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Synthesis, experimental and theoretical investigations of $Zn_{1-x}Cu_xO$ nanopowders

N. Ghajari[a], A. Kompany[a], T. Movlarooy[b,*], F. Roozban[a], M. Majidiyan[a]

[a] Department of Physics (Materials and Electroceramics Laboratory), Ferdowsi University of Mashhad, Iran
[b] Department of Physics, Shahrood University of Technology, Shahrood, Iran

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ABSTRACT

$Zn_{1-x}Cu_xO$ composition (x=0.00, 0.02, 0.04) has been synthesized via gel-combustion method. The prepared powders were characterized using XRD, TEM and UV–vis spectroscopy. The band structure and the total density of states have been calculated for $Zn_{1-x}Cu_xO$ (x=0.0000, 0.0625, 0.1250, 0.1875) using density functional theory (DFT), employing full-potential linearized augmented plane wave method with the generalized gradient approximation (GGA). Our results revealed that with the increasing Cu concentration in ZnO, the energy band gap decreases. Also using GGA+U showed that Cu dopant in ZnO causes the spin polarization expecting the appearance of the magnetic properties in $Zn_{1-x}Cu_xO$ compound.

1. Introduction

Zinc oxide is a II–VI semiconducting compound which has a direct band gap of 3.34 eV and a large exiton binding energy of about 60 meV [1]. The stable phase of zinc oxide is hexagonal wurtzite structure with 186_P63mc space group, at ambient temperature and pressure. ZnO has been extensively used in fabricating electrical, optoelectronic and gas sensing devices [2]. Furthermore, ZnO because of having low toxicity and antibacterial activity has medical applications [3]. It has been shown that adding suitable impurities such as IB elements to ZnO improves its electrical and optical properties. Among these elements Cu seems to be the best candidate, because the ionic radii of Cu and Zn are very close (Cu^{+2}=0.72 Å, Zn^{+2}=0.74 Å). It has been reported that in Cu-doped ZnO thin films, the presence of Cu reduces the energy band gap of ZnO [4–6]. Fu et al. [7] prepared Cu-doped ZnO nanopowders via sol–gel method and showed that Cu enhances the photo catalytic activity of ZnO. Theoretically, Ye et al. [8] investigated the ferromagnetic property of Cu-doped ZnO, using full-potential linearized augmented plane wave method. Similar results were obtained by Ferhat et al. [9]. Bai et al. [10] have investigated optical and electronic properties of wurtzite structure of Mg-doped ZnO alloys, using DFT approach. The electronic and optical properties of wurtzite $Zn_{1-x}Cu_xO$ have been studied by first principles using CASTEP code [11]. In this work we have investigated both experimentally and theoretically the electronic and optical properties of Cu-doped ZnO for different percentages of Cu content. The nanopowders were prepared employing a gel-combustion route and were characterized using XRD, TEM techniques and UV–vis spectroscopy. Also the electronic structure of Cu-doped ZnO was studied theoretically, using DFT with WIEN2k code [12–14]. In our calculations both GGA and GGA+U approaches were used and it was found that the results obtained by GGA+U are much closer to the experimental data comparing to the GGA method. Our results, both experimentally and theoretically revealed that substitution of Zn by Cu decreases the energy band gap of ZnO.

2. Experimental: results and discussion

$Zn_{1-x}Cu_xO$ nanopowders were synthesized by gel-combustion method. The starting materials used were zinc acetate dehydrate ($Zn(CHCOO)_2$, $2H_2O$), copper acetate monohydrate ($Cu(CH_3COO)_2$,H_2O), acetic acid and diethanolamine (DEA). Appropriate amounts of zinc and copper acetates were dissolved in a mixture of isopropanol and distilled water, keeping at 40 °C and stirred for 30 min. Then, certain amounts of DEA and acetic acid were added to this solution and stirred for 10 min. After refluxing the obtained solution and heating in an oil bath at 80 °C for 16 h, the gel was formed. In gel-combustion method, the gel drying

* Corresponding author. Tel.: +98 2733395270; fax: +98 2733395270.
E-mail addresses: web2_tayebeh.movlarooy@shahroodut.ac.ir, tayebeh.movlarooy@yahoo.com (T. Movlarooy).

