

Effect of Cu doping on Electrical, Photoluminescence and Band Gap Engineering of Mg Doped ZnO Nanoparticles

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ABSTRACT: In the present investigation Cu, Mg co doped ZnO nanoparticles were synthesized using co-precipitation method by adding PVP as capping agent at pH of 9. Magnesium (Mg) doping in ZnO is a good method for tuning of band gap. Doping of copper (Cu) in ZnO:Mg enhances the photoluminescence. The X-ray diffraction patterns confirmed the wurtzite hexagonal structure without disturbing the lattice constant. The growth of particle size decreases from 40 nm to 26 nm with increasing the concentration of Cu. As the concentration of Cu increases in ZnO:Mg, the optical band gap was found to be decreased from 3.1 eV to 2.88 eV. The photoluminescence studies revealed that the visible PL emission was enhanced with increasing doping concentration of Cu in ZnO:Mg.

Keywords: capping agent, co-precipitation method, EDAX, photoluminescence, SEM.

I. INTRODUCTION

The Zinc oxide (ZnO) is an inorganic compound which is insoluble in water and widely used as an additive in numerous materials and products including rubbers, plastics, ceramics, glass, cement, paints, lubricants, ointments, adhesives, batteries, fire retardants and first aid tapes. ZnO exhibits direct optical transitions with an optical band gap of 3.3 eV suitable for short wavelength optoelectronic applications [1]. ZnO exhibits hexagonal wurtzite structure with large exciton binding energy (60 meV) and high chemical and thermal stability [2, 3]. It has very short luminescence life time and allows variation in the material properties to improve mechanical properties [4, 5]. By proper doping, the physical, electrical, mechanical and optical properties will be improved [6]. Incorporation of various elements into ZnO host lattice has significance for its use in industries as fluorescent lamps, information storage materials, control panel displays, plasma display panels, gas sensors and chemical sensors [7, 8]. The ionic radii of Zn⁺² is 0.074 nm and O⁻² is 0.140 nm which are preferred for the formation of wurtzite as well as strong piezo-electric nature of ZnO [9]. Incorporation of two or more metals into ZnO host lattice increases the saturation magnetization of ZnO samples and influences the electrical, optical, and magnetic properties [10]. Cu is selected as one of the doped material for ZnO due to its similar electronic shell structure, physical and chemical properties. Incorporation of Cu in ZnO lattice creates the localized impurity level and modifies the luminescence of ZnO and has great interest due to their application in the field of lasing devices, light emitting diodes and optical sensing devices [11]. Doping of ZnO with Mg changes the value of the band gap and increases the UV luminescence properties [12, 13]. So, it is relevant to choose Mg and Cu as co doping for reducing band gap and optical properties of ZnO nanoparticles. In the present study, Cu co-doping concentrations are varied with constant Mg doping in capped ZnO (Zn_{0.96-x}Mg_{0.04}Cu_xO, x= 0.00, 0.02, 0.04, 0.06) nanoparticles prepared by co precipitation method and studied the structure, morphology, composition, optical and photoluminescence properties.

II. EXPERIMENTAL AND CHARACTERIZATION TECHNIQUES

For the synthesis of ZnO:Mg, Cu nanoparticles, analytical grade (AR) high purity chemicals such as Zinc acetate dehydrated ((ZnO₂CCH₃). 2H₂O), Magnesium nitrate (Mg (NO₃)₂. 6H₂O), hydrated Copper acetate (C₄H₆CuO₄.H₂O), NaOH and Polyvinylpyrrolidone (PVP) in suitable quantities were used as precursors. Initially, appropriate amount of Zinc acetate and Magnesium nitrate was dissolved in 100 ml double distilled water and stirred for 15 minutes until a clear solution obtained. 0.5 gm of PVP was added as capping agent to the solution. After that NaOH solution was added drop wisely until it maintained the acidic medium level of pH 9 at room temperature. The mixed solution was stirred for 3 hours. The white precipitate formed while stirring was filtered and washed several times to remove the impurities. Same procedure was adopted for Mg and Cu co-doping. The 4 at.% magnesium doped ZnO was co-doped with copper (x= 0.00, 0.02, 0.04 and 0.06) such that

