CHAPTER – 5

STRUCTURAL, OPTICAL, ELECTRICAL AND MAGNETIC PROPERTIES OF ZnO NANOPARTICLES CO-DOPED WITH Co AND Cu

5.1. Introduction

ZnO is a promising semiconducting material for various applications such as light-emitting diodes, gas sensors, UV detectors, cosmetics and biomaterials due to its large band gap and exciton binding energy [1-3]. TM doping into ZnO have also attracted researchers due to its possible multifunctional device applications [4].

Thota et al. [5] reported the solubility limit of Ni, Co and Mn into ZnO structure i.e. the concentration after which secondary phase formation took place. The thermal, structural and magnetic properties of TM-doped ZnO depend on the kind of TM and their concentrations. Among the different metallic doping elements (Cu, Al, Co, Ga, etc) Cu and Co are important because they are prominent luminescence activator and have similar electronic shell structure, physical and chemical properties to those of Zn [6-8].

Many synthesis methods have been employed for the preparation of TM doped ZnO nanocrystals including sol–gel processes [9], co-precipitation [10], aqueous solution deposition [11] and mechano-chemical processing [12]. Among the different methods, the co-precipitation is one of the most important methods to prepare the nanoparticles. The enhanced ferromagnetic order was observed in Co and Cu doped ZnO powder where Cu acted as an acceptor [13]. Chakraborti et al. indicated that itinerant electrons were responsible for the ferromagnetism in Co, Cu co-doped ZnO system [14]. Sato et al. predicted that the addition of 3d transition metal ions such as
Mn, Fe, Co, and Ni showed ferromagnetic ordering in ZnO [15]. Hou et al. observed that the transition temperature of Zn$_{0.98}$Cu$_{0.02}$O was to be about 350 K but it was decreased to 320 K by nitrogen doping [16]. The influence of shape and hydrogenation on ferromagnetic properties of Zn$_{0.93}$Co$_{0.05}$Cu$_{0.02}$O nanoparticles at room temperature was demonstrated by Xu et al. [17].

Even though some of the research works have been carried out on Cu and Co co-doped ZnO system [13,14,17], most of the works are on the thin films and the comprehensive study of the structural and optical properties of Cu and Co co-doped ZnO nanoparticles is still scanty. Therefore, in the present investigation, Zn$_{0.96-x}$Cu$_{0.04}$Co$_x$O (0 $\leq$ x $\leq$ 0.04) nanoparticles are synthesized by co-precipitation method. Initial doping of Cu into Zn-O lattice increases the carrier concentration and the further doping of Cu would be expected to create a secondary phase (CuO) and thereby decrease the carrier concentration [13]. Since, Cu related phases like CuO are observed in primary lattice system at higher concentrations [18,19], Cu and Co doping concentration is limited to 4%. Due to the considerable variation of band gap with small doping percentages of Co, the Co and Cu co-doped ZnO is considered as an excellent candidate for optoelectronic applications. The modifications in structural, optical, electrical and magnetic behavior by Co and Cu substitution into ZnO have been studied and discussed in detail.

5.2. Experimental procedure

5.2.1. Preparation of Zn$_{0.96-x}$Cu$_{0.04}$Co$_x$O (0 $\leq$ x $\leq$ 0.04) nanoparticles

The high purity chemicals (Merc, > 99% purity) such as zinc nitrate hexahydrate (Zn(NO$_3$)$_2$.6H$_2$O), copper (II) nitrate trihydrate (Cu(NO$_3$)$_2$.3H$_2$O) and cobalt (II) nitrate hexahydrate (Co(NO$_3$)$_2$.6H$_2$O) were used as precursors for the synthesis of
Zn\(_{0.96-x}\)Cu\(_{0.04}\)Co\(_x\)O nanoparticles. Required amount of zinc nitrate hexahydrate was dissolved in double distilled water and continuously stirred to get a clear and homogeneous solution. Copper (II) nitrate trihydrate and cobalt (II) nitrate hexahydrate were dissolved in the initial solution one by one with 30 min interval. Separately, NaOH solution was prepared by dissolving appropriate amount of NaOH in 50 ml double distilled water. The NaOH solution was added drop wise into the initial solution. The mixed solution was kept under constant stirring for two hours at room temperature. The final precipitates were filtered and washed many times to avoid the impurities. Then, the filtered precipitates were dried using micro-oven at 80°C for 2 h. The dried precipitates were collected and grounded using an agate mortar. Finally, the synthesized nanoparticles were annealed at 500°C in air atmosphere for 2 h and left furnace cooling. The same procedure was repeated for remaining samples.

5.2.2. Characterization techniques

The crystal structure of Zn\(_{0.96-x}\)Cu\(_{0.04}\)Co\(_x\)O (x = 0, 0.01, 0.02, 0.03 and 0.04) nanoparticles was determined by powder X-ray diffraction. The surface morphology of Zn\(_{0.96-x}\)Cu\(_{0.04}\)Co\(_x\)O nanoparticles were studied using scanning electron microscope. The topological features and composition of Zn, O, Cu and Co were determined by energy dispersive X-ray spectrometer on K and L lines. The UV–Visible optical absorption and transmission studies were carried out to explore their optical properties. The photoluminescence (PL) spectra of Zn\(_{0.96-x}\)Cu\(_{0.04}\)Co\(_x\)O nanoparticles had been carried out between the wavelengths ranging from 350 nm to 600 nm using a fluorescence spectrophotometer at room temperature. The presence of chemical bonding in Zn\(_{0.96-x}\)Cu\(_{0.04}\)Co\(_x\)O samples was studied by FTIR spectrometer from
400 cm\(^{-1}\) to 4000 cm\(^{-1}\). Dielectric and ac conductivity measurements were carried out in the frequency range from 50 Hz to 200 kHz using LCR meter at room temperature. The magnetization (M) and magnetic field (M-H) hysteresis loops were measured at room temperature using vibrating sample magnetometer. The detailed description about the characterization instruments are given in the section 2.2 of chapter 2.

