CHAPTER 8

STRUCTURAL, OPTICAL AND ELECTRICAL

PROPERTIES OF Mn DOPED CuO NANOPARTICLES

8.1. Introduction:

Synthesis and properties of one-dimensional nanostructured materials is one of the most important areas in modern materials science and technology. Nanomaterials are not only a kind of ideal system for the study of many physical properties, but also possess potential applications in fabrication of electronic and optical nano-devices. Metal oxides span a broad range of properties from wide band-gap insulators to metallic and superconducting which creates a significant interest in the synthesis of metal oxide nanomaterials. Intensive research efforts have been devoted to the synthesis and investigation of the physical and chemical properties of semiconducting oxides such as ZnO, SnO\textsubscript{2}, TiO\textsubscript{2}, In\textsubscript{2}O\textsubscript{3}. Cupric oxide (CuO) is one of an important semiconducting oxide with a monoclinic structure and direct band gap of 1.85 eV [1,2]. It has potential applications in solar cells [3], catalysis [4-6], sensors [7-11], electrode materials [12], magnetic storage media [13], lithium ion batteries [14-16] and high Tc superconductors [17]. Study on the synthesis and characterization of CuO nanoparticles is the least explored area compared to other transition metal oxides like ZnO, SnO\textsubscript{2}, TiO\textsubscript{2} and Fe\textsubscript{2}O\textsubscript{3}, making it an interesting candidate to investigate its properties. Furthermore, the doping of the semiconductor
nanoparticles with impurity metal ions is one of the most important methods to modify the characteristics of the material. Many authors have reported the improvement in material’s characteristic properties using various dopants. The band gap narrowing of Ni doped SnO$_2$ nanoparticles was observed by Ahmed et al. [18], Das et al. reported the tuning of emission properties of Mn doped Cu$_2$O nanoparticles [19]. Study of Mn doped CuO is a least explored area till now.

This chapter presents the effect of manganese (Mn) doping on the structural, electrical and optical properties of CuO nanoparticles synthesized by sol-gel combustion route.

8.2. Experimental:

8.2.1. Synthesis:

In a typical synthesis procedure, Cu(NO$_3$)$_2$.3H$_2$O, Mn(NO$_3$)$_2$.6H$_2$O and citric acid were used as starting materials. Required amounts of metal nitrates were dissolved in distilled water with a molar ratio of 1:1 between metal nitrate and citric acid. The solution was stirred with magnetic stirrer at 100 $^\circ$C. Stirring continues till the formation of gel. After the formation of gel it was allowed to burn at 200 $^\circ$C. A light fluffy mass was obtained as a result of combustion, which was further annealed at 400 $^\circ$C to obtain the crystalline Mn doped CuO nanoparticles. The amount of Mn dopant was varied from 0% to 15%. The CuO nanoparticles thus obtained were characterized by XRD, SEM, EDAX, FTIR, UV-Visible
spectroscopy, photoluminescence and LCR meter for their structural, optical and electrical properties.

**8.2.2. Characterization:**

The crystallinity, structure and crystallite size of Mn-doped CuO nanoparticles were determined by X-ray diffraction (XRD) using Cu-Kα radiations (\(\lambda=0.15406\) nm) in 2θ range from 20° to 80° and the morphological analysis of the sample was carried out on a FE-SEM (JEOL). The compositional analysis was carried out using EDAX attached with the FE-SEM. Fourier transform infrared (FT-IR) spectra of as-prepared samples were recorded using a Fourier transform infrared spectrometer (Spectrum 65, Perkin Elmer) in the range of 1000–400 cm\(^{-1}\) with a resolution of 1 cm\(^{-1}\). The PL measurements were carried out using a luminescence spectrometer (LS-55B, Perkin Elmer) with a Xenon lamp as the excitation source at room temperature. The excitation wavelength used for the experiment was 350 nm. The samples were pelletized for electrical measurements and silver coated on both surfaces of pellets for dielectric measurements. Electrical and dielectric measurements were carried out using LCR meter (Agilent 4245A).

