PREPARATION AND CHARACTERIZATION OF Cu DOPED ZnO POWDER AND ITS ELECTRICAL AND OPTICAL PROPERTIES

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Abstract

The main aim of the research work is to study the preparation and characterization of Cu doped ZnO powder and its electrical and optical properties. Cu doped ZnO nanocrystalline powder was prepared by using a sol-gel method. Cu doped ZnO powder ($Zn_{(1-x)}Cu_xO$) was prepared by using different dopant concentration of Cu (x = 0.03, 0.05). $Zn_{(1-x)}Cu_xO$ (x = 0.03, 0.05) was synthesized via the sol-gel technique using new organic precursors pectin and sucrose. The prepared Cu doped ZnO powder was characterized by TG - DTA , XRD, FT IR and SEM analyses.TG-DTA analysis of the synthesized Cu doped ZnO powder was carried out to determine the appropriate calcination temperature. From XRD analysis, it was observed that the crystallite size of the prepared $Zn_{(1-x)}Cu_xO$ (x= 0.03, 0.05) are 74 and 72 nm. FT IR spectra of Cu doped ZnO powder, the prominent peak of OH stretching, C-H stretching, O-C-O sym stretching and M-O stretching vibrations was observed. Morphological studies were conducted using SEM to comfirm the grain size and texture. The ac conductivities and dielectric properties of the prepared Cu doped ZnO samples was investigated in the frequency range 10 kHz – 100 kHz by LCR meter. The experimental results indicated that the ac conductivity (σ_{ac}) , dielectric loss factor (tan δ) and dielectric constant (έ) depend on the frequency. It was observed that ac conductivity is inversely proportional to the dielectric loss factor and dielectric constant. UV-Visible spectrum showed absorbance peaks in the 200-800 nm region. It was found that the absorbance does not significantly change with doping. From UV-Visible spectral data, it was found that the band gap values of $Zn_{(1-x)}Cu_xO$ (x = 0.03, 0.05) are 3.2 and 3.0 eV.

Keywords: sol-gel, dielectric loss factor, dielectric constant, ac conductivity

Introduction

Metal oxides like zinc oxide (ZnO), tin oxide (SnO_2) and indium oxide (In_2O_3) in their pure forms and also in doped forms have been extensively investigated in recent years. Among these, ZnO has gained prominence because of its abundance and non-toxicity and also because it is inexpensive compared to others. Zinc oxide (ZnO) is a II-IV semiconductor with a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature (Soitah *et al*., 2010).

Nanoparticles of ZnO are used in a variety of applications. They can be used as UV absorbent, antibacterial treatment material, catalytic agent and as an additive material in several industrial products. It is currently being used in the fabrication of solar cells, gas sensors, luminescent materials, transparent conductors, heat mirrors and coatings. (Ghosh *et al*., 2015)

Many physical properties of ZnO, such as piezoelectricity, electrical conductivity and defect structures, are greatly influenced by the presence of impurity. Several dopants (Fe, Cr, Al, Cu, Co, Mn, Mg, S, P, etc.) can lead to an increase in the surface area of the ZnO based powders. The dopants stabilize the ZnO surface, and they also promote changes in the grain size.

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The dielectric properties of pure ZnO are dependent on the presence of interstitial zinc atoms and lack of oxygen at O sites. As pure ZnO is sensitive to oxidation, absorption of O_2 results in a decrease of its dielectric properties. Therefore, different dopants have been introduced into ZnO to modify its dielectric and other properties depending on the desired applications. In many cases, when ZnO has been doped, the dielectric properties were reported to be change because of the extrinsic defects (Zhang *et al*., 2010).

Methods such as pulsed laser deposition, vapour phase transport and chemical vapour deposition have been developed for the preparation of nanostructures of ZnO. Sol-gel method is one of the most important wet chemical methods used for the preparation of metal oxide nanoparticles. ZnO nanoparticles have been obtained through the sol-gel method using both conventional and new organic precursors (sucrose and pectin).

The aim of this study is to investigate electrical and optical properties of Cu doped ZnO nanocrystalline powder by using the sol-gel method, replacing the organic compounds with commercial sucrose and pectin from banana peels. Structural and morphological characterizations of the samples were performed using powder X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. Electrical properties were investigated using inductance capacitance resistance (LCR) measurements and optical properties by UV-Visible (UV-Vis) spectroscopy.

