CHAPTER-VI

RESULTS ON MAGNETIC PROPERTIES OF Cu SUBSTITUTED Ni-Zn NANOCRYSTALLINE FERRITES

6.1 Introduction

This chapter contains complete details about the magnetic properties of Cu substituted Ni\(_{0.65}\)Zn\(_{0.35}\)\(_x\)Cu\(_x\)Fe\(_2\)O\(_4\) and Ni\(_{0.5}\)Zn\(_{0.5}\)\(_x\)Cu\(_x\)Fe\(_2\)O\(_4\) ferrite systems (x=0.00 to 0.25 in steps of 0.05). The magnetic properties of ferrite materials can be discussed on the basis of saturation magnetization, corecevity, Bhor magnetrons, magnetic loss and net magnetic moment etc. The applications of ferrite materials are completely depend on the magnetic properties. The magnetic properties of ferrites are depends on the method of preparation, doping concentration, grain size, porosity percentage, sintering conditions and cation distribution in both tetrahedral and octahedral sites [1].

The study of magnetic properties are important to understand the various parameters such as soft and hard magnetic nature of material, magnetic anisotropy, domain wall motion of the material and magnetic strength of the material etc. In general ferrites exhibit similar magnetic properties to that of ferromagnetic materials. When the external magnetic field is applied to the ferrite material the magnetization arises from zero to saturation region. This Hysteresis behavior is explained by the Weiss domain theory [2]. According to Weiss theory the resultant magnetic moment of the material is a vector sum of magnetic moment of every domain. The net result of the magnetization value is in between zero to saturation region. According to Neel [3] the coercive force is completely related to the saturation magnetization, anisotropy constant, internal stress and porosity [4]. The saturation magnetization and shape of hysteresis loop are very sensitive to structural properties. The magnetization studies of ferrite material give information about saturation magnetization, coercive force and remenance ratio. In general low coercive force ferrites are known as soft ferrites which do not retain permanent magnetism; these are used in high frequency applications. High coercive force ferrites are known as hard ferrites. These are retain permanent magnetism and also difficult to magnetize and demagnetize. These hard ferrites are used to create permanent magnets.
6.2 Magnetic properties

6.2.1 Saturation Magnetization

The saturation magnetization \( M_s \) of the material is defined as the magnetic moment per unit volume. The magnetization of the material is represented as

\[
M = n \mu_m
\]

Where \( M_s \) is saturation magnetization, \( n \) is the number of dipoles per unit volume and \( \mu_m \) is the magnetic dipole moment.

The room temperature magnetization data of as prepared Cu substituted Ni\(_{0.65}\)Zn\(_{0.35-x}\)Cu\(_x\)Fe\(_2\)O\(_4\) and Ni\(_{0.5}\)Zn\(_{0.5-x}\)Cu\(_x\)Fe\(_2\)O\(_4\) ferrite systems (\( x=0.00 \) to \( 0.25 \) in steps of \( 0.05 \)) were shown in Figure 6.1 and Figure 6.2 respectively. From both Figures 6.1 and 6.2 it is observed that all samples exhibit the ferromagnetic nature. The narrow type hysteresis loops with low coercivity and remanence indicates that all samples belong to soft ferrites.

![Figure 6.1: Saturation magnetization of Ni\(_{0.65}\)Zn\(_{0.35-x}\)Cu\(_x\)Fe\(_2\)O\(_4\) system at 300K](image)
Figure 6.2: Saturation magnetization of Ni$_{0.5}$Zn$_{0.5}$Cu$_x$Fe$_2$O$_4$ at 300K

From Figure 6.1 and Figure 6.2 are indicating that the saturation magnetization of the Cu substituted both Ni$_{0.65}$Zn$_{0.35}$Cu$_x$Fe$_2$O$_4$ and Ni$_{0.5}$Zn$_{0.5}$Cu$_x$Fe$_2$O$_4$ ferrite systems was decreased with increasing of Cu concentration. And also the values of saturation magnetization, coercive field and remanent magnetization were reported in Table 6.1. The compositional variation of saturation magnetization of both systems were shown in Figure 6.3.