5.3. Results and discussion

5.3.1. X-ray diffraction (XRD) – Structural study

The typical XRD spectra of Zn\(_{0.96-x}\)Cu\(_{0.04}\)Co\(_x\)O (x = 0, 0.01, 0.02, 0.03 and 0.04) nanoparticles are shown in Fig. 5.1. The XRD spectra of Zn\(_{0.96-x}\)Cu\(_{0.04}\)Co\(_x\)O nanoparticles clearly shows the crystalline nature with the sharp peaks corresponding to the positions 31.57° (100), 34.26° (002), 36.10° (101), 47.38° (102), 56.44° (110), 62.75° (103), 66.27° (200), 67.89° (112) and 69.03° (201). The standard diffraction peaks show the crystal structure of Zn\(_{0.96-x}\)Cu\(_{0.04}\)Co\(_x\)O nanoparticles is hexagonal wurtzite and very close to the standard data of pure ZnO (a = 3.2488 Å, c = 5.2061 Å, space group P6\(_3\)mc, 186, JCPDS data card No. 36-1451) with preferred orientation along (101) plane in all the samples. It is evident from the XRD spectra that there are no extra peaks corresponding to Cu/Co, oxides of Cu/Co or Cu/Co related secondary and impurity phases which may be attributed to the incorporation of Cu\(^{2+}\) and Co\(^{2+}\) into Zn\(^{2+}\) lattice site.

The inset of Fig. 5.1 clearly shows the variation of XRD intensity and the peak position (2\(\theta\)) along (101) plane as a function of 2\(\theta\) values from 35.8° to 36.6°. It is noticed that the peak position is shifted to higher 2\(\theta\) side (\(\Delta 2\theta = 36.25 - 36.1 \sim 0.15°\)) when 1% of Co is introduced into the Zn–Cu–O lattice. Further increase of Co shifts the peak position to lower 2\(\theta\) side by very small amount (\(\Delta 2\theta = 0.03°\)) up to Co = 3%.
Fig. 5.1: Powder X-ray diffraction pattern of Zn$_{0.96-x}$Cu$_{0.04}$Co$_x$O ($0 \leq x \leq 0.04$) nanoparticles. The inset shows the magnified image of peak corresponding to (101) plane.
Again the peak position is shifted to higher $2\theta$ side ($\Delta 2\theta \approx 0.07^\circ$) for Co = 4% doping. The peak intensity of Cu, Co co-doped samples is always less than the Cu mono-doped samples. During the simultaneous substitution of Co and Cu, the peak intensity gradually decreases up to Co = 2% and the further increase of Co doping increases the peak intensity. A strong coulomb interaction between Zn$^{2+}$ (3d$^{10}$S$^0$) and O$^{2-}$ (2p$^6$) forming Zn–O bond and the bond is dominantly ionic, whereas Co–O and Cu–O bonds are principally covalent instead of ionic [20]. The strong covalency of Co–O and Cu–O makes the interaction of Cu and Co with O is stronger than Zn with O. The existing stronger interaction with O reduces the oxygen defects in the lattice and hence promotes the crystallinity of nanoparticles [21].

Thus, the Co doping increases the stability and quality of the crystal lattice which leads to increase the peak intensity at higher Co doping concentrations. Dinesha et al. also showed that Co-doping is able to promote the crystallinity of materials [22]. The change in peak intensity is due to the size or micro-strain or size and micro-strain [23].

Table 5.1: The variation of full width at half maximum (FWHM, $\beta$) value, average crystallite size (D) and micro-strain ($\varepsilon$) of Zn$_{0.96-x}$Cu$_{0.04}Co_x$O ($0 \leq x \leq 0.04$) nanoparticles

<table>
<thead>
<tr>
<th>Samples</th>
<th>FWHM, $\beta$ (degrees)</th>
<th>Average crystallite size, D (nm)</th>
<th>Micro-strain, $\varepsilon$ ($10^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$<em>{0.96}$Cu$</em>{0.04}$O</td>
<td>0.3097</td>
<td>27</td>
<td>1.2848</td>
</tr>
<tr>
<td>Zn$<em>{0.95}$Cu$</em>{0.04}$Co$_{0.01}$O</td>
<td>0.3254</td>
<td>25.7</td>
<td>1.3494</td>
</tr>
<tr>
<td>Zn$<em>{0.94}$Cu$</em>{0.04}$Co$_{0.02}$O</td>
<td>0.3352</td>
<td>24.9</td>
<td>1.3901</td>
</tr>
<tr>
<td>Zn$<em>{0.93}$Cu$</em>{0.04}$Co$_{0.03}$O</td>
<td>0.3172</td>
<td>26.3</td>
<td>1.3156</td>
</tr>
<tr>
<td>Zn$<em>{0.92}$Cu$</em>{0.04}$Co$_{0.04}$O</td>
<td>0.2901</td>
<td>28.8</td>
<td>1.2029</td>
</tr>
</tbody>
</table>
Table 5.1 shows the variation of full width at half maximum (FWHM) value, average crystallite size (D) and micro-strain (ε) of Zn$_{0.96-x}$Cu$_{0.04}$Co$_x$O (0 ≤ x ≤ 0.04) nanoparticles. The FWHM has the maximum value at Co = 2% and then gradually decreased when Co doping concentration increased from 2% to 4%. The substitution of Co$^{2+}$ ions into Zn–Cu–O lattice decreases the crystallite size up to Co = 2%. When Co concentration is increased beyond 2%, the crystal quality is improved and hence crystallite size is increased.

