CHAPTER 5

SYNTHESIS, CHARACTERIZATION AND EFFECT OF COPPER CONCENTRATION IN COBALT FERRITE NANOPARTICLES BY CO-PRECIPITATION METHOD

5.1 INTRODUCTION

Cobalt ferrite, a ferromagnetic ceramic has emerged as one of the important magnetic materials due to its high electrical resistance and low eddy current losses. These nanoparticles have cubic spinel structure and have been extensively studied because of their interesting magnetic and electrical properties. Structural stability of the cobalt ferrite nanoparticles is essential in all technical applications. Their physical properties depend on several factors such as the method of preparation, chemical composition, sintering temperature and distribution of cations among the two sublattices: tetrahedral (A) and octahedral (B) (Gnanaprakash et al 2007). Also the magnetic properties of CoFe$_2$O$_4$ strongly depend on the size and the shape of the nanoparticles which are closely related to the preparation method. Nanoparticles of CuFe$_2$O$_4$ have also been shown to have a catalytic effect in CO$_2$ decomposition, hydrogen production and in gas sensors (Deepa Thapa et al 2010). These Copper ferrites are mostly inverse spinel and due to a relatively small energy difference between Cu$^{2+}$ ions at the tetrahedral (A-) and octahedral (B-) sites, cation redistribution is possible and strongly dependent on the annealing temperature, cooling rate and microstructure (Goya et al 1998).
The inclusion of Cu$^{2+}$ ions in the structure of CoFe$_2$O$_4$ is therefore expected to modify its structural, magnetic and dielectric properties, making it suitable for different types of applications. To obtain these nanosized ferrite particles, various preparation techniques have been developed, such as hydrothermal synthesis (Cheng et al 2005, Deng et al 2005, Wang et al 2005, Zhao et al 2007, Jing Feng et al 2007, Xuan et al 2007), co-precipitation (Bee et al 1995, Cushing et al 2004, Willis et al 2005), sol-gel (Areán et al 1999, Christoskova et al 2001) and microemulsion processes (Moumen et al 1995, Nagesh S. Kommareddi et al 1996, Liu et al 2000, Woo et al 2003, Ge et al 2006). Among these preparation techniques the co-precipitation method is adopted in the present work for preparing Co-Cu mixed ferrites. The significant effect of concentration of Cu in cobalt mixed ferrite is analyzed.

5.2 MATERIALS AND METHODS

Nanocrystalline copper doped cobalt ferrites Co$_{(1-x)}$Cu$_x$Fe$_2$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 cobaltous chloride [CoCl$_2$.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 contents. 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.
5.3 RESULTS AND DISCUSSION

5.3.1 FT-IR Spectral Analysis

Ferrites possess the structure of spinel (MgAl$_2$O$_4$) that crystallizes in the cubic form (White & De Angelis 1967). The magnetic properties of ferrites are decisively dependent on the precise configuration of the atoms and ions in the structure. Therefore, the non-destructive spectroscopy is especially suited for such investigations.

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

**Figure 5.1** FT-IR spectra of Co$_{(1-x)}$Cu$_x$Fe$_2$O$_4$ (a) $x = 0.2$ (b) $x = 0.4$ (c) $x = 0.6$ nanoparticles sintered at 130°C

Figures 5.1, 5.2 and 5.3 show the FT-IR spectra of the sample of cobalt-copper mixed ferrites Co$_{(1-x)}$Cu$_x$Fe$_2$O$_4$ ($x = 0.2$, 0.4, 0.6) sintered at
130°C, 600°C and 900°C respectively, recorded at room temperature in the wave number range 4000 cm⁻¹ - 400 cm⁻¹. According to Waldron (1955) the ferrites can be considered as continuously bonded crystals, meaning that the atoms are bonded to all the nearest neighbours by equivalent forces. In ferrites the metal ions are situated in two different sublattices designated tetrahedral (A-site) and octahedral (B-site) according to the geometrical configuration of the oxygen nearest neighbours. Also, Waldron (1955) and Hafner & Krist (1961) have attributed the band around 600 cm⁻¹ to stretching vibrations of tetrahedral groups (v₁) and that around 400 cm⁻¹ to the octahedral group (v₂). In the present study the absorption bands for mixed Co-Cu ferrites are found to be in expected range.