Figure 6.3: Compositional variation of saturation magnetization
The obtained variation of saturation magnetization can be explained on the basis of super exchange interactions between both octahedral [B] and tetrahedral [A] sites in the spinel system. This was observed from Neel’s two sub-lattice model in spinel ferrites. The observed variation in the saturation magnetization can be understood from the Neel’s two sub-lattice model [5]. In spinel ferrites the magnetization is known to be strongly influenced by the exchange interaction between the magnetic ions in the tetrahedral (A) and octahedral (B) crystallographic sites i.e. inter sub-lattice interaction between (A-B) and inter sub-lattice exchange interaction between (A-A) and (B-B). Among these three exchange interaction, intra sub-lattice interaction (A-B) is predominant over inter sub-lattice interactions. Therefore the resultant magnetic moment is the difference between magnetic moment of A and B sites.

\[
M_B - M_A
\]

From above discussion it is very clear that the resultant magnetization is completely depended on the distribution of the cation in both A and B sites. In present study Cu\textsuperscript{2+} ion substitution in place of Zn\textsuperscript{2+} ion in both Ni\textsubscript{0.65}Zn\textsubscript{0.35-x}Cu\textsubscript{x}Fe\textsubscript{2}O\textsubscript{4} and Ni\textsubscript{0.5}Zn\textsubscript{0.5-x}Cu\textsubscript{x}Fe\textsubscript{2}O\textsubscript{4} ferrite systems. The Zn\textsuperscript{2+} ions are preferentially occupying A-sites while Ni\textsuperscript{2+}, Fe\textsuperscript{3+} and Cu\textsuperscript{2+} ions have a strong preference to occupy the B-sites [6-7]. It is known that the magnetic moment of Ni\textsuperscript{2+} in spinel ferrite is 2\(\mu\)B [8]; however, the magnetic moment of Cu\textsuperscript{2+} (1\(\mu\)B), Fe\textsuperscript{3+} (5\(\mu\)B) and Zn\textsuperscript{2+} is zero. In the present work as Cu ions occupy B-sites results in the migration of some of the Fe\textsuperscript{3+} ions in to tetrahedral sites. This arrangement increases the magnetic moment of A-site and decreases net magnetic moment. The decreasing of saturation magnetization is explained as follows.

i) If the x is increases then the Cu\textsuperscript{2+} ion replace the Fe\textsuperscript{3+} ions in A site according to Neel’s then the net magnetic moment of present system is increased with increasing the Cu concentration. This results that the value of saturation magnetization is increased with increasing of Cu concentration.

ii) If Cu\textsuperscript{2+} ions are distributed into both A and B sites, thus the abnormal variations in saturation magnetization will observe.
iii) If all the Cu ions completely occupy B site, then the net magnetic moment of the B site is decreases with increasing of Cu concentration. This results that the value of saturation magnetization is decreased monotonically with increasing of Cu concentration. In the present two systems clearly observed that the value of saturation magnetization is decreased with increasing of composition. Thus the occupancy of Cu$^{2+}$ ions completely in B site as observed in Figure 6.3. The occupancy of Cu$^{2+}$ ion in B site is estimated from X-ray intensity calculations and Infrared spectra which were reported in chapter-IV. The similar type of reports was observed in existing available literature.

Table 6.1: Saturation magnetization (Ms), corecivity (Hc) and remenance force (Mr) of Ni$_{0.65}$Zn$_{0.35}$xCu$_x$Fe$_2$O$_4$ and Ni$_{0.5}$Zn$_{0.5}$xCu$_x$Fe$_2$O$_4$ samples with composition

<table>
<thead>
<tr>
<th>Composition (x)</th>
<th>Ni$<em>{0.65}$Zn$</em>{0.35}$xCu$_x$Fe$_2$O$_4$</th>
<th>Ni$<em>{0.5}$Zn$</em>{0.5}$xCu$_x$Fe$_2$O$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ms (emu/gm)</td>
<td>Hc (Oersted)</td>
</tr>
<tr>
<td>0.00</td>
<td>59.68</td>
<td>106.46</td>
</tr>
<tr>
<td>0.05</td>
<td>58.18</td>
<td>131</td>
</tr>
<tr>
<td>0.10</td>
<td>56.49</td>
<td>135</td>
</tr>
<tr>
<td>0.15</td>
<td>55.35</td>
<td>115</td>
</tr>
<tr>
<td>0.20</td>
<td>49.08</td>
<td>155</td>
</tr>
<tr>
<td>0.25</td>
<td>46.46</td>
<td>141.34</td>
</tr>
</tbody>
</table>