Table 5.2 shows the peak position (2θ), d-value, cell parameters ‘a’ and ‘c’, c/a ratio, stress (σ), bond length and volume of Zn$_{0.96-x}$Cu$_{0.04}$Co$_x$O (0 ≤ x ≤ 0.04) nanoparticles. The decrease in d-value, cell parameters, bond length and volume of Zn$_{0.96-x}$Cu$_{0.04}$Co$_x$O nanoparticles compared with Zn$_{0.96}$Cu$_{0.04}$O nanoparticle is due to the substitution of smaller ionic radii Co$^{2+}$ (0.58 Å) into the position of larger ionic radii Zn$^{2+}$ (0.60 Å) in Zn–Cu–O lattice [24]. These values are linearly increased by very small amount when Co concentration changes from 1% to 3%. The distortion produced around doping impurity is responsible for such a small increase in d-value, cell parameters, bond length and volume. However, the noticed remarkable shift in peak position towards higher 2θ side, decrease in d-value, cell parameters ‘a’ and ‘c’, bond length and volume at Co = 4% are due to the solubility limit of Co atoms in ZnO lattice. Thus, the solubility limit of proposed nanoparticles is fixed at 3% for present preparation condition.
Table 5.2: The variation of peak position (2θ), d-value, cell parameters ‘a’ and ‘c’, c/a ratio, stress (σ), bond length (l) and volume (V) of Zn$_{0.96-x}$Cu$_{0.04}$Co$_x$O (0 ≤ x ≤ 0.04) nanoparticles

<table>
<thead>
<tr>
<th>Samples</th>
<th>Peak position, 2θ(˚)</th>
<th>d-value (Å)</th>
<th>Cell parameters (Å)</th>
<th>c/a ratio</th>
<th>Stress, σ (GPa)</th>
<th>Bond length, l (Å)</th>
<th>Volume, V (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$<em>{0.96}$Cu$</em>{0.04}$O</td>
<td>36.10</td>
<td>2.4860</td>
<td>3.2660 5.2284</td>
<td>1.601</td>
<td>-0.9962</td>
<td>1.9871</td>
<td>48.2951</td>
</tr>
<tr>
<td>Zn$<em>{0.95}$Cu$</em>{0.04}$Co$_{0.01}$O</td>
<td>36.25</td>
<td>2.4761</td>
<td>3.2510 5.2082</td>
<td>1.602</td>
<td>-0.0958</td>
<td>1.9785</td>
<td>47.6687</td>
</tr>
<tr>
<td>Zn$<em>{0.94}$Cu$</em>{0.04}$Co$_{0.02}$O</td>
<td>36.22</td>
<td>2.4783</td>
<td>3.2540 5.2119</td>
<td>1.602</td>
<td>-0.2614</td>
<td>1.9802</td>
<td>47.7918</td>
</tr>
<tr>
<td>Zn$<em>{0.93}$Cu$</em>{0.04}$Co$_{0.03}$O</td>
<td>36.19</td>
<td>2.4801</td>
<td>3.2569 5.2155</td>
<td>1.602</td>
<td>-0.4198</td>
<td>1.9818</td>
<td>47.9108</td>
</tr>
<tr>
<td>Zn$<em>{0.92}$Cu$</em>{0.04}$Co$_{0.04}$O</td>
<td>36.28</td>
<td>2.4742</td>
<td>3.2483 5.2036</td>
<td>1.602</td>
<td>-0.1119</td>
<td>1.9768</td>
<td>47.5488</td>
</tr>
</tbody>
</table>

The stress is decreased from -0.9962 GPa (Co = 0%) to -0.0958 GPa (Co = 1%) when Co is introduced in Zn–Cu–O. The negative sign of stress indicates that the stress is tensile. The stress is gradually increased when Co is increased from 1% to 3%. This increase of tensile stress is due to lattice distortion produced around Co atom inside the Zn–Cu–O lattice. At 4% Co doping, the tensile stress is completely relieved and the lattices are relaxed due to better crystallization. The observed constant c/a ratio revealing that there is no change in hexagonal wurtzite structure by Co doping. The observed shift in XRD peak position, change in peak intensity, d-value, cell parameters, bond length, volume and stress confirms the substitution of Co into Zn–Cu–O lattice.

5.3.2. Scanning electron microscope (SEM) and Energy dispersive X-ray (EDX) spectra

The surface morphology of Zn$_{0.96-x}$Cu$_{0.04}$Co$_x$O (x = 0, 0.02 and 0.04) nanoparticles is shown in Figs. 5.2a–c. Fig. 5.2a shows the surface morphology of Zn$_{0.96}$Cu$_{0.04}$O nanoparticles. It has mixture of spheroid-like and hexagon-like particle
structure with grain size around 20 nm to 40 nm having better crystal quality.
Fig. 5.2b shows the morphology of $\text{Zn}_{0.94}\text{Cu}_{0.04}\text{Co}_{0.02}\text{O}$ nanoparticles. They are homogeneous and uniformly distributed throughout the structure. It is observed from Fig. 5.2b that the size of the particle get reduced and the particles are agglomerated each other with grain size around 10 nm to 30 nm. The initial distortion produced around Co atom inside the Zn–Cu–O lattice is responsible for the reduction in size. Fig. 5.2c shows ($\text{Zn}_{0.92}\text{Cu}_{0.04}\text{Co}_{0.04}\text{O}$ nanoparticles) the well agglomerated and uniform spheroid-like particle structure around 25 nm to 40 nm. At Co = 4%, tensile stress is completely relieved and the lattices are relaxed which depress the lattice depression and create the better crystallization. A good correlation is found to exist between mathematical calculations from XRD and SEM studies.