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process is completed by using a fuel such as glycine, urea or nitric acid. In this work, nitric acid was added as the fuel to the gel in order to complete the drying process. The molar ratio of the fuel to cations was chosen as 3. Finally, the produced powder was calcined at 500 °C for 2 h. Fig. 1, shows the XRD patterns of the prepared $Zn_{1-x}Cu_xO$ nanopowders (x=0.00,0.02,0.04) calcined at 500 °C, which confirms the wurtzite structure of the prepared powders with the lattice constants $a=b=3.20443$ Å, $c=5.33581$ Å with $c/a=1.66$. However, for $x=0.04$ a secondary monoclinic phase is also observed which is due to the CuO. This secondary phase was also observed by recent works [15–17]. Although Zheng et al. [18] used sol–gel method for the synthesis of Cu-doped ZnO, but they have not observed this second phase. Fig. 2, shows the TEM image of pure ZnO in which the particles mostly

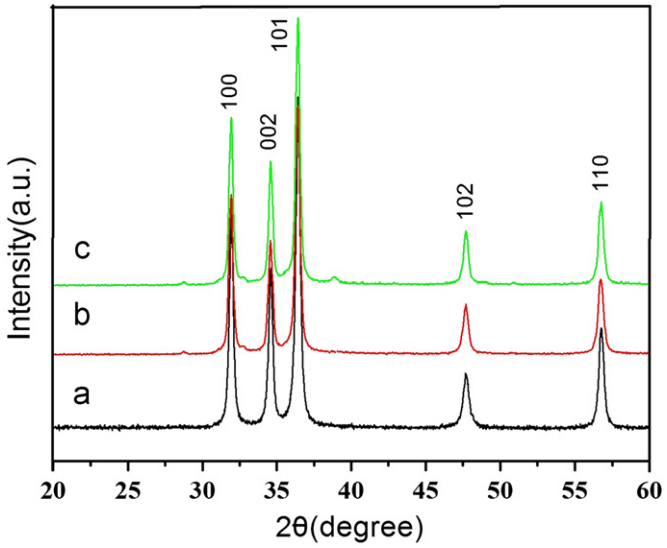

Fig. 1. XRD pattern of the $Zn_{1-x}Cu_xO$ nanopowders (a) x=0.00, (b) x=0.02, (c) x=0.04.

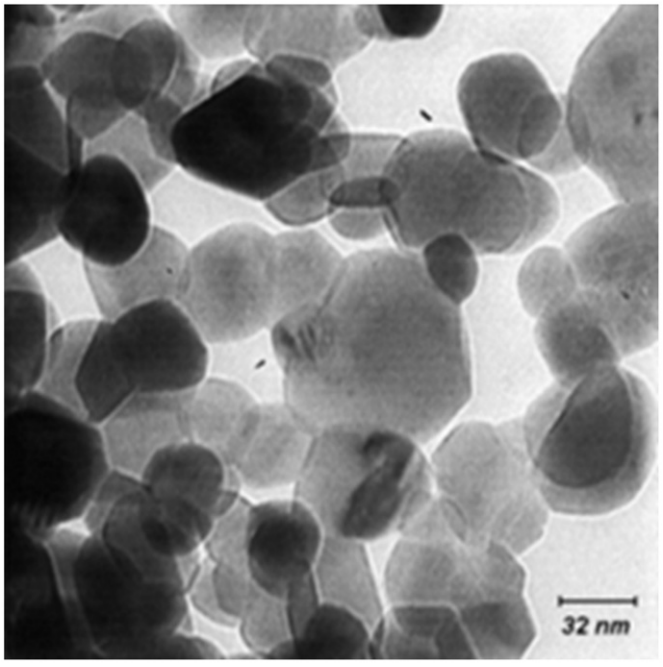

Fig. 2. TEM image of ZnO nanopowder.

have hexagon shape and the average size of the particles is about 38 nm. In order to prepare a sample for UV–vis spectroscopy, the nanopowders were ultrasonically and centrifugally dispersed in distilled water. The UV absorbance spectra of pure and Cu-doped ZnO nanopowders are shown in Fig. 3a). An absorption peak is evident in all UV spectra corresponding to the absorption edge. As it can be seen, the absorption edge wavelengths for all the three samples are very close. Since the average size of the particles is about 38 nm, therefore we have used the absorbance spectra for determining the optical energy band gap by first derivative of absorbance in terms of photon energy spectra [19]. As shown in Fig. 3b)., the value of the optical gap for the pure ZnO, $Zn_{0.98}Cu_{0.02}O$ and $Zn_{0.96}Cu_{0.04}O$ is found to be 3.27, 3.23 and 3.22 eV, respectively. The slight decrease of ZnO band gap energy with Cu content can be due to the strong hybridization of O–p and Cu–d orbitals.

