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Research Article

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Wet chemical synthesis and characterization of copper doped zinc oxide particle

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ABSTRACT

Synthesis of transition metal doped zinc oxide particles in aqueous phase was studied by adopting a low cost, easy and environmental friendly route. The precursors used in the preparation of Cu doped ZnO ($Zn_{0.95}Cu_{0.05}O$) and ZnO ($Zn_{0.9o}Cu_{0.1}O$) by wet process are zinc acetate dehydrate, copper chloride, sodium hydroxide, di-ethylene glycol and double distilled water. The doped ZnO particles were characterized by using scanning electron microscope (SEM), energy dispersive X-ray (EDX), Fourier transforms infrared spectroscopy (FTIR). The study constitutes the basis for developing versatile applications of transition metal doped ZnO microstructures.

Key words: Transition metal, zinc oxide, doped, SEM, FTIR

INTRODUCTION

Zinc oxide have attracted a wide attention due to their unique properties like optical properties, magnetric properties gas senesing properties and immense potential application in nano device fabrication. Zinc oxide (ZnO), a direct wide bandgap (3.4 eV at Room temperature) *II-VI* compound n-type semiconductor, has a stable wurtzite structure with lattice spacing a = 0.325 nm and c = 0.521 nm and composed of a number of alternating planes with tetrahedrally-coordinated O^{2-} and Zn^{2+} ions, stacked alternately along the c-axis. These metal oxide nanoparticles were extensively investigated due to their extented applications in the field of spintronics [1], photoelectronic [2], sensor [3], lasing devices [4] and light emitting diodes [5], etc. All these predominant properties make ZnO a great potential in the field of nanotechnology.

Nano zinc oxide is non-toxic, with wide band gap has also been identified as a promising semiconductor material for exhibiting ferromagnetism (RTFM) at room temperature when doped with most of the transition metal elements [6].

Various efforts have been made to investigate the effect of doping elements (such as Ni, Co, Al, Li, Fe, Ce, Eu, etc.) on its electrical, optical and magnetic properties, essentially for practical industrial applications [7,8,9,10]. Transition metal doped nanostructure is an effective method to adjust the energy level surface states of ZnO, which can further improve by the changes in doping concentrations of doped materials and hence in its physical and especially optical properties [11]. Doping of copper with ZnO has effected the photoluminescence and magnetic behaviour of ZnO based host material. Luminescence properties of ZnO are of great interest due to their application in the field of lasing devices, light emitting diodes and optical sensing devices etc. Photoluminescence properties of ZnO nanoparticles are very sensitive to the surface defects and size.

When transition metals are doped in ZnO host, they increase the defect density in the host and enhance the defect related emissions which put forward transition metals as suitable candidates for luminescence properties as well. Out of a variety of transition metals, copper is one of the most promising dopant because of its comparable size to Zn ion, which can easily substitute it.

Beside the magnetic and optical properties Cu doped ZnO nano particle, it acts as a sensor a few research on the effects of Cu doping on the sensing properties of ZnO has been reported. Sonawane et. al.[12] reported gas sensing properties of nanocrystalline ZnO: Cu for different concentrations of Cu and found for 1 wt% Cu in zinc oxide a higher response and selectivity to H_2. Paraguay et. al. [13] used the spray pyrolysis technique to obtain ZnO films doped with Cu and investigated the ethanol sensing at temperatures ranging between 435 and 675 K. Gong et al. [14] used co-sputtering technique to obtain Cu-doped ZnO films for CO sensing at temperatures of 150–400◦C. More recently Zhao et al. [15] used electrospinning to fabricate Cu-doped ZnO nanofibers for H_2S sensing application. Ghosh et al. [16] investigated the effect of Cu doping on the liquid propane gas sensing properties of soft chemically grown nano-structured ZnO thin films.

Various types of nano structured materials are synthesized by using different physical methods such as simple vapor transport and condensation process [17], sol-gel method [18], solid state reaction method[19], radio-frequency (rf) magnetron sputtering technique[20] , facile low temperature synthesis[21], chemical co-precipitation method[22], etc. In the present work aqueous phase synthesis or wet process was used for the synthesis of copper doped zinc oxide. The $Zn_{1-x}Cu_xO$; x=0.05.0.1 particles were successfully synthesized.