Chemical purity and stoichiometry of the samples were tested by EDX spectra. The typical EDX spectra of $\text{Zn}_{0.96-x}\text{Cu}_{0.04}\text{Co}_x\text{O}$ (x = 0, 0.02 and 0.04) nanoparticles are shown in Figs. 5.3a–c. The quantitative atomic percentage of the compositional elements such as Zn, Cu, Co and O present in $\text{Zn}_{0.96-x}\text{Cu}_{0.04}\text{Co}_x\text{O}$ nanoparticles under different Co substitution are given as inset of Fig. 5.3. The EDX analysis confirms the presence of Cu and Co in ZnO and purity of system. The atomic percentage of Cu/(Zn+Cu+Co) ratio is derived to be 4.22%, 4.32% and 4.15% for $\text{Zn}_{0.96}\text{Cu}_{0.04}\text{O}$, $\text{Zn}_{0.94}\text{Cu}_{0.04}\text{Co}_{0.02}\text{O}$ and $\text{Zn}_{0.92}\text{Cu}_{0.04}\text{Co}_{0.04}\text{O}$ nanoparticles, respectively. The atomic percentage of Zn is increased from 39.06% to 46.77% whereas O percentage is decreased from 59.22% to 50.03% when Co concentration is increased from 0% to 2%. The atomic percentage of Co/(Zn+Cu+Co) ratio is derived to be 2.08% and 4.23% for $\text{Zn}_{0.94}\text{Cu}_{0.04}\text{Co}_{0.02}\text{O}$ and $\text{Zn}_{0.92}\text{Cu}_{0.04}\text{Co}_{0.04}\text{O}$ nanoparticles, respectively.
Fig. 5.2: Scanning electron microscope (SEM) images of (a) $\text{Zn}_{0.96}\text{Cu}_{0.04}\text{O}$, (b) $\text{Zn}_{0.94}\text{Cu}_{0.04}\text{Co}_{0.02}\text{O}$ and (c) $\text{Zn}_{0.92}\text{Cu}_{0.04}\text{Co}_{0.04}\text{O}$ nanoparticles
Fig. 5.3: Energy dispersive X-ray spectra of (a) Zn$_{0.96}$Cu$_{0.04}$O, (b) Zn$_{0.94}$Cu$_{0.04}$Co$_{0.02}$O, and (c) Zn$_{0.92}$Cu$_{0.04}$Co$_{0.04}$O nanoparticles. The inset table shows the quantitative atomic percentage of the compositional elements.
When Co concentration is increased from 2% to 4%, the atomic percentage is increased proportionally from 1.04% to 2.09% but Zn is decreased from 46.77% to 45.26%. Decreasing of Zn atomic percentage and increasing of Co atomic percentage confirms the incorporation of Co into Zn–Cu–O lattice in which Zn is substituted by Co. The calculated atomic percentages are nearly equal to their nominal stoichiometry within the experimental error. Table 4.3 shows the quantitative analysis of compositional elements present in the Zn$_{0.96-x}$Cu$_{0.04}$Co$_x$O ($x = 0, 0.02$ and $0.04$) nanoparticles.

**Table 5.3:** The quantitative analysis of the compositional elements present in Zn$_{0.96-x}$Cu$_{0.04}$Co$_x$O ($x = 0, 0.02$ and $0.04$) nanoparticles using EDX analysis

<table>
<thead>
<tr>
<th>Samples</th>
<th>O</th>
<th>Zn</th>
<th>Cu</th>
<th>Co</th>
<th>Cu/(Zn+Cu+Co) ratio</th>
<th>Co/(Zn+Cu+Co) ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$<em>{0.96}$Cu$</em>{0.04}$O</td>
<td>59.22</td>
<td>39.06</td>
<td>1.72</td>
<td>-</td>
<td>4.22</td>
<td>-</td>
</tr>
<tr>
<td>Zn$<em>{0.94}$Cu$</em>{0.04}$Co$_{0.02}$O</td>
<td>50.03</td>
<td>46.77</td>
<td>2.16</td>
<td>1.04</td>
<td>4.32</td>
<td>2.08</td>
</tr>
<tr>
<td>Zn$<em>{0.92}$Cu$</em>{0.04}$Co$_{0.04}$O</td>
<td>50.60</td>
<td>45.26</td>
<td>2.05</td>
<td>2.09</td>
<td>4.15</td>
<td>4.23</td>
</tr>
</tbody>
</table>

5.3.3. UV–Visible spectra – Optical study

The absorbance is expected to depend on several factors, such as band gap, oxygen deficiency surface roughness and impurity centers [25]. The UV–Visible optical absorption spectra of Zn$_{0.96-x}$Cu$_{0.04}$Co$_x$O nanoparticles have been taken out at room temperature from 300 nm to 600 nm and shown in Fig. 5.4a. The inset of Fig. 5.4a shows the enlarged and clear picture of the absorption changes from 320 nm to 350 nm. It is noticed from Fig. 5.4a that the absorption is increase to its maximum value when 1% of Co is introduced into Zn–Cu–O lattice which may be due to the created charge carries by Co-doping. When Co concentration is increased beyond 1%,
the absorption is gradually deceased due to the increase of distortion. The distortion affects the carrier density and hence the absorption gets decreases. The position of the absorption peak is shifted towards the lower wavelength side when increasing Co doping concentration. The observed blue shift can be explained by the Burstein-Moss effect [26]. This is the phenomenon that the Fermi level merges into the conduction band with an increase of the carrier concentration and hence the value of band gap increases. Thus the low energy transitions are blocked. The results are in good agreement with the results reported by Sakai et al. [27].