3. Theoretical: results and discussion

The calculations have been performed within the framework of density functional theory (DFT) with the generalized gradient approximation GGA and GGA+U methods using WIEN2k package [12–14]. The method is based on solving the Kohn–Sham equation, which was performed by solutions self-consistent field manner. Besides, the valence electron configurations for the oxygen, zinc and copper atoms are as $2s^2\ 2p^4$, $3d^{10}\ 4s^2$ and $3d^{10}\ 4s^1$, respectively. In our calculations, the supercell employed contains 32 atoms, which corresponds to a $2\times2\times2$ supercell of ZnO. The muffin-tin radii of Cu, Zn, and O were chosen to be 1.8, 1.9 and 1.7a.u, respectively. The iteration halted when the charge difference was less than 0.001e between steps as convergence criterion. The cut-off energy, which defines the separation of the valence and core states, was chosen as −7 Ry. Because of the narrow band (e.g. d-band) of ZnO corresponding to high localization, comparing to s and p bands, GGA approach is not able to describe the position of ZnO energies, properly. So, we used an orbital-dependent potential which adds an extra coulomb interaction U (GGA+U) [20]. In using GGA+U, choosing proper value for U is very important. Actually, U acts as a fitting parameter to reproduce the experimentally observed position of the d states. By employing ultraviolet photoemission spectroscopy of ZnO Powell et al. [21] found out that Zn-3d core level is located at about 7.5 eV below the Fermi level. Fig. 4, shows the DOS of ZnO using GGA+U method. By entering the spin-polarized in GGA+U, DOS spectrum divided into two spin-up and spin-down. There is no significant difference between the two spectra and also both are entirely below the Fermi level, indicating that ZnO is non-magnetic. Also it is revealed that by employing U in the calculations the value of the band gap has increased from 0.8 eV to 1.4 eV, which is closer to the experimental results. Fig. 5 shows the band structure of ZnO calculated by both GGA and GGA+U methods in the energy region −3 to 3 eV. All the observed energy bands from −2 up to Fermi level belong to the hybridization of Zn-3d and O-2p orbitals.

Fig. 6, shows the total density of states (DOS) for ZnO and $Zn_{0.9375}Cu_{0.0625}O$ in wurtzite phase from −10 eV to 10 eV, using GGA approach. Zn-3d and O-2p states can easily hybridize with each other due to their close energy in pure ZnO, but in Cu-doped ZnO the hybridization between Cu-3d and O-2p states is much stronger, as shown in Fig. 7, leading to reduction of the band gap which is in good agreement with the previous theoretical [9,11] and experimental [22] results. Fig. 8 shows the electronic band structure of $Zn_{0.9375}Cu_{0.0625}O$. The bands close to the Fermi level correspond to Cu 3d bands.

As shown in Fig. 9, the injection of spin-polarized in GGA+U approach for $Zn_{0.9375}Cu_{0.0625}O$ causes the shift of spin-up of DOS