EXPERIMENTAL SECTION

Synthesis of copper doped zinc oxide ($Zn_{1-x}Cu_xO$; x=0.05.0.1) particles

The precursors used in the synthesis ZnO by wet process are zinc acetate dehydrate, copper chloride, sodium hydroxide, diethylene glycol and distilled water were used for this study. For preparing 5% Cu doped ZnO($Zn_{0.95}Cu_{0.05}O$) and for preparing 10% Cu doped ZnO ($Zn_{0.90}Cu_{0.1}O$), zinc acetatedehydrate and copper chloride were taken according to calculated stoichiometric ratio were taken in a beaker containing water. Then of diethylene glycol was added to above solution and were stirred for 10-15 minutes. NaOH solution was mixed in it dropwise and stirred. The NaOH was added till the pH was maintained to 10-12, again it was stirred. The solution was divided into three parts. First part was heated at 100 ^{0}C for half hour. Second part was heated at 100 ^{0}C for one hour and the third part for one and half hour. It was then filtered and washed first by water and then by ethanol. Then the precipitate were dried in the oven and weighed.

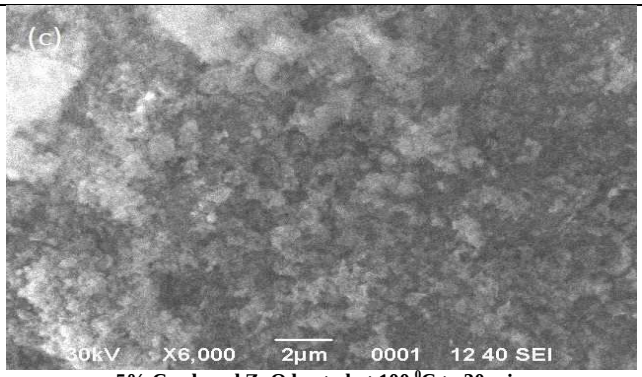
$Zn^{2+} + 2OH^-$	⟷	$Zn(OH)_2$	(1)
$Zn(OH)_2 + 2OH^-$	⟷	$[Zn(OH)_4]^{2-}$	(2)
$[Zn(OH)_4]^{2-}$	⟷	$ZnO_2^{2-} + 2H_2O$	(3)
$ZnO_2^{2-} + H_2O$	⟷	$ZnO + 2OH^-$	(4)
$ZnO + OH^-$	⟷	$ZnOOH^-$	(5)

Characterization

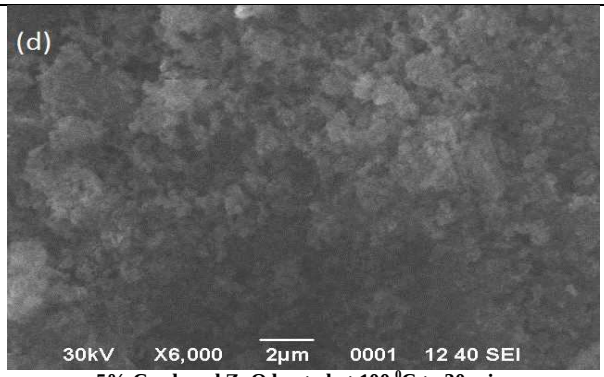
In order to investigate various properties of the prepared sample, number of characterizations techniques has been performed. The results show the different optical and structural properties of the prepared sample. Chemical composition and morphology of the samples were carried out using a scanning electron microscope, SEM (JSM-6490 LV) equipped with Energy Dispersive X-ray (EDX) thermo electron corporation. The mean particle size and corresponding standard deviation of the ZnO particles were determined by image analyses of SEM micrographs. FTIR (IR Spectrometer, Hicolet^{TM}–6700 of thermo scientific USA) was used to study absorbance properties.

