Synthesis, XRD, TEM, EPR, and Optical Absorption Spectral Studies of CuZnO$_2$ Nanocompound

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1. Introduction

Semiconducting compounds have drawn much attention during the last few years because of their unique properties and immense potential applications. In recent years, zinc-oxide (ZnO) has also been studied for its use as a promising material for UV light emitting diodes and diode lasers because of its wide band gap energy 3.4 eV and high binding energy (~60 meV). ZnO has a stable wurtzite structure (hexagonal) with lattice constants $a = 3.25 \text{ Å}$ and $c = 5.25 \text{ Å}$ and is composed of a number of alternating planes of tetrahedrally coordinated O$^{2-}$ and Zn$^{2+}$ ions stacked alternately along the C-axis [1]. Zinc-oxide is an n-type semiconductor. When transition metal elements are doped, the compound exhibits ferromagnetism at room temperature. This type of doping is helpful in adjusting the energy level states of ZnO and hence its properties change [2]. Due to structural stability and other parameters transition metal doped zinc-oxides are used in gas sensors.

Theionic radius of Cu(II) is 0.73 Å and that of Zn(II) is 0.84 Å and the charges are the same. Therefore Cu and Zn are mutually replaceable and are surrounded by oxygen molecules in the oxide form, since Cu$^{2+}$, being a d$^9$ system, is prone to Jahn-Teller distortion. Hence a EPR study of these ions will provide information about the type of distortion and nature of bonding between metal and ligand. In the present investigation, XRD, TEM, optical absorption, and NIR and EPR techniques are used to know the crystalline phase and site symmetry of Cu$^{2+}$ in the material.

2. Synthesis of Nano CuZnO$_2$

9.98 g of cupric acetate (0.05 moles) and 10.97 g of zinc acetate (0.05 moles) are dissolved separately in 100 mL of
demineralized water. The solutions are then transferred into a conical flask and 1 mL of glacial acetic acid is added to the mixture. The solution is transferred to a reflux flask which is then kept in a CATA 2R microwave reactor (MWR) and heated to boiling. The heating is continued for five minutes with constant stirring. The color of the solution changes from blue to greenish brown. Then 0.8 gm of NaOH is added and heating and stirring are continued in MWR for about 5 minutes. The color of the solution changes from bluetogreenish brown. Then 0.8 gm of NaOH is added and heating and stirring are continued in MWR and heated to boiling. The heating is continued for five minutes with constant stirring. The color of the solution changes from blue to greenish brown. Then 0.8 gm of NaOH is added and heating and stirring are continued in MWR and heated to boiling. The heating is continued for five minutes with constant stirring.

\[
\text{Cu(CH}_3\text{COO)}_2 + \text{Zn(CH}_3\text{COO)}_2 + 4\text{NaOH} \rightarrow \text{CuZnO}_2 + 4\text{CH}_3\text{COO}Na + 2\text{H}_2\text{O} \quad (1)
\]

X-ray powder diffraction pattern of CuZnO\(_2\) compound is recorded using Philips X-ray diffractometer operated in reflection geometry at 30 mA, 40 kV with Cu-K\(_\alpha\) (\(\lambda = 1.54060 \ \text{Å}\)) source at 25°C in the range of 10°–75°. Data are collected using a continuous scan rate of one degree per 2 minutes, which are then refined into 2\(°\) theta steps of 0.02°. The TEM images are obtained on a transmission electron microscope, Philips CM 200, operating at 200 keV having a 0.23 nm resolution. EPR spectra of the powdered sample are recorded at room temperature and then filtered by suction and washed with deionised water and ethanol. The precipitate is dried in open air for about 3 days:

\[
\text{Cu(CH}_3\text{COO)}_2 + \text{Zn(CH}_3\text{COO)}_2 + 4\text{NaOH} \rightarrow \text{CuZnO}_2 + 4\text{CH}_3\text{COO}Na + 2\text{H}_2\text{O} \quad (1)
\]

\[
X = \frac{\text{CuZnO}_2 + 4\text{CH}_3\text{COO}Na + 2\text{H}_2\text{O}}{\text{MWR at 100°C}}
\]

\[
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\]

The strain induced in powder due to crystal imperfection and distortion is calculated using

\[
\varepsilon = \frac{\beta_{hkl}}{4\tan\theta} \quad (4)
\]