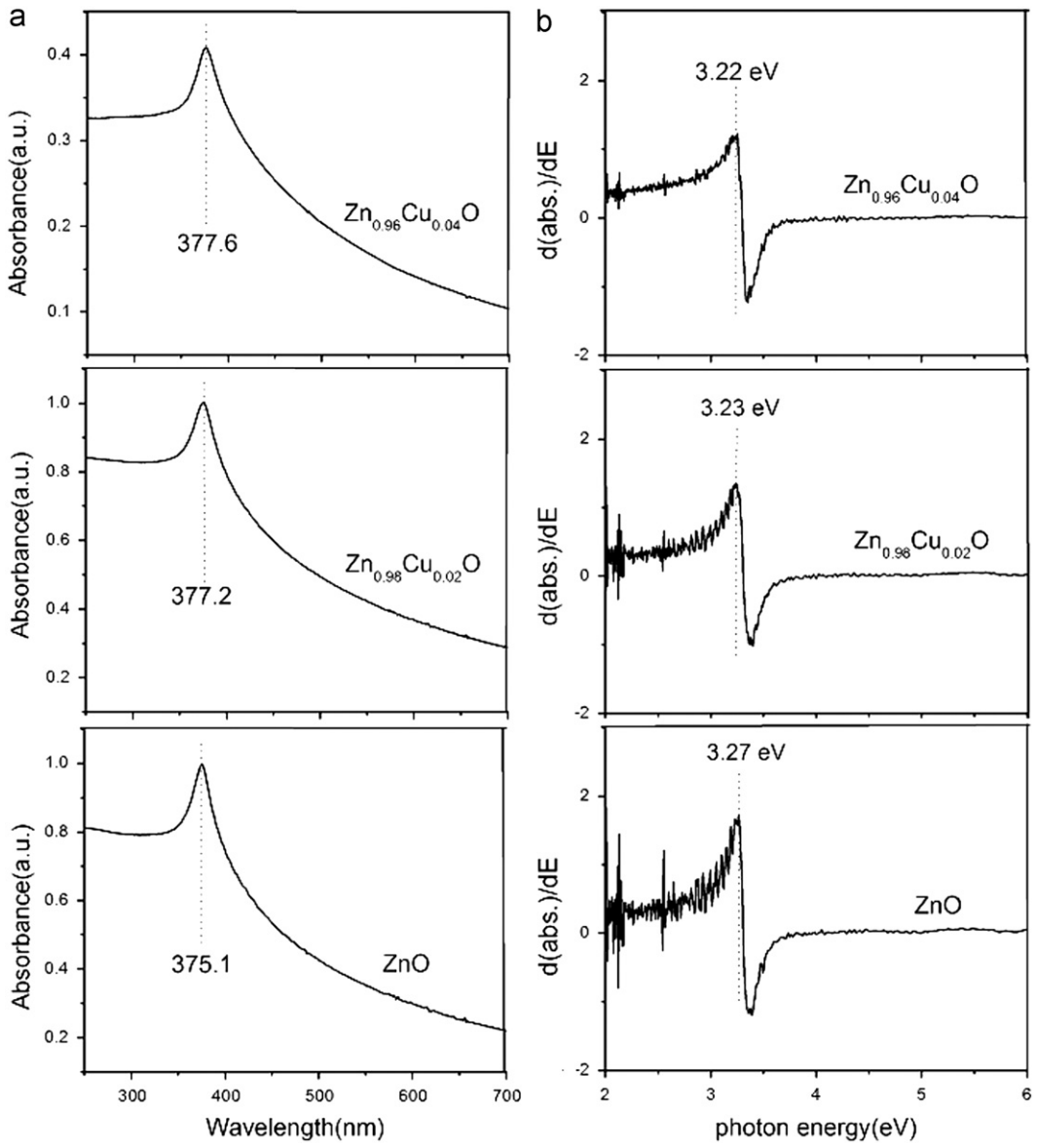

Fig. 3. (a) Optical absorbance in term of photon energy, (b) first derivative of absorbance in term of photon energy.

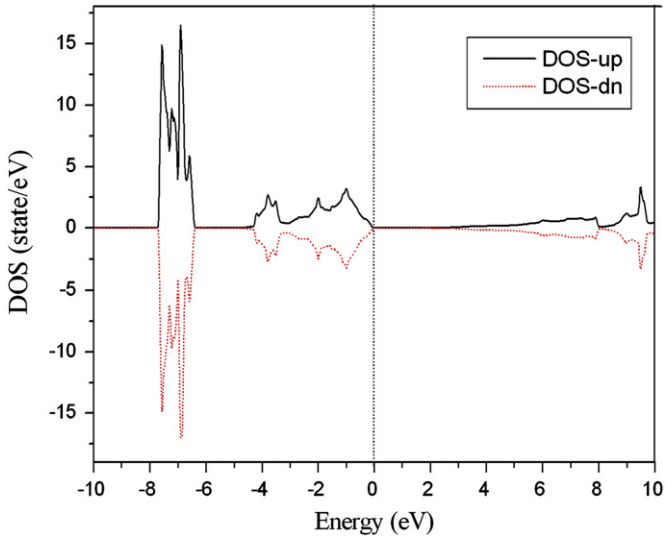

Fig. 4. DOS spectra of ZnO by GGA+*U* method.

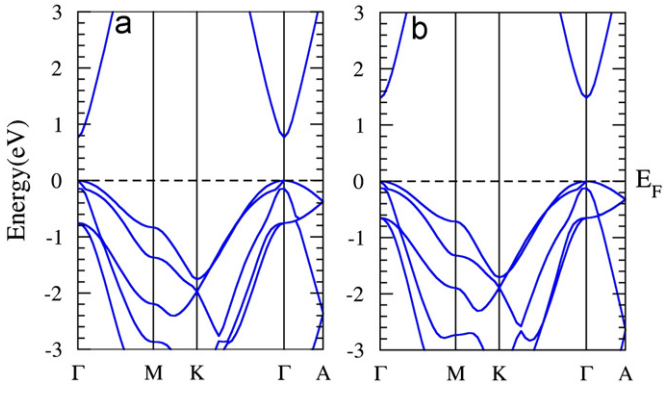

Fig. 5. Band structure of ZnO with (a) GGA, (b) GGA+*U* approach.

spectrum to lower energies, while the spin-down spectrum has shifted to upper energies. This reveals the presence of magnetic properties in $Zn_{0.9375}Cu_{0.0625}O$, which is in good agreement with the experimental data published previously [23].

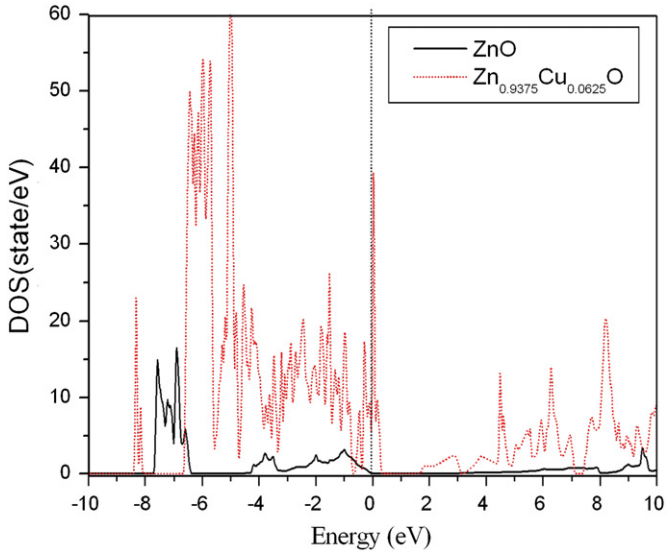

Fig. 6. DOS of ZnO and $Zn_{0.9375}Cu_{0.0625}O$.

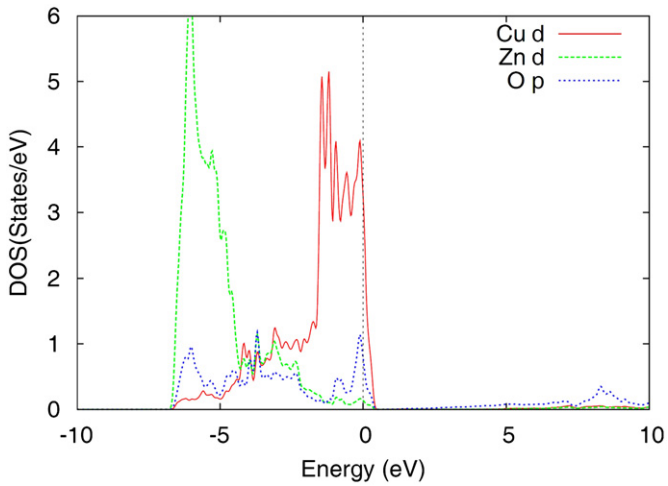

Fig. 7. The partial density of states(PDOS) of $Zn_{0.875}Cu_{0.125}O$.

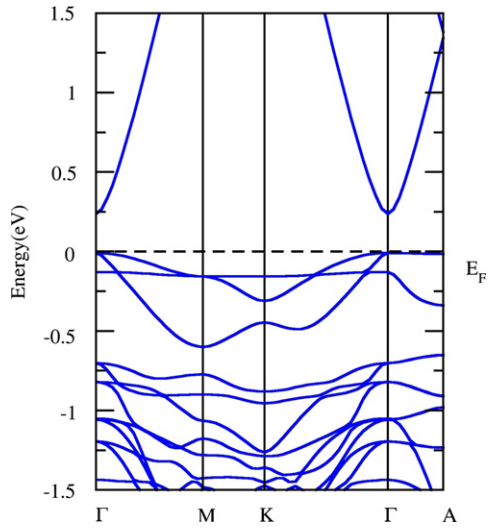

Fig. 8. Band structure of $Zn_{0.9375}Cu_{0.0625}O$ with GGA method.