the stoichiometry $Zn_{0.96-x}O:Mg_{0.04}Cu_x$ is obtained. The precipitate form was filtered and washed several times to remove the impurities. The final precipitate was dried at $80^\circ C$ using an oven and the dried precipitates were collected and grounded using mortar. The structure of the samples was studied by using X-ray powder diffraction (XRD), using CuK_α radiations ($\lambda = 1.54 \text{ \AA}$) in 2θ range from 20° to 80° . The morphology and grain size distribution of the samples were investigated using SEM. The compositional analysis was carried out using EDAX attached with SEM. UV visible absorption spectra were recorded using Perkin Elmer Lambda 35 UV/vis spectrometer. Fourier transformation infrared (FTIR) analysis was done using (spectrum 65, Perkin Elmer in the range of $4500-400\text{cm}^{-1}$ with a resolution of 1 cm^{-1}). The photoluminescence (PL) spectra of ZnO:Mg, Cu nanoparticles was carried out between the wavelength ranging from 350-600nm using FLS980 EDIN BURCH instruments at room temperature.

III. RESULT AND DISCUSSION

3.1 Structural Analysis

Figure 1 shows the XRD pattern of Mg, Cu co-doped ZnO nanoparticles. The intense diffraction peaks of the ZnO appeared at $31.75, 34.39, 36.29, 47.5, 56.57, 62.8, 66.25, 67.9, 69.1$ which corresponds to the lattice planes (100), (002), (101), (102), (110), (103), (200), (112) and (201). The peak position of each sample exhibited hexagonal wurtzite structure of ZnO which were confirmed from the JCPDS Card No.80-0075. Without disturbing the hexagonal wurtzite structure of ZnO, Mg^{+2} and Cu^{+2} ions were supplemented into Zn^{+2} ion lattice sites. With increasing the concentration of Cu (4 mol%) in the ZnO:Mg lattice, a phase related to Cu corresponding to (111) plane was observed between 35° and 45° without disturbing the crystal structure (JCPDS Card No.05-0661). The new phase was due to the presence of unreacted Cu^{+2} ions present in the sample. Similar results were observed by Sharma et al [19] at higher dopant concentrations of Cu. The crystalline sizes of the samples are calculated according to the Scherer's formula and are given in table 1.

Table 1. Crystallite size of the $Zn_{0.96-x}Mg_{0.04}Cu_xO$ nanoparticles

Sample composition	Crystalline size (nm)
$Zn_{0.96}Mg_{0.04}O$	40
$Zn_{0.94}Mg_{0.04}Cu_{0.02}O$	30
$Zn_{0.92}Mg_{0.04}Cu_{0.04}O$	27
$Zn_{0.90}Mg_{0.04}Cu_{0.06}O$	28

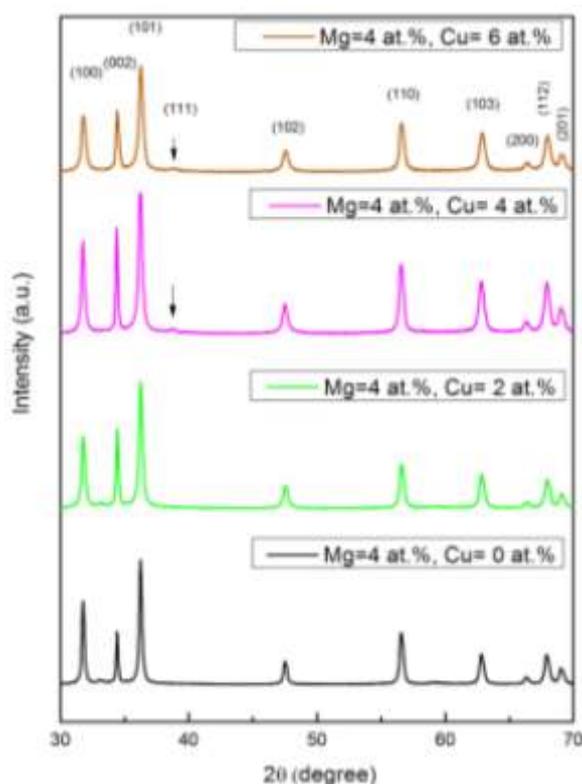


Fig. 1: XRD patterns of ZnO:Mg, Cu nanoparticles synthesized with different doping concentration of Cu

Increase in particle size at higher concentration of Cu may be due to Cu-Cu interactions in the ZnO host lattice.

$$D = \frac{0.94\lambda}{\beta_{hkl} \cos \theta}$$

Where, D is the average Particle size, β_{hkl} is full width at half maximum of XRD peak expressed in radians and θ is the position of the diffraction peak., λ = wave length of x-ray (1.54 Å).