The typical room temperature transmittance spectra of Zn$_{0.96-x}$Cu$_{0.04}$Co$_x$O nanoparticles are shown in Fig. 5.4b. The transmission spectra of the Zn$_{0.96-x}$Cu$_{0.04}$Co$_x$O nanoparticles show just opposite trend of the optical absorption spectra. All samples shows poor transmittance in UV region and transparent to visible light with an average transmittance value of ~80% (except Co = 1%), which indicating a good optical quality with low scattering or absorption losses.

The optical band gap of the Zn$_{0.96-x}$Cu$_{0.04}$Co$_x$O nanoparticles are estimated by plotting $(\alpha h\nu)^2$ versus $h\nu$ as shown in Fig. 5.5. The extrapolation of the straight line to the energy ($h\nu$) axis gives the band gap of the material. The observed band gap of Zn$_{0.96-x}$Cu$_{0.04}$Co$_x$O nanoparticles is increased from 3.66 eV to 3.74 eV when Co concentration is increased from 0% to 4%. The blue shift in band gap is due to Burstein-Moss effect. This is also in good agreement to the quantum confinement effect of the nanoparticles [28]. Similar blue shift in band gap was reported in the previous literature for Co doped ZnO [22,29].
Fig. 5.4: (a) UV-Visible absorption spectra and (b) Transmittance spectra of Zn$_{0.96-x}$Cu$_{0.04}$Co$_x$O ($0 \leq x \leq 0.04$) nanoparticles. The inset shows enlarged absorption spectra from 320 nm to 350 nm.
Fig. 5.5: The $(\alpha h \nu)^2$ versus $h \nu$ curves of Zn$_{0.96-x}$Cu$_{0.04}$Co$_x$O (0 $\leq$ x $\leq$ 0.04) nanoparticles for optical band gap calculation.
5.3.4. Photoluminescence (PL) spectra - Optical study

The room temperature PL spectra of undoped and Co-doped Zn$_{0.96}$Cu$_{0.04}$O nanoparticles with different Co concentrations from 0% to 4% between 350 nm and 600 nm are shown in Fig. 5.6. PL spectra of undoped Zn$_{0.96}$Cu$_{0.04}$O contains four bands; (i) a high intensity peak centered at 391 nm corresponding to ultraviolet (UV) band, (ii) a peak centered at 417 nm corresponding to violet band, (iii) a low intensity peak centered at 478 nm corresponding to blue band, and (iv) a low intensity and broad peak centered at 523 nm corresponding to green band. The intensity of UV band is less than the violet band in undoped Zn$_{0.96}$Cu$_{0.04}$O while the intensity of UV band is higher than violet band in Co-doped Zn$_{0.96}$Cu$_{0.04}$O.

Strong UV emission around 382-391 nm are observed for all the samples and can be assigned as a near-band-edge (NBE) emission originating from the recombination of excited electrons from a localized levels below the conduction band with the holes in valence band. The intensity of UV emission decreases by Co-doping followed by the maximum intensity observed at Co = 1% doped Zn$_{0.96}$Cu$_{0.04}$O nanoparticles. In addition, a slight shift of UV peaks towards lower wavelength side by the substitution of Co$^{2+}$ ions is found, this can be attributed to the blue shift of band gap by Co-doping. The noticed blue shift in the UV emission peak is due to the Burstein-Moss effect [28]. The Fermi level merges into the conduction band with an increase of carrier concentration and hence the band gap gets increase.

The violet band centered at 417 nm (shoulder with UV emission) can be originating from the transition of electrons from shallow donor levels (Zn$_i$) to valence band. Electrons in the conduction band first relaxed to a shallow donor levels (Zn$_i$)
Fig. 5.6: The room temperature PL spectra of Zn$_{0.96-x}$Cu$_{0.04}$Co$_x$O (0 ≤ x ≤ 0.04) nanoparticles as a function of wavelength between 350 nm and 600 nm.
due to the long life time of these levels and then recombined with the holes in the valence band [30]. Since shallow donor levels (Zn_i) lies below the conduction band, the emission wavelength during the electrons transition from shallow donor levels (Zn_i) to valence band have slightly larger than the excitons transition from conduction band to valence band. On the other hand, the metal-ion doping could rise to deep acceptor levels in the band gap of matrix material. Hence, the shoulder in the UV band at higher wavelength side may results from the recombination of excited electrons in the conduction band with the holes in the Cu/Co impurity levels [31].