The presence of water in the sample sintered at 130°C is observed in the IR spectra of Figure 5.1. The nonlinear, triatomic molecule of water has three main vibration modes: symmetric stretching, asymmetric stretching and scissoring vibration modes. The first and second vibrations are observed at 3669 and 3780 cm⁻¹ and the scissoring vibration exists for this nonlinear molecule at 1627 cm⁻¹ and besides that, the strong absorption bands in the region 3700 - 3100 cm⁻¹ usually results from a stretching vibration between hydrogen and oxygen atoms (Douglas A. Skoog 1985, Saafan et al 2010). Therefore, it can be concluded that the absorption bands in Figure 5.1 around those mentioned values are assigned to water. The absence of those bands in Figures 5.2 and 5.3 confirms that the water molecules are completely removed as the samples are sintered at 600°C and 900°C. The small absorption bands around 2363 cm⁻¹ and 1020 cm⁻¹ are due to traces of adsorbed or atmospheric CO₂.
Figure 5.2  FT-IR spectra of $\text{Co}_{(1-x)}\text{Cu}_x\text{Fe}_2\text{O}_4$ (a) $x = 0.2$ (b) $x = 0.4$ (c) $x = 0.6$ nanoparticles sintered at $600^\circ\text{C}$

Figure 5.3  FT-IR spectra of $\text{Co}_{(1-x)}\text{Cu}_x\text{Fe}_2\text{O}_4$ (a) $x = 0.2$ (b) $x = 0.4$ (c) $x = 0.6$ nanoparticles sintered at $900^\circ\text{C}$
The main absorption band $\nu_1$ appearing around 572 cm$^{-1}$ is due to tetrahedral sites and is found to be shifted to lower values on doping with copper. The band $\nu_2$ around 409 cm$^{-1}$ is due to octahedral sites and is shifted to higher values upon increasing the concentration of copper ions. These observations may be attributed to the fact that the absorption bands for pure copper ferrite appear around 565 cm$^{-1}$ and 416 cm$^{-1}$ respectively and it is evident that the inclusion of copper is responsible for shifting the bands appropriately to lower values for $\nu_1$ and higher values for $\nu_2$. It is also observed from the Figures 5.2 and 5.3 the broad absorption band appear for tetrahedral sites on sintering the samples at 600°C and 900°C. This might be due to the fact that upon sintering, the cations migrate from octahedral sites to tetrahedral sites.

5.3.2 Structural Analysis

Figures 5.4, 5.5 and 5.6 show the XRD patterns of the cobalt-copper mixed ferrites $\text{Co}_{(1-x)}\text{Cu}_x\text{Fe}_2\text{O}_4$ ($x = 0.2, 0.4, 0.6$) nanoparticles synthesized at pH equal to 8 and sintered at 130°C, 600°C and 900°C respectively. Analysis of the diffraction pattern confirms the formation of cubic spinel structure for all the samples. The experimentally observed d-spacing values and relative intensities are in good agreement with those reported in the powder diffraction file of JCPDS card no. (22-1086) and (34-0425) for cobalt and copper ferrites. The strongest reflection comes from the $(311)$ plane, which denotes the spinel phase. All the compositions have a spinel structure. The peaks indexed to $(111)$, $(220)$, $(311)$, $(222)$, $(400)$, $(422)$, $(511)$, $(440)$, $(620)$, $(533)$, $(622)$, $(444)$ and $(642)$ planes of a cubic unit cell, correspond to cubic spinel structure. The diffraction patterns indicate amorphous nature for the samples sintered at 130°C. As the sintering temperature increases, there is a development of the sample’s
crystalline structure (the relative intensities increase and full-width at half-maximum decreases).

