CHAPTER 7

STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF Ni DOPED CuO NANOPARTICLES

7.1. Introduction:

Transition metal oxides (TMOs), such as TiO$_2$, ZnO and Fe$_2$O$_3$ nanocrystals, have attracted much attention in recent years because of their size dependent optical properties and electronic structure [1–3]. Nanomaterials, which have attracted major attention in recent years, are characterized by a large amount of surfaces and interfaces. Particle sizes in the nano regime and specific crystal morphologies are expected to enhance the performance and allow the fine tuning of the properties of these materials. Giant dielectric permittivity in nanomaterials will play a key role in the advances of electronic devices. Recent discovery of giant dielectric response in oxide materials has attracted tremendous research interest because of their potential applications [4–11]. Among the oxides of transition metals, copper oxide (CuO) nanoparticles are of special interest from technological point of view. Copper oxide has shown industrial importance in applications, such as gas sensors, magnetic storage media, solar energy transformation, semiconductors and catalysis [12–14]. Opposite to n-type semiconducting metal oxides, cupric oxide (CuO) is a p-type semiconductor with a band gap of 1.85 eV [15]. Investigations on the synthesis and characterization of CuO nanoparticles are relatively few compared to other transition metal
oxides like ZnO, SnO₂, TiO₂ and Fe₂O₃, making it an interesting candidate to study. Moreover the doping of the semiconductor nanoparticles with impurity metal ions is one of the most important methods to modify the characteristics of the material. The engineering of band gap and influencing physical, chemical, and electronic properties of the semiconductors are possible by the use of the right dopants. Several authors have reported the improvement in material’s characteristic properties using various dopants. The band gap narrowing of Ni doped SnO₂ nanoparticles was observed by Ahmed et al. [16], Das et al. reported the tuning of emission properties of Mn doped Cu₂O nanoparticles [17]. Some methods for the preparation of pure and doped nanocrystalline CuO have been reported such as the sonochemical method [18], sol–gel technique [19], one-step solid state reaction method at room temperature [20], electrochemical method [21], thermal decomposition of precursors [22].

This chapter presents the effect of Ni doping on the structural, electrical and optical properties of CuO nanoparticles synthesized by sol–gel combustion route.

7.2. Experimental:

7.2.1. Synthesis:

In a typical synthesis procedure, Cu(NO₃)₂.3H₂O, Ni(NO₃)₂.6H₂O 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 °C. Stirring continues till the formation of gel. As the gel is formed it is allowed to burn at 200 °C. A light brown fluffy mass is obtained as a result of combustion, which was further annealed at 400 °C to obtain the crystalline Ni doped CuO nanoparticles. The doping concentration of Ni was varied from 0% to 15%. The CuO nanoparticles thus obtained were characterized by XRD, FTIR, UV-Visible spectroscopy and dielectric spectroscopy.

7.2.2. Characterization:

Structural characterization was carried out by X-ray diffraction using Rigaku X-ray diffractometer with Cu-Kα radiation having wavelength $\lambda = 1.5406\text{Å}$ in the $2\theta$ range from $20^\circ$ to $80^\circ$. Morphological analysis was carried out on a FEI FE-SEM. The compositional analysis was carried out using EDAX attached with the FE-SEM. The samples were coated with a thin layer of gold to prevent charging of the samples. FT-IR spectroscopy measurements were carried out on a Perkin Elmer spectrophotometer using KBr pellets. Electrical analysis was carried out using Agilent 4245 A impedance analyzer. The samples were pelletized for electrical measurements and silver coated on both sides for dielectric measurements. Optical absorbance spectra were taken using Perkin Elmer UV-Visible spectrophotometer at room temperature.
Fluorescent emission spectra were recorded on a Varian Fluorescence spectrophotometer (Carry Eclipse).