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\]

\[
\text{Cu(II) has an electronic configuration [Ar] 3d}^9. \text{In an octahedral crystal field, the corresponding ground state electronic configuration is t}_{2g}^6\text{e}_g^3, which yields an } 2\text{E}_g \text{ term. The excited electronic configuration, } t_{2g}^5\text{e}_g^4, \text{corresponds to a } 2T_{2g} \text{ term. Hence single electron transition } 2\text{E}_g \rightarrow 2T_{2g} \text{ is expected in an octahedral crystal field. Normally, the ground } 2\text{E}_g \text{ state splits due to Jahn-Teller effect and hence lowering of symmetry is expected for Cu(II) ion. This state splits into two states, that is, } 2\text{B}_{1g} (d_{x^2}^2d_{y^2}^2) \text{ and } 2\text{A}_{1g} (d_{x^2}^2), \text{in tetragonal symmetry and the excited term } 2T_{2g} \text{ also splits into } 2\text{B}_{2g} (d_{xy}) \text{ and } 2\text{E}_g (d_{xz}, d_{yz}) \text{ levels. In a rhombic field, } 2\text{E}_g \text{ ground state splits into } 2\text{A}_{1g} (d_{x^2}^2d_{y^2}^2) \text{ and } 2\text{A}_{2g} (d_{z^2}) \text{ states whereas the } 2T_{2g} \text{ splits into } 2\text{B}_{1g} (d_{xy}), 2\text{B}_{2g} (d_{xz}), \text{and } 2\text{B}_{3g} (d_{yz}) \text{ states. Thus three bands are expected for tetragonal (C}_{4v}\text{) symmetry and four bands are expected for rhombic (D}_{4h}/(C}_{2v}) \text{ symmetry. The wave numbers of the three transitions in the tetragonal field are given by the following equations [3]}:
\]

\[
2\text{B}_{1g} \rightarrow 2\text{A}_{1g} : 4D_1 + 5D_t
\]

\[
2\text{B}_{1g} \rightarrow 2\text{B}_{2g} : 10D_\eta
\]

\[
2\text{B}_{1g} \rightarrow 2\text{E}_g : 10D_\eta + 3D_t - 5D_t
\]

In the above formula, \(D_1\) is the crystal field and \(D_t\) and \(D_\eta\) are tetragonal field parameters.

4. Results and Analysis

4.1. X-Ray Diffraction Results. Figure I(a) shows the X-ray diffraction pattern of CuZnO\(_2\) recorded on Philips diffractometer at 25°C. In Figure I(a) all major peaks were indexed using Scherrer formula. The calculated unit cell constants are \(a = 3.1\ \text{Å}\) and \(c = 3.4786\ \text{Å}\), respectively. The unit cell constants are different from wurtzite (hexagonal) [1]. This behaviour of change of lattice constant is attributed to the substitutional effect of \(\text{Zn}^{2+}\) ions of larger ionic radius (0.84 Å) by smaller \(\text{Cu}^{2+}\) (0.73 Å) ions, due to this ionic radius of lattice decreases. Hence the cell size decreases and thus shows low cell constant. Thus we expect that a nanocompound is formed. The calculated unit cell constants suggest that the nano CuZnO\(_2\) compound possesses tetragonal structure. The crystallite size of the compound is evaluated from the line broadening of the peak using Debye-Scherrer equation:

\[
D_{(002)} = \frac{k\lambda}{\beta_{1/2}\cos\theta} \quad (3)
\]

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\]

(see [4]). Here \(D\) is the crystallite size of the compound; \(\lambda\) (1.54060 Å) is the wavelength of incident X rays; \(\theta\) is the corresponding Bragg angle; \(\beta_{1/2}\) is the full width at the half maximum (FWHM) of the peak. \(k\) is shape constant \((k = 0.9)\). The crystallite size of the nanocompound is calculated as 115 nm.

The strain induced in powder due to crystal imperfection and distortion is calculated using

\[
\varepsilon = \frac{\beta_{hkl}}{4\tan\theta} \quad (4)
\]

(see [4]). The above two equations confirmed that the peak width from crystallite size varies as \(1/\cos\theta\) and strain varies as \(\tan\theta\). Assuming that the particle size and strain contributions to line broadening are independent of each other and both have a Cauchy-like profile, the observed line breadth is simply the sum of the two above two equations. \(\beta_{hkl} = k\lambda/D \cos\theta + 4\varepsilon\tan\theta\). By rearranging we have \(\beta_{hkl} \cos\theta = k\lambda/D + 4\varepsilon\sin\theta\). A plot is drawn with \(4\sin\theta\) along the X-axis.
and $\beta_{hkl}$ along Y-axis for the prepared CuZnO$_2$ nanoparticles as shown in Figure 1(b). From the linear fit to the data, the crystalline size has been estimated from the Y-intercept as 115 nm. This value exactly coincides with the value obtained from the Debye-Scherrer equation value. Further, strain $\epsilon$, calculated from the slope of the fit, is 0.2948.