Materials and Methods

Sample collection

Zinc(II)sulphate heptahydrate (BDH), copper(II)sulphate pentahydrate (BDH), sucrose and pectin from banana peels. Distilled water was used as the solvent in all analyses.

Preparation of 0.03 mol and 0.05 mol Copper Doped Zinc Oxide by Sol-gel Method

The common salts $ZnSO_4.7H_2O$ and $CuSO_4.5H_2O$ (0.03 mol and 0.05 mol) were used as zinc and copper precursors. Zinc(II)sulphate was dissolved in distilled water on a warming plate at 100 °C. Next, the copper sulphate for a final composition of 0.03 mol and 0.05 mol CuO to ZnO were calculated and added to the solution. After the homogenization, a sucrose and pectin mixture with a mass ratio of 1:0.02 was added to the mixture solution under continuous stirring. The thermal treatment continues and the mixture is dried at 90-100 °C and is allowed to stand for 2 h. During this, the solution becomes highly viscous and the gel was formed. The gel was dried completely at an oven at 120 °C for 4 h. The dried gels were grounded with motar and pestle. The prepared sample was calcinated at 900 °C for 4 h. Finally, Cu doped ZnO powder was obtained.

Preparation of Copper Doped Zinc Oxide Pellets

The obtained powder (0.03 mol and 0.05 mol Cu doped ZnO) were pressed into pellets with diameter 1.5 cm and thickness 0.16 cm using MAEKAWA Testing machine.

Characterization of the Prepared Copper Doped Zinc Oxide Samples

Thermal properties of the prepared Cu doped ZnO were evaluated by TG-DTA. The powder X-ray diffraction methods are used to study the structural properties and the phase purity of the samples. The functional group of prepared Cu doped ZnO was analysed using FT IR. The morphological structure of the prepared Cu doped ZnO was characterized by SEM. The dielectric

properties and frequency dependent electrical conductivity were also determined by LCR meter in the frequency range of 10-100 kHz. The optical properties of prepared Cu doped ZnO by UV-vis spectrophotometer in the range of 200 to 800 nm was presented.

Thermogravimetric analysis of smples were performed by using TG-DTA apparatus, (Hi-TGA 2950 model). The temperature range between 0 °C and 600 °C under nitrogen gas (at a rate of 50mL/min).

X-ray diffraction (XRD) analysis was carried out using Rigaku X-ray Diffractometer, RINI 2000/PC software, Cat.No 9240 J 101, Japan. Copper tube with nickel filter was used. The diffraction pattern was recorded in terms of 2θ in the range of 10-70 °.

FT IR spectrum was recorded in the range of 4000-400 $cm^{-1}$by using 8400 SHIMADZU, Japan FT IR spectrophotometer.

The scanning electron microscopy (SEM) images were obtained by using JSM-5610 Model SEM, JEOL-Ltd., Japan.

For the electrical conductivity measurements, the obtained samples were pressed in the form of pellet using MAEKAWA Testing machine. The dielectric permittivities such as dielectric constant έ, dielectric loss factor tan δ and ac conductivity were determined using LCR-B110G meter (DC 20-10 MHz) in the frequency ranged of 10-100 kHz at ambient temperature. Frequency dependent electrical conductivity was evaluated by using dielectric equation;

$$C = \frac{\acute{\varepsilon}\,\varepsilon_0 A}{d}$$

$$\omega = 2\pi f$$

$$\sigma_{ac} = \acute{\varepsilon}\,\varepsilon_o \tan\delta\,\omega$$

where, C is capacitance (F), έ is dielectric constant, ε_0 is electrical permittivity in vacuum (8.85×10^{-14} Fcm^{-1}), d is sample thickness (cm), A is sample area ($2\pi r^2$)(cm^2), ω is circular frequency (kHz), tan δ is dielectric loss factor and σ_{ac} is electrical conductivity (μScm^{-1})