RESULTS AND DISCUSSION

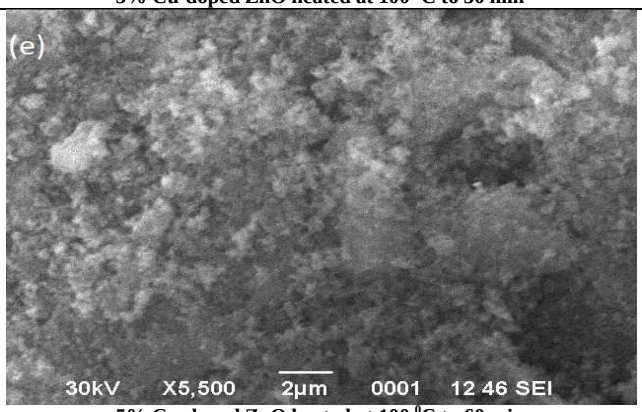
Scanning Electron Microscope (SEM), Energy Dispersive X-ray (EDX) and Fourier Transforms Infrared Spectroscopy (FTIR) methods were employed to characterize the copper doped zinc oxide, the $Zn_{1-x}Cu_xO$; x=0.05.0.1 particles. SEM micrographs (Figure-1) revealed spherical submicro particles, however there is wide size distribution from 0.2µm to 1 µm. Further, spherical particles tending to attain one dimensional(1-D) structures (figure-2;a,b,c,d,e,f,g,h,k).



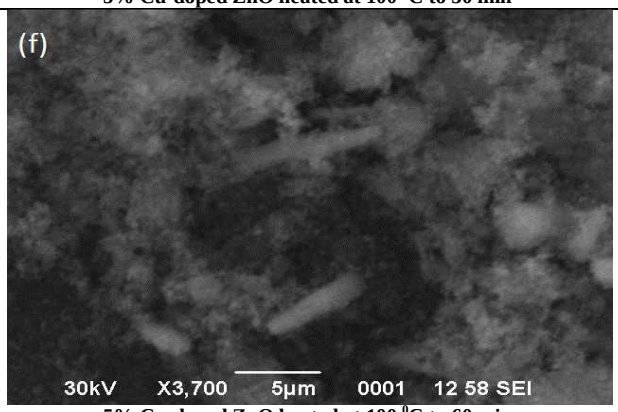
5% Cu-doped ZnO heated at 100 ^{0}C to 30 min



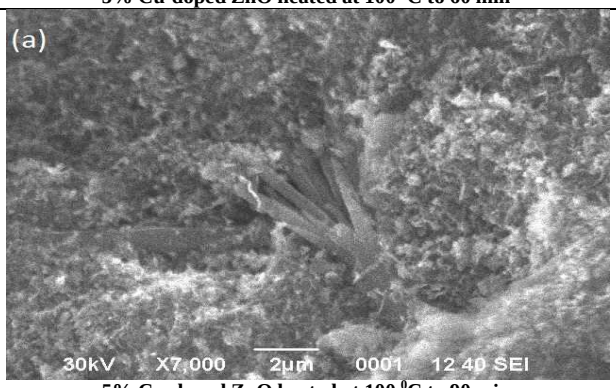
5% Cu-doped ZnO heated at 100 ^{0}C to 30 min



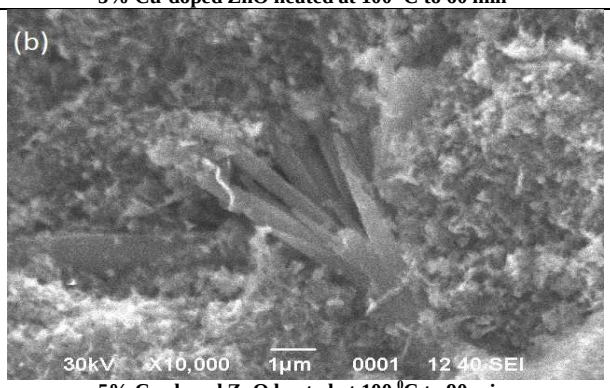
5% Cu-doped ZnO heated at 100 ^{0}C to 60 min