7.3. Results and discussion:

7.3.1. Structural analysis:

The typical XRD spectra of pure and Ni doped CuO nanoparticles annealed at 400 °C is shown in Fig. 7.1. The peak positions of 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. 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 7.1. Lattice parameters shown in Table 7.1 are very close to the standard lattice parameters reported in ICDD card no. 801916. It is clear from Table 7.1 that the crystallite size and lattice parameters slightly decrease with the increase in dopant concentration, which can be attributed to the smaller ionic radii of Ni\(^{+2}\) (69 pm) ions compared to Cu\(^{+2}\) (73 pm). It can be seen from XRD spectra that there is no shift in peak positions of Ni-doped CuO nanoparticles up to 9% doping beyond which there is a clear shift in peak positions for 15% doping indicating no change in the monoclinic symmetry of the system with doping up to 9%. At higher doping concentration (15%) there is a clear shift in XRD peaks.
towards larger angle which indicates a slight distortion in the symmetry of the system due to the creation of defects and vacancies in the system.

![XRD spectra of pure and Ni doped CuO nanoparticles](image)

**Fig. 7.1.** XRD spectra of pure and Ni doped CuO nanoparticles

<table>
<thead>
<tr>
<th>Dopant Concentration (%)</th>
<th>Crystallite size (nm)</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Cell volume (Å³)</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>20</td>
<td>4.712</td>
<td>3.425</td>
<td>5.132</td>
<td>81.66</td>
</tr>
<tr>
<td>3</td>
<td>18</td>
<td>4.710</td>
<td>3.422</td>
<td>5.131</td>
<td>81.56</td>
</tr>
<tr>
<td>5</td>
<td>17</td>
<td>4.710</td>
<td>3.421</td>
<td>5.130</td>
<td>81.52</td>
</tr>
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<td>7</td>
<td>16</td>
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<td>3.419</td>
<td>5.129</td>
<td>81.42</td>
</tr>
<tr>
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<td>15</td>
<td>4.707</td>
<td>3.417</td>
<td>5.128</td>
<td>81.34</td>
</tr>
<tr>
<td>15</td>
<td>13</td>
<td>4.699</td>
<td>3.415</td>
<td>5.124</td>
<td>81.09</td>
</tr>
</tbody>
</table>

**Table 7.1.** Variation of crystallite size, lattice parameters and cell volume with dopant concentration
Fig. 7.2 shows the typical morphology of pure (Fig. 7.2a) and 9% Ni doped (Fig. 7.2b) CuO nanopowder. Samples were in the powder form for SEM analysis. Powder was stick on the sample holder using double sided tape and gold coated with sputter coater. SEM micrographs clearly exhibit the presence of spherical aggregates of smaller individual nanoparticles. It can also be seen from Fig. 7.2 that Ni doped CuO have smaller particles size as compared to pure CuO. Average particle size of pure CuO was found to be 35 nm while it was 32 nm for 9% Ni doped CuO. This decrease 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.7.2.** FE-SEM images of (a) pure CuO (b) 9% Ni doped CuO nanoparticles
The presence of Ni in doped samples was confirmed from the selective area EDAX analysis. EDAX spectra of pure and Ni doped CuO is shown in Fig. 7.3. It is clear from Fig. 7.3 (a) & (b) that Ni was successfully incorporated in the system. It can be verified from the results of XRD and EDAX that the Ni is successfully doped in the CuO nanocrystals.

![EDAX spectra of pure and Ni doped CuO nanoparticles](image)

**Fig. 7.3.** EDAX spectra of (a) pure CuO (b) Ni doped CuO nanoparticles

### 7.3.2. Electrical properties:

To explore the electrical behavior of Ni doped CuO nanoparticles the electrical parameters like dielectric constant, loss tangent, ac conductivity and impedance of Ni-doped CuO nanoparticles were studied over a wide range of frequency at room temperature using ac technique of complex impedance spectroscopy. Impedance spectroscopy is a technique for the measurement of
electrical impedance of the materials over a suitable frequency range which depends upon particular study of interest. Impedance spectroscopy is also used to determine the relationship between material’s electrical properties and other physical and chemical properties. Material’s properties are monitored by observing a frequency response of a small AC signal. Changes in the frequency response thus reflect the changes in the physical and chemical properties.