Figure 5.4  XRD pattern of Co_{(1-x)}Cu_xFe_2O_4 (a) x = 0.2 (b) x = 0.4 (c) x = 0.6 nanoparticles sintered at 130°C

Figure 5.5  XRD pattern of Co_{(1-x)}Cu_xFe_2O_4 (a) x = 0.2 (b) x = 0.4 (c) x = 0.6 nanoparticles sintered at 600°C
The degree of crystallinity of the sample increases with increase of the sintering temperature to 600 °C and 900 °C, suggesting the enhancement of crystallinity due to sintering. The absence of extra peaks confirms the phase purity, i.e. there is no phase change on annealing. The annealing process results in a decrease in the defects and internal strains due to coalescence of crystallites, which in turns results in an increase in the average size of the nanoparticle (Raming et al 2002).

![Figure 5.6 XRD pattern of Co(1-x)Cu_xFe_2O_4 (a) x = 0.2 (b) x =0.4 (c) x = 0.6 nanoparticles sintered at 900 °C](image)

The lattice parameters are calculated for all the compositions and are listed in Table 5.1. It is observed that the lattice parameter decreases on inclusion of copper content (i.e) for Co(1-x)Cu_xFe_2O_4 (x = 0.2, 0.4) as could be evidenced from Table 5.1. The decrease in lattice parameter with increase in copper content is due to the replacement of larger Co^{2+} cations by smaller Cu^{2+} cations. It is also observed that the lattice parameter increases on further addition of copper for
The induced microstrain in the crystallites has been calculated for all the compositions of Co – Cu mixed ferrites Co\(_{(1-x)}\)Cu\(_x\)Fe\(_2\)O\(_4\) \((x = 0.2, 0.4, 0.6)\) sintered at 900°C and is found to be 0.000735, 0.000735, 0.000654 respectively. It is found that the strain is maximum for cobalt rich samples and decreases as copper concentration increases.

Table 5.1 Structural parameters of Co\(_{(1-x)}\)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>Co(<em>{0.8})Cu(</em>{0.2})Fe(_2)O(_4)</td>
<td>8.3076</td>
<td>8.3695</td>
</tr>
<tr>
<td>Co(<em>{0.6})Cu(</em>{0.4})Fe(_2)O(_4)</td>
<td>8.3046</td>
<td>8.3353</td>
</tr>
<tr>
<td>Co(<em>{0.4})Cu(</em>{0.6})Fe(_2)O(_4)</td>
<td>8.3098</td>
<td>8.3601</td>
</tr>
</tbody>
</table>

The crystallite size of each composition is then determined by the Debye-Scherrer relation and listed in Table 5.1. It varies with the composition and is found to decrease with the substitution of copper which indicates that the addition of Cu has a great effect in obstructing the grain growth of the spinel (Gabal et al 2011).

5.3.3 SEM Analysis

The microstructure plays an important role in realizing many application-oriented ferrite properties. The SEM micrographs are taken to understand the microstructure of the prepared cobalt-copper mixed ferrites Co\(_{(1-x)}\)Cu\(_x\)Fe\(_2\)O\(_4\) \((x = 0.2, 0.4, 0.6)\) nanoparticles sintered at 600°C with different magnifications and are shown in Figures 5.7, 5.8 and 5.9.
Figure 5.7 SEM micrographs of $\text{Co}_{0.8}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4$ nanoparticles sintered at 600°C

Figure 5.8 SEM micrographs of $\text{Co}_{0.6}\text{Cu}_{0.4}\text{Fe}_2\text{O}_4$ nanoparticles sintered at 600°C
Figure 5.9 SEM micrographs of $\text{Co}_{0.4}\text{Cu}_{0.6}\text{Fe}_2\text{O}_4$ nanoparticles sintered at 600°C

The micrographs give the appearance of a sponge structure with a large number of pores and this might be due to the fact that the copper is immiscible with cobalt.