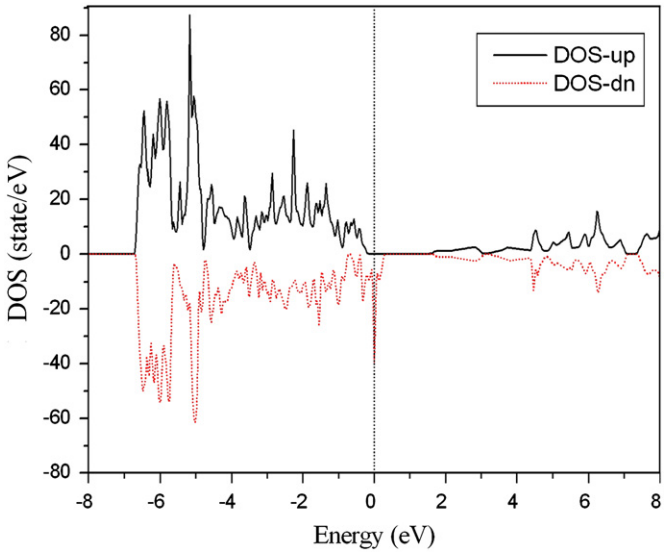

Fig. 9. DOS of $Zn_{0.9375}Cu_{0.0625}O$ using GGA+U method.

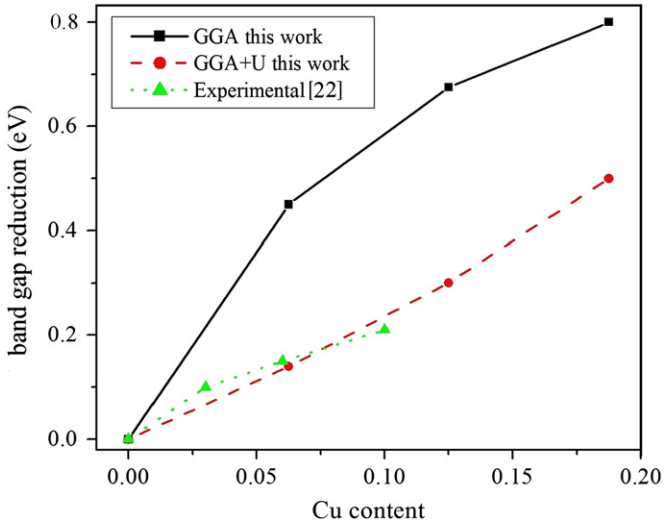

Fig. 10. Comparing band gap reduction by increasing Cu content.

Fig. 10 shows the plot of $Zn_{1-x}Cu_xO$ the band gap reduction, $\Delta E_g = E_g(\text{ZnO}) - E_g(\text{Cu-ZnO})$, using both GGA and GGA+U methods. These results are compared with the experimental data [22]. As it can be seen, the calculated results using GGA+U are very close to the experimental.

4. Conclusion

The electronic structure and optical properties of Cu-doped ZnO for different percentages of Cu content were studied both theoretically and experimentally. $Zn_{1-x}Cu_xO$ composition (x=0.00, 0.02, 0.04) was prepared by gel-combustion method. XRD, TEM and UV–vis techniques were used to characterize the structure and morphology of the prepared nanopowders. Analyzing of the UV–vis spectra of the samples revealed that by increasing Cu concentration, optical band gap energy decreases. The value of the optical gap for pure ZnO, $Zn_{0.98}Cu_{0.02}O$ and $Zn_{0.96}Cu_{0.04}O$ was found to be 3.27, 3.23 and 3.22 eV, respectively. The electronic structure of $Zn_{1-x}Cu_xO$ (x=0.0000, 0.0625, 0.1250, 0.1875) based on DFT using GGA and GGA+U approaches has been calculated. Our electronic calculations revealed an energy

band gap reduction by increasing Cu concentration in ZnO which is in agreement with the experimental data. By doping Cu, $Zn_{1-x}Cu_xO$ showed ferromagnetic behavior and the Fermi level of $Zn_{1-x}Cu_xO$ shifts upward into the valance band due to the strong hybridization between Cu-d and O-p states.

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