**8.3. Results and discussion:**

**8.3.1. Structural analysis:**

The typical XRD patterns of pure and Mn doped CuO nanoparticles annealed at 400 °C is shown in Fig. 8.1. It is clear from Fig. 8.1 that all the samples exhibit the monoclinic structure of CuO
which was confirmed from the ICDD card No. 801916. Further, no other impurity peak was observed in the XRD pattern showing the single phase sample formation of CuO nanoparticles up to 7%, beyond which an impurity phase of CuMn$_2$O$_4$ was detected in higher dopant concentration (9% and 15%). The crystallite size was calculated using Scherrer formula, \(D = \frac{0.9 \lambda}{\beta \cos \theta}\), where \(\lambda\) is the wavelength of X-ray radiation, \(\beta\) is the full width at half maximum (FWHM) of the peaks at the diffracting angle \(\theta\). Crystallite size, lattice parameters and cell volume are tabulated in Table 8.1. Lattice parameters shown in Table 8.1 are very close to the standard lattice parameters reported by ICDD card no. 801916. It is clear from Table 8.1 that the crystallite size and lattice parameters slightly increase with the increase in dopant concentration up to 7% after which they decrease for higher doping concentration (9% and 15%). This is due to the fact that up to 7% Mn goes in the lattice in the form of Mn$^{+2}$ replacing Cu$^{+2}$ beyond which an impurity phase of CuMn$_2$O$_4$ comes into the picture for 9% and 15% doping in which the oxidation state of Mn is +3 state. Therefore, in case of 9% and 15% Mn doped CuO there is a co-existence of Mn$^{+2}$ and Mn$^{+3}$ valence states. Rao et al. have also shown the formation of CuMn$_2$O$_4$ in 10% Mn doped CuO (Cu$_{0.9}$Mn$_{0.1}$O), in which Mn$^{+3}$ valence state comes into existence [20]. The ionic radii of Mn$^{+2}$ and Mn$^{+3}$ are 0.83 Å and 0.58 Å respectively, i.e. in the first case it is larger whereas in the second case it is smaller compared to the Cu$^{+2}$ ionic radius (0.73 Å) [21]. Since ionic
size of Mn$^{+2}$ is larger than Cu$^{+2}$, crystallite size increases slightly up to 7% Mn doping. On the other hand, ionic radius of Mn$^{+3}$ is smaller than that of Cu$^{+2}$, that is why crystallite size decreases for higher doping concentration.

It can be seen from XRD spectra that there is a clear shift in peak positions of Mn-doped CuO nanoparticles towards larger angles, which indicates a slight distortion in the symmetry of the system due to the creation of defects and vacancies in the system. Defects generated in the system can be attributed to the charge imbalance arised from Mn doping (Mn$^{+3}$ repalcing Cu$^{+2}$).

Fig. 8.1 XRD patterns of pure and Mn doped CuO nanoparticles
<table>
<thead>
<tr>
<th>Dopant Concentration (%)</th>
<th>Crystallite size (nm)</th>
<th>Lattice parameters</th>
<th>Cell Volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a (Å)</td>
<td>b (Å)</td>
</tr>
<tr>
<td>0</td>
<td>20</td>
<td>4.712</td>
<td>3.425</td>
</tr>
<tr>
<td>3</td>
<td>22</td>
<td>4.713</td>
<td>3.425</td>
</tr>
<tr>
<td>5</td>
<td>23</td>
<td>4.713</td>
<td>3.425</td>
</tr>
<tr>
<td>7</td>
<td>25</td>
<td>4.715</td>
<td>3.426</td>
</tr>
<tr>
<td>9</td>
<td>21</td>
<td>4.710</td>
<td>3.422</td>
</tr>
<tr>
<td>15</td>
<td>16</td>
<td>4.708</td>
<td>3.420</td>
</tr>
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</table>

**Table 8.1.** Variation of crystallite size and lattice parameters with doping

Fig. 8.2 shows the typical morphology of pure (Fig. 8.2a), 5% (Fig. 8.2b) and 15% Mn doped (Fig. 8.2c) CuO nanopowder. Powder samples were used for SEM analysis. Powder was sprinkled on the sample holder using double sided tape and gold coated with sputter coater. SEM micrographs clearly exhibit almost spherical morphology of all the samples. It can also be seen from Fig. 8.2 that 5% Mn doped CuO have slightly larger particles size as compared to pure CuO, while 15 % Mn doped CuO samples have smaller particle size compared to pure sample. Average particle size of pure CuO was found to be 35 nm while it was 39 nm and 31 nm for 5% and 15%Mn doped CuO respectively. The variation in particle size matches well with the XRD results. However, the average particle size obtained from SEM analysis is slightly greater than the values calculated from
XRD measurements. It may be due to the aggregation of smaller particles during sample preparation for SEM analysis.