The blue and green emission bands are originating from the intrinsic defects and donor-accepter pair recombination involving Cu and Co impurity acceptors [32]. The transition of electrons from shallow donor levels (Zn_i) to shallow accepter levels (V_m) let to emit the blue emission at 478 nm; while the green emission centered at 523 nm arises from the oxygen vacancies in Zn–Cu–Co–O lattices [33]. Even though the intensity and the broadening are modulated by Co-doping, there is no change in the peak position of blue and green emissions. The substitution of Co^{2+} in the Zn–Cu–O lattice absorbs the energy from the defect emission, because the defect state energy is very close to the photon energy which excites the transitions of Co^{2+}. Thus, the doped Co^{2+} ions provide competitive pathways for recombinatio n and result in quenching of the broad, visible emission [34,35]. The increases of Co-doping tend to increase the distortion centers in the lattice and surface defects, which cause the absorption of the nanoparticle and hence the emission decreases with the increase of Co doping concentration.
5.3.5. Fourier Transform Infrared (FTIR) study

The band positions and numbers of absorption peaks are depending on crystalline structure, chemical composition and also on morphology [36]. The characteristic peaks exhibited by FTIR spectra of Zn$_{0.96-x}$Cu$_{0.04}$Co$_x$O ($0 \leq x \leq 0.04$) nanoparticles are shown in Fig. 5.7a. The broad absorption peaks around 2900-3600 cm$^{-1}$ and 1096-1117 cm$^{-1}$ are attributed to normal polymeric O–H stretching vibration of H$_2$O in Zn–Cu–Co–O lattice [37,10] which may be due to moisture in the solution and the atmosphere. The absorption around 2936 cm$^{-1}$ are due to C–H mode, which is absent in Zn$_{0.96}$Cu$_{0.04}$O and present on other samples. Another sharp peak around 1631-1714 cm$^{-1}$ is attributed to H–O–H bending vibration, which is assigned to a small amount of H$_2$O in the ZnO nanocrystals [38]. The principal absorption peaks observed between 1394-1438 cm$^{-1}$ are corresponding to the asymmetric and symmetric stretching of carboxyl group (C=O). The absorption peaks observed between 2357 and 2371 cm$^{-1}$ are because of the existence of CO$_2$ molecule in air [39].

The characteristic IR peaks below 1000 cm$^{-1}$ is very important to study the presence or absence of Zn–O / Co–O / Cu–O bonds and the functional groups. The enlarged spectrum in the wave number range below 1000 cm$^{-1}$ is shown in Fig. 5.7b. The medium to weak bands around 717-758 cm$^{-1}$ are assigned to the vibrational frequencies due to the change in the microstructural features by the addition of Co into Zn–Cu–O lattice. The change in intensity and FWHM corresponding to the frequency around 717-758 cm$^{-1}$ represents a change in density of defect states surrounding to Cu and Co ions in Zn–Cu–Co–O lattice. The medium to weak bands around 470-490 cm$^{-1}$ are assigned to the vibrational frequency of Zn–Cu–O lattice [40]. FTIR spectra exhibit strong vibrations around 621-632 cm$^{-1}$ which are assigned to
Fig. 5.7: (a) FTIR spectra of $\text{Zn}_{0.96-x}\text{Cu}_{0.04}\text{Co}_x\text{O}$ ($0 \leq x \leq 0.04$) nanoparticles and (b) The enlarged FTIR spectra in the wave number range < 1000 cm$^{-1}$
stretching frequency of Co–O bond [41]. The Co-O bond is assigned to the stretching frequency at 621 cm \(^{-1}\) for pure Co = 0% which is shifted to higher frequency as 624 cm \(^{-1}\) for Co = 1%; 626 cm \(^{-1}\) for Co = 2%; 633 cm \(^{-1}\) for Co = 3% and 632 cm \(^{-1}\) for Co = 4%. Co atom is slightly lighter than Zn atom, so, according to the well-established theories of vibrational modes in mixed crystals the substitution should result in an upward shift of the fundamental transverse optical phonon mode [42]. The transmittance percentage is increased with Co concentrations and maximum for Co = 4%. The change in the characteristic frequency and the percentage of transmittance of Co–O and Zn–O bands reflects that Zn–O–Cu network is perturbed by the presence of Co in its environment. Therefore, the FTIR results also indicate that Co is occupying Zn position in ZnO matrix as observed in XRD measurements.

5.3.6. Dielectric constant (\(\varepsilon'\)) and dielectric loss (tan \(\delta\))

Fig. 5.8a shows the change in dielectric constant (\(\varepsilon'\)) as a function of frequency between 50 Hz and 200 kHz at room temperature for Zn\(_{0.96-x}\)Cu\(_{0.04}\)Co\(_x\)O (x = 0, 0.02 and 0.04) nanoparticles and the inset of Fig. 5.8a shows the plot for Zn\(_{0.96}\)Cu\(_{0.04}\)O nanoparticles. All samples exhibit rapid dielectric dispersion at lower frequencies but it becomes sluggish at medium frequencies and nearly frequency independent behavior at higher frequencies. Co doped Zn\(_{0.96}\)Cu\(_{0.04}\)O nanoparticles have higher dielectric constant than undoped Zn\(_{0.96}\)Cu\(_{0.04}\)O nanoparticles where 2% of Co doped Zn\(_{0.96}\)Cu\(_{0.04}\)O has maximum value and the further increase of Co decreases the dielectric constant at a particular frequency.

The Maxwell-Wagner (MW) interfacial model suggests that the dielectric medium is considered to be composed of double layer such as well conducting grains which are separated by poorly conducting (or resistive) grain boundaries [43].
Based on MW model, Gupta et al. proposed that each nano grains act as nanodipoles and they showed that when the size of the grains become low, the number of nanodipoles per unit volume increases and hence the dielectric constant increased [44]. Lanje et al. also found the similar size dependent dielectric properties in their studies [45].