The UV-Visible spectra of powder samples are observed in the 200-800 nm range by using UV-Visible spectrophotometer. The energy band gap is determined by using the relationship;

$$\alpha = A\,(h\upsilon - E_g)^n$$

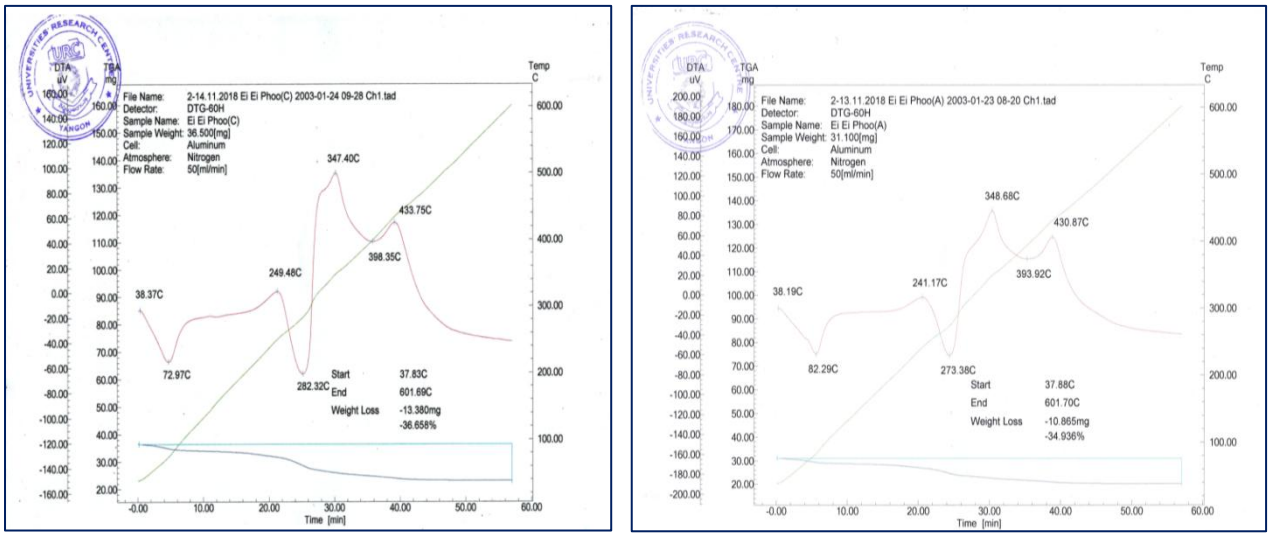
Where, hυ is photon energy, α is Absorption coeffiecient ($\alpha = 4\pi k/\lambda$), k is the absorption index or absorbance, λ is wavelength in nm, E_g is energy band gap, A is constant and n = ½ for allowed direct band gap.

Results and Discussion

0.03 mol and 0.05 mol of Cu doped ZnO powder were prepared by sol-gel method using sucrose and pectin. The resultant prepared samples were characterized by modern techniques (TG-DTA, XRD, FT IR and SEM). Moreover, their electrical and optical properties were investigated by LCR meter and UV-vis spectrophotometer.

Thermal Analysis of the Prepared Cu Doped ZnO Powder

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) thermograms of prepared $Zn_{1-x}Cu_xO$ (x = 0.03 and 0.05) are shown in Figure 1. Weight loss percent of 0.03 and 0.05 mol Cu doped ZnO are listed in Table 1. TGA curve of prepared Cu doped ZnO indicates that there are three stages of decomposition (Figure 1 (a)). Endothermic peaks observed at 72 °C and 82 °C for 0.03 and 0.05 mol of Cu doped ZnO with 5.22 and 5.36% weight loss are due to the evaporation of water presence in the Zn-Cu precursors. Endothermic peaks observed at 282 °C and 273 °C for 0.03 and 0.05 mol of Cu doped ZnO with 15.06 and 17.86% weight loss are due to the dehydroxylation of $Zn(OH)_2$. Exothermic peaks observed at 347 °C and 348 °C for 0.03 and 0.05 mol of Cu doped ZnO with the 15.34 and 17.38% weight loss are due to the decomposition of organic residues. Total weight loss of 0.03 mol and 0.05 mol Cu doped ZnO are given in Table 1.