**Fig. 8.2.** FE-SEM micrographs of (a) pure CuO (b) 5% Mn doped CuO (c) 15% Mn doped CuO nanoparticles

The presence of Mn in doped samples is confirmed from the selective area EDAX analysis. EDAX spectra of pure and Mn doped CuO nanoparticles are shown in Fig. 8.3. It is clear from Fig. 8.3 (a), (b) and (c) that Mn is successfully incorporating in the system. It can be concluded from the results of XRD and EDAX that the Mn is successfully doped in the CuO nanocrystals.
8.3.2. Electrical properties:

Electrical properties of Mn doped CuO nanoparticles were studied using impedance spectroscopy. Various electrical parameters like dielectric constant, loss tangent, ac conductivity, real and imaginary components of impedance were measured over a wide range of frequency at room temperature for all the samples.

8.3.2.1. Dielectric constant:

The dielectric constant of pure and Mn doped CuO was calculated using equation 3.6 given in chapter 3. Fig. 8.4 shows dielectric behavior of pure and Mn doped CuO with frequency and composition. It is clear from Fig. 8.4 that the dielectric constant decreases with the increase in frequency in low frequency region and then it shows frequency independent behavior for all the samples.
This can be attributed to the fact that at low frequencies, the hopping plays in unison with the applied ac field, but at the elevated frequencies, the hopping ceases to follow the rapid fluctuation of the field and hence $\varepsilon'$ decreases due to random orientation and chaotic dipolar distribution up to certain frequency and show the frequency independent behavior at higher frequencies. Further, it can be seen from Fig. 8.4 that the dielectric constant increases with doping up to 7% Mn doping beyond which it is reduced at higher doping (9% and 15%). This is due to the fact that dielectric polarizability of Mn$^{\text{2+}}$ is larger than that of Cu$^{\text{2+}}$ [22]. It is evident from XRD spectra that up to 7% doping Mn$^{\text{2+}}$ is going in the system replacing the Cu$^{\text{2+}}$ after which Mn$^{\text{3+}}$ comes into picture for 9% and 15% doping whose ionic radius is smaller than that of Cu$^{\text{2+}}$. Since dielectric polarizability is directly proportional to the cube of ionic radius, dielectric constant decreases for higher dopant concentration [23].

![Fig. 8.4. Variation of dielectric constant with frequency and composition](image)
Variation of dissipation factor or loss tangent (tan δ) with frequency and composition is shown in Fig. 8.5. All the samples exhibit the peaking behavior which is occurred when the hopping frequency of metal ions becomes equal to the frequency of applied field. It has been observed that the peaking frequency shifts towards higher frequency with doping up to 7% Mn doping after which it is again shifted towards low frequencies at higher doping. This indicates that the hopping frequency of metal ions increases with doping up to 7% beyond which it decreases for higher dopant concentrations. This is due to the fact that at higher doping (9% & 15%) there is the coexistence of Mn$^{+2}$ and Mn$^{+3}$ in the system which generates the charge imbalance in the system resulting the formation of defects and vacancies which tend to segregate at the grain boundaries. This in turn forms a barrier for hopping of charge carriers between the grains. This results in the decrease of hopping frequency at high doping concentration. These results correlate very well with the results of ac conductivity which are described in next paragraph.
8.3.2.2. AC conductivity:

Fig. 8.6 shows the variation of ac conductivity with frequency and composition. It can be seen from Fig. 8.6 that ac conductivity exhibit the general trend of increasing with the frequency of applied ac field for all the samples. It may be due to the increase in the rate of hopping with the applied field frequency. The ac conductivity of CuO nanoparticles follows the frequency dependence of ac conductivity given by the power law according to relation:

\[ \sigma_{ac} = A \omega^n \]

where \( \omega \) is the angular frequency, \( A \) is a constant of proportionality and \( n \) is an exponent that depends on both the temperature and frequency.
To investigate the conduction mechanism involved variation of exponent $n$ with frequency and composition was studied. Values of exponent $n$ were calculated from the linear fits of the curves between $\log \sigma_{ac}$ and $\log \omega$ for different dopant concentration as shown in Fig. 8.7. The slope of the curve gives the value of $n$. 