It is concluded from the above discussion that the observed higher dielectric constant in 2% of Co doped Zn$_{0.96}$Cu$_{0.04}$O nanoparticles at lower frequencies is due to the smaller average crystallite size (24.9 nm). The better crystallization with average crystallite size of 28.8 nm at Co = 4% doped Zn$_{0.96}$Cu$_{0.04}$O nanoparticles causes the reduction in dielectric constant. Even though the average crystallite size of 4% Co doped Zn$_{0.96}$Cu$_{0.04}$O nanoparticles is higher (28.8 nm) than undoped Zn$_{0.96}$Cu$_{0.04}$O nanoparticles (27 nm), the dielectric constant also higher than undoped Zn$_{0.96}$Cu$_{0.04}$O nanoparticles. The observed higher dielectric constant in Co = 4% doped Zn$_{0.96}$Cu$_{0.04}$O is due to the availability of higher charge carriers by Co doping. At higher frequencies, electric dipoles existing in the material begin to lag behind the applied alternating electric field and dielectric constant decreases exponentially. However, the dipoles are no longer follows the alternating field; they unable to follow the external field at higher frequencies and hence the frequency independent behavior is noticed.

Fig. 5.8b shows the variation in dielectric loss (tan $\delta$) of Zn$_{0.96-x}$Cu$_{0.04}$Co$_x$O ($x = 0, 0.02$ and $0.04$) nanoparticles as a function of frequency between 50 Hz and 200 kHz at room temperature. Generally, the dielectric loss has higher value at lower frequencies; exhibit exponential decrease at medium frequencies and almost constant at higher frequencies. Even though undoped Zn$_{0.96}$Cu$_{0.04}$O nanoparticles follow the general trend of dielectric loss, Co-doped Zn$_{0.96}$Cu$_{0.04}$O nanoparticles exhibit small peaks at low frequencies which is absent in undoped Zn$_{0.96}$Cu$_{0.04}$O nanoparticles.
Fig. 5.8: The variation of (a) Dielectric constant and (b) Dielectric loss (tan δ) of Zn$_{0.96-x}$Cu$_{0.04}$Co$_x$O ($x = 0, 0.02$ and $0.04$) nanoparticles as a function of frequency between 50 Hz and 200 kHz at room temperature.
These characteristic peaks (referred as relaxation peaks) occur when frequency of localized charge carrier matches with the frequency of external applied ac electrical field [46]. It is noticed from Fig. 5.8b that the \( \text{Zn}_{0.94}\text{Cu}_{0.04}\text{Co}_{0.02}\text{O} \) nanoparticles have higher dielectric loss and the relaxation peak exist at higher frequency side. The increase of Co concentration from 2% to 4% shifts the relaxation peak position to lower frequency side. The observed peak position shift towards lower frequency side in 4% of Co doped \( \text{Zn}_{0.96}\text{Cu}_{0.04}\text{O} \) is due to the existence of higher number defects in the nanoparticles. The low dielectric constant and dielectric loss at high frequency region makes it to be a suitable material for high frequency applications.

5.3.7. Electrical ac conductivity study

Fig. 5.9 shows the variation of ac conductivity of \( \text{Zn}_{0.96-x}\text{Cu}_{0.04}\text{Co}_x\text{O} \) (\( x = 0, 0.02 \) and 0.04) nanoparticles as a function of frequency between 50 Hz and 200 kHz at room temperature. The change in ac conductivity is almost zero at lower frequencies and increase slowly with the increase of frequency and a rapid increase is noticed at higher frequencies. According to Maxwell-Wagner interfacial model, the each grain interfacial act as potential barrier and the charge carrier in the grains behaves like charges in the potential well [47]. The charge carriers easily move within the grains and cannot migrate between grains due to resistive interfacial. At low frequencies, there is some possibility for tunneling of few charge carriers from one grain to another, thus the small amount of conduction takes place. When frequency increases, the more charge carrier tunneling let to increase the ac electrical conductivity with the increase of frequency. As frequency increases beyond certain value, the charge carriers get sufficient energy to overcome the barrier and hence the rapid increase in ac conductivity is noticed at higher frequency.
Fig. 5.9: ac electrical conductivity of $\text{Zn}_{0.96-x}\text{Cu}_{0.04}\text{Co}_x\text{O}$ ($x = 0, 0.02$ and $0.04$) nanoparticles as a function of frequency between $50$ Hz and $200$ kHz at room temperature.

The graph shows the conductivity of the nanoparticles at room temperature, with three curves representing different concentrations of cobalt ($Co=0\%$, $2\%$, and $4\%$). The conductivity increases as the frequency increases, indicating a better electrical conductivity at higher frequencies.
Undoped Zn$_{0.96}$Cu$_{0.04}$O has low value of electrical conductivity which is changed to high value when 2% of Co is substituted into Zn–Cu–O lattice. The further increase of Co concentrations from 2% to 4% decreases the electrical conductivity. The observed higher electrical conductivity of 2% of Co doped Zn$_{0.96}$Cu$_{0.04}$O along the entire frequency region is due to the availability of high density of charge carriers in the grains by Co-doping [48]. The decrease of electrical conductivity at higher doping (Co = 4%) is due to the fact that the generation of more defects. This high density defect sites formed by Co-doping scatter the charge carriers and decrease the electrical conductivity during the conduction. The number of defect sites are low at lower doping concentration (Co = 2%), hence the less number of scattering results the increase of electrical conductivity.