4.2. EPR Spectral Analysis. EPR spectrum of CuZnO$_2$ nanocompound recorded at room temperature is given in Figure 2. The spectrum indicates a strong resonance signal around 380 mT in the high field region. This signal gives a “$g$” value of 1.76. Such a low value of “$g$” may not be due to Cu(II). Generally, if Cu(II) is present in higher concentration in the compound it gives a single resonance signal with “$g$” which is greater than 2.0, since the compound contains zinc, copper, and oxygen and this may be due to Zn(II) or O$^{2-}$. But generally, a free radical of O$^{2-}$ gives a signal around DPPH. Therefore it is assigned to Zn(II) in the compound [5]. On the low field side two resonances are observed with $g$ values of 2.31 and 2.05. These are due to Cu(II) which is in tetragonal distortion. The copper complex exhibits $g_{\parallel}$ at 2.31 and $g_{\perp}$ at 2.05 and $A_{\parallel}$ is 13.3 mT. These values indicate that the ground state of Cu(II) is $d_{x^2-y^2}$. Using the above values the covalency parameter $\alpha^2$ is calculated with the equation [6]:

$$\alpha^2 = -\left(\frac{A_{\parallel}}{0.036}\right) + (g_{\parallel} - g_e) + \frac{3}{7}(g_{\perp} - g_e) + 0.04. \quad (5)$$

If $\alpha^2$ is 0.5, it indicates a pure covalent bonding and if $\alpha^2$ is 1.0, it indicates a complete ionic bonding between metal ion and the ligands. In the present case, the observed value of $\alpha^2$ is 0.74 which is less than unity and indicates that the compound has some covalent character existing in the ligand environment. Hence the compound is electrically less conductive.

4.3. Transmission Electron Microscope (TEM). TEM is employed to visualize the size and shape and to confirm the nanocrystalline nature of the synthesized copper doped zinc-oxide. Figure 3(a) shows the typical bright field TEM images of the synthesized CuZnO$_2$ nanoparticles. It is observed from the image that the particles are clearly well separated and essentially no aggregation is found. Several uniform bright rings are also noticed. These are in spherical shape with almost the same dimension. This property suggests that the nanocrystals have preferential instead of random orientations. Further TEM images are showing that the metal ion may be in hexagonal structure with oxygen ligands. The particle size is about 100 nm. This value of the crystallite size is coinciding with XRD value.

Figure 3(b) shows the selected-area electron diffraction (SAED) pattern of the nano CuZnO$_2$ particles. The electron diffraction (ED) pattern consists of concentric rings with spots over the rings. This feature indicates that the samples are crystalline in nature. The rings in ED confirm the wide size distribution of CuZnO$_2$ nanoparticles.
4.4. Optical Absorption Spectral Analysis. The total optical absorption spectrum of nano CuZnO$_2$ compound that is recorded in the mull form at room temperature (RT) from 200 to 2500 nm is shown in Figure 4(a). The band component analysis is conveniently divided into several ranges, as shown in Figures 4(b)–4(f).

4.4.1. 200–500 nm Spectral Region. Figure 4(b) shows optical absorption spectrum of the material at room temperature in the range of 200–500 nm. The spectrum shows three sharp peaks. They are at 48780 (205 nm), 44440 (225 nm), 37735 (260 nm), and 35715 (280 nm) cm$^{-1}$. The high intensity band at 48780 (205 nm) cm$^{-1}$ and low intensity band at 44440 (225 nm) cm$^{-1}$ are due to metal-ligand charge transfer transitions. The moderate intensity band with components at 37735 (260 nm) and 35715 (280 nm) cm$^{-1}$ are due to metal-ligand charge transfer transitions. The moderate intensity band with components at 37735 (260 nm) and 35715 (280 nm) cm$^{-1}$ gives energies of 3.4 and 3.3 eV. This may be due to the presence of copper in the zinc oxide. Thus the optical absorption spectral measurements indicate red shift in the absorption band due to the presence of copper oxide.