6.2.2 Coercivity

Measurement of coercivity from hysteresis curve is one of the best ways to understand magnetic nature of the materials. In general coercivity of a ferrite material is the intensity of applied external field to reduce the magnetization to be zero after the maximum magnetization it reaches to saturation region. Measurement of
coercivity is describes the resistance of a ferrite material to becoming demagnetized. From Figure 6.1 and Figure 6.2 it is very clear that all samples exhibit in ferromagnetic nature and also exhibit that low coercivity value which confirms that all samples belong to soft ferrites. The coercivity of ferrite material is completely depend on the density, particle size, magnetic anisotropy, dislocations in crystals, percentage of porosity and shape of the material.

6.2.2.1.1 Coercivity of Cu substituted Ni-Zn nano ferrites

The obtained variations in coercivity of Cu substituted both systems Ni$_{0.65}$Zn$_{0.35-x}$Cu$_x$Fe$_2$O$_4$ and Ni$_{0.5}$Zn$_{0.5-x}$Cu$_x$Fe$_2$O$_4$ ferrites (x=0.00 to 0.25 in steps of 0.05) were shown in Figure 6.4. The value of coercivity in Ni$_{0.65}$Zn$_{0.35-x}$Cu$_x$Fe$_2$O$_4$ is increased with increasing of Cu concentration up to x=0.10 and decreases for x=0.15 and 0.25 concentrations. In Ni$_{0.5}$Zn$_{0.5-x}$Cu$_x$Fe$_2$O$_4$ ferrite system the value of coercivity is increased with increasing of Cu concentration up to x=0.20 and decreases for higher concentrations.

![Graph of Coercivity vs Composition](image)

**Figure 6.4. Compositional variation of coercivity of Cu substituted Ni-Zn ferrites**

The variations in coercivity are observed from estimated cation distributions reported in chapter-IV of both systems. The coercivity of the ferrite material inversely proportional to the grain size of the material. Larger grain size samples have more domain walls. Hence larger grain size samples have low coercivity and also it is well known that porosity of material is directly proportional to the coercivity of the
material. The porosity values and grain size of the present systems were reported in chapter-IV.

6.2.3 Curie temperature

The variation of Curie temperature with Cu concentration is observed from temperature variation initial permeability measurements as discussed in section 6.4. It is very clear that the Curie temperature of both systems was increased with increasing of Cu concentration. Curie temperature is intrinsic property of ferrites; in general it does not vary for a particular composition in case of bulk ferrites. In nanoferrites this contention may not be true and for a particular composition Curie temperature might depend on the distribution of cations which is often sensitive to the method of processing. Similar methods of processing Curie temperature have been reported by M. A. Ahmad et al [9]. The observed variations in the Curie temperature can also be explained on the basis of superexchange interactions among tetrahedral and octahedral cations in the spinel lattice. As it is already mentioned above; the Curie temperature is the net magnetic moment of the lattice is the difference between the magnetic moment of the B and A sublattices, and it is found that increased with increasing of Cu concentration in both systems. It is obvious that the exchange interactions among the ions would increase with both the density of magnetic ions and their magnetic moments. Hence, it is therefore expected that greater amount of thermal energy will be required to off-set the influence of exchange interactions. The paramagnetic Cu ions prefer to occupy octahedral [B] sites and decrease the density of magnetic ions at the B-sublattice. The B-sublattice magnetic moment and A-B site superexchange interactions are expected to decrease with the substitution of Cu ion. Hence the substitution of Cu ion improves the Curie temperature.

6.2.4 Initial Permeability

High initial permeability and low magnetic loss are very important parameters to understand the performance of the ferrite material. In general the initial permeability of the ferrite material is completely depend on the many parameters such as stoichiometry, impurity concentration, grain structure, saturation magnetization, crystal anisotropy, magnetostriction and porosity of the material. [10]. Higher permeabilities are favoured by large grain size, high saturation magnetization, low
porosity, low crystal anisotropy, low magnetostriction and high purity of the material. Therefore, it is very necessary to consider above all aspects before conclusion for the variation in initial permeability with addition of Cu concentration. The detailed experimental procedure of the measurement of initial permeability has been described in chapter-II.