5.3.4 EDX Analysis

Chemical composition analysis through EDX is carried out for cobalt-copper mixed ferrites $\text{Co}_{0.6}\text{Cu}_{0.4}\text{Fe}_2\text{O}_4$ sample sintered at 600°C and is shown in Figure 5.10. EDX spectroscopy results confirm the stoichiometry of the sample without the impurity.
Figure 5.10 EDX spectrum of Co$_{0.6}$Cu$_{0.4}$Fe$_2$O$_4$ nanoparticles sintered at 600°C

5.3.5 TEM Analysis

TEM provides insight into the morphologies and structural details of the system. Figure 5.11 shows a typical TEM image of Co$_{0.6}$Cu$_{0.4}$Fe$_2$O$_4$ nanoparticles sintered at 600°C. The image shows agglomerates of rather roughly spherical nanoparticles with an average size of 50 nm, which agrees well with that obtained from XRD measurement.
Figure 5.11 TEM micrographs of Co$_{0.6}$Cu$_{0.4}$Fe$_2$O$_4$ nanoparticles sintered at 600$^\circ$C

5.3.6 SAED Analysis

Figure 5.12 shows the SAED pattern of Co$_{0.6}$Cu$_{0.4}$Fe$_2$O$_4$ nanoparticles sintered at 600$^\circ$C. The SAED pattern reveals that the particles have high crystallinity. Each ring corresponds to the lattice parameter obtained in the XRD.

Figure 5.12 SAED pattern of Co$_{0.6}$Cu$_{0.4}$Fe$_2$O$_4$ nanoparticles sintered at 600$^\circ$C
5.3.7 Magnetic Measurements using VSM

Figures 5.13, 5.14 and 5.15 show the typical magnetic hysteresis loops obtained from room temperature VSM measurement for copper substituted cobalt ferrites $\text{Co}_{(1-x)}\text{Cu}_x\text{Fe}_2\text{O}_4$ (where $x = 0.2, 0.4, 0.6$) sintered at 130°C, 600°C and 900°C respectively.

(a) 

(b) 

(c) 

Figure 5.13 VSM measurements for $\text{Co}_{(1-x)}\text{Cu}_x\text{Fe}_2\text{O}_4$ (a) $x = 0.2$ (b) $x = 0.4$ (c) $x = 0.6$ nanoparticles sintered at 130°C
Figure 5.14 VSM measurements for $\text{Co}_{(1-x)}\text{Cu}_x\text{Fe}_2\text{O}_4$ (a) $x = 0.2$ (b) $x = 0.4$ (c) $x = 0.6$ nanoparticles sintered at 600°C
The saturation magnetization ($M_s$), remanent magnetization ($M_r$), coercivity ($H_c$) and squareness ratio values are listed in Table 5.2.
Table 5.2 The saturation magnetization \((M_s)\), remanent magnetization \((M_r)\), coercivity \((H_c)\) and squareness ratio values of \(\text{Co}_{(1-x)}\text{Cu}_x\text{Fe}_2\text{O}_4\) \((x = 0.2, 0.4, 0.6)\) nanoparticles

