

These calculated values of $\sin^2 \Theta_{hkl}$ were then compared with the observed $\sin^2 \Theta$ values of the diffracted pattern. The closely matched values will be taken for calculations for lattice parameters,

For, $\sin^2 \Theta_{100} = A$

Or, 0.07487 = $\frac{\lambda^2}{3a^2}$

Or, $a^2 = \lambda^2/(3*0.07487)$

$a = 3.2533 \text{ Å}$

This is very close to the reference value. Again the observed value for

$\sin^2 \Theta_{002} = 4C$

Or, 0.08754 = $4(\frac{\lambda^2}{4c^2})$

Or, $c^2 = \frac{\lambda^2}{4*0.08754}$

$c = 5.211 \text{ Å}$
III. RESULT AND DISCUSSION

Our main object is to study the structural property of Cu-doped ZnO. The structural analysis was performed using X-ray diffraction measurement model: D2 PHASER (BRUKER). The typical X-ray diffraction pattern of Zn$_{0.99}$Cu$_{0.01}$O & Zn$_{0.90}$Cu$_{0.10}$O powder is shown in Fig. 3.2, 3.3 & 3.4 the possible phase and $d_{hk}$ values of different samples have been calculated by using equation (2.2). The $d_{hl}$ values of different samples are given in Table 3.1 and 3.2.

### Table: 3.1 The $d_{hl}$ values of Zn$_{0.99}$Cu$_{0.01}$O sample.

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>$2\theta$ (Degree)</th>
<th>$d_{hl}$ (Exp.) (Å)</th>
<th>$d_{hl}$ (from JCPDS) (Å)</th>
<th>Intensity (%)</th>
<th>Standard Indices (hkl)</th>
<th>Possible phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>31.86</td>
<td>2.816</td>
<td>2.814</td>
<td>2.04</td>
<td>100</td>
<td>ZnO</td>
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<tr>
<td>2</td>
<td>34.50</td>
<td>2.598</td>
<td>2.603</td>
<td>1.76</td>
<td>002</td>
<td>ZnO</td>
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<tr>
<td>3</td>
<td>36.34</td>
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<td>2.476</td>
<td>3.76</td>
<td>101</td>
<td>ZnO</td>
</tr>
<tr>
<td>4</td>
<td>47.66</td>
<td>1.907</td>
<td>1.911</td>
<td>0.52</td>
<td>102</td>
<td>ZnO</td>
</tr>
<tr>
<td>5</td>
<td>56.72</td>
<td>1.623</td>
<td>1.625</td>
<td>1.18</td>
<td>110</td>
<td>ZnO</td>
</tr>
</tbody>
</table>

### Table: 3.2 The $d_{hl}$ values of Zn$_{0.90}$Cu$_{0.10}$O sample.

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>$2\theta$ (Degree)</th>
<th>$d_{hl}$ (Exp.) (Å)</th>
<th>$d_{hl}$ (from JCPDS) (Å)</th>
<th>Intensity (%)</th>
<th>Standard Indices (hkl)</th>
<th>Possible phase</th>
</tr>
</thead>
<tbody>
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<td>1</td>
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<tr>
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<tr>
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<td>2.476</td>
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<td>ZnO</td>
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<tr>
<td>4</td>
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<td>1.908</td>
<td>1.911</td>
<td>0.40</td>
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<td>ZnO</td>
</tr>
<tr>
<td>5</td>
<td>56.70</td>
<td>1.622</td>
<td>1.625</td>
<td>0.14</td>
<td>110</td>
<td>ZnO</td>
</tr>
</tbody>
</table>

![Fig.3.1 Variation of lattice constant with doping of Cu into ZnO](image-url)
Structural Characterization of Cu-Doped ZnO (Zn$_{1-x}$Cu$_x$O) Using Solid State Reaction Method.

The X-ray diffraction patterns for Cu doped ZnO samples are shown in Fig.3.2, 3.3 and 3.4. The ZnO characteristic peaks are very sharp and no shoulder is found for other phase along with major crystallographic planes. The peaks were identified as (100), (002), (102), (110) comparing with the standard JCPDS card no 80-00075 (Grant Aid report in 1987). Three main ZnO peaks are found at around 31.80 (100), 34.52 (002) and 36.36 degrees in 2θ scale of Bragg angle. From X-ray diffractogram, it is clear that as synthesized samples are crystalline and well oriented.
Copper doped Zinc oxide (Zn$_{0.99}$Cu$_{0.01}$O & Zn$_{0.90}$Cu$_{0.10}$O) has been successfully prepared using Solid state reaction method. The XRD pattern for Zn$_{1-x}$Cu$_x$O samples are shown in Fig.3.2-3.4 and Fig.3.1 shows lattice constant with doping concentration. From spectrogram it is clear that all the samples are almost monophase and crystalline in nature. This XRD pattern shows the crystalline structure of the Zn$_{1-x}$Cu$_x$O samples. The peaks were identified as (100), (002) and (101) comparing with the standard JCPDS card no 80-00075 (Grant Aid report in 1987). The crystal structure of the synthesized samples could be indexed with hexagonal wurtzite structure by Hess-Lipson method. The peak position, lattice parameter, corresponding Miller indices and possible phase of the samples are tabulated in Table (3.1 to 3.2). From Fig’s it is also observed that the intensity of some peaks are gradually increased and few peaks disappear with the increasing doping concentration of Cu. It is found that the lattice parameters decreased with the increased of doping concentration Cu.

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References