(a) (b)

Figure 1 TG-DTA thermograms of prepared (a) 0.03 mol and (b) 0.05 mol of Cu doped ZnO Powder

Table 1 Total Weight Loss Percent of Prepared 0.03 mol and 0.05 mol of Cu Doped ZnO from TG-DTA Analyses

Sample	Temperature range(°C)	Nature of peak	Weight Loss (%)	Total Weight Loss (%)
Cu doped	38-120	endo	5.22	
ZnO	120-310	endo	15.06	36.06
(0.03 mol)	310-600	exo	15.78	
Cu doped	38-120	endo	5.36	
ZnO	120-310	endo	16.14	34.94
(0.05 mol)	310-600	exo	13.44	

XRD Analysis of the Prepared Cu Doped ZnO Powder

The powder x-ray diffraction methods are used to study the structural properties and the phase purity of the samples. Figures 2 (a-b) represent the XRD pattern of prepared 0.03 mol and 0.05 mol of Cu doped ZnO. In Figure 2, the X-ray diffractions of prepared Cu doped ZnO show sharp peaks at 2θ (36.23 °) for 0.03 mol and at 2θ ~ 36.25 ° for 0.05 mol respectively. The particle size of prepared samples were determined using the Debye Scherrer equation.

$$D = k\lambda/\beta Cos\theta$$

where k is constant equal to 0.94, D and λ are the particle size in nanometers and wavelength of the radiation (1.54056 Å for Cu kα radiation), respectively.β and θ are the peak width at half-maximum intensity (FWHM) and peak position.

The particles size for 0.05 mol Cu doped ZnO was found to be 72 nm which is lower than 74 nm for 0.03 mol Cu doped ZnO. The decrease in the particle size was attributed to disorders created by the copper ions in the ZnO lattice structure. From the study it was assumed that for a smaller amount of Cu^{2+}, its ions substitute well with Zn^{2+} ions, but increasing Cu concentration causes a CuO cluster to form and isolate as an impurity phase.

The volume of unit cell and Zn-O bond length for 0.03 mol and 0.05 mol Cu doped ZnO are given in Table 2. It is observed that with the increase in Cu content, bond length increases which is attributed to the segregation of Cu. This is visible as some low-intensity peaks in XRD as the dopant concentration increases. This suggests that the crystalline quality of ZnO is improved by Cu doping.