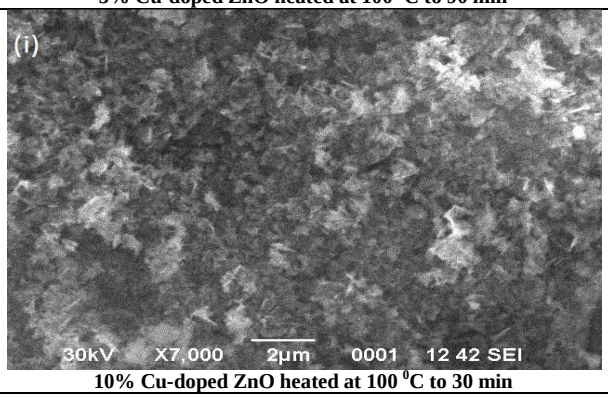
5% Cu-doped ZnO heated at 100 ^{0}C to 60 min



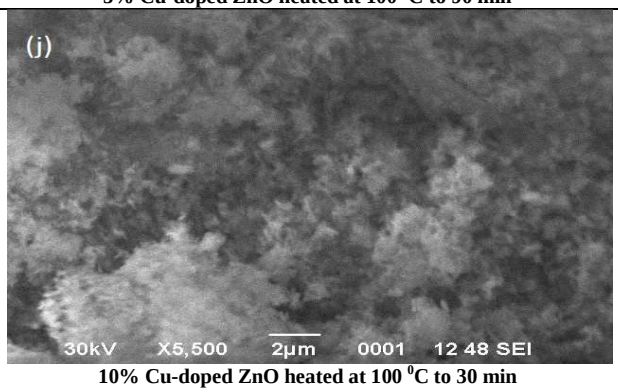
5% Cu-doped ZnO heated at 100 ^{0}C to 90 min



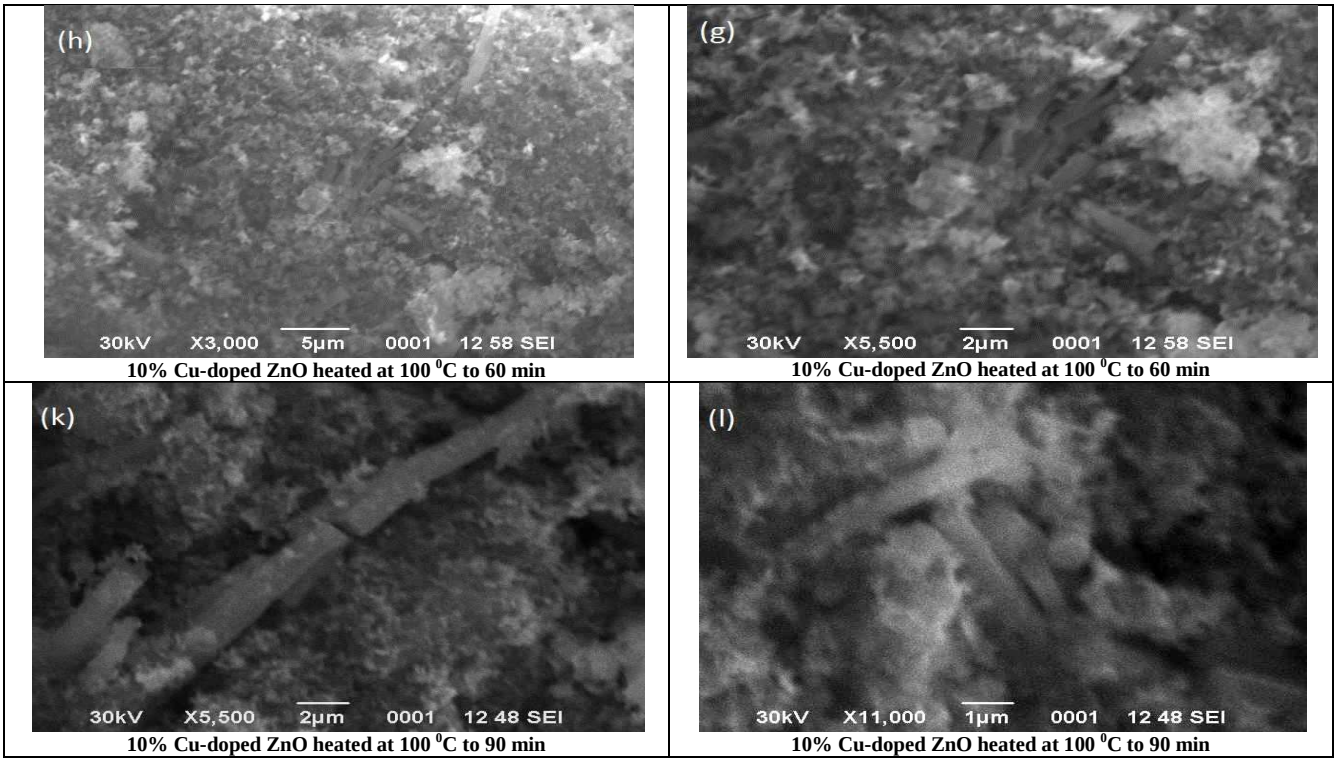
5% Cu-doped ZnO heated at 100 ^{0}C to 90 min