5.3.8. Magnetic study

Fig. 5.10a shows magnetization versus magnetic field (M-H) curves for Zn$_{0.96-x}$Cu$_{0.04}$Co$_x$O ($x = 0, 0.02$ and $0.04$) nanoparticles measured at room temperature. Figs. 5.10b and c shows the magnified M-H curves of Zn$_{0.94}$Cu$_{0.04}$Co$_{0.02}$O and Zn$_{0.92}$Cu$_{0.04}$Co$_{0.04}$O nanoparticles, respectively to view the clear RTFM. Even though all the samples exhibit ferromagnetic nature at room temperature, the substitution of Co into Zn–Cu–O lattice decreases the saturation magnetization and retentivity. Co ions substituted for Zn sites in Zn–Cu–O lattice undergo trigonal distortion. The trigonally distorted environment near Co$^{2+}$ affects the magnetic [49] and optical properties [50] of Co-based DMSs though their relationship remains unclear.

There can be several possible reasons for RTFM in Cu doped ZnO nanoparticles. Cao et al. demonstrated that p-type carrier generated by Cu doping is considered to be
Fig. 5.10: (a) Magnetization versus magnetic field (M-H) curves of Zn$_{0.96-x}$Cu$_{0.04}$Co$_x$O ($x = 0, 0.02$ and $0.04$) nanoparticles at room temperature. Magnified M-H curves of (b) Zn$_{0.94}$Cu$_{0.04}$Co$_{0.02}$O and (c) Zn$_{0.92}$Cu$_{0.04}$Co$_{0.04}$O nanoparticles
a main factor to induce RTFM [51]. Carrier induced RTFM (RKKY mechanism) in Cu doped ZnO rod array was reported by Xia et al. [52]. The point defects such as Zn interstitial and oxygen vacancies are also the possible reasons for RTFM [53,54]. There are no clustering and other phases observed in the XRD spectrum and hence ferromagnetic ordering may be intrinsic and may not be due to any other magnetic phases or Cu clusters.

Even though the charge carrier concentration is increased by Co-doping in Zn\textsubscript{0.96}Cu\textsubscript{0.04}O as discussed in the electrical properties, the decrease in the saturation magnetization and retentivity is unexpected in our investigation. The observed suppression of RTFM may be due to the enhanced antiferromagnetic interaction between neighbouring Cu-Cu ion [55]. Theoretical modeling of the Cu doped ZnO system indicates that the location of Cu atom and its relation with other atoms can strongly affect the magnetic properties of the system [56-58]. Substitution of Co into Zn–Cu–O lattice decreases the bond length and volume which leads to decrease the relative distance between Cu ions and enhanced the antiferromagnetic order. Since, we could not find any secondary phases like Cu/Co oxides or any signal of Cu/Co clusters in the XRD, the observed RTFM in the samples could arise from the homogeneous doping of Co into Zn–Cu–O which follows the RKKY mechanism.

5.4. Conclusion

Cu doped and Cu, Co co-doped ZnO nanoparticles (Zn\textsubscript{0.96-x}Cu\textsubscript{0.04}Co\textsubscript{x}O, 0 ≤ x ≤ 0.04) were synthesized successfully by co-precipitation method. All the samples exhibited a hexagonal wurtzite structure with different microstructure. The average crystallite size was decreased from 27 nm to 24.9 nm when Co doping concentration increasing up to 2%.
The increased crystallite size beyond 2% was due to low strain present in the Zn–Cu–Co–O lattice. Beyond Co = 2%, the existing stronger interaction with O reduced the oxygen defects in the lattice and hence promoted the crystallinity of nanoparticles. The observed shift in XRD peak position, changes in peak intensity, d-value, cell parameters, bond length, volume and stress confirmed the substitution of Co into Zn–Cu–O lattice. The energy dispersive X-ray spectra confirmed the presence of Cu and Co in ZnO system and the atomic percentage was nearly equal to their nominal stoichiometry.

The optical absorption spectra showed that all the prepared nanoparticles had high absorption in UV region and poor in visible region. The observed blue shift in optical absorption and band gap, 3.66–3.74 eV, could be explained by the Burstein-Moss effect. Low transmittance in UV region and more than 80% transparency in visible region in all the samples indicated the good optical quality with low scattering or absorption losses. PL spectra of undoped and Co-doped Zn$_{0.96}$Cu$_{0.04}$O samples showed four distinct bands, i) ultra violet emission bands around 382-391 nm, ii) violet emission band centered at 417 nm, iii) blue emission bands centered at 478 nm and iv) green emission bands centered at 523 nm. The substitution of Co$^{2+}$ into Zn–Cu–O lattice provided competitive pathways for recombination and result in quenching of the broad, visible emissions. The noticed change in the characteristic frequency and the percentage of transmittance from FTIR spectra demonstrated that Zn–O–Cu network was perturbed by the presence of Co in its environment.

Co-doped Zn$_{0.96}$Cu$_{0.04}$O samples had high dielectric constant, dielectric loss and ac conductivity than undoped Zn$_{0.96}$Cu$_{0.04}$O samples. The observed higher dielectric constant, dielectric loss and ac conductivity in Co = 2% doped Zn$_{0.96}$Cu$_{0.04}$O samples was explained in terms of average crystallite size and number of nano-dipoles.
Undoped $\text{Zn}_{0.96}\text{Cu}_{0.04}\text{O}$ sample had higher magnetization and it was suppressed by Co-doping due to the enhanced antiferromagnetic interaction between neighbouring Cu–Cu ions. Since there were no signal of secondary phases like Cu/Co oxides or Cu/Co clusters in the XRD, it was proposed that changes in RTFM could arise only by doping of Co into Zn–Cu–O lattice.
References