**6.2.4.1 Compositional variation of initial permeability**

The compositional variation of initial permeability at 1 kHz frequency of Cu substituted Ni-Zn ferrite systems sintered at 900°C were shown in Figure 6.5.

![Figure 6.5: Room temperature compositional variation of initial permeability of Cu substituted Ni-Zn ferrite systems](image)

From Fig.5 it is very clear that initial permeability of Ni$_{0.65}$Zn$_{0.35-x}$Cu$_x$Fe$_2$O$_4$ ferrite is initially decreased and increased for higher concentrations. The maximum permeability is observed at $x=0.10$ concentration. From Fig.5 the permeability of Ni$_{0.5}$Zn$_{0.5-x}$Cu$_x$Fe$_2$O$_4$ ferrite is increased with increasing of Cu concentration up to $x=0.15$ and then decreases for higher concentrations. The maximum permeability of Ni$_{0.5}$Zn$_{0.5-x}$Cu$_x$Fe$_2$O$_4$ ferrite system is observed at $x=0.15$ concentration. As mentioned above several parameters will influence the initial permeability. From those parameters some of the variations explained below.
i) The variations in permeability attributed mainly due to substitution of Cu in place of Zn ion in both systems will modify the cation distribution. In spinel Ni-Zn ferrites the Ni$^{2+}$ ions strongly prefer to occupy octahedral (B) sites, Zn$^{2+}$ ions are prefer to occupy tetrahedral (A) sites, substitution of Cu$^{2+}$ ion in place of Zn$^{2+}$ ion due to the paramagnetic nature of Cu$^{2+}$ ion will strongly prefer to occupy the octahedral (B) site and Fe$^{3+}$ ions will distributed in both A and B sites. The saturation magnetization and initial permeability are interdependent properties.

ii) The relation between initial permeability and grain size is given below

$$\mu \propto D^{1/3}$$

Where $\mu$ the initial permeability of the material and D is is the grain diameter.

The compositional variation of initial permeability with a function of grain size is shown in Figure 6.6 and Figure 6.7. These figures depicts that the highest initial permeability of both systems is observed at highest grain size of the material. The initial permeability and grain size both are follow same trend.

![Figure 6.6: Compositional variation of initial permeability and grain size of Ni$_{0.65}$Zn$_{0.35-x}$Cu$_x$Fe$_2$O$_4$ ferrite](image-url)
Figure 6.7: Compositional variation of initial permeability and grain size of Ni$_{0.5}$Zn$_{0.5-x}$Cu$_{x}$Fe$_2$O$_4$ ferrite

6.2.4.2 Frequency variation of initial permeability

The room temperature frequency variation of Cu substituted Ni-Zn ferrite both systems sintered at 900$^\circ$C temperature for 4 hr were shown in Figure 6.8 and Figure 6.9.

Figure 6.8: Frequency variation of initial permeability with composition of Ni$_{0.65}$Zn$_{0.35-x}$Cu$_{x}$Fe$_2$O$_4$ ferrite sintered at 900$^\circ$C
From Figure 6.8 and Figure 6.9 the permeability of the all samples were mostly stable for few many orders of frequency 7MHz and after this frequency some rise in permeability is observed for both ferrite systems. The cut-off frequencies of the samples were observed at above 15MHz. Since the highest frequency applied in the present case was insufficient to observe complete resonance peaks. From figs it is very clear that the permeability remain nearly constant up to 10 MHz and there on increases with increasing frequency. A step rise beyond $10^7$Hz is clearly observed in the plots drawn for the doping concentrations of Cu. It is clear that the resonance frequency appears to shift towards higher frequencies with increasing of Cu concentration. The observation of constant permeability over large frequencies shows the stability and quality of the ferrite material. The flat frequency region is known as zone of utility of ferrite and the stable frequency of the material is a desirable characteristic for electromagnetic applications.

### 6.2.4.3 Temperature variation of initial permeability

Study of temperature variation initial permeability is very important for MLCI applications. The temperature variation of initial permeability in the range of 40°C to 475°C of Ni$_{0.65}$Zn$_{0.35-x}$Cu$_x$Fe$_2$O$_4$ and Ni$_{0.5}$Zn$_{0.5-x}$Cu$_x$Fe$_2$O$_4$ nano crystalline ferrites were shown in Figure 6.10 and Figure 6.11 respectively.
Figure 6.10: Temperature variation of initial permeability of 
\[ \text{Ni}_{0.65}\text{Zn}_{0.35-x}\text{Cu}_x\text{Fe}_2\text{O}_4 \]

Figure 6.11: Temperature variation of initial permeability of 
\[ \text{Ni}_{0.5}\text{Zn}_{0.5-x}\text{Cu}_x\text{Fe}_2\text{O}_4 \]
From Figure 6.10 it is clear that the initial permeability is initially decreased for \(x=0.05\) concentration and increased for \(x=0.10\) concentration of Cu ion, again decreased for \(x=0.15\) concentration and increased for remaining higher concentrations. These variations explained on the basis of grain size of the material. Generally the initial permeability of the material is directly proportional to the grain size. From Figure 6.11 it is clear that the initial permeability is increased with increasing Cu concentration upto \(x=0.15\) and then decreases for higher concentrations.

Increasing of temperature the initial permeability is almost constant for particular temperature and increases to Hopkinson value and then suddenly falls to low value the sharp falling of initial permeability with temperature is suggests that the formation single phase of ferrites[11]. Beyond a temperature, when the permeability observed to decreased and indicates the Curie transition temperature. At that temperature the samples may transform form ferromagnetic state to paramagnetic state. From Figure 6.10 and Figure 6.11 it was clearly observed that the Curie transition temperature is increased with increasing of Cu concentration. The highest initial permeability is found at \(x=0.10\) for \(\text{Ni}_{0.65}\text{Zn}_{0.35-x}\text{Cu}_x\text{Fe}_2\text{O}_4\) and \(x=0.15\) for \(\text{Ni}_{0.5}\text{Zn}_{0.5-x}\text{Cu}_x\text{Fe}_2\text{O}_4\).

This variation of initial permeability is may be attributed to the interaction between A-B ions in both tetrahedral and octahedral sublattices in the composition. From scanning electron microscopy studies which is clear that highest grain size is observed at \(x=0.10\) for \(\text{Ni}_{0.65}\text{Zn}_{0.35-x}\text{Cu}_x\text{Fe}_2\text{O}_4\) and \(x=0.15\) for \(\text{Ni}_{0.5}\text{Zn}_{0.5-x}\text{Cu}_x\text{Fe}_2\text{O}_4\) which may cause to increase in initial permeability at \(x=0.10\) for \(\text{Ni}_{0.65}\text{Zn}_{0.35-x}\text{Cu}_x\text{Fe}_2\text{O}_4\) and \(x=0.15\) for \(\text{Ni}_{0.5}\text{Zn}_{0.5-x}\text{Cu}_x\text{Fe}_2\text{O}_4\) respectively.

The variations in initial permeability are expressed as follows: the saturation magnetization and anisotropy constant are decreases with increasing of temperature. The anisotropy constant is inversely proportional to the initial permeability. The relation between anisotropy constant, saturation magnetization, grain size and initial permeability are given in following equation [12-13].

\[
\mu_i = \frac{M_s^2 D}{K_i}
\]
Where $\mu_i$ initial permeability, $M_s$ is saturation magnetization, $D$ is average grain size and $K_1$ is anisotropy constant.

The obtained anisotropy of both Cu substituted Ni-Zn ferrites are shown in Figure 6.12 from Figure 6.12. It is very clear that the obtained anisotropy constant and initial permeability shows the inverse trend with increasing of Cu substitution in both systems. The obtained highest permeability of the samples indicates that these Cu substituted Ni-Zn ferrites are well suitable soft magnetic materials for MLCI applications.

![Figure 6.12: compositional variation of anisotropy constant of Cu substituted Ni-Zn nanocrystalline ferrites](image)

Figure 6.12: compositional variation of anisotropy constant of Cu substituted Ni-Zn nanocrystalline ferrites
6.3 References