4.4.2. 500–1300 nm Spectral Region. Figure 4(c) represents optical absorption spectrum of the compound in the range of 500–1300 nm. The optical absorption spectrum is analyzed as follows.

The broad band observed at 9130 cm$^{-1}$ (1095 nm), intense band at 10750 cm$^{-1}$ (930 nm), and a profile of bands with high intensity at 14390 cm$^{-1}$ (690 nm) with components on either side at 12345 (810 nm), 13160 (755 nm), and 15870 (630 nm) cm$^{-1}$ are due to Cu$^{2+}$ in the material. The observed three bands are assigned to Cu$^{2+}$ in tetragonal symmetry. Accordingly three bands observed at 9130 (1095 nm) and 10750 (930 nm) cm$^{-1}$ and a heap of bands with maximum intensity at 14390 (690 nm) cm$^{-1}$ are assigned to $^2B_1 \rightarrow ^2A_1, ^2B_1 \rightarrow ^2B_2$, and $^2B_1 \rightarrow ^2E$ transitions, respectively. The crystal field ($D_q$) and tetragonal ($D_s$ and $D_t$) parameters are evaluated using the expressions given in theory [3]. The parameters evaluated are $D_q = 1075$ cm$^{-1}$, $D_s = 1824$ cm$^{-1}$, and $D_t = 366$ cm$^{-1}$. The same sign for $D_s$ and $D_t$ indicated axial elongation of the tetragonal field [7]. This also confirms that the ground state is $d_{x^2-y^2}^2$ [8].

Figure 3: TEM micrographs of nano CuZnO$_2$ compound.
Using the EPR and optical absorption results, the spin-orbit coupling constant $\lambda$ is calculated with the formulae [8]:

$$g_{\text{aver}} = \frac{1}{3} \left[ g_{\parallel} + 2 g_{\perp} \right]$$

$$g_{\text{aver}} = 2 \left[ 1 - \frac{2\lambda}{10D_q} \right].$$

(6)

The $\lambda$ obtained is 366 cm$^{-1}$ (for free Cu(II) is ~832 cm$^{-1}$) which indicates some part of covalent bond existing between metal and ligand.

4.5. NIR Studies. H$_2$O has C$_{2v}$ symmetry. It gives three fundamental modes. They are $v_1$, $v_2$, and $v_3$. $v_1$ represents symmetric OH stretch, $v_2$ the asymmetric OH stretch, and $v_3$ the H-O-H bend, respectively. In vapour phase $v_1$ occurs at 3652, $v_2$ at 1595, and $v_3$ at 3756 cm$^{-1}$, respectively [9]. In liquid phase they are shifted to 3219, 1645, and 3445 cm$^{-1}$, whereas in solid phase they are shifted to 3200, 1640, and 3400 cm$^{-1}$. The shifts of $v_1$ and $v_3$ towards the lower frequency side and $v_2$ towards the higher frequency side are characteristic of hydrogen bonding [10].

The results of the band component analysis of the NIR spectra recorded at room temperature of the compound are split into different regions. From the figures, it is evident that several sharp absorptions with maximum intensity are observed in the sample. These are divided as 1300 to
1800 nm [shown in Figure 4(d)], 1800 to 2250 nm [shown in Figure 4(e)], and 2250 to 2500 nm [shown in Figure 4(f)]. The very sharp bands observed [Figure 4(e)] at 8230 (1215 nm) and 8400 (1190 nm) cm$^{-1}$ are assigned to the combination of $v_1 + v_2 + v_1$ (3200 + 1640 + 3400 = 8240 cm$^{-1}$) of water fundamentals. This may be occurred as contaminated water while synthesizing the compound.

4.5.1. The 1300 to 1800 nm Spectral Region. NIR spectrum of nanomaterial recorded from 1300 to 1800 nm is shown in Figure 4(d). Figure shows two sets of profile bands around 6710 cm$^{-1}$ (1490 nm) with components and with the highest intensity in the entire region of the spectrum and another group of bands at 5800 cm$^{-1}$ (1490 nm) with components on either side. In general whenever water is present in compound two characteristic bands appear around 7000 cm$^{-1}$ (1430 nm) due to $2v_2$ and 5200 cm$^{-1}$ (1925 nm) due to $(v_2 + v_3)$. When the bands are broad, it indicates that water molecules are relatively disordered and when the bands are sharp it indicates that water molecules are located in well-defined ordered sites [10]. These water molecules may be due to oxygen bonded or due to interstitial presence of water in the compound. These will not contribute to the formation of the compound.