**Fig. 8.6.** Variation of ac conductivity with frequency and composition
Fig. 8.7. Variation of log $\omega$ vs log $\sigma_{ac}$ for different compositions

The value of $n$ has been found to lie between 0 and 1 for all the compositions indicating the hopping conduction of charge carriers. The variation of $n$ with composition is shown in Fig. 8.8. It is clear from Fig. 8.8 that $n$ increases as a function of doping composition up to 7% after which it decreases for 9% and 15%, which clearly indicates the reduction of rate of hopping for 9% and 15% doping. It is clear from Fig. 8.8 that value of $n$ is maximum for 7% Mn doped CuO nanoparticles. This may be due to replacement Cu$^{+2}$ by Mn$^{+2}$ up to 7% beyond which Mn$^{+3}$ also comes into the picture for 9% and 15% doping as shown in XRD results (evolution of secondary phase due to Mn$^{+3}$). Thus at higher doping 9% and 15% excess charge carriers started to segregate the grain boundaries which blocks the
hopping of charge carriers between two grains. This is why ac conductivity for 7% Mn doped CuO is maximum.

Fig. 8.8. Frequency exponent (n) as a function of dopant concentration

Moreover, it has been observed that the conductivity increases with doping up to 7% beyond which it shows decreasing trend for 9% and 15% Mn doping. This result correlate very well with that of loss tangent where the hopping rate of charge carriers was found to increase up to 7% Mn doping beyond which it decreases for higher doping. The reduction in the rate of hopping is attributed to the barrier produced by the segregation of large number of defects and vacancies at grain boundaries in case of higher doping. Similar reduction of ac conductivity has also been observed in Ni and Mn.
doped SnO\textsubscript{2} due to the formation of grain boundary defect barriers [24].

**8.3.2.3. Impedance analysis:**

The total impedance of any system is given by 
\[ Z = Z' + Z'' \], where 
\( Z' \) is the real part of impedance which is related to a pure resistance \( R \), 
\( Z'' \) is the imaginary part of impedance that can be related to a capacitance \( C \) where 
\[ Z'' = 1/j\omega C, \quad j = \sqrt{-1}. \]

The variation of real part of impedance \( Z' \) with frequency is exhibited in Fig. 8.9 for all the samples. It has been observed that \( Z' \) decreases with the increase in frequency for all the compositions. Generally, grain boundaries which are resistive in nature are active at low frequencies, that is why resistance is high in low frequency region, while grains which are conductive in nature are active in high frequency region due to which \( Z' \) is small at high frequencies. Moreover, \( Z' \) was observed to decrease as a function of composition up to 7\% Mn doping beyond which it increases for 9\% and 15\% Mn doping. This decrease in real impedance corroborate very well with the variation of ac conductivity which shows the opposite behavior to that of impedance.
Fig. 8.9. Variation of real impedance with frequency and composition

Variation of imaginary part of impedance $Z''$ with frequency corresponding to different composition is shown in Fig. 8.10. It has been observed that $Z''$ also follows the similar trend as $Z'$ with frequency and dopant concentration.

Fig. 8.10. Variation of imaginary impedance $Z''$ with frequency and composition
When the impedance data of materials having capacitive and resistive components is plotted in a complex plane plot it appears in the form of a sequence of semicircles representing electrical phenomenon due to bulk (grain) material, grain boundary and interfacial phenomenon, if any. Since the grains are effective in high frequency region while the grain boundaries are effective in low frequency region, the semicircle appearing in the high frequency region corresponds to grain contribution while in low frequency region corresponds to the grain boundary contribution. Fig. 8.11 shows the Nyquist plots corresponding to various dopant concentration. It has been observed that all the samples exhibit the single semicircular behavior occurring due to the dominance of grain boundary conduction over grain contribution.

