CHAPTER 6

EFFECT OF COPPER ON STRUCTURAL, MAGNETIC AND DIELECTRIC PROPERTIES OF NICKEL FERRITE NANOPARTICLES BY CO-PRECIPITATION METHOD

6.1 INTRODUCTION

Spinel ferrites and substituted nickel ferrites are found to be very attractive and versatile magnetic materials. Nickel ferrite is the most suitable one in which the magnetic and transport properties are affected by the substituents (Roy et al 2008). The substitution can be divided into the following types: direct replacement of Fe$^{3+}$ on tetrahedral (A) or octahedral (B) sublattice by the substituent ion, with consequential redistribution of Fe$^{3+}$ ions among A- or B- sublattices which lead to the change of ferrimagnetic spin structure. The amount of replaced iron is given dictated by the valency of the substituent ions. The extent of iron redistribution depends on the specific nature of the substituting ion.

Diamagnetic substitutions in super and mixed ferrites have received a great deal of attention over the past few years. The substitutions of various magnetic and non-magnetic ions at different sublattices in ferrite materials have provided interesting magnetic structures and electrical properties. The size of the magnetic domain is smaller than the size of the corresponding bulk materials. Novel magnetic behaviour is observed for the nanosized magnetic particles when compared to that of the bulk. Due to
their small sizes, nanoparticles exhibit novel material properties that largely differ from the bulk solid state. Many investigators have carried out research work on nickel ferrite containing various cations such as Zn and Cu (Mazen et al 1982, Ahmed et al 2003, Ahmed et al 2007, Roy et al 2008, Jadhav et al 2009, Gabal 2009, Jozef Sláma et al 2009).

The substitution of Cu brings about a structural phase transition accompanied by a reduction in the crystal symmetry due to cooperative Jahn-Teller effect (Verma et al 2000, Dimri et al 2006), which ultimately results in some interesting electrical and magnetic properties. Hence in the present study, an attempt has been made to study the structural, magnetic and dielectric properties of copper doped nickel ferrite nanoparticles prepared by co-precipitation method.

6.2 MATERIALS AND METHODS

Nanocrystalline copper doped nickel ferrites $\text{Ni}_{(1-x)}\text{Cu}_x\text{Fe}_2\text{O}_4$ (where $x = 0.2, 0.4, 0.6$) are prepared by co-precipitation method. The desired composition is obtained by using stoichiometric amounts of nickel chloride [NiCl$_2$.6H$_2$O], cupric chloride [CuCl$_2$.2H$_2$O] and anhydrous ferric chloride [FeCl$_3$] dissolved in distilled water. The neutralization is carried out with sodium hydroxide solution and the reaction temperature is maintained at 60°C. The pH of the solution is maintained at 8 and it is stirred for 2 hrs. The precipitate is thoroughly washed with distilled water until it is free from impurities. The product is dried at a temperature of 100°C to remove the water content. The dried powder is mixed homogeneously and sintered at 130°C, 600°C and 900°C. These samples are characterized using FT-IR, XRD, SEM, EDX, TEM, VSM and LCRZ meter and the results are discussed.
6.3 RESULTS AND DISCUSSION

6.3.1 FT-IR Spectral Analysis

FT-IR absorption spectra of nickel-copper ferrites of different compositions $\text{Ni}_{(1-x)}\text{Cu}_x\text{Fe}_2\text{O}_4$ ($x = 0.2, 0.4, 0.6$) sintered at 130°C, 600°C and 900°C and recorded in the range 4000 cm$^{-1}$ - 400 cm$^{-1}$ are shown in Figures 6.1, 6.2 and 6.3 respectively. The main absorption bands ($\nu_1$ and $\nu_2$) observed in almost all spinel ferrites - around 600 and 400 cm$^{-1}$ respectively, are attributed to tetrahedral and octahedral site clusters in spinel structure (Priyadarsini et al 2009). The higher values of $\nu_1$ compared to $\nu_2$ indicate that the normal mode of vibration of the tetrahedral cluster is higher than that of the octahedral cluster. This is attributed to the shorter bond length of the tetrahedral cluster than that of the octahedral cluster (Mazen et al 2009).