7.3.2.1. Dielectric properties:

The complex dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ of pure and Ni doped CuO nanoparticles was measured as a function of frequency at room temperature, where $\varepsilon'$ is real part of dielectric constant and describes the stored energy while $\varepsilon''$ is imaginary part of dielectric constant, which describes the dissipated energy. Generally, the dielectric response involves effects from ‘dipolar’ and ‘charge carrier’ behaviours. The former is responsible for the restoration of the zero residual polarization after discharging while the later is associated with partial recovery on discharge but always leaves a finite polarization in the system.
The dielectric constant as a function of frequency for all compositions is shown in Fig. 7.4. It is clear from Fig. 7.4 that dielectric constant shows the general decreasing trend with the increase in frequency for both pure and doped samples. This can be attributed to the fact that $\varepsilon'$ and conductivity have the same root of origin via hopping between metal ions (Cu$^{+2}$, Cu$^{+1}$ and Ni$^{+2}$). At low frequencies, the hopping plays in unison with the applied a.c. 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. Further, it has been observed that the dielectric constant increases with doping concentration up to 9% doping beyond which there is an abrupt decrease in dielectric constant for 15% Ni doped CuO. The increment
in dielectric constant with Ni doping may be attributed to the enhanced electro-negativity of Ni compared to Cu in the system. The electro-negativity of Ni and Cu are 1.9 and 1.8 respectively on Pauling scale. The coordination of atoms in CuO is that each atom has four nearest neighbors of the other kind. Each Cu atom is linked to four nearly coplanar O atoms at the corner of an almost rectangular parallelogram. The O atom is coordinated to four Cu atoms in the form of a distorted tetrahedron. In case of pure CuO electron density will exist near central oxygen atom in distorted tetrahedron as shown in Fig. 7.5(a). Due to the shifting of electron density towards central oxygen atom bond angles are wide with small value of resultant polarization. As Ni is introduced in the system electro-negativity of Cu-Ni system slightly increases leading to the shift of electron density towards outer Cu-Ni atom, which in turn decreases the bond angles resulting the increase in resultant polarization and thereby increasing the dielectric constant up to 9%. This phenomenon is shown in Fig. 7.5(b). Beyond 9% Ni doping, a large number of defects and vacancies are developed in the system which distorts the already distorted tetrahedron configuration as shown in Fig. 7.5(c). The distortion in case of 15% is also evident from shifting of XRD peaks towards larger angles (Fig. 7.1). As a result of this the overall dipole moment of system falls abruptly decreasing the dielectric constant.
**Fig. 7.5.** (a) Oxygen atom surrounded by four Cu atoms in pure CuO  
(b) Oxygen is surrounded by Cu$_{1-x}$Ni$_x$ of higher electronegativity  
(c) Distortion of already distorted tetrahedron with higher doping (15%). Purple color shows the electron density
Loss tangent $\tan \delta$ is derived from the phase difference due to the loss of energy within the sample at a particular frequency according to the relation:

$$\tan \delta = \frac{1}{\tan \theta},$$

where $\theta$ is the phase difference.

![Graph showing variation of $\tan \delta$ with frequency and composition](image)

**Fig. 7.6.** Variation of $\tan \delta$ with frequency and composition

Generally, at low frequencies dipoles follow the applied ac field with small phase difference leading to the large value of loss tangent. As frequency increases dipoles begin to lag behind the field leading to the increase in phase difference which in turn decreases the $\tan \delta$. At high frequencies dipoles do not follow applied ac field where $\tan \delta$ shows the frequency independent behavior [23]. Variation of loss factor with frequency for all the compositions is shown in Fig. 7.6. It is clear from Fig. 7.6 that the loss tangent exhibits the relaxation
peak for all the compositions, which occurs when the applied frequency becomes equal to the hopping frequency between metal ions. Moreover, it is interesting to see that the relaxation peak is shifting towards the higher frequency with dopant concentration up to 9% Ni doping beyond which the relaxation peak again shifted towards low frequency. This phenomenon clearly indicates the increase in the hopping frequency with doping up to 9% after which (for 15% Ni doped CuO) peak shifts towards lower frequency side indicating the decrease in hopping frequency.