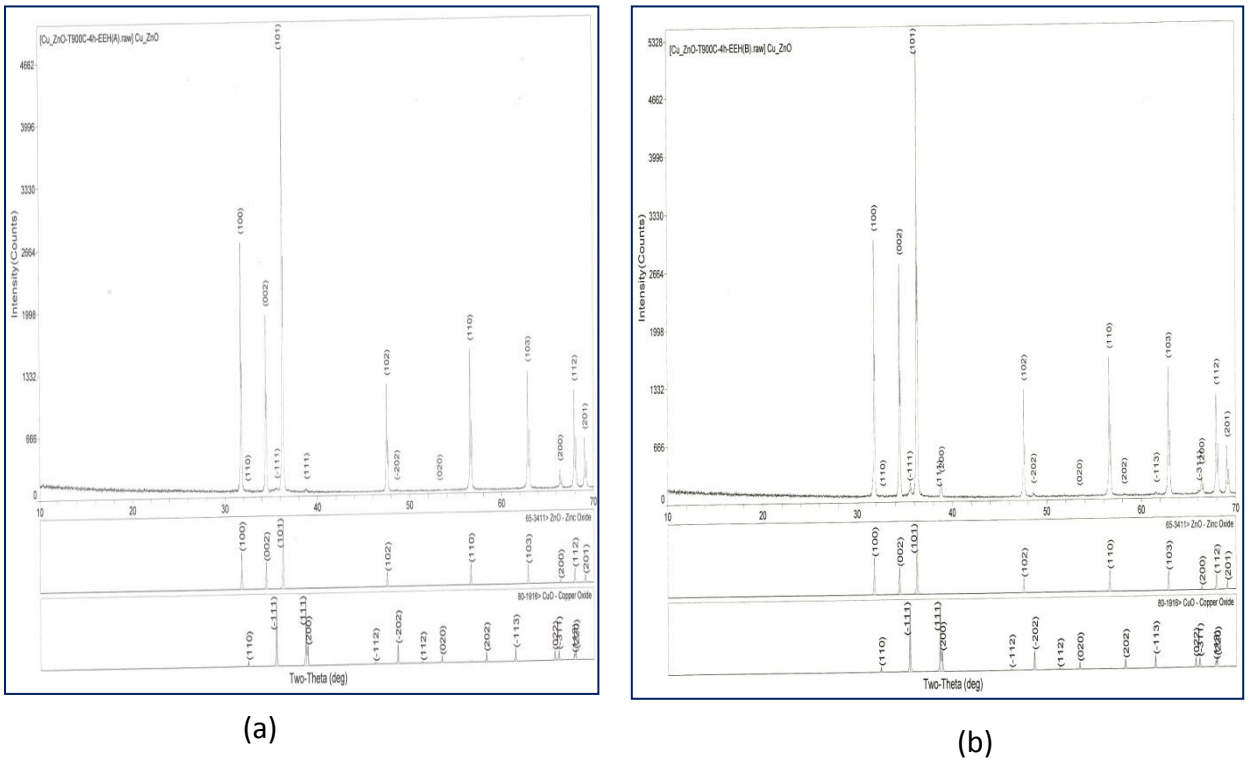


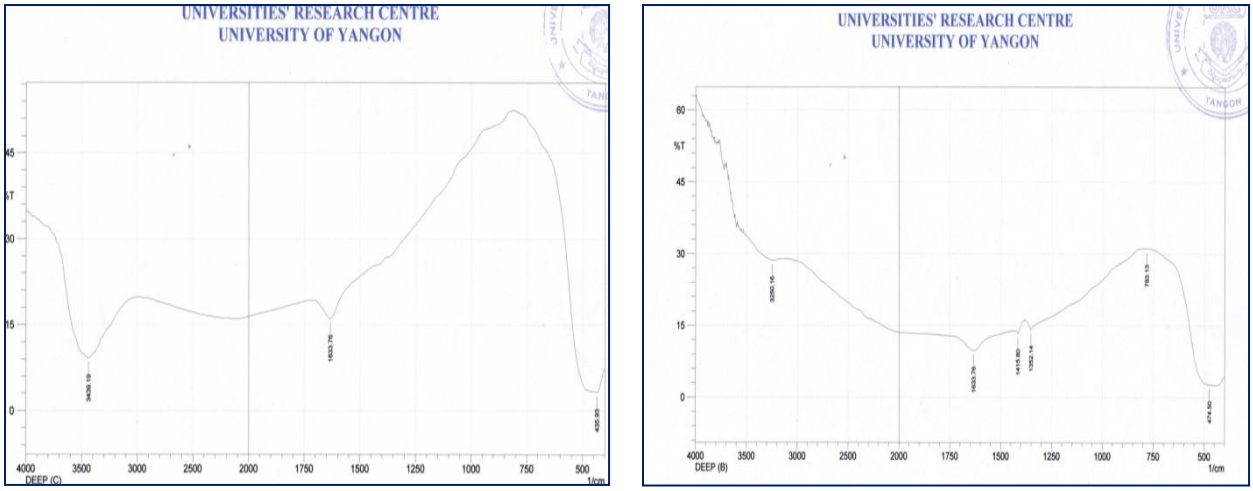
Figure 2 XRD patterns of prepared (a) 0.03 mol and (b) 0.05 mol Cu doped ZnO powder at 900 °C for 4 h

Table 2 XRD analyses of prepared 0.03 mol and 0.05 mol of Cu doped ZnO powder

Peak	(hkl)	Average Crystallite size from XRD (nm)		By using Debye Scherrer (nm)		Volume of Unit Cell (Å)^3		Zn-O bond length (Å)	
		Cu doped ZnO (0.03 mol)	Cu doped ZnO (0.05 mol)	Cu doped ZnO (0.03 mol)	Cu doped ZnO (0.05 mol)	Cu doped ZnO (0.03 mol)	Cu doped ZnO (0.05 mol)	Cu doped ZnO (0.03 mol)	Cu doped ZnO (0.05 mol)
1	100	63	100	46	83				
2	110	26.3	39.9	23	33				
3	002	100	100	76	84				
4	$\bar{1}11$	29.4	53.7	25	40				
5	101	77.7	76.1	50	50				
6	111	49.2	37.2	37	30				
7	102	100	100	73	77				
8	$\bar{2}02$	38	50.7	28	36				
9	020	56.5	100	38	62	45.81	46.06	1.95	1.96
10	110	100	100	65	67				
11	103	100	100	58	53				
12	200	90.6	77.2	46	42				
13	112	100	100	55	53				
14	201	100	100	59	54				
15	200	-	52.2	-	38				
16	202	-	37.8	-	26				
17	$\bar{1}13$	-	43.3	-	29				
18	$\bar{3}11$	-	25.7	-	17				
Average		74	72	49	48				

