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Synthesis and Characterization of $Zn_{1-X}Cu_XO$ (X=0.0, 0.02, 0.04, 0.06) Nano-Powder via Sol-gel Method

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Abstract

In the present work, Cu-doped ZnO nanopowder was synthesized via a sol-gel method for doping concentration 2, 4, 6 mole %. The synthesized powder was sintered at 500◦C for six hours. Further, all samples were studied by means of X-ray diffraction(XRD), Field Emission Scanning electron Microscopy(FESEM) , UV-visible spectroscopy. XRD study indicates that undoped and doped ZnO have a hexagonal wurtzite structure and also, the traces of any impure phase was not observed within the detection limit of XRD. The crystalline size varies from ~16 to 13nm. The morphology was examined from FESEM micrograph and showed spherical in nature. The particles size observed from FESEM fluctuate in the range ~ 62-37 nm. The optical band gap was calculated from absorption spectra obtained from UV-visible spectroscopy. The energy band gap is found to be in the range ~ 3.19-2.98 eV and decreases with increase in doping concentration

Keywords: ZnO, Copper doped, Sol-gel, Energy Band Gap

1. INTRODUCTION

During last two decade, metal oxide semiconductors like TiO_2, SnO_2, CeO_2, ZnO etc. have been paid more attention due to their attractive applications in the various fields

of science and technology. The wide band gap semiconductor ZnO, is one of them, which has excellent properties like high chemical stability, nontoxicity and biocompatibility. Furthermore it is inexpensive, easy to synthesize [1]. Over a past few years, nanoparticles of ZnO have also been received more attention due to its various types of applications for luminescence, solar cells, sensors, spintronic devices etc. [2]. The applications of ZnO can be improved by suitable dopant, as physical/optical properties depend upon the dopant and synthesis conditions. Different transition metals such as Fe, Mn, Co, Ni, Cr have been doped in ZnO to tune the optical, electrical and magnetic properties [3]. Undoped and doped ZnO have been synthesized by various methods such as sol-gel [1], co-precipitation [2], ball milling [3], etc. by various researchers. To understand the structural and optical properties, the choice of synthesis method have its great importance. During synthesis process the dopant ion should substitute the host material ion and should give homogeneous mixing within host materials. The sol-gel method is preferred here as it is easy, cheap, require less time, yields fine nanoparticles, homogeneous mixing of dopant, doping concentration and temperature can be controlled effectively.

2. EXPERIMENTAL DETAILS

Undoped and copper doped ZnO nanocrystalline powder were synthesized by a sol-gel method using Zinc nitrate {Zn (NO3)2·6H2O} and Copper Nitrate {Cu (NO3)2·3H2O}as precursors. The precursors are mixed in an appropriate ratio in distilled water to get doping concentration 2, 4, 6 mole %. The solution was stirred on a magnetic stirrer for four hours to get a homogeneous solution. Further, the mixture was poured into citric acid, which acts as a chelator in the reaction. The solution was dried at 90◦C to get the gel and which was further kept at the same temperature to get dried materials. The dried materials were grinded with mortar and pestle to get a fine powder and which was further sintered at 500◦C for six hours.

The crystal structure and phase analysis were studied by X-ray diffractometer (Rigaku Japan). Morphology of nanoparticles was analyzed using micrograph obtained from FESEM (Hitachi SU-8010 FE-SEM). Energy band gap was evaluated from UV–visible absorption spectra of the samples recorded by UV-Visible Spectrometer (Perkin Elemer Lambda 650)**.**

3. RESULT AND DISCUSSION

The XRD patterns for $Zn_{1-x}Cu_xO$ (x = 0, 0.02, 0.04, 0.06) are depicted in Fig.1. The patterns were obtained at room temperature by X-ray diffractometer with CuKα radiations (λ = 1.5416 Å) in the scanning range 25˚ to 65˚. All the synthesized samples

have single phase hexagonal wurtzite structure. The peaks were compared with standard data i.e. JCPDS file No.21-1486 and indexed. With doping, the shift towards the higher angle, for the most intense peak (101), was observed as compared with undoped ZnO as shown in the inset of fig.1. It indicates that Cu^{2+} ions substitute Zn^{2+} ions in the host materials without any change in crystal structure. Further, the decrease and broadening of peaks are observed, which is the consequences of smaller radii of Cu^{2+} than that of Zn^{2+} [4]. The average crystalline size 'D' was calculated using Debye Scherrer's formula i.e.