### 7.3.2.2. AC conductivity:

The ac conductivity of pure and Ni doped CuO was investigated as a function of frequency and composition. Variation of ac conductivity with frequency for different compositions is shown in Fig. 7.7. It has been observed that the ac conductivity increases with the increase in frequency for all the compositions.
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. 7.8. The slope of the curve gives the value of $n$. 

**Fig. 7.8.** Variation of $\log \omega$ vs $\log \sigma_{ac}$
The value of \( n \) was 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. 7.9. It is clear from Fig. 7.9 that \( n \) increases as a function of doping composition up to 9% after which it decreases for 15%.

![Graph showing variation of exponent \( n \) with dopant concentration.](image)

**Fig. 7.9.** Variation of frequency exponent with dopant concentration

Thus the increase in conductivity with frequency can be attributed to the increase in the hopping frequency of charge carriers with the increase in applied frequency. Furthermore, it can also be seen from Fig. 7.7 that ac conductivity shows increasing trend with dopant concentration up to 9% beyond which it decreases for 15% Ni doping. This can be attributed to the fact that hopping frequency is increasing up to 9% and then decreases for higher doping (15%).
which is also evident from the results of loss tangent where relaxation peak is shifting towards low frequency for 15% Ni doped CuO. The decrease in hopping may be attributed to the large amount of defects and vacancies generated in the system at higher doping, which segregate at the grain boundaries blocking the transportation of charge carriers between the grains [24]. This in turn reduces the rate of hopping at higher dopant concentration. The values of frequency exponent n also verify the results of conductivity variation with dopant concentration.

### 7.3.3.3. Impedance analysis:

The total impedance of the system can be given in the form $Z = Z' + Z''$, where $Z'$ is the real part of impedance that can be related a pure resistance $R$, $Z''$is the imaginary part of impedance that can be related to a capacitance $C$ where $Z'' = 1/j\omega C$, $j = \sqrt{-1}$.

![Fig.7.10. Variation of $Z'$ with frequency for all the compositions](image.png)
The variation of real part of impedance $Z'$ with frequency is shown in Fig. 7.10. It is clear from Fig. 7.10 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, no clear pattern of $Z'$ was observed as a function of composition. However, it shows a decreasing trend for higher dopant concentration.

Variation of imaginary part of impedance $Z''$ with frequency is shown in Fig. 7.11. It is clear from Fig. 7.11 that $Z''$ follow the similar trend as $Z'$ with frequency. Further, $Z''$ was observed to decrease with the increase in dopant concentration up to 9% after which it increased for 15% doping which agrees well with the results of dielectric constant and ac conductivity.
Dielectric constant which is directly proportional to capacitance ($C$) was found to increase with doping up to 9% beyond which it decreases for 15% (Fig. 7.4). Since $Z''$ is inversely proportional to the capacitance according to the relation:

$$Z'' = \frac{1}{j\omega C}$$

It decreases with doping up to 9% and increases thereafter for 15%.

Impedance data of materials that have capacitive and resistive components, when plotted in a complex plane plot (Nyquist plot), appear in the form of a succession of semicircles representing electrical phenomenon due to bulk (grain) material, grain boundary and interfacial phenomenon, if any. Generally, the grains are effective in high frequency region while the grain boundaries are effective in low frequency region. Thus, the semicircle appearing in the high frequency region corresponds to grain contribution while in
low frequency region corresponds to the grain boundary contribution. Fig. 7.12 exhibits the Nyquist plots between $Z'$ and $Z''$ for different compositions. It is evident from Fig. 7.12 that all the samples show single semicircular behavior indicating the predominance of grain boundaries over grain conduction in all the samples. This could be attributed to smaller size of nanoparticles. In case of nanomaterials, interface area (grain boundary) to bulk (grain) ratio increases as a result of which grain boundary contribution in conduction process becomes dominant over grain contribution.

**Fig.7.12.** Nyquist plots for pure and Ni doped CuO nanoparticles
The semicircles obtained in Nyquist plot can be represented by an equivalent circuit consisting of a resistance and a capacitor connected in parallel as shown in Fig. 7.13.

![Equivalent circuit for Nyquist plots](image)

**Fig.7.13.** Equivalent circuit for Nyquist plots

The values of various impedance parameters were obtained by analyzing the impedance plots using non linear least square fitting method. These values are tabulated in Table 7.2.

<table>
<thead>
<tr>
<th>Dopant concentration (mol %)</th>
<th>$R_{gb}$ (MΩ)</th>
<th>$C_{gb}$ (nF)</th>
<th>$T_{gb}$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>23.61</td>
<td>1.369</td>
<td>32.32</td>
</tr>
<tr>
<td>3</td>
<td>21.62</td>
<td>1.497</td>
<td>32.36</td>
</tr>
<tr>
<td>5</td>
<td>4.385</td>
<td>7.442</td>
<td>32.63</td>
</tr>
<tr>
<td>7</td>
<td>2.923</td>
<td>11.16</td>
<td>32.62</td>
</tr>
<tr>
<td>9</td>
<td>2.099</td>
<td>15.50</td>
<td>32.53</td>
</tr>
<tr>
<td>15</td>
<td>20.68</td>
<td>1.569</td>
<td>32.44</td>
</tr>
</tbody>
</table>

**Table 7.2.** Variation of various impedance parameters with compositions

It is clear from Table 7.2 that $R_{gb}$ decreases with doping up to 9% and then increases for 15%, which agrees well with the results of
ac conductivity. Moreover, $C_{gb}$ was observed to increase up to 9% beyond which it decreases for 15%. These results agree well with the results of dielectric constant which increases up to 9% and then decreases for 15%.

7.3. Optical Properties:

UV-Visible absorption spectroscopy is one of an important tool to investigate the optical properties of semiconducting nanoparticles. Absorption spectra of pure and Ni doped CuO nanoparticles were taken using Perkin Elmer UV-visible spectrophotometer. The absorption spectra of pure and Ni doped CuO nanoparticles is shown Fig. 7.14. Fig. 7.14 exhibits an absorption edge at around 275 nm for all the samples which is smaller than absorbance for bulk CuO which is 310 nm as reported by Zhang et al. [25]. This shift towards lower wavelength could be attributed to the quantum confine effect of nanoparticles. It is interesting to see that the absorption edge is slightly red shifted towards higher wavelength side with doping concentration even the particle size is decreasing with doping, which is in contradiction with the quantum confinement effect.
Absorbance spectra of pure and Ni doped CuO nanoparticles

This indicates the decrease in band gap with doping. Optical band gap for all the samples was calculated using well known Tauc relation given by:

\[ a h \nu = A' \, h \nu - E_g^n \]

where \( a =2.303A/t \) 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 is evident from Tauc plots (Fig. 7.15) that band gap of pure CuO nanoparticles is 2.6 eV which is higher than that of bulk CuO (1.85 eV). This increase has been attributed to the quantum confinement effect of nanoparticles. Moreover, it has been observed that the band gap decreases with Ni doping along with the decrease in particle size. The red shift in the band gap can be attributed to the presence of intra
gap defects in doped samples. Intra gap defects have also been reported to decrease the band gap of CuO nanoparticles by Rehman et al.[26]. Ovchinnikov et al. have discussed the role of electronic defects in CuO. They have suggested that the presence of dopants or valence defects (e.g. O vacancies and Cu$^{+1}$) in CuO nanoparticles leads to the development of intraband states within the band gap and these are the sources of observed decrease in the band gap [27]. Similar decrease in band gap of Ni doped SnO$_2$ has also been observed in our previous work [28], where band gap decreases with Ni doping along with the reduction in size.