10% Cu-doped ZnO heated at 100 ^{0}C to 30 min



10% Cu-doped ZnO heated at 100 ^{0}C to 30 min

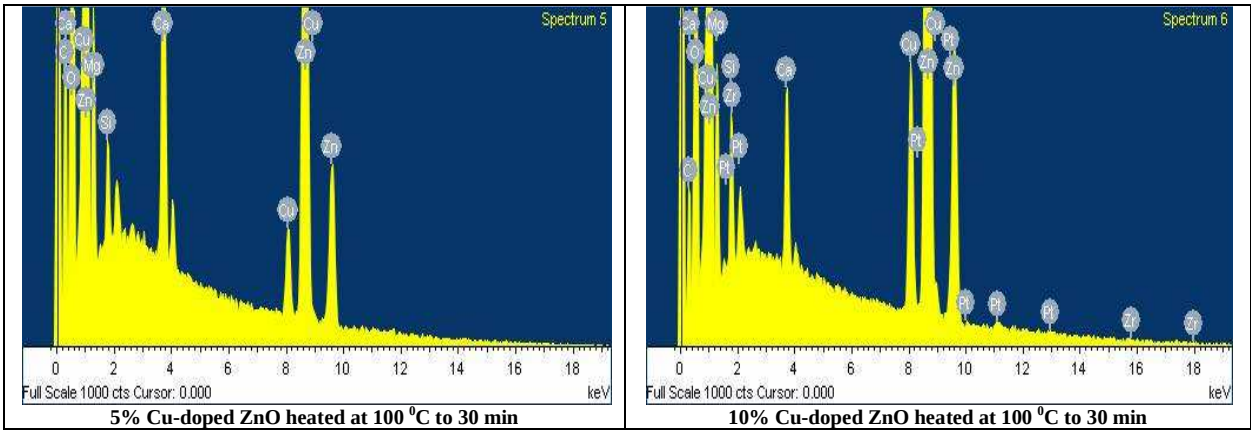


10% Cu-doped ZnO heated at 100 ^{0}C to 60 min **10% Cu-doped ZnO heated at 100 ^{0}C to 60 min**

10% Cu-doped ZnO heated at 100 ^{0}C to 90 min **10% Cu-doped ZnO heated at 100 ^{0}C to 90 min**

Figure-1 SEM micrograph for 5%, 10%Cu-doped ZnO heated at temperature 100 ^{0}C to different time 30, 60 and 90 minutes at different resolution of SEM

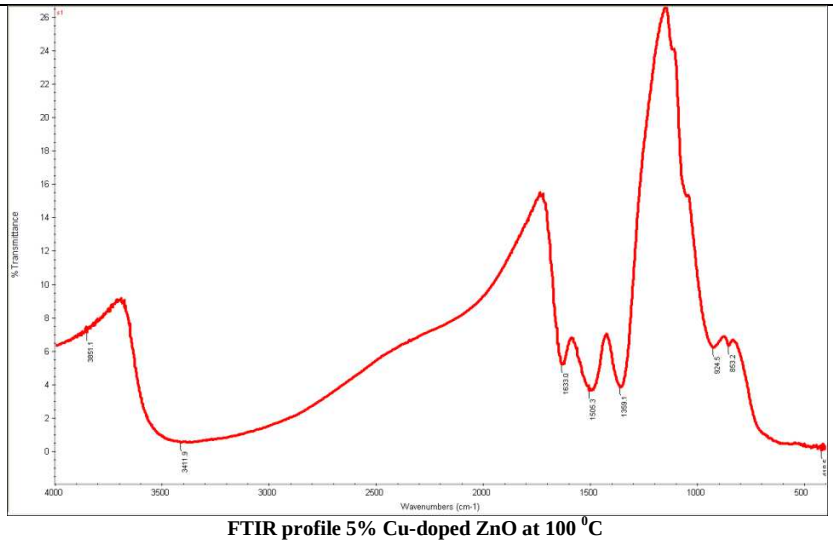
Morphology and elemental analysis were carried out by Energy Dispersive Spectra (EDX). EDX (Fig.2) data shows composition of Cu, Zn are present in sample and other impurities such as Mg, Ca, Al, Si ,C and O present in atmosphere. Zn:Cu:O ratio has been calculated to be 0.95:0.05:1 and 0.90:0.0.1:1 for 5% Co-doped ZnO and 10% Cu-doped ZnO respectively. Other peaks corresponds to Al, Ca, Mg, Si,C and O are seen due to some impurities.



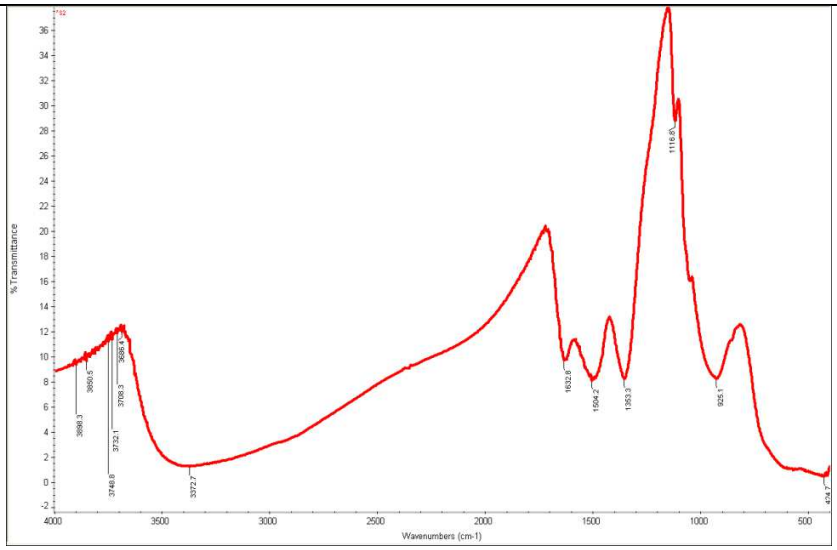
5% Cu-doped ZnO heated at 100 ^{0}C to 30 min **10% Cu-doped ZnO heated at 100 ^{0}C to 30 min**

Figure 2 Shows EDX image and spectra of Cu-doped ZnO partical with different concentration 5%, 10% of Cu in ZnO at 100 ^{0}C

In the FTIR pattern (Fig.- 3) the broad and intense peak at 3398 cm^{-1} corresponds to O-H due to presence of hydrated H_2O molecules. A part from this duplet peaks at 1486 cm^{-1}, 1394 cm^{-1} due to CH_2 bending and CH_2 wagging of diethylene glycol molecules. The other peak at 855 is due to C-C stretching of diethylene glycol. All the peaks corresponds to diethylene glycol shows some downward shifts as compared to pure diethylene glycol indicating adsorption of diethylene glycol at doped ZnO particles surface.



FTIR profile 5% Cu-doped ZnO at 100 ^{0}C



FTIR profile 10% Cu-doped ZnO with 30 minutes at 100 ^{0}C

Figure-3 FT -IR Spectra of Cu-doped ZnO particles

CONCLUSION

Nanocrystals of 5% and 10% Cu doped ZnO particles were successfully prepared by wet chemical aqueous phase synthetic method and characterized by SEM, EDX and FTIR. The effects of dopant contents and synthesis process on the structural and FTIR pattern of the products were discussed. Further studies on this environmentally benign system may provide many interesting aspect in the field of material science.

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