FT IR Analysis of the Prepared Cu Doped ZnO Powder

Figure 3 shows the FT IR spectrum of prepared Cu doped ZnO powder. The assignment data is summarized in Table 3. In the spectrum of 0.03 mol and 0.05 mol Cu doped ZnO, the peak observed at 3439 cm^{-1} corresponds to O-H stretching vibration and the peak at 1633 cm^{-1} corresponds to O-H bending vibration. Which are related to the absorbed water on the surface of nanomaterial. Another intense absorption peak at 435 cm^{-1} is related to the stretching vibrations of the Zn-O bond is described in Table 3 (Silverstein *et al*., 2003).



(a) (b)

Figure 3 FT IR spectra of the prepared (a) 0.03 mol and (b) 0.05 mol Cu doped ZnO powder

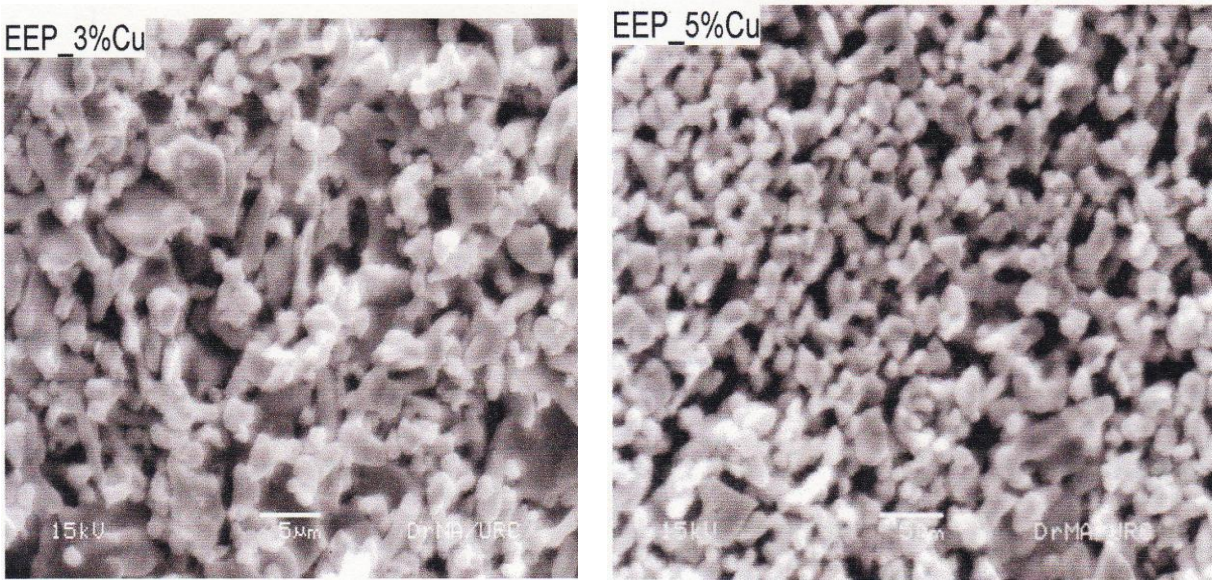
SEM Analysis of the Prepared Cu Doped ZnO Powder

Figures 4 (a-b) show the morphological differences between the 0.03 mol and 0.05 mol Cu doped ZnO. The SEM images reveal the formation of homogeneous and uniform distributed nanopowder. The average particle size was found to decrease with the increase in Cu doping into the ZnO matrix. The decrease in the particle size is mostly ascribed to the formation of Cu-O-Zn on the surface of the doped nanoparticles, which prevents the growth of crystal grains and assists separation of particles.

Table 3 FT IR Band Assignments of the Prepared 0.03 mol and 0.05 mol Cu doped ZnO Powder

Observed wave number (cm^{-1})		*Literature wave number (cm^{-1})	Band Assignment
0.03 mol Cu doped ZnO	**0.05 mol Cu doped ZnO**		
3439	3250	3500-3200	O-H stretching
1633	1633	1655-1630	O-H bending
-	1415 1352	1450-1350	O-C-O sym stretching
-	783	790-750	C-H bending out of plane
435	474	550-420	Zn-O stretching (or) Cu-O stretching

* Silverstein *et al*., 2003

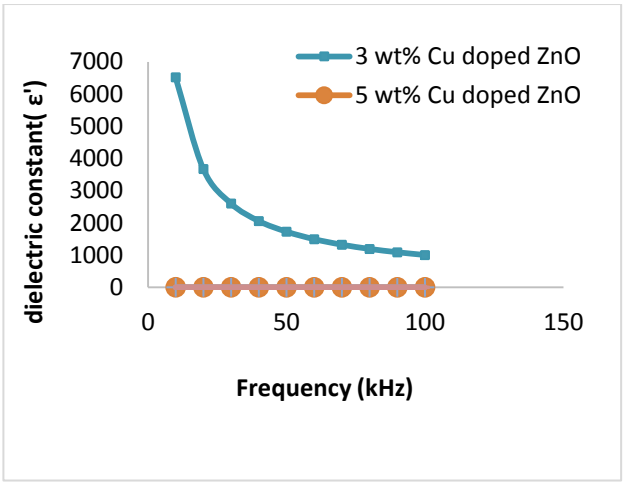


(a) (b)

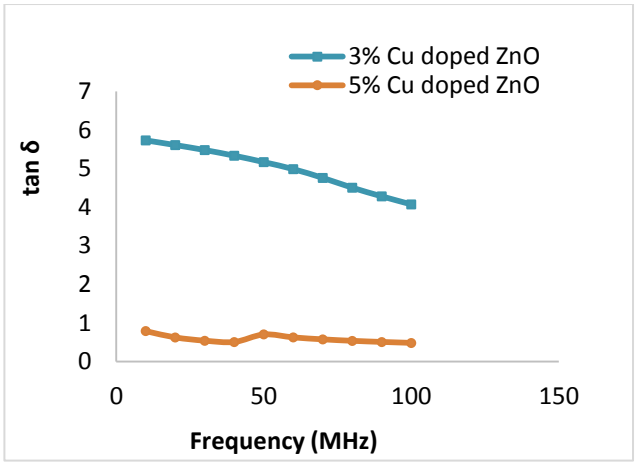
Figure 4 SEM micrographs of the prepared (a) 0.03 mol and (b) 0.05 mol Cu doped ZnO powder

Dielectric Properties

The frequency dependent dielectric permittivities such as έ, tan δ and ac conductivity of prepared 0.03 mol and 0.05 mol Cu doped ZnO are presented in Figures 5 (a-c). It is seen that the ac conductivity increases slightly with frequency. This type of frequency response indicates localized conduction in the ZnO samples, where ac conductivity increases with frequency. Higher conductivity is found in 0.03 mol Cu and the level decreases with the increase in Cu doping. This may be attributed to the fact that the Cu dopant introduces defect ions (such as zinc interstitials and oxygen vacancies) in the ZnO system. Figure 5(a) presents the dielectric constant with frequency of 0.03 mol and 0.05 mol Cu doped ZnO, showing that dielectric constant decreases with increase in frequency, which can be considered as a normal dielectric behavior. The space charge polarization occurring at the interfaces at lower frequency can also be contributed to the dielectric permittivity at lower frequencies. The dielectric constant initially decreases abruptly with increase in frequency. However, it remains almost constant at higher frequencies for all samples. The reason is that beyond a particular frequency of the applied electric field, the electron exchange does not follow the alternating field. Hence, the polarization decreases causing a decrease in dielectric constant έ.



(a)



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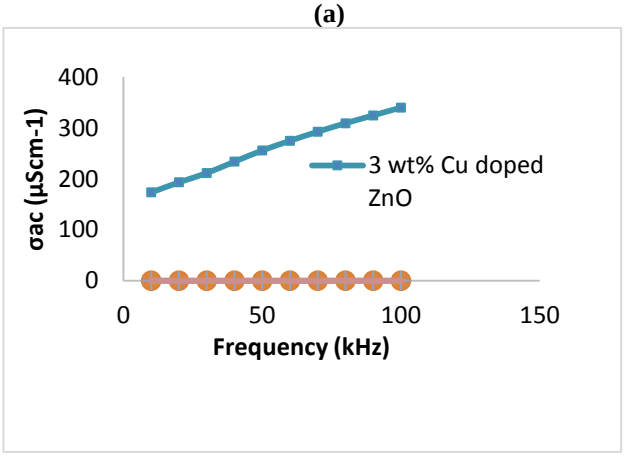
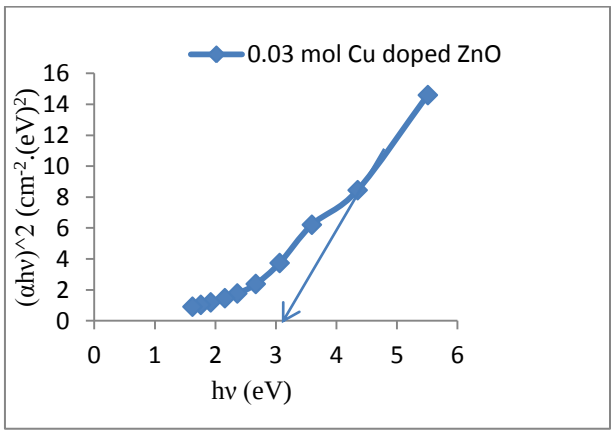


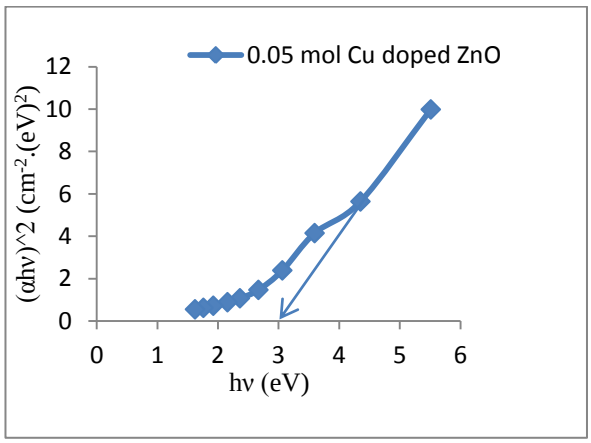
(c)

Figure 5 Plots of Relationship between (a) dielectric constant (b) dielectric loss factor and (c) electrical conductivity of prepared 0.03 mol and 0.05 mol of Cu doped ZnO powder at 4 V potential

The dielectric loss factor of 0.03 mol and 0.05 mol Cu doped ZnO as a function of frequency is shown in Figure 5(c). In nanomaterials, impurities, defects and space charge formation in the interface layers together produce an absorption current gets reduced, and hence the dielectric loss will be reduced.



(a)



(b)

Figure 6 Variation of $(\alpha h\nu)^2$ and photon energy (hν) of prepared (a) 0.03 mol and (b) 0.05 mol Cu doped ZnO powder

Optical Properties

UV-Visible studies are conducted with an intention of measuring the optical band gap of nanocrystals. The optical band gap values were evaluated using Taucs' relation. The electronic transition is represented in Figure 6. The transition energy can be easily deduced from the zero crossing of the second derivative of the absorption spectrum. According to Fermi exclusion principle, for higher photon energies, optical transitions can only occur from the valence band up to the conduction band. Band gap gradually decreases with the doped amount of Cu. The impurity energy levels and defects always contribute to the decrease of energy gap. This implies that the addition of Cu enhances the conductance of the sample expected. However 0.05 mol of energy gap is smaller than the 0.03 mol Cu doped ZnO. By adding a trace amount of Cu, the conductivity of ZnO can be improved without altering the other properties of ZnO.

Conclusion

In this study, the structural, electrical and optical properties of 0.03 mol and 0.05 mol Cu doped ZnO powder prepared by using sol-gel method. The structural analysis confirms the formation of ZnO in both 0.03 mol and 0.05 mol Cu doped samples. Change in crystalline size is observed with the increasing doping concentration of Cu. Electrical studies confirmed that the conductivity increases slightly with frequency but decreases with doping at higher concentration whereas it increases as the concentration decrease.

Optical properties and band gap were determined by UV-Visible spectra. The energy band gap values for 0.03 mol and 0.05 mol Cu doped ZnO were found to be decreased from 3.2 to 3.0 eV. The observations of Cu doped ZnO reveal that this sample can be chosen as a semiconductor material.

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