<table>
<thead>
<tr>
<th>Sintering Temperature (^\circ\text{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>(\text{Co}<em>{0.8}\text{Cu}</em>{0.2}\text{Fe}_2\text{O}_4)</td>
<td>1.7826</td>
<td>0.00296</td>
<td>8.14</td>
<td>0.00166</td>
</tr>
<tr>
<td></td>
<td>(\text{Co}<em>{0.6}\text{Cu}</em>{0.4}\text{Fe}_2\text{O}_4)</td>
<td>4.160</td>
<td>0.0164</td>
<td>7.0179</td>
<td>0.00394</td>
</tr>
<tr>
<td></td>
<td>(\text{Co}<em>{0.4}\text{Cu}</em>{0.6}\text{Fe}_2\text{O}_4)</td>
<td>0.803</td>
<td>0.00125</td>
<td>8.3422</td>
<td>0.00155</td>
</tr>
<tr>
<td>600</td>
<td>(\text{Co}<em>{0.3}\text{Cu}</em>{0.2}\text{Fe}_2\text{O}_4)</td>
<td>38.202</td>
<td>16.234</td>
<td>1514.4</td>
<td>0.4249</td>
</tr>
<tr>
<td></td>
<td>(\text{Co}<em>{0.6}\text{Cu}</em>{0.4}\text{Fe}_2\text{O}_4)</td>
<td>35.035</td>
<td>13.784</td>
<td>1402.1</td>
<td>0.3934</td>
</tr>
<tr>
<td></td>
<td>(\text{Co}<em>{0.4}\text{Cu}</em>{0.6}\text{Fe}_2\text{O}_4)</td>
<td>46.72</td>
<td>22.192</td>
<td>1554</td>
<td>0.475</td>
</tr>
<tr>
<td>900</td>
<td>(\text{Co}<em>{0.3}\text{Cu}</em>{0.2}\text{Fe}_2\text{O}_4)</td>
<td>67.45</td>
<td>30.88</td>
<td>1184.2</td>
<td>0.4578</td>
</tr>
<tr>
<td></td>
<td>(\text{Co}<em>{0.6}\text{Cu}</em>{0.4}\text{Fe}_2\text{O}_4)</td>
<td>58.66</td>
<td>19.12</td>
<td>679.15</td>
<td>0.3259</td>
</tr>
<tr>
<td></td>
<td>(\text{Co}<em>{0.4}\text{Cu}</em>{0.6}\text{Fe}_2\text{O}_4)</td>
<td>49.31</td>
<td>12.84</td>
<td>425.94</td>
<td>0.26039</td>
</tr>
</tbody>
</table>

It is observed that the saturation magnetization \((M_s)\), remanent magnetization \((M_r)\) and coercivity \((H_c)\) decrease with increase in the copper substitution for the samples sintered at 900 \(^\circ\text{C}\) (Gabal et al 2011). The saturation values are explained by assuming that the A - B interaction favours anti-parallel coupling of A-site and B-site groups and is strong enough to overcome any tendency for A - A or B - B couplings to disrupt the parallel alignment of all spins within the A-site or B-site groups separately. The magnetic order in the ferromagnetic spinels is due to a super-exchange interaction mechanism occurring between the metal ions in the tetrahedral A-sites and octahedral B-sites (Köseoğlu et al 2009). The replacement of \(\text{Co}^{2+}\) ions by \(\text{Cu}^{2+}\) ions, which have preferential octahedral site occupancy, results in the reduction of the super-exchange
interaction between the A and B sites. In other words, as the copper concentration increases, the magnetization of the B-site decreases and the net magnetization decrease. The $H_c$ values decrease with increasing copper content and this behaviour can be interpreted if we take into consideration the decrease in the crystallite size on increasing the copper content. In this case, the variation of $H_c$ with particle size can be explained on the basis of domain structure, critical diameter and the anisotropy of the crystal (Farghali et al 2007). A crystallite will spontaneously break up into a number of domains in order to reduce the large magnetization energy it would have if it were a single domain. Thus, the coercivity of the magnetic particles decreases with particle size. It is also observed that the saturation magnetization ($M_s$), remanent magnetization ($M_r$) and coercivity ($H_c$) decrease and then increase for all the compositions of cobalt-copper mixed ferrites sintered at 600°C. It is evident from the fact that the particle size decreases for Co$_{0.6}$Cu$_{0.4}$Fe$_2$O$_4$ sample sintered at 600°C.

It is further observed that the saturation magnetization ($M_s$) and remanent magnetization ($M_r$) increase on annealing the samples to 600°C and 900°C. This could be explained on the basis of increasing of the crystallite size and homogenous and clear microstructure. Furthermore, the saturation magnetization significantly increases mainly because of a decrease in internal strain and defects density (Rashad et al 2009). But the coercivity increases on annealing the sample from 130°C to 600°C and then decreases for annealing at 900°C. These variations in coercivity can be related with particle growth and could be described on the basis of magnetic domain theory (Muller and Schuppel 1996). The increase in coercivity of the samples annealed at 600°C may be due to the transfer of the single magnetic domain into pseudo single-domain of the annealed particles. Similarly the decrease in coercivity on annealing at 900°C is due
to transition of the magnetic single-domain to magnetic multi-domain during growth of the particles.

The change in magnetic properties can be attributed to the increase in the crystallinity of the sample (Zhang et al 2007) and the same could be observed in pure cobalt ferrite and copper ferrite. From the hysteresis loops, the squareness ratio of the samples (i.e) remanent to the saturation magnetization ($M_r / M_s$) are derived and listed in Table 5.2. It is found that there exist magnetostatic interactions for all the compositions of cobalt-copper ferrites sintered at 130°C, 600°C and 900°C.

### 5.3.8 Dielectric Properties

The variation of dielectric constant ($\varepsilon'$) with logarithmic frequency $f$ in the frequency range 100 Hz - 5 MHz of cobalt-copper mixed ferrites $\text{Co}_{(1-x)}\text{Cu}_x\text{Fe}_2\text{O}_4$ ($x = 0.2, 0.4, 0.6$) nanoparticles sintered at 130°C, 600°C and 900°C are shown in Figures 5.16, 5.17 and 5.18 respectively.

It is observed that dielectric constant decreases rapidly in the low frequency region whereas the decrease is quite slow in the high frequency region. This type of dielectric behaviour in the ferrites has been explained by the Maxwell-Wagner and Koops phenomenological theory (Koops 1951). In this model, a dielectric medium is assumed to be made up of highly conducting grains and poorly conducting grain boundaries. The grain boundaries are more effective at lower frequencies while the grains are found to be more effective at higher frequencies. Dielectric constant of the material come into play from the space charge polarization produced inside the material.
Figure 5.16 Variation of dielectric constant with respect to log frequency for Co_{(1-x)}Cu_xFe_2O_4 (x = 0.2, 0.4, 0.6) nanoparticles sintered at 130 °C

Figure 5.17 Variation of dielectric constant with respect to log frequency for Co_{(1-x)}Cu_xFe_2O_4 (x = 0.2, 0.4, 0.6) nanoparticles sintered at 600 °C
In the ferrites, electrons are the main charge carriers and the motion of electrons takes place between Fe\textsuperscript{2+} ions and Fe\textsuperscript{3+} ions present at crystallographically equivalent sites, i.e., octahedral sites. This is known as the hopping mechanism of electron transfer. The observed decrease in dielectric constant with the increase in frequency is due to the fact that the electron hopping between Fe\textsuperscript{3+} - Fe\textsuperscript{2+} ions at octahedral sites cannot follow the alteration of ac electric field at higher frequencies. The electrons have to pass through the well-conducting grains and the poorly conducting grain boundaries. As the grain boundaries have large resistance, the electrons pile up there and produce large space charge polarization. Therefore, the dielectric constant has larger values in the low frequency range. With further increase in the frequency, the electrons change their direction of motion rapidly, which hinders the movement of electrons inside the dielectric material and accumulation of charge at the grain boundaries.
decreases. This decreases the space charge polarization and therefore, the value of the dielectric constant is also reduced.

It is observed from the Figure 5.16 that the dielectric constant decreases with increasing concentration of Cu\(^{2+}\) ions for the sample sintered at 130°C (Ahmed et al 2012). This may be due to the fact that when Cu\(^{2+}\) is substituted for Co\(^{2+}\), it occupies the octahedral B sites. Due to this some of the Fe\(^{3+}\) ions migrate from the octahedral B sites to tetrahedral A sites. Therefore the hopping between Fe\(^{2+}\) and Fe\(^{3+}\) ions decreases in the octahedral sites. As a result, the polarization and hence, the dielectric constant decreases. It is further observed that the dielectric constant reaches the constant value for all the compositions at higher frequencies. It is also observed from the Figures 5.17 and 5.18 that on sintering the samples to 600°C and 900°C the dielectric constant found to decrease which may be due to the decrease in the concentration of Fe\(^{2+}\) / Fe\(^{3+}\) ion pairs at the B-site and reaches a constant value for higher frequencies.

Figures 5.19, 5.20 and 5.21 show the variation of dissipation factor as a function of frequency in the range from 100 Hz to 5 MHz at room temperature for cobalt-copper mixed ferrites \(\text{Co}_{(1-x)}\text{Cu}_x\text{Fe}_2\text{O}_4\) (\(x = 0.2, 0.4, 0.6\)) nanoparticles sintered at 130°C, 600°C and 900°C.

It is noted from the Figure 5.19 that the dissipation factor decreases with increasing frequency followed by the relaxation peak. The appearance of relaxation peak can be explained according to the Debye relaxation theory (Tridevi et al 2005). The loss peak occurs when the applied field is in phase with the dielectric and the condition \(\omega \tau = 1\) is satisfied, where \(\omega = 2\pi f\), \(f\) is being the frequency of the applied field.
Figure 5.19 Variation of dissipation factor with respect to log frequency for $\text{Co}_{(1-x)}\text{Cu}_x\text{Fe}_2\text{O}_4$ ($x = 0.2, 0.4, 0.6$) nanoparticles sintered at $130^\circ\text{C}$

Figure 5.20 Variation of dissipation factor with respect to log frequency for $\text{Co}_{(1-x)}\text{Cu}_x\text{Fe}_2\text{O}_4$ ($x = 0.2, 0.4, 0.6$) nanoparticles sintered at $600^\circ\text{C}$
In the present investigation, it is evident from the Figure 5.19 that the relaxation peak appeared between the frequency 10 KHz to 1 MHz for the composition $x = 0.2$ and shifts towards higher frequencies between 100 KHz to 5 MHz for the compositions $x = 0.4$ and 0.6. The shifting of these peaks towards the higher frequency region may be attributed to the increase in the rate of hopping of charge carriers. It is apparent from the Figure 5.20 that on sintering the samples to 600°C in which the relaxation peak appears between the frequency 10 KHz to 1 MHz for the composition $x = 0.2$ and shifts towards lower frequencies between 1000 Hz to 100 KHz for the composition $x = 0.6$ and no peak appears for the composition $x = 0.4$. The shifting towards lower frequencies may be due to the strengthening of the dipole - dipole interactions causing hindrance to the rotation of the dipoles (Singh et al 2002) and approaches very low value at higher frequencies. It is evidenced from the Figure 5.21 that no such peak appears.
appears for all the compositions of the samples sintered at 900°C and the
dissipation factor reaches very low values at higher frequencies.

5.4 CONCLUSION

Copper doped Cobalt ferrites $\text{Co}_{(1-x)}\text{Cu}_x\text{Fe}_2\text{O}_4$ (where $x = 0.2, 0.4, 0.6$) are prepared by co-precipitation method and are sintered at 130°C, 600°C and 900°C. The FT-IR spectra show the absorption band around 572 cm$^{-1}$ which is attributed to the stretching vibrations of tetrahedral complexes and it shifts to lower values on doping with copper. The band at 409 cm$^{-1}$ is attributed to the stretching vibrations of octahedral complexes and it shifts to higher values upon increasing the concentration of copper ions. The XRD spectra reveal the average crystallite size to be in the range 37 - 52 nm and this is found to be in agreement with TEM results. The particle size is observed to decrease with increase in copper concentration. The lattice parameter decreases on inclusion of copper content. It is also observed that the saturation magnetization ($M_s$), remanent magnetization ($M_r$) and coercivity ($H_c$) decrease with increase in copper substitution. The SEM micrographs show the appearance of a sponge like structure. The EDX spectra confirm the presence of metallic compounds without impurities. The dielectric constant decreases with increasing concentration of Cu$^{2+}$ ions for the sample sintered at 130°C. The dissipation factor decreases with increasing frequency followed by a relaxation peak for all the compositions and it approaches very low values at higher frequencies.