$$D = \frac{k\lambda}{\beta \mathrm{Cos}\theta} \qquad (1)$$

where λ, β, k and θ represents the wavelength of the incident beam, Full Width Half Maxima (FWHM) of the diffraction peak, shape factor (i.e. 0.9) and scattering angle of reflection. The average crystalline size for samples X = 0, 0.02, 0.04 and 0.06 is found 16.30 nm, 15.85 nm, 14.60 nm, and 13.17 nm respectively. Hence, it is suggested that the average crystalline size decrease with increase in dopant concentration. This indicates that with an increase in dopant concentration, dopant suppresses the growth of the crystal. Furthermore, no extra peaks related to oxides of copper are not observed within the detection limit of XRD.

The morphological of all the samples was investigated using micrograph, as shown in fig.2, obtained from FESEM. The average particle sizes of all the samples were estimated and found to be 62 nm, 45 nm, 42 nm and 37 nm for doping concentration 0, 2, 4 and 6 mole %, respectively.

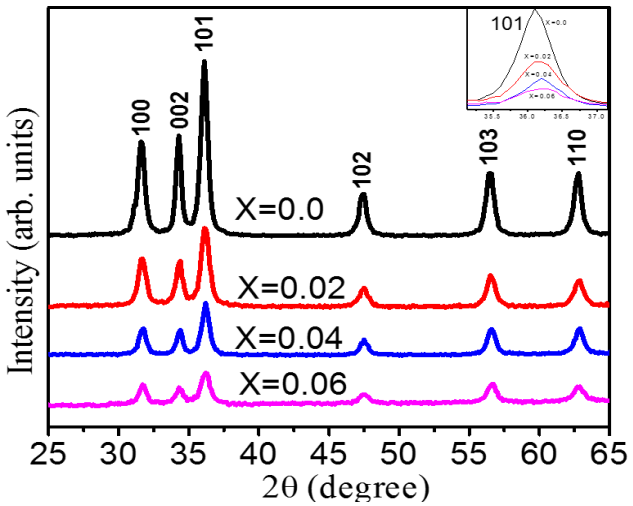

Figure 1: X-ray diffraction patterns of undoped and doped ZnO

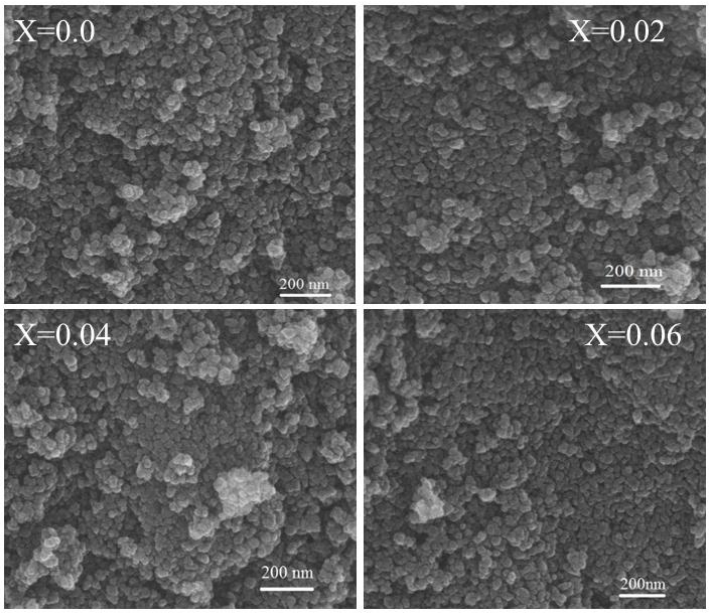

Figure 2: FESEM micrographs of undoped and doped ZnO

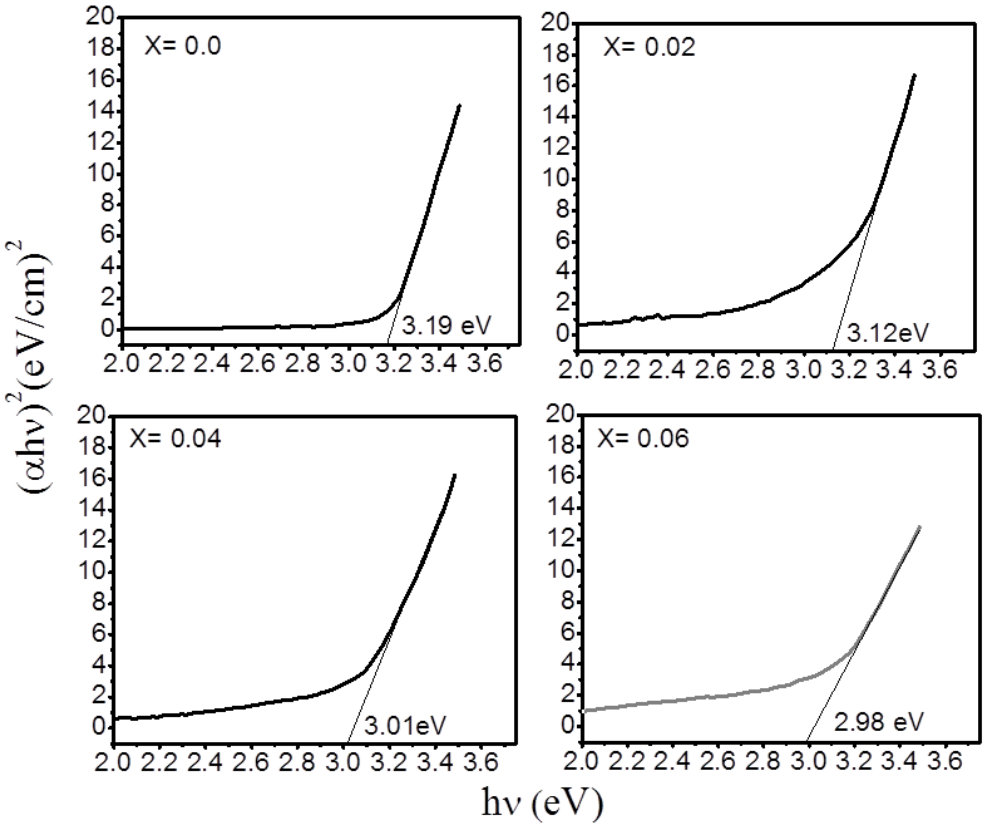

Figure 3: Tauc plot for undoped, and doped ZnO

In order to study the energy band gap of all the samples, the absorption spectra were obtained from UV–vis diffuse reflectance spectroscopy. Further, the Tauc plots $(\alpha h\nu)^2$ vs. $(h\nu)$ of all studied samples were drawn as depicted in Fig. 3. The band gaps for all samples were calculated from the graph using the Tauc equation:

$$\alpha h\nu = A(h\nu - E_g)^2 \qquad (2)$$

where α is the absorption coefficient, $h\nu$ is the photon energy and E_g is Band gap. The energy band gap values have been obtained from the extrapolation of the rising part of the plots to the energy-axis. The estimated bandgap for X=0.0, 0.02, 0.04 and 0.06, samples were found to be 3.19, 3.12, 3.01 and 2.98eV, respectively. The decrease in band gap is due to band gap renormalization effect. According to which the shrinkage in the band gap is due to the s–d and p–d exchange interactions, which give rise to a negative and a positive correction to the conduction-band and valence-band edges, respectively [5]. Thus, in our synthesized samples the decrease in the band gap with doping is due to the s-d and p-d exchange interaction of band electron of host materials ZnO and d electrons of dopant copper. Hence, copper doping can tune the band gap of ZnO host materials and influences the local structural environment of host ZnO lattice.

CONCLUSION

Nanocrystalline powder of undoped and copper doped ZnO was synthesized successfully via the sol-gel method. XRD and FESEM analysis confirmed the single phase hexagonal wurtzite crystal structure of undoped and doped samples. The particles size varies from 62 nm to 37 nm with doping. The decrease in energy band gap is observed with doping and varies from 3.19 eV to 2.98 eV. It is suggested that the decrease in band gap is due to s-d and p-d exchange interaction of band electron of host materials and dopant.

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