![Fig. 8.11. Nyquist plots corresponding to various dopant concentrations](image)
The semicircles obtained in Nyquist plot are represented by an equivalent circuit consisting of a resistance and a capacitor connected in parallel as shown in Fig. 8.12.

![Equivalent circuit of Nyquist plots](image)

**Fig.8.12.** Equivalent circuit of Nyquist plots

Various electrical parameters like $R_{gb}$, $C_{gb}$, $\tau_{gb}$ were calculated using Non-linear least square (NLLS) fitting which are presented in Table 8.2. It is clear from Table 8.2 that $R_{gb}$ decreases up to 7% doping and then increases at 9 and 15% doping concentration, while the $C_{gb}$ shows the opposite behavior. These results agree well with the results of ac conductivity and dielectric constant.

<table>
<thead>
<tr>
<th>Dopant Concentration (%)</th>
<th>$R_{gb}$ (MΩ)</th>
<th>$C_{gb}$ (nF)</th>
<th>$\tau_{gb}$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>33.84</td>
<td>0.960</td>
<td>32.49</td>
</tr>
<tr>
<td>3</td>
<td>22.08</td>
<td>1.470</td>
<td>32.46</td>
</tr>
<tr>
<td>5</td>
<td>21.62</td>
<td>1.490</td>
<td>32.21</td>
</tr>
<tr>
<td>7</td>
<td>0.159</td>
<td>197.7</td>
<td>31.43</td>
</tr>
<tr>
<td>9</td>
<td>1.220</td>
<td>25.40</td>
<td>30.99</td>
</tr>
<tr>
<td>15</td>
<td>1.830</td>
<td>16.94</td>
<td>31.00</td>
</tr>
</tbody>
</table>

**Table 8.2.** Variation of electrical parameters with dopant concentration
8.3.3. Optical properties:

UV-Visible absorption spectroscopy has been used to investigate the optical properties of Mn doped CuO nanoparticles. Absorption spectra of pure and Mn doped CuO nanoparticles were recorded using Perkin Elmer UV-visible spectrophotometer. The absorption spectra of pure and Mn doped CuO nanoparticles is shown Fig. 8.12. It has been observed that all the samples exhibit an absorption edge at around 275 nm which is smaller than absorbance for bulk CuO which occurs at 310 nm as reported by Zhang et al. [25]. Moreover, It is clear from Fig. 8.13 that there is a clear blue shift in case of higher Mn doping concentration (9% and 15%). This shift towards lower wavelength could be attributed to the quantum confinement effect of nanoparticles.

![Absorbance spectra of pure and Mn doped CuO nanoparticles](image)

**Fig.8.13.** Absorbance spectra of pure and Mn doped CuO nanoparticles
Optical band gap for all samples was calculated using well known Tauc relation given by:

\[ \alpha h \nu = A' (h \nu - E_g)^n \]