![FT-IR spectra of Ni$_{(1-x)}$Cu$_x$Fe$_2$O$_4$](image)

**Figure 6.1** FT-IR spectra of Ni$_{(1-x)}$Cu$_x$Fe$_2$O$_4$ (a) $x = 0.2$ (b) $x = 0.4$ (c) $x = 0.6$ nanoparticles sintered at 130°C
Figure 6.2  FT-IR spectra of \( \text{Ni}_{(1-x)}\text{Cu}_x\text{Fe}_2\text{O}_4 \) (a) \( x = 0.2 \) (b) \( x = 0.4 \) (c) \( x = 0.6 \) nanoparticles sintered at \( 600^\circ C \)

Figure 6.3  FT-IR spectra of \( \text{Ni}_{(1-x)}\text{Cu}_x\text{Fe}_2\text{O}_4 \) (a) \( x = 0.2 \) (b) \( x = 0.4 \) (c) \( x = 0.6 \) nanoparticles sintered at \( 900^\circ C \)
It is observed from the spectra that there is a long shoulder around 554 cm\(^{-1}\) - 547 cm\(^{-1}\) for the tetrahedral site band and also the depth increases as the concentration of copper increases. This may be attributed to the presence of lower ionic states in that site i.e. diffusion of Ni\(^{2+}\) (Pradeep et al 2008) and Cu\(^{2+}\) by the replacement of Fe\(^{3+}\) in the A-site. The octahedral site band appears around 450 cm\(^{-1}\). The spectra also shows a small subsidiary band around 435 cm\(^{-1}\) as observed for the pure nickel ferrite and it is more pronounced for Ni\(_{0.4}\)Cu\(_{0.6}\)Fe\(_2\)O\(_4\) sample sintered at 900°C. The inclusion of copper shifts the band \(\nu_1\) to lower values and small shoulders around are observed 693 cm\(^{-1}\) and 671 cm\(^{-1}\) as reported for pure nickel ferrite. These bands completely disappeared for the sample sintered at 900°C. The absorption bands around 3500 cm\(^{-1}\) and 1600 cm\(^{-1}\) are assigned to the stretching (\(\nu\)) vibrations of the free or absorbed water on the surface of nickel-copper ferrite nanoparticles as shown in Figures 6.1 & 6.2 and the absence of band in Figure 6.3 implies that the hydroxyl groups are completely removed as the samples are sintered at 900°C.

### 6.3.2 Structural Analysis

XRD patterns of nickel-copper mixed ferrites of different compositions Ni\(_{(1-x)}\)Cu\(_x\)Fe\(_2\)O\(_4\) (x = 0.2, 0.4, 0.6) synthesized at pH equal to 8 and sintered at 130°C, 600°C and 900°C are shown in Figures 6.4, 6.5 and 6.6 respectively. The experimentally observed d spacing values and relative intensities of the diffraction peaks are compared and indexed using JCPDS Card No (74-2081) and (34-0425) for nickel and copper ferrites.
Figure 6.4  XRD pattern of Ni_{(1-x)}Cu_xFe_2O_4 (a) x = 0.2 (b) x = 0.4 (c) x = 0.6 nanoparticles sintered at 130°C

The diffraction patterns indicate amorphous nature of the sample sintered at 130°C. With increase in sintering temperature to 600°C and 900°C the diffraction peaks become sharper and narrower thereby indicating the crystalline nature of the samples. An impurity peak of hematite (α-Fe_2O_3) is observed for the sample Ni_{0.4}Cu_{0.6}Fe_2O_4 sintered at 600°C and 900°C. The formation of α-Fe_2O_3 has been attributed to preferential loss of one or more of divalent cations during the washing and drying stages (Mangalaraja et al 2004, Suwalka et al 2007). The percentage of α-Fe_2O_3 is known to be dependent on pH and the temperature of the solution at the precipitation stage.
Figure 6.5  XRD pattern of Ni_{1-x}Cu_xFe_2O_4 (a) x = 0.2 (b) x = 0.4 (c) x = 0.6 nanoparticles sintered at 600°C

Figure 6.6  XRD pattern of Ni_{1-x}Cu_xFe_2O_4 (a) x = 0.2 (b) x = 0.4 (c) x = 0.6 nanoparticles sintered at 900°C
The lattice parameter of Ni-Cu ferrite for all the compositions sintered at 600°C and 900°C calculated from the (311) diffraction peak are listed in Table 6.1. The lattice parameter depends upon the composition and sintering temperature. As shown in Table 6.1 the lattice constant increases as the sintering temperature increases (Tania Jahanbin et al 2010). The lattice expansion may be attributed to the reduction of Fe$^{3+}$ and formation of Fe$^{2+}$ ions while the ionic radius of the Fe$^{2+}$ (0.77 Å) is larger than that of the Fe$^{3+}$ (0.63 Å). It can also be observed from the Table 6.1 that the increase in the lattice parameter with increasing Cu content is attributed to the greater ionic radius of Cu$^{2+}$ (0.72 Å) in comparison to Ni$^{2+}$ (0.69 Å) and indicates the occupancy of copper ions in the B-sites of the spinel structure (Gabal et al 2011). The microstrain is found to be 0.001331, 0.001646, 0.002439 for Ni-Cu mixed ferrites Ni$_{(1-x)}$Cu$_x$Fe$_2$O$_4$ (x = 0.2, 0.4, 0.6) respectively sintered at 900°C and is observed to increase with increase in copper concentration. This can be attributed to the doping of Cu$^{2+}$ ions in the Ni$^{2+}$ sites which increases the strain in lattice due to larger ionic radii of Cu$^{2+}$ ions which in turn decreases the crystallite size.

Table 6.1 Structural parameters of Ni$_{(1-x)}$Cu$_x$Fe$_2$O$_4$ (x = 0.2, 0.4, 0.6) nanoparticles sintered at 600°C and 900°C

<table>
<thead>
<tr>
<th>Composition</th>
<th>Lattice Parameter (a) Å</th>
<th>Crystallite Size (D) nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>600°C</td>
<td>900°C</td>
</tr>
<tr>
<td>Ni$<em>{0.8}$Cu$</em>{0.2}$Fe$_2$O$_4$</td>
<td>8.2978</td>
<td>8.3046</td>
</tr>
<tr>
<td>Ni$<em>{0.6}$Cu$</em>{0.4}$Fe$_2$O$_4$</td>
<td>8.3060</td>
<td>8.3159</td>
</tr>
<tr>
<td>Ni$<em>{0.4}$Cu$</em>{0.6}$Fe$_2$O$_4$</td>
<td>8.3421</td>
<td>8.4725</td>
</tr>
</tbody>
</table>

The crystallite size of each composition is determined by the Debye-Scherrer relation and listed in Table 6.1. The average crystallite sizes of different compositions for x values of 0.2, 0.4 and 0.6 of the
sample Ni$_{(1-x)}$Cu$_x$Fe$_2$O$_4$ sintered at 600°C are found to be 6 nm, 10 nm and 12 nm respectively and are found to increase as the samples are sintered at 900°C. This is due to the fact that two or more particles fuse together due to melting of their surfaces through the sintering process. At higher sintering temperatures, the grain growth is stimulated but the influence of copper controls and retains the smaller particle size.

It is observed from the Table 6.1 that the crystallite size decreases with Cu substitution, which indicates that the addition of Cu has a great effect on obstructing the grain growth of the spinel. The same trend was observed in Cu-Ni ferrite prepared using the solid-state method (Msomi & Moyo 2009) and through oxalate impregnation method, where the introduction of Cu in the NiFe$_2$O$_4$ structure appears to lead to finer grains of a more reduced size (Gabal et al 2011).