![Fig.7.15. Tauc Plots for all the samples](image)
The room temperature Photoluminescence behaviour of pure and Ni doped CuO nanoparticles was investigated using fluorescence spectrophotometer and the results are shown in Figure 7.16. PL spectra were taken at an excitation wavelength of 350 nm. It can be seen from PL spectra that the samples exhibit three emission peaks. A sharp emission band occurred in the UV region at 361 nm, while two weak emission bands located at 470nm (visible region) and 715 nm were also observed. It is believed that the emission wavelength of the oxide material depends mainly on the particle’s shape, size, and excitation wavelength. The first emission peak at 361 nm can be attributed to the band edge emission [29, 30, 31]. The second weak peak occurred in the visible region can be assigned to the defects and vacancies generated due to non-stoichiometric CuO [32]. Non stoichiometry is generated in CuO due to the existence of Cu vacancies [33]. The third PL peak occurring at 715 nm was found to be due to band impurity transition resulting in the recombination of electron bound to donor and free holes [31]. Band impurity transition is also verified from absorbance results where band gap was found to decrease with doping due to the existence of impurity or defect states within the band gap. It can be seen from Fig. 7.16 that there is no change in PL peak positions with doping. However, a slight increase in the intensity of luminescent emission was observed with doping which can be attributed to the defects such as oxygen interstials and Cu vacancies in the doped samples. The shifting in XRD peaks of
highly doped CuO nanoparticles confirms the generation of lattice defects in the system.

![Photooluminescence (PL) spectra of pure and Ni doped CuO nanoparticles.](image)

**Fig. 7.16.** Photoluminescence (PL) spectra of pure and Ni doped CuO

FTIR spectra have long been utilized as a powerful tool to provide supplementary information on the nature of copper oxides [34]. Fig. 7.17 shows the FTIR spectra of pure and Ni doped CuO nanoparticles. It is clear from Fig. 7.17 that all the samples show strong bands at around 490 cm\(^{-1}\), 535 cm\(^{-1}\) and 589 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 [34]. Moreover, it can be seen from Fig. 7.15 that the intensity of FTIR peaks decreases while the
Fig. 7.1. FTIR spectra of pure and Ni doped CuO nanoparticles

Broadening increases with the increase in doping concentration. This is due to the reduction of particle size with doping. H. Zhang et al. have also reported the broadening of IR bands with the decrease in particle size [35]. As the particle size decreases, defects and local lattice distortions appear in the system lowering the crystal symmetry leading to the broadening of FTIR peaks [35]. Similar broadening have also been observed by Fangxin et al. in nanosized ZrO$_2$ [36].

7.4. Conclusions:

Nickel-doped CuO nanoparticles were successfully synthesized using sol-gel combustion route. The XRD patterns confirm the formation of single phase CuO nanoparticles. No impurity phase has been observed in XRD. The particle size, lattice parameters and cell
volume were observed to decrease with the increase in nickel concentration. The data revealed that the dielectric constant increases with doping up to 9% and decreases for higher doping (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 9% beyond which it again shifted towards low frequency at 15%. It is interesting to see that dielectric constant is high for higher doping (9%) while loss tangent is very small in high frequency region for the same dopant concentration (9% and 15%) 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. 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 have been carried out using optical absorbance and fluorescence spectroscopies. The band gap of the doped samples show a narrowing effect as measured from the Tauc relation. The fluorescence spectra show a broad visible emission peak which may be due to the surface defect levels. The intensity of luminescent emission slightly increases as the dopant concentration increases. Thus the nickel doping in CuO improves the electrical and optical properties of the CuO nanoparticles.
References:


