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# Structural, Morphological and Magnetic Properties of Cu<sup>2+</sup> Doped ZnO Nanoparticles

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**Abstract.** Investigations on the structural, morphological and magnetic properties of Zn<sub>1-x</sub>Cu<sub>x</sub>O (x= 0.00 and 0.05) nanoparticles synthesized via simple and low cost sol-gel auto combustion technique. The synthesized samples were characterized by X-ray diffraction technique (XRD), and vibrating sample magnetometer (VSM). XRD pattern reveals the formation of single phase with hexagonal wurtzite structure of both the synthesized samples. It also confirms the successful incorporation of dopant (Cu<sup>2+</sup>) into the ZnO lattice. The lattice parameter of Cu<sup>2+</sup> doped ZnO is slightly greater than that of pure ZnO nanoparticles. The crystallite size of synthesized samples are as 21 and 19 nm in range. Magnetic study carried out by VSM at room temperature and shows the diamagnetic nature of pure ZnO nanoparticles. After the doping of Cu<sup>2+</sup> ions in ZnO changes to ferromagnetic nature. The appearance of ferromagnetism due to the presence of free carriers induced by Cu<sup>2+</sup> doped into ZnO nanoparticles.

## 1. Introduction

In the recent year ZnO is one of the most important functional material and it exhibit novel optical, electrical and magnetic properties. ZnO is one of the most important oxide material with a wide bandgap of 3.37 eV and has a large exciton binding energy (60 meV) useful for various applications such as optoelectronic devices, piezoelectronic transducers, high frequency electronic devices, solar cells, spintronic devices, etc [1-5]. A number of synthesis techniques have been used for the fabrication of transition metal doped nanocrystalline ZnO, these techniques give different particle morphologies, size as well as it modifies the properties of the material. In literature sol gel auto combustion technique



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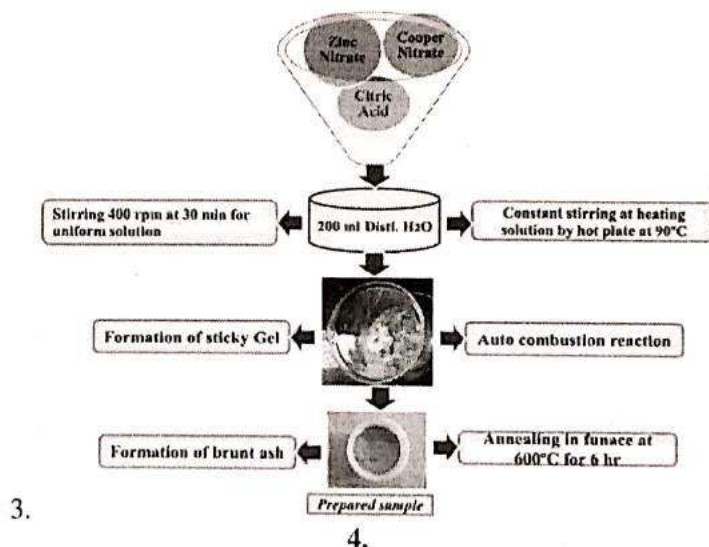


[6-9], ball milling technique [10-14], spray pyrolysis for thin film deposition [15-17], hydrothermal technique [18, 19], co-precipitation technique [20, 21], chemical electrodeposition [22, 23] etc were successfully adopted for the synthesis of transition metal doped nanocrystalline ZnO. Among these established techniques, sol gel auto combustion technique is one of great importance for the production of tailored oxide nanoparticles. Since, it is simple, inexpensive, less time consuming and easy control of particle size. Also by adopting sol gel auto combustion technique we get accurate composition and constituent phases mixed at molecular level, assures high purity and well crystallized powders[24].