6.3.3 SEM Analysis

Figures 6.7, 6.8 and 6.9 show the micrographs of Ni$_{(1-x)}$Cu$_x$Fe$_2$O$_4$ (x = 0.2, 0.4, 0.6) nanoparticles sintered at 600°C with different magnifications. The micrographs show the formation of multigrain agglomerations consisting of very fine crystallites with different shapes and sizes.
Figure 6.7 SEM micrographs of $\text{Ni}_{0.8}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4$ nanoparticles sintered at 600°C

Figure 6.8 SEM micrographs of $\text{Ni}_{0.6}\text{Cu}_{0.4}\text{Fe}_2\text{O}_4$ nanoparticles sintered at 600°C
Figure 6.9 SEM micrographs of $\text{Ni}_{0.4}\text{Cu}_{0.6}\text{Fe}_2\text{O}_4$ nanoparticles sintered at 600°C

6.3.4 EDX Analysis

EDX analysis as shown in Figure 6.10 gives the qualitative composition of nickel-copper mixed ferrites $\text{Ni}_{0.6}\text{Cu}_{0.4}\text{Fe}_2\text{O}_4$ nanoparticles sintered at 600°C. It indicates the quantitative presence of Ni, Cu, Fe and O in the samples. It also confirms the absence of impurities in these samples.
Figure 6.10 EDX spectrum of Ni$_{0.6}$Cu$_{0.4}$Fe$_2$O$_4$ nanoparticles sintered at 600°C

6.3.5 TEM Analysis

TEM micrographs of Ni$_{0.6}$Cu$_{0.4}$Fe$_2$O$_4$ nanoparticles sintered at 600°C are shown in Figure 6.11. The micrographs indicate the nanostructure nature with platelet shape. From the TEM, the average crystallite size of the samples is around 12 to 22 nm which is in agreement with that calculated from XRD.
6.3.6 SAED Analysis

SAED pattern of \( \text{Ni}_{0.6}\text{Cu}_{0.4}\text{Fe}_2\text{O}_4 \) nanoparticles sintered at 600°C are shown in Figure 6.12. The ring shape of electron diffraction pattern confirms the formation of \( \text{Ni}_{0.6}\text{Cu}_{0.4}\text{Fe}_2\text{O}_4 \) nanoparticles.
6.3.7 Magnetic Measurements using VSM

The magnetic properties of nickel-copper mixed ferrites $\text{Ni}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ ($x = 0.2, 0.4, 0.6$) nanoparticles are investigated with a VSM at room temperature and are shown in Figures 6.13, 6.14 and 6.15 for the samples sintered at 130°C, 600°C and 900°C respectively. It shows the magnetic properties of the samples are affected by the composition and cation distribution. Various cations can be placed in tetrahedral (A) sites and octahedral (B) sites to tune its magnetic properties (Ahmed et al 2003, Akther Hossain et al 2004).
Figure 6.13 VSM measurements for Ni\(_{(1-x)}\)Cu\(_x\)Fe\(_2\)O\(_4\) (a) \(x = 0.2\) (b) \(x = 0.4\) (c) \(x = 0.6\) nanoparticles sintered at 130° C
Figure 6.14 VSM measurements for Ni_{(1-x)}Cu_xFe_2O_4 (a) x = 0.2 (b) x = 0.4 (c) x = 0.6 nanoparticles sintered at 600°C

Figure 6.15 VSM measurements for Ni_{(1-x)}Cu_xFe_2O_4 (a) x = 0.2 (b) x = 0.4 (c) x = 0.6 nanoparticles sintered at 900°C
The saturation magnetization ($M_s$), remanent magnetization ($M_r$), coercivity ($H_c$) and squareness ratio values are listed in Table 6.2. It is observed that the saturation magnetization ($M_s$) and remanent magnetization ($M_r$) decrease with increase in copper concentration for the samples sintered at 600°C. But the coercivity ($H_c$) found to increase with increase in copper concentration (Gabal et al 2011). The increase in coercivity ($H_c$) may be due to the increase in the grain size as found from XRD analysis. This may be attributed to the magnetization mechanism, which is a domain rotation process. The $H_c$ is in direct proportion to the volume single-domain grains. Therefore, $H_c$ becomes gradually larger as the single-domain particle size increases (Zhang et al 2007).

### Table 6.2 The saturation magnetization ($M_s$), remanent magnetization ($M_r$), coercivity ($H_c$) and squareness ratio values of Ni$_{(1-x)}$Cu$_x$Fe$_2$O$_4$ ($x = 0.2$, $0.4$, $0.6$) nanoparticles

<table>
<thead>
<tr>
<th>Sintering Temp °C</th>
<th>Composition</th>
<th>Saturation Magnetization ($M_s$) emu/g</th>
<th>Remanent Magnetization ($M_r$) emu/g</th>
<th>Coercivity ($H_c$) G</th>
<th>Squareness Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>130</td>
<td>Ni$<em>{0.8}$Cu$</em>{0.2}$Fe$_2$O$_4$</td>
<td>0.32664</td>
<td>0.01099</td>
<td>412.76</td>
<td>0.03364</td>
</tr>
<tr>
<td></td>
<td>Ni$<em>{0.6}$Cu$</em>{0.4}$Fe$_2$O$_4$</td>
<td>0.54180</td>
<td>0.01508</td>
<td>400.29</td>
<td>0.02783</td>
</tr>
<tr>
<td></td>
<td>Ni$<em>{0.4}$Cu$</em>{0.6}$Fe$_2$O$_4$</td>
<td>1.0364</td>
<td>0.03720</td>
<td>408.58</td>
<td>0.03589</td>
</tr>
<tr>
<td>600</td>
<td>Ni$<em>{0.8}$Cu$</em>{0.2}$Fe$_2$O$_4$</td>
<td>33.370</td>
<td>11.930</td>
<td>375.88</td>
<td>0.3575</td>
</tr>
<tr>
<td></td>
<td>Ni$<em>{0.6}$Cu$</em>{0.4}$Fe$_2$O$_4$</td>
<td>29.616</td>
<td>11.168</td>
<td>396.19</td>
<td>0.37709</td>
</tr>
<tr>
<td></td>
<td>Ni$<em>{0.4}$Cu$</em>{0.6}$Fe$_2$O$_4$</td>
<td>8.9462</td>
<td>3.7859</td>
<td>657.16</td>
<td>0.42318</td>
</tr>
<tr>
<td>900</td>
<td>Ni$<em>{0.8}$Cu$</em>{0.2}$Fe$_2$O$_4$</td>
<td>34.610</td>
<td>14.001</td>
<td>350.85</td>
<td>0.40453</td>
</tr>
<tr>
<td></td>
<td>Ni$<em>{0.6}$Cu$</em>{0.4}$Fe$_2$O$_4$</td>
<td>41.358</td>
<td>16.917</td>
<td>349.55</td>
<td>0.40903</td>
</tr>
<tr>
<td></td>
<td>Ni$<em>{0.4}$Cu$</em>{0.6}$Fe$_2$O$_4$</td>
<td>14.982</td>
<td>6.772</td>
<td>562.51</td>
<td>0.4520</td>
</tr>
</tbody>
</table>
It is also observed that the saturation magnetization ($M_s$) and remanent magnetization ($M_r$) increase with increase in copper concentration for the samples sintered at 130°C and 900°C and are found to decrease for the sample $\text{Ni}_{0.4}\text{Cu}_{0.6}\text{Fe}_2\text{O}_4$ sintered at 900°C. The enhancement of saturation magnetization with the increase in Cu contents is observed up to $x = 0.4$. This may be due to the occupancy of Cu$^{2+}$ substituted ions in the tetrahedral sites causing transfer of Fe$^{3+}$ ions from there to the octahedral sites. This increases the concentration of Fe$^{3+}$ ions in octahedral sites and so increases the magnetization in the octahedral sublattice, which in turn enhances the magnetization of the nanoparticles. But the reduction in saturation magnetization $M_s$ for the sample with $x = 0.6$ could be due to the Cu$^{2+}$ ions moving from the tetrahedral to octahedral sites, which have smaller ionic magnetic moment in contrast to the Ni$^{2+}$ ions and half of the Fe$^{3+}$ ions fill the A sites, reducing the super-exchange interactions between octahedral and tetrahedral sites, which in turn causes the decrease in the $M_s$ value. Secondly, the occurrence of $\alpha$-$\text{Fe}_2\text{O}_3$ impurity phase as evidenced from XRD analysis could also be the reason for the drastic reduction in $M_s$ value (Laokul et al 2011). The coercivity ($H_c$) decreases with increase in copper concentration for $x = 0.2$ and 0.4 and is found to increase for the sample $x = 0.6$ sintered at 130°C and 900°C. This may be due to the fact that the particle size decreases with addition of copper.

The saturation magnetization ($M_s$) and remanent magnetization ($M_r$) increase on annealing the samples of all the composition of nickel-copper ferrites which can be attributed to the influence of the average particle size induced by the annealing temperature (Xiao et al 2008) and the coercivity ($H_c$) decreases on annealing except for the $\text{Ni}_{0.4}\text{Cu}_{0.6}\text{Fe}_2\text{O}_4$ sample for which the coercivity at first increases and then decreases.
6.3.8 Dielectric Properties

The dielectric constant of the nickel-copper mixed ferrites \( \text{Ni}_{(1-x)}\text{Cu}_x\text{Fe}_2\text{O}_4 \) (\( x = 0.2, 0.4, 0.6 \)) nanoparticles sintered at 130\(^\circ\) C, 600\(^\circ\) C and 900\(^\circ\) C with varying log frequency (f) are shown in Figures 6.16, 6.17 and 6.18. It can be seen from the figures that the dielectric constant decreases with increasing frequency. The decrease of dielectric constant with increase of frequency as observed in the case of mixed Ni-Cu ferrites is a normal dielectric behaviour of spinel ferrites. The dispersion in dielectric constant is analogous to Maxwell-Wagner interfacial polarization (Wagner 1913, Maxwell 1929) and in agreement with Koops phenomenological theory (1951).

![Figure 6.16 Variation of dielectric constant with log frequency for Ni\(_{(1-x)}\)Cu\(_x\)Fe\(_2\)O\(_4\) (x = 0.2, 0.4, 0.6) nanoparticles sintered at 130\(^\circ\) C](image)

\( x = 0.2 \)  \( x = 0.4 \)  \( x = 0.6 \)
Figure 6.17 Variation of dielectric constant with log frequency for $\text{Ni}_{(1-x)}\text{Cu}_x\text{Fe}_2\text{O}_4$ (x = 0.2, 0.4, 0.6) nanoparticles sintered at 600°C

Figure 6.18 Variation of dielectric constant with log frequency for $\text{Ni}_{(1-x)}\text{Cu}_x\text{Fe}_2\text{O}_4$ (x = 0.2, 0.4, 0.6) nanoparticles sintered at 900°C
Figure 6.16 shows that the dielectric constant increases with increase in concentration of Cu\(^{2+}\) ions for the sample sintered at 130°C. This is due to the fact that the Cu\(^{2+}\) ions replace the Fe\(^{3+}\) ions at the A-site. The replaced Fe\(^{3+}\) ions migrate from A-site to the B-site, which increases the concentration of Fe\(^{2+}\) / Fe\(^{3+}\) ion pairs at the B-site and therefore the amount of space charge polarization increases, which leads to increase in the values of dielectric constants for \(x = 0.4\) (Navneet Singh et al 2011). On further increase of copper ions (i.e) at \(x = 0.6\), the dielectric constant is found to decrease and this may be attributed to the decrease in concentration of Fe\(^{2+}\) / Fe\(^{3+}\) ion pairs at the B-site. It is also noted that the dielectric constant reaches a constant value for all the compositions at higher frequencies. It is further observed from the Figures 6.17 and 6.18 that on sintering the samples at 600°C and 900°C, the dielectric constant decreases drastically for all the compositions and reaches a constant value. This decrease in dielectric constant is due to the presence of \(\alpha\)-Fe\(_2\)O\(_3\) phase as evidenced from XRD (Figures 6.5 and 6.6). The presence of this phase creates a decrease in resistivity of the samples. However the value of the dielectric constant is observed to increase for samples sintered at 130°C because of the absence of the \(\alpha\)-Fe\(_2\)O\(_3\) phase.

The dielectric loss arises when the polarization lags behind the applied alternating field and is caused by the impurities and imperfections in the crystal lattice. Figures 6.19, 6.20 and 6.21 show the variation of dissipation factor as a function of logarithmic frequency in the range from 100 Hz to 5 MHz at room temperature for nickel-copper mixed ferrites Ni\(_{(1-x)}\)Cu\(_x\)Fe\(_2\)O\(_4\) (\(x = 0.2\), 0.4, 0.6) nanoparticles sintered at 130°C, 600°C and 900°C respectively.
Figure 6.19 Variation of dissipation factor with log frequency for Ni_{(1-x)}Cu_xFe_2O_4 (x = 0.2, 0.4, 0.6) nanoparticles sintered at 130 °C

Figure 6.20 Variation of dissipation factor with log frequency for Ni_{(1-x)}Cu_xFe_2O_4 (x = 0.2, 0.4, 0.6) nanoparticles sintered at 600 °C
Figure 6.21 Variation of dissipation factor with log frequency for Ni\(_{1-x}\)Cu\(_x\)Fe\(_2\)O\(_4\) \((x = 0.2, 0.4, 0.6)\) nanoparticles sintered at 900°C

The dielectric loss gives the loss of energy from the applied field into the sample. This is caused by domain wall resonance. At higher frequencies the losses are found to be low, since domain wall motion is inhibited and magnetization is forced to change rotation. There is a strong correlation between the conduction mechanism and the dielectric behaviour of ferrites (Iwachi & Ikeda 1986). From Figure 6.19, it is apparent that dielectric loss decreases for \(x = 0.4\) compared to other compositions. It shows the relaxation peak for the copper doped nickel ferrites for \(x = 0.4\) between the frequency range 100 KHz - 5 MHz and for \(x = 0.6\) between the frequency range 1 KHz - 100 KHz for the sample sintered at 130°C. The shifting of the relaxation peak towards lower frequency side with an increase in copper content \((x)\) is due to the strengthening of the dipole-dipole interactions causing hindrance to the rotation of the dipoles (Singh et al 2002). Therefore the resonance between rotation of the dipoles and
applied field takes place at lower frequency. It is seen from the Figure 6.20 on sintering the samples at 600°C the relaxation peak appears for \( x = 0.2 \) between 100 Hz - 10 KHz and no such peak appears for any other compositions and the dissipation factor approaches a very low value at higher frequencies. It is found from the Figure 6.21 that on sintering the samples at 900°C no relaxation peak appears for any of the compositions which may be due to high resistivity and the dissipation factor approaches very low values at higher frequencies.

6.4 CONCLUSION

Copper doped nickel ferrites \( \text{Ni}_{(1-x)}\text{Cu}_x\text{Fe}_2\text{O}_4 \) (where \( x = 0.2, 0.4, 0.6 \)) nanoparticles are prepared by co-precipitation method and sintered at 130°C, 600°C and 900°C. The XRD study confirms the formation of single-phase cubic spinel Ni-Cu ferrites. The lattice constant ‘a’ is found to increase with increase in copper content. The crystallite size is found to be approximately 28 nm which is in agreement with TEM results. But the particle size decreases with Cu substitution, indicating that the addition of Cu has a great effect on obstructing the grain growth of the spinel ferrites. SEM micrographs show the formation of multigrain agglomerates with very fine crystallites. EDX analysis confirms the presence of Ni, Cu, Fe and O without any impurities. FT-IR spectra confirm the characteristic absorption bands of ferrites around 554 cm\(^{-1}\) - 547 cm\(^{-1}\) for the tetrahedral sites and around 448 cm\(^{-1}\) - 450 cm\(^{-1}\) for the octahedral sites. The inclusion of copper shifts the tetrahedral band \( \nu_t \) to lower values. The Cu content has a significant effect on the magnetic and dielectric properties. The variation of saturation magnetization, remanent magnetization, coercivity and squareness ratio are discussed for all the compositions. The saturation magnetization \( (M_s) \) and remanent magnetization \( (M_r) \) decrease with increase in copper concentration and the
coercivity ($H_c$) is found to increase for all the compositions sintered at 600°C. The dielectric constant increases with increase in concentration of $\text{Cu}^{2+}$ ions for $x = 0.4$ and is found to decrease for $x = 0.6$. 