3.2 Morphological and compositional studies

SEM was used to study the morphology of Mg doped ZnO and Mg, Cu co-doped ZnO nanoparticles (Fig.2). From the SEM micrographs, it was observed that, the particle size decreased with dopant concentration. Slight agglomeration was observed in all the samples. The stoichiometry of the samples was examined by EDAX. Zinc, magnesium, oxygen for ZnO:Mg are detected in Fig3(a) and Zinc, copper, magnesium, and oxygen are detected for ZnO:Mg, Cu in Fig3(b), (c) and (d). EDAX profiles confirm the effective doping of Cu and Mg into ZnO host lattice.

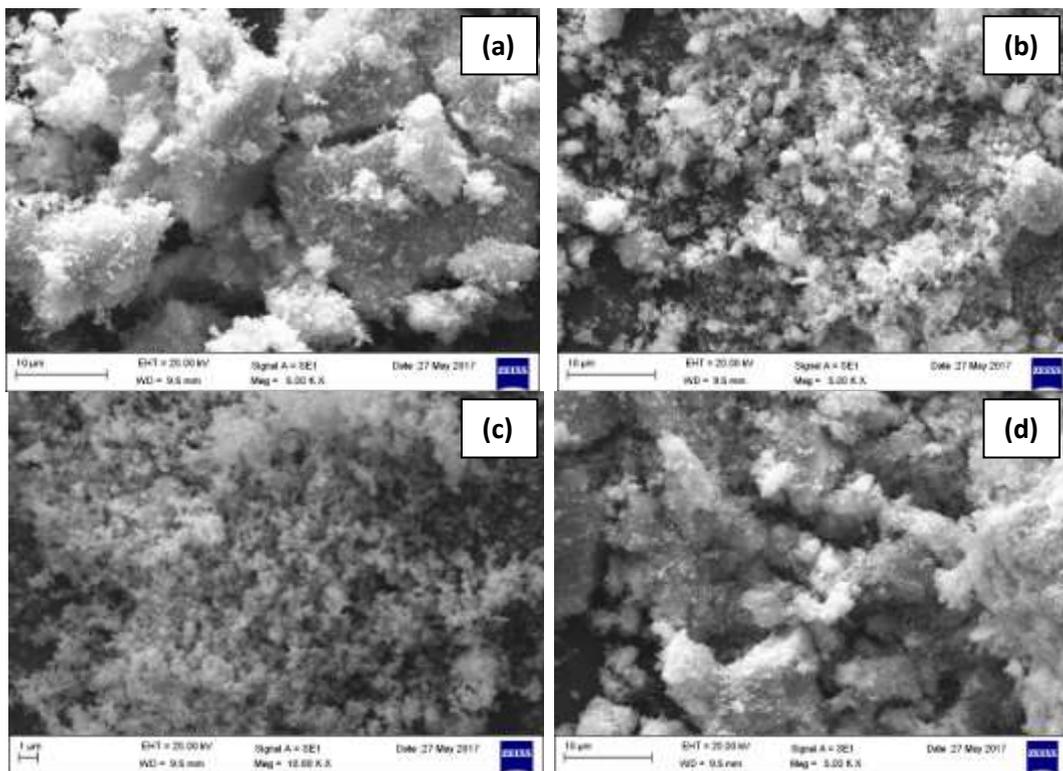


Fig.2 SEM images of ZnO:Mg, Cu nanoparticles with different concentration of Cu(0,2, 4 and 6 at.%)

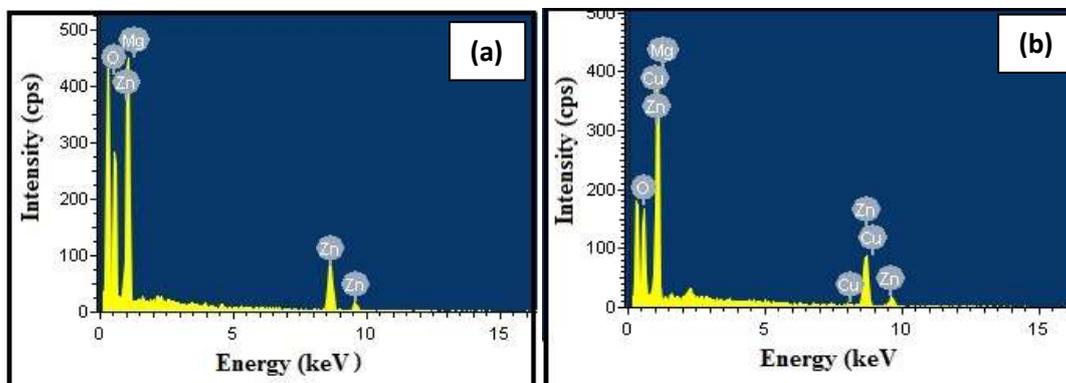


Fig.3. The EDAX profile of ZnO:Mg, Cu nanoparticles with (a) 0 and (b) 2 at.% of Cu

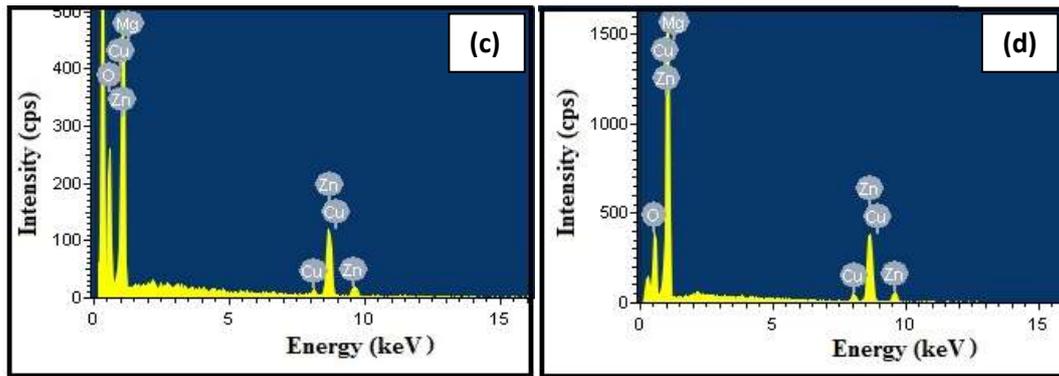


Fig.3. The EDAX profile of ZnO:Mg, Cu nanoparticles with (c) 4 and (d) 6 at.% of Cu

3.3 UV visible absorption Studies

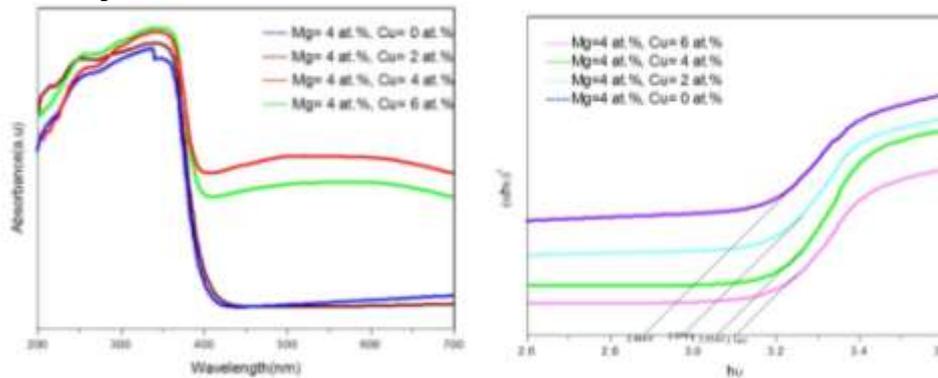


Fig-4(a) Absorption of Cu doped ZnO: Mg

Fig.5 Band gap measurement for n=1/2 excitonic state nanoparticles different Cu concentrations

The optical properties of the as deposited nanoparticles were measured using UV-Vis spectrophotometer. The absorption spectra of the $Zn_{0.96-x}Mg_{0.04}Cu_xO$ nanoparticles were given in Fig.4. ZnO:Mg sample exhibit absorption peak centered at 351nm is shifted to red region from 351nm to 357nm due to fundamental absorption of excitons with Mg and Cu co-doping(22). Initially substitution of Mg without Cu doping (ZnMgO) caused a reduction in the charge carriers density and hence absorption is increased. With Cu doping it may be induced the charge carriers which suppressed the absorption(23).The red shift observed with increase of Cu doping concentration is initially assigned to decrease in band gap .The band gap decreases from 3.1eV to 2.8eV with Cu doping as shown in Fig 5.This shows good application in optoelectronic, spintronic and gas sensor properties.

3.4 FTIR studies

From Fig 6 there are series of absorption bands at around $3311cm^{-1}$, $1511cm^{-1}$, $1036 cm^{-1}$, $829 cm^{-1}$, $697cm^{-1}$, $412cm^{-1}$ in the spectrum. The band $3311cm^{-1}$ corresponds to the hydroxyl band i.e O-H mode.

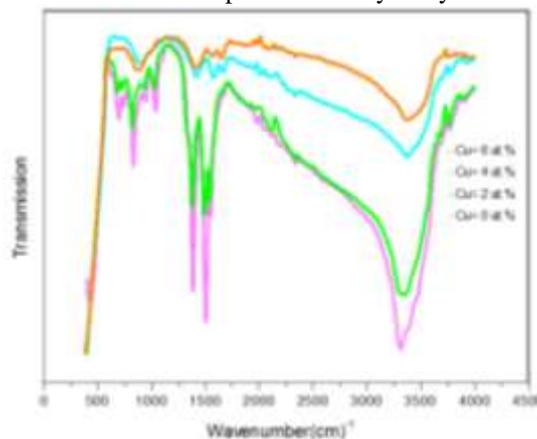


Fig.6. FTIR spectra of ZnO:Mg nanoparticles co-doped with different concentration of Cu(0, 2, 4 and 6 at.%)

1511 cm^{-1} is due to bending vibration of free water. This vibration indicates the presence of bound H_2O on the surface of the sample. The band located at $412\text{--}690\text{ cm}^{-1}$ can be attributed to the ZnO stretching mode in the ZnO lattice which is absent when Cu co-doped on ZnO:Mg. As the concentration of Cu in ZnO:Mg increases the absorption decreases and $O-H$ mode shifted towards 3400 cm^{-1} from 3311 cm^{-1} (24, 25).

3.5 Photoluminescence studies

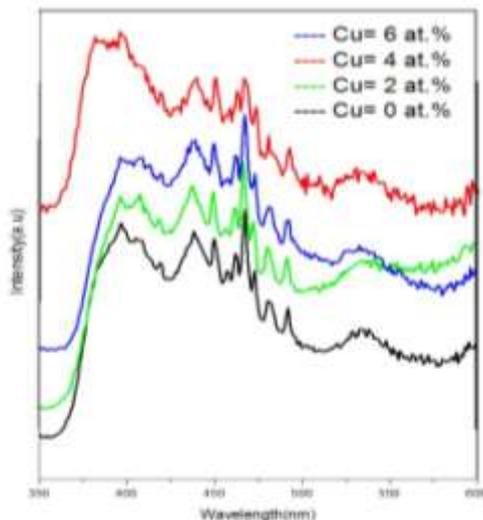


Fig7. The room temperature PL spectra of $\text{Zn}_{0.96-x}\text{Mg}_{0.04}\text{Cu}_x\text{O}$ ($x = 0, 4, 6\%$) nanoparticles

PL measurement has been carried out at room temperature between 350 nm to 600 nm. Fig 7 shows the PL spectra of $\text{Zn}_{0.96-x}\text{Mg}_{0.04}\text{Cu}_x\text{O}$ ($x = 0.00, 0.02, 0.04$ and 0.06) samples at room temperature. ZnO has one sharp band associated with near band edge emission at 396 nm and another broad emission in the visible region around 533 nm. The emission peaks in the visible region confirm the existence of the defect states by Mg and Cu co-doped with ZnO and peak position shift is due to Cu doping. Three well defined emission peaks (ultra violet, blue and green regions) are noticed in all the four samples even though the intensity position and width of peaks are different. The intensity of broad deep level emission increases with increase of Cu doping in ZnMgO lattice. The incorporation of Mg^{+2} and Cu^{+2} in ZnO lattice causes the formation of different intrinsic defect such as Zinc vacancies and oxygen interstitials which lead to enhance visible emission (26-29).

IV. CONCLUSION

Cu, Mg co doped ZnO nanoparticles were synthesized using co-precipitation method by adding PVP as capping agent at pH of 9. The X-ray diffraction patterns confirmed the wurtzite hexagonal structure without disturbing the lattice constant. The growth of particle size decreases from 40 nm to 26 nm with increasing the concentration of Cu. As the concentration of Cu increases in ZnO:Mg, the optical band gap was found to be decreased from 3.1 eV to 2.88 eV. EDAX confirms the effective doping of Cu and Mg into ZnO host lattice. The photoluminescence studies revealed that the visible PL emission was enhanced with increasing doping concentration of Cu in ZnO:Mg.

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