Transition metal doped ZnO nanomaterials has great interest in research field that it was induced to tune the optical, magnetic and electrical properties. Due to the exchange interaction between s and p electron of host ZnO and d electron of transition metal, also it changes its electronic structure. Many researchers have studied the changes predicted by doping of transition metal ions into ZnO lattice [25-27]. The transition metals such as Mn, Fe, Cu, Ni, Co etc. doped with ZnO lattice which have remarkable change in structural, optical, electrical and magnetic properties for potential application in semiconductor devices [21, 28, 29]. Among all these transition metal elements, copper has much interest since it exhibits a drastic change in optical, electrical and magnetic properties of ZnO, which will increase its practical applications.  $\text{Cu}^{2+}$  ions are easily incorporated on  $\text{Zn}^{2+}$  site such as ionic radii of  $\text{Cu}^{2+}$  ( $0.73\text{\AA}$ ) close to ionic radii of  $\text{Zn}^{2+}$  ( $0.74\text{\AA}$ ) ions. Few reports are available on ferromagnetism in  $\text{Cu}^{2+}$  doped ZnO nanoparticles. In the present work the preparation of  $\text{Zn}_{1-x}\text{Cu}_x\text{O}$  with composition 0.00 and 0.05 via sol gel auto combustion technique and effect of  $\text{Cu}^{2+}$  ions on the structural, morphological and magnetic properties of the ZnO was investigated using XRD, TEM/SAED and VSM characterization techniques.

## 2. Experimental Procedure

### 2.2. Synthesis



5. Figure 1. systematic presentation of synthesis of  $\text{Zn}_{1-x}\text{Cu}_x\text{O}$  ( $x=0.00$  and  $0.05$ ) nanoparticles.

The synthesis of  $\text{Zn}_{1-x}\text{Cu}_x\text{O}$  ( $x=0.00$  and  $0.05$ ) nanoparticles were carried out using, the high purity (A R. grade, 99% pure) chemicals using zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), citric acid monohydrate ( $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ ) as starting material and copper nitrate trihydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ) as doping source. Zinc nitrate and copper nitrate acted as oxidant while citric acid as fuel during the reaction. The ratio of fuel and oxidant were taken as 1:3 by propellant chemistry. Zinc nitrate and copper nitrate were dissolved in 100 ml distilled water to get a homogeneous solution for 30 min by using magnetic stirrer. Citric acid had been dissolved separately in 100 ml distilled water for 30 min

and the add to the nitrate solution. Then the solution was stirring and continuously heating at 90°C until water gets evaporated, thus the sol is converted in to gel. The gel subsequently in to bulge form and it get strong self combustion reaction to give the fine powder shown in Figure 1. All the samples are ground by pestle and mortar, powdered samples were sintered at 600°C for 6h in muffle furnace. The final powder of pure ZnO is in white color and Cu<sup>2+</sup> doped ZnO is in moss green color.

### 5.2. Characterizations

The structural analysis was carried out by X-ray diffraction technique (XRD) analysis (BRUKERD8 ADVANCE) with Cu K $\alpha$  radiation in the 2 $\theta$  range of 30°-80°. Field dependent magnetization studies were carried out by vibrating sample magnetometer (VSM) at room temperature.

## 6. Results and Discussions

### 6.2. XRD

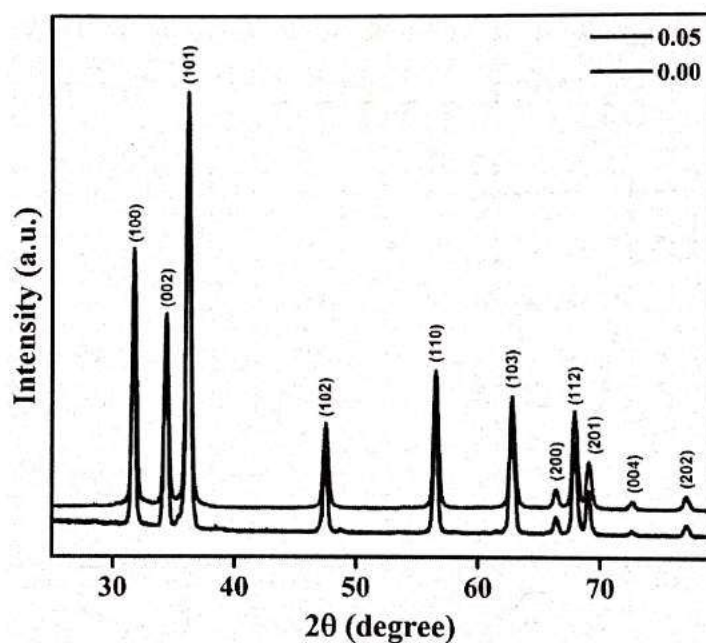


Figure 2. XRD pattern of pure and Cu<sup>2+</sup> doped ZnO nanoparticles.

The X-ray diffraction pattern of the Zn<sub>1-x</sub>Cu<sub>x</sub>O (x=0.00 and 0.05) nanoparticles are shown in Figure 2. XRD analysis were used to determine the phases as well as crystal structure of the samples. Each XRD peaks identified the single phase with hexagonal wurtzite structure of ZnO nanocrystal. The XRD pattern can seen the formation of strong and narrow diffraction peaks which shows good crystallinity. Form Figure 2, it is clearly observed that variation has been observed in the peak intensities value with doping of Cu<sup>2+</sup> ions in ZnO nanoparticles[30, 31]. The slightly shifting of the peak position shows the Cu<sup>2+</sup> ions were incorporated into Zn position in the ZnO lattices. The lattice parameters *a* and *c* of the pure and Cu<sup>2+</sup> doped ZnO nanoparticles were estimated using the Eq. 1[32].

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



where,  $\theta$  is the diffraction angle,  $\lambda$  is incident wavelength ( $\lambda = 0.15406$  nm) and  $h$ ,  $k$ , and  $l$  are the Miller indices. The lattice parameter  $a$  and  $c$  of  $\text{Cu}^{2+}$  doped ZnO nanoparticles slightly greater than that of pure ZnO nanoparticles shown in Table 1, because the ionic radius of  $\text{Cu}^{2+}$  ions is larger than that of Zn ions. The change of the lattice parameter shows that  $\text{Cu}^{2+}$  ions systematically induced in to ZnO lattice.

The average crystallite size of doped and undoped ZnO nanoparticles were estimated using the Debye-Scherrer's Eq. 2[33].

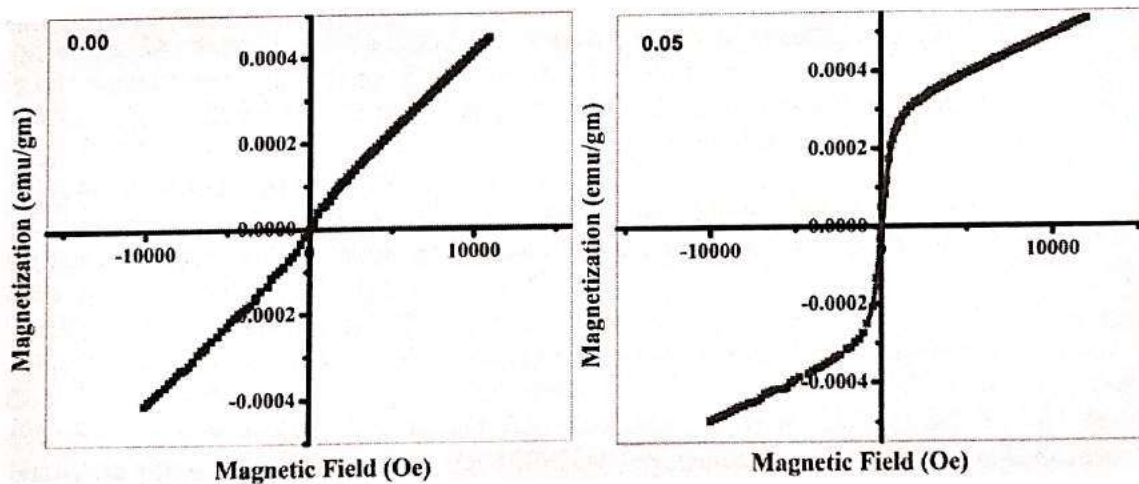
$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (2)$$

where,  $D$  is average crystalline diameter,  $\lambda$  is the wavelength of X-ray radiation,  $\beta$  is full width at half maximum (FWHM) and  $\theta$  is the Bragg angle. The crystallite size of  $\text{Cu}^{2+}$  doped ZnO nanoparticle is smaller than those of the pure ZnO nanoparticles shown in Table 1. The decreasing crystallite size is due to the distortion in ZnO lattice by the presence of  $\text{Cu}^{2+}$  reduces nucleation and interference growth rate of ZnO nanoparticles.

**Table 1.** Lattice parameter and crystallite size of pure and  $\text{Cu}^{2+}$  doped ZnO nanoparticles.

$\text{Zn}_{1-x}\text{Cu}_x\text{O}$	Lattice Parameter		Crystallite size D (nm)
	a ( $\text{\AA}$ )	c ( $\text{\AA}$ )	
X= 0.00	3.251	5.216	21
X= 0.05	3.254	5.217	19

### 6.3. VSM



**Figure 3.** M-H plot of pure and  $\text{Cu}^{2+}$  doped ZnO nanoparticles.

The magnetic study of pure and  $\text{Cu}^{2+}$  were carried out by vibrating sample magnetometer at room temperature. Pure ZnO nanoparticles clearly shows the paramagnetic behavior at room temperature from Figure 3. According to Langvins theory, paramagnetic nature is linear at normal temperature with regular field strength. The presence of magnetic ions by electric or magnetic field which gives the paramagnetic nature. The paramagnetic behavior for pure ZnO was found in our case where magnetic ions are not presented. This was observed due to the Zn vacancies presented during synthesis of pure



ZnO nanoparticles.  $\text{Cu}^{2+}$  doped ZnO nanoparticles shows the ferromagnetic behavior show in Figure 3. for 0.05 concentration. The origin of ferromagnetism in  $\text{Cu}^{2+}$  doped ZnO nanoparticles due to the different extrinsic and intrinsic defects. Extrinsic defect as secondary phase formation by doping metal ions and intrinsic defect as zinc and oxygen vacancies. The appearance of ferromagnetism in  $\text{Cu}^{2+}$  doped ZnO nanoparticles due to the oxygen vacancies and exchange interaction of  $\text{Cu}^{2+}$  with oxygen ions with spin moment. The transformation of paramagnetic to ferromagnetic due to  $\text{Cu}^{2+}$  doped into ZnO lattice[34].

## 7. Conclusions

In this present study, sol gel auto combustion technique for synthesis of pure and Ni doped ZnO nanoparticles were successfully achieved. The influence of  $\text{Cu}^{2+}$  ions on to structural, morphological and magnetic properties of ZnO nanoparticles were investigated. The structural analysis by XRD shows the single phase hexagonal wurtzite crystal structure were observed for pure and  $\text{Cu}^{2+}$  doped ZnO nanoparticles. The lattice parameter  $a$  and  $c$  of  $\text{Cu}^{2+}$  doped ZnO nanoparticles slightly greater than that of pure ZnO nanoparticles. The crystallite size of  $\text{Cu}^{2+}$  doped ZnO nanoparticle is smaller than those of the pure ZnO nanoparticles. Morphological study by TEM/SAED confirms the spherical morphology with agglomeration of pure and  $\text{Cu}^{2+}$  doped ZnO nanoparticles. The magnetic study show the transformation of paramagnetic to ferromagnetic behavior by doping of  $\text{Cu}^{2+}$  into ZnO nanoparticles, which is applicable for the spintronic devices.

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