Figure 4(d) shows a sharp band at 6710 cm$^{-1}$ (1490 nm) and is resolved into one sharp peak at 6710 (1410 nm) and four weak bands at 7170 (1395 nm), 6970 (1435 nm), 6495 (1540 nm), and 6360 cm$^{-1}$ (1575 nm). These are shifted to lower wave numbers and appear with distorted modes in the compound. It may also be explained that the possible substitution of Cu for Zn is responsible for the complexity of bands in the spectra. Bands from 7170 (1395 nm) to 6500 cm$^{-1}$ (1540 nm) correspond to the overtones of OH stretching vibrational mode. Bands appearing as shoulders to the sharp peak at 6710 cm$^{-1}$ (1490 nm) may be attributed to the combination of OH stretching fundamental and metal-OH deformation modes. The sharp band observed at 5800 cm$^{-1}$ (1725 nm) with components on either side is identified as $v_5$ of H$_2$O molecule.

4.5.2. 1800 to 2250 nm Spectral Region. Figure 4(e) shows two sets of sharp bands one centered at 5195 cm$^{-1}$ (1925 nm) and another at 4760 cm$^{-1}$ (2100 nm). Each band is resolved into two or three components. The two prominent features involve the fundamental stretching combined with the fundamental Cu-O-H bend to give the band at 4760 cm$^{-1}$ (2100 nm) with the first overtone of the band at 5800 cm$^{-1}$ (1725 nm) [11]. One set of sharp bands centered around 5195 cm$^{-1}$ (1925 nm) is the combination of the frequency lattice modes with the combination band at 4760 cm$^{-1}$ (2100 nm) [12].

4.5.3. 2250 to 2500 nm Spectral Region. Figure 4(f) shows a very sharp group of sharp bands with components and a moderate intensity band at 4050 cm$^{-1}$ (2470 nm). The most pronounced band centered at 4330 cm$^{-1}$ (2310 nm) in the nanocompound with split component almost equal in width on either side at 4395 (2275 nm) and 4255 cm$^{-1}$ (2350 nm) is due to the fundamental bending mode combined with the lowest frequency of OH stretching fundamental.

The bands in between 4500 and 4300 cm$^{-1}$ (2220–2325 nm) appear due to the combination of OH stretching and M-OH bending modes and the bands in the range of 4300–4200 cm$^{-1}$ (2325–2380 nm) are attributed to M-OH vibrations [13]. These bands are assigned due to true OH vibrations. The low wave number bands near 4050 cm$^{-1}$ (2470 nm) may be attributed to metal-OH units.

5. Conclusions

(1) CuO and ZnO are given equal proportions and CuZnO$_2$ nanocompound is synthesized by thermal decomposition method.

(2) XRD results indicate that CuZnO$_2$ is in tetragonal symmetry with cell constants $a = 3.1$ Å and $c = 3.4786$ Å. Further the crystallite size calculated for the prominent peak as 115 agrees with the TEM results.

(3) EPR results suggest that the nano CuZnO$_2$ compound Cu(II) ion has undergone Jahn-Teller distortion and is in the tetragonal elongated symmetrical environment which is further supporting the XRD results. Using EPR covalency character has been (calculated as 0.74) enhanced between metal and ligand in the compound. Hence the compound is electrically less conductive.

(4) TEM results clearly indicate that the particles are spherical in shape with almost the same dimension and they are clearly well separated. Hence no aggregation is found. Further TEM images show that the metal ion may be in tetragonal structure with oxygen ligands. The particle size is about 100 nm. This value of the crystalite size is coinciding with XRD value. The selected-area electron diffraction (SAED) pattern of the nano CuZnO$_2$ compound suggest that wide size distribution of nanoparticles is present in the compound.

(5) Optical absorption spectrum is due to Cu(II) and is placed in distorted octahedral environment. The crystal field parameters calculated are indicating that Cu(II) is in elongated tetragonal octahedral geometry. Using EPR and optical absorption results, the spin-orbit coupling constant $\lambda$ is calculated as 366 cm$^{-1}$ which indicates some covalent bond existing between metal and ligand.

(6) NIR results are due to water fundamentals and hydroxyls which indicate that the oxygens are not free but are bound to the metal ion as ligand atoms. During the synthesis of nano CuZnO$_2$ some of the water molecules may be bound and it may be reflected in the NIR spectrum.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.
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