where \( \alpha = 2.303A/t \) is called the absorption coefficient, \( A \) is the absorbance, \( t \) is the path length of wave which is equal to the thickness of the cuvette, \( A' \) is the proportionality constant, \( E_g \) is the band gap, \( h \nu \) is the photon energy and \( n = 1/2 \) and 2 for direct and indirect band gap semiconductors respectively. It can be seen from Tauc plots (Fig. 8.14) that band gap of pure CuO nanoparticles is 2.6 eV which is larger than that of bulk CuO (1.85 eV). This increase has been attributed to the quantum confinement effect of nanoparticles. Moreover, it is clear from Tauc plots that the band gap decreases initially with Mn doping up to 7% beyond which it was found to increase for higher doping 9% and 15%. This is due to the increase in particle size with Mn doping up to 7% after which particle size decreases for 9% and 15% Mn doping as shown in Table 8.1.
Fig. 8.14. Tauc plots of pure and Mn doped CuO nanoparticles
Room temperature photoluminescence spectra of Mn doped CuO nanoparticles are shown in Fig. 8.15. Emission spectra were taken using an excitation wavelength of 350 nm. It is observed from Fig. 8.15 that all the samples exhibit strong emission peaks at 546 nm, 612 nm and 680 nm along with several weak emissions in the region 370-470 nm. The appearance of emission bands in the lower wavelength region (UV region) may be attributed to the near band edge emission (NBE). It is generally considered that the UV emission is related to the near band edge emission. R. Elilarassi et al. have also reported the near band edge emission in the UV region in Cu doped ZnO [26]. Furthermore, the origin of defect related visible emission in oxide nanomaterials is generally ascribed to the oxygen vacancies and intrinsic defects. It is generally accepted that the green and red emissions are associated with oxygen vacancies and interstitial metal ions in the oxide [27-30]. One can evaluate the concentration of structural defects by comparing the PL intensity ratio of UV near band edge emission to green deep level emission. It is clear from the Fig. 8.15 that the PL intensity of green and red emission peaks at 546 and 680 nm occurred in the visible region is enhanced much more compared to UV emission peaks in the doped samples. The PL intensity ratio of UV emission to green emission becomes very small in 15% Mn doped CuO indicating the increase in the concentration of defects in doped samples, which corroborates well with XRD results.
**Fig. 8.15.** Photoluminescence spectra of Mn doped CuO nanoparticles

FTIR spectra were taken using Perkin Elmer FTIR spectrophotometer. Fig. 8.16 shows the FTIR spectra of pure and Mn doped CuO nanoparticles. It is clear from Fig.8.16 that all the samples exhibit vibrations in the region 400-600 cm\(^{-1}\), which can be attributed to the vibrations of Cu(II)-O bond. Zhang et al. have also reported that the vibrations at 588, 534 and 480 cm\(^{-1}\) confirms the Cu(II)-O phase of Copper oxide [31]. FTIR spectra clearly show the vibrations at 450 cm\(^{-1}\), 530 cm\(^{-1}\) and 585 cm\(^{-1}\), which agree well with the values reported in the literature. Moreover, it can be seen from Fig. 8.16 that there is clear a shift in the position of peaks of 9% and 15% Mn doped samples which is related to quantum size and surface effects of nanomaterials [32].Similar quantum size and surface
effects have also been reported by L. Fangxin et al. in nanogranular ZrO$_2$ [32].

![FTIR spectra of pure and Mn doped CuO nanoparticles](image)

**Fig. 8.16.** FTIR spectra of pure and Mn doped CuO nanoparticles

### 8.4. Conclusions:

Manganese-doped CuO nanoparticles were successfully synthesized using sol-gel combustion route. The XRD spectra confirm the formation of single phase CuO nanoparticles. No impurity phase was observed in XRD up to 7% beyond which a small amount of impurity phase corresponding to CuMn$_2$O$_4$ was observed for higher Mn doped samples (9% and 15%). The particle size and lattice parameters were observed to increase slightly with the increase in manganese concentration up to 7% and thereafter it
tends to decrease for 9% and 15% Mn doped samples. The data revealed that the dielectric constant increases with doping up to 7% and decreases for higher doping (9% and 15%). Loss tangent $\tan\delta$ exhibit peaking behavior for all the samples where peak was found to shift towards higher frequency with doping up to 7% beyond which it again shifted towards low frequency at 9% and 15%. It is interesting to see that dielectric constant is high compared to loss tangent indicating the importance of this material to be used for high frequency device applications. The ac conductivity shows the frequency and composition dependent behaviour. It increases with the increase in frequency and dopant concentration up to 7% and then decreases for higher dopant concentration. Complex impedance spectra show single semicircular behavior for all the samples suggesting the dominance of grain boundary contribution over grain contribution in conduction process. All the electrical parameters correlate well with each other. The optical studies confirmed that the band gap of the doped samples decreases initially up to 7% Mn doping after which it started to increase for 9% and 15% doping concentration. The fluorescence spectra showed intense green and red emission peaks in the visible region which may be due to the surface defect levels. The intensity of visible emission increases as the dopant concentration increases. In conclusion, the manganese doping in CuO improves the electrical and optical properties of the CuO nanoparticles.
References:


