Chapter III
MAGNETIC PROPERTIES

Introduction

Magnetic properties of nanocrystalline materials have been extensively studied because of their technological and fundamental scientific importance. Spinel ferrites MFe$_2$O$_4$ (M = Ni, Zn etc) are among the most important class of magnetic materials and one of the unique feature of these materials is their superparamagnetism. Nanocrystalline ferrites exhibit unusual magnetic properties such as single domain behaviour, superparamagnetism and reduced magnetization, which are not observed in the bulk material. Superparamagnetism is only one and important characteristic of magnetism in the nanosized magnetic materials. Understanding and controlling the superparamagnetic features of these ferrite nanoparticles are important for many applications. In nanoparticles the structure can substantially deviate from the bulk counterpart which depends upon the method of preparation and reaction conditions [1]. Some nanocrystalline spinel ferrites show different cation distribution and as a consequence, exhibit diverse magnetic properties when compared with corresponding bulk counterparts [2,3].

The magnetic properties of a magnetic material depend largely on particle size distributions, domain structure and magnetization process [4]. If the particle size is quite large it consists of several domains. These domains are oriented in the direction of applied magnetic field, which takes place by domain wall displacement as well as by domain rotation. If the volume of the particles is reduced in such a way that they contain only single domain, change in magnetization takes place by rotation only. As a result the coercivity increases. If the volume of particle is further reduced, then at a particular temperature, the thermal energy becomes greater than anisotropy energy in the presence of an applied magnetic field. As a result a global magnetization is observed which is field dependent and exhibits no magnetic hysteresis. This behavior is termed as superparamagnetic behavior [4].

Recently, Ni-Cu-Zn ferrites with high permeability and high Curie temperature have been widely studied for scientific, practical and microwave applications [5-7]. Ni-Cu-Zn ferrite is the material of choice that fulfils most of the requirements quite well. The applications of Ni-Cu-Zn ferrite ensures effective
sintering at a low temperature (<950°C) for better magnetic properties. The permeability spectra of ferrites depend not only on the chemical compositions of the ferrites but also on the microstructure such as grain size, intra and intergranular pores [8-10]. Nanocrystalline ferrite materials with definite particle size distribution and thermal relaxation of the magnetic vectors exhibit superparamagnetism above and magnetic hyperfine structure below the particular temperature [11].

Magnetic nano-particles of mixed spinel ferrites have been the subject of current interest because of their interesting magnetic, electric, dielectric and optical properties, which are considerably different from that of their bulk counterparts. These systems are commercially important for their several applications in electromagnetic devices operating in the radio frequency region where the superparamagnetic (SPM) properties have a strong influence on enhancing their quality of applications [8,12,13]. A nanoparticle of these materials exhibits interesting phase transitions from super paramagnetic to ferri/ferro-magnetic state or vice versa with variation of temperatures depending on their sizes. Major factors that control superparamagnetism are magnetic anisotropy and volume of nanoparticles. The factors that govern the value of magnetic anisotropy are electron spin-orbital angular momentum coupling at lattice sites, dipole-dipole interaction among the magnetic ions, shape of nanoparticles etc. The strength of the spin-orbital angular momentum coupling depends mainly on the value of magnetic moment of the atoms involved in the coupling, their relative distance and the symmetry of the lattice site. To achieve SPM properties with relatively large sizes of nanoparticles, these factors can be systematically varied, particularly in the case of mixed spinel ferrites [13-16]. The ferrite grain size has important influence on the domain wall contribution in the magnetization processes at low frequency [17].
Section A: Vibrating Sample Magnetometer [VSM]

3. A.1. Introduction

The magnetic materials can be studied by applying external magnetic field to the specimen under investigation at room temperature or with varying temperature to determine the saturation magnetization, coercive strength and retentivity of the material. There are various methods to determine the above said properties. But the most advanced technique for the study of magnetization is the vibrating sample magnetometer (VSM). Magnetic measurement over a broad range of magnetic fields and temperatures are also possible. A vibrating sample magnetometer (VSM) works on Faraday’s law of induction, which tells us that a changing magnetic field will produce an electric field. This electric field can be measured to give us information about the change in magnetic field.

3. A.2. Experimental

The actual photograph of the magnetometer (VSM MODEL – LAKESHORE-7307) with EM7-HV electromagnet and 665 MPS is shown in Fig. 3.1.

![Figure 3.1: Vibrating sample magnetometer set up](image)

The powder sample to be studied is taken in sample holder, a small capillary of 3mm (0.13”) diameter x 6.35 mm (0.25”) length. It is kept in constant magnetic field strength. If the sample is magnetized this constant magnetic field will magnetize the sample by aligning the magnetic domains, or the individual magnetic spins, in the direction of the field. The stronger constant field generates higher magnetization. The
magnetic dipole moment of the sample will create a magnetic field around the sample. Sometimes this field is called the magnetic steady field. As the sample is moved up and down, this magnetic steady field changes as a function of time and can be sensed by a set of pick-up coils. The alternating magnetic field will cause an electric field in the pick-up coils according to Faraday’s law of induction. The current will be proportional to the magnetization of the sample. The greater the magnetization, the greater is the induced current. The induction current is amplified by a trans-impedance amplifier and lock-in amplifier. The various components are hooked up to a computer interface. Using controlling and monitoring software, the system can tell us how much the sample is magnetized and how its magnetization depends on the strength of the magnetic materials. Computer interface device collects the data from which a plot of magnetization (M) versus magnetic field strength (H) can be obtained. From the graph, saturation magnetization (Ms), retentivity (Mr) and coercivity (Hc) can be easily determined.

The saturation magnetization in emu/gm was calculated by using relation

\[ M_s = (1-p) \rho_x \]

where, \( \rho_x \) is x-ray density and ‘p’ is porosity.

The magnetic moment \( n_B \) per atom in Bohr magnetron for each composition is calculated using the experimental value of saturation magnetization (Ms) and the relation [18]

\[ n_B = \frac{(M \times M_s)}{(N \times \beta)} \]

where, ‘M’ = molecular weight of the sample  
‘N’ = Avogadro’s number \( (6.024 \times 10^{23} \text{gm.mol}^{-1}) \)  
‘B = the conversion factor to express the magnetic moment per atom in Bohr magnetron \( (9.273 \times 10^{-21} \text{erg/ gauss}) \)

The anisotropy constant is calculated using the Brown’s relation [19]

\[ H_c \geq \left( \frac{2K}{\mu_0 M_s} \right) \]

\[ k = \frac{M_s H_c}{0.96} \]

where, ‘K’ is the anisotropy constant
3. A.3 Results and Discussion

The room temperature hysteresis loops of \( \text{Ni}_{0.5-x} \text{Cu}_x \text{Zn}_{0.3} \text{Mg}_{0.2} \text{Fe}_2 \text{O}_4 \) nanoparticles with different Cu-content (x=0, 0.1, 0.3, 0.4, and 0.5) are shown Fig. 3.2 in which a typical nature of soft magnetic material is observed. The saturation magnetization (Ms), remanent magnetization (Mr) and coercivity (Hc) values are listed in Table 3.1. The experimental magnetic moment (n_B) calculated from the saturation magnetization data and is presented in Table 3.1.

Table 3.1 Data on Ms, Hc, Mr, Mr/Ms, K and n_B for \( \text{Ni}_{0.5-x} \text{Cu}_x \text{Zn}_{0.3} \text{Mg}_{0.2} \text{Fe}_2 \text{O}_4 \) ferrites.

<table>
<thead>
<tr>
<th>Cu Content (x)</th>
<th>Saturation Magnetization, Ms (emu/g)</th>
<th>Coercivity Hc (G)</th>
<th>Retentivity Mr (emu/g)</th>
<th>Mr/Ms</th>
<th>Anisotropy Constant K (erg/gm)</th>
<th>Magnetic moment (Bohr Megton) n_B</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>70.23</td>
<td>32.81</td>
<td>2.9</td>
<td>0.041</td>
<td>2400.25</td>
<td>3.5</td>
</tr>
<tr>
<td>0.1</td>
<td>64.38</td>
<td>58.83</td>
<td>4.10</td>
<td>0.063</td>
<td>3963.67</td>
<td>2.0</td>
</tr>
<tr>
<td>0.2</td>
<td>60.07</td>
<td>27.34</td>
<td>3.6</td>
<td>0.059</td>
<td>1710.74</td>
<td>3.35</td>
</tr>
<tr>
<td>0.3</td>
<td>46.55</td>
<td>41.00</td>
<td>1.66</td>
<td>0.035</td>
<td>1988.07</td>
<td>2.13</td>
</tr>
<tr>
<td>0.4</td>
<td>37.81</td>
<td>24.61</td>
<td>2.73</td>
<td>0.072</td>
<td>969.27</td>
<td>1.69</td>
</tr>
<tr>
<td>0.5</td>
<td>31.42</td>
<td>13.67</td>
<td>0.49</td>
<td>0.015</td>
<td>447.40</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Fig. 3.2 The room temperature hysteresis loops of \( \text{Ni}_{0.5-x} \text{Cu}_x \text{Zn}_{0.3} \text{Mg}_{0.2} \text{Fe}_2 \text{O}_4 \) nanoparticles with different Cu-contents (x=0, 0.1, 0.3, 0.4 and 0.5)
i) **Effect of Cu-content on magnetization**

It is evident from Fig. 3.2 that the hysteresis loops for these nanocrystals get saturated with magnetic field up to 5 kOe for all samples. Fig. 3.2 also shows that saturation magnetization decreases with increasing copper content. This decrease is slow in the region from x=0 to 0.2, after which a rapid change in the saturation magnetization is observed from x=0.3 to x=0.5. A sharp decrease in saturation magnetization (31.42 emu/g) was observed for the tetragonal phase of copper ferrite. The remanent magnetization sharply decreases with increasing Cu-content. On the other hand, the coercivity gradually decreases up to the copper content of x=0.5, which indicates the soft nature of the ferrite. The present decrease in saturation magnetization is found to be in good agreement with the data reported for Ni-Cu ferrites prepared by other methods [20, 21]. In the present case, the saturation magnetization (Ms) is smaller than that observed for the bulk counterpart (73emu/g) [12].

It is shown that there is reduction in saturation magnetization for magnetic nanoparticles on comparing with their bulk counterparts. In general the smaller particles give larger deviation [22]. The magnetization behaviour of nickel ferrite can be understood in terms of the cation distribution and Neel’s two sublattice model. Nickel ferrite (Ni Fe$_2$O$_4$) with an inverse spinel structure, shows ferrimagnetism that originates from the magnetic moment of antiparallel spins between Fe$^{3+}$ ions at tetrahedral sites and Ni$^{2+}$ ions at octahedral sites. The observed saturation magnetization of 70.23 emu/g for x = 0 measured at 5 kOe, is comparatively close to the theoretical saturation magnetization of 50 emu/g measured at 3 kOe [23]. These values are in good agreement with the values observed for nickel ferrite synthesized by other methods [24-26]. The saturation magnetization of 31.42 emu/g observed in the present work agrees well with that observed for the sample prepared through the combustion reaction of ureate precursors method (24.8 emu/g) [27].

ii) **Effect of microstructure on magnetization**

Another important factor which influences the magnetization in ferrites is the microstructure. The magnetization is a result of simultaneous influence of several intrinsic and extrinsic factors such as density and porosity [28]. The microstructure depends upon sintering conditions such as sintering temperature and rate of cooling. These factors determine the grain size. The larger grains have lower porosity. The presence of pores breaks the magnetic circuit among the grains which results in net
reduction of magnetization. The lower firing temperature may result in closed chains which decrease magnetization. The presence of copper in the sintering process increases the average grain size and decreases porosity [17].

The decrease in saturation magnetization is explained by assuming that the A–B interaction favors 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 occurring between the metal ions in the tetrahedral A-sites and octahedral B-sites [29]. It must be considered that magnetic moment of Cu\(^{2+}\) ions (1.3 \(\mu_B\)) is lower than that of Ni\(^{2+}\) ions (2.3 \(\mu_B\)) consequently, the replacement of nickel with copper decreases saturation magnetization [30], which is consistent with our results. Its 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.

From Table 3.1 it is evident that the Hc values decrease with increasing copper content. Yan at el. [31] observed the decrease in coercivity beyond 550\(^\circ\)C and is attributed to particles exceeding the critical single domain size and becoming multidomain due to sintering. Large grains obtained at higher annealing temperature consist of a greater number of domain walls. The magnetization or demagnetization caused by domain wall movement requires less energy than that required by single domain rotation. As the number of domain walls increases with increasing grain sizes, the contribution of wall movement to magnetization or demagnetization is greater than domain rotation, therefore samples having relatively large grains are expected to have low coercivity. Similar trend was reported by Jahanbin et al. [32] for Ni-Zn ferrites at different sintering temperature.

Kenfack and Langbein [21] suggested that the presence of the Cu\(^{2+}\) ions in the A-sites displaces the same amount of Fe\(^{3+}\) ions towards the B-sites. This influence can compensate the decrease of the magnetization by the substitution of Ni\(^{2+}\) by Cu\(^{2+}\). Reddy et al. [33] synthesized iron deficient soft Ni-Cu-Zn spinel ferrites using microwave sintering method. It reveals that increase of Ni\(^{2+}\) ion concentration decreases saturation magnetization.

Xia et al. [34] prepared Ni-Zn-Cu ferrite with different coprecipitator via chemical co-precipitation method. He observed that the saturation magnetization of
specimens with NaOH as coprecipitator is lower than that with Na\textsubscript{2}CO\textsubscript{3} as coprecipitator.

Ghasemi et al. [30] prepared fine particles of Ni\textsubscript{0.6-x}Cu\textsubscript{x}Zn\textsubscript{0.4}Fe\textsubscript{2}O\textsubscript{4} (x=0.0 to 0.5) ferrite by reverse micelle method. He found an increase in saturation magnetization with decrease in copper content. He observed that values of saturation magnetizations for fine particles are much lower than that of bulk ferrite.

Wei-Chih Hsu et al. [35] have reported that Cu substitution for Ni in Ni-Zn ferrite enhances the densification of ferrites and subsequently increases the permeability as well as Ms and decrease in Hc value. For the sample Cu\textsubscript{0.4}Zn\textsubscript{0.6}Fe\textsubscript{2}O\textsubscript{4}, he observed a very low value of Ms due to small particle size (27 nm) and presence of a small fraction (0.4) of copper. Similar results were observed in case of nanocrystalline Ni\textsubscript{0.2}Zn\textsubscript{0.6}Cu\textsubscript{0.2}Fe\textsubscript{2}O\textsubscript{4} ferrite [36].

Singh et al. [37] observed that the saturation magnetization first increases with the addition of Cu up to x=0.2 and then decreases with further increase in Cu content. Our results are comparable with these.
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Figs. 3.3 (a-b-c) M-H loops of $\text{Ni}_{0.5-x} \text{Cu}_x \text{Zn}_{0.3} \text{Mg}_{0.2} \text{Fe}_2 \text{O}_4$ with different Cu-contents ($x=0, 0.1, \text{and} 0.5$)

- **Fig. 3.3 (b)**
  - $M_s=47 \text{emu/g}$
  - $M_r=2 \text{emu/g}$
  - $H_c=34 \text{Oe}$

- **Fig. 3.3 (C)**
  - $M_s=30.65 \text{emu/g}$
  - $M_r=1.8 \text{emu/g}$
  - $H_c=18 \text{Oe}$
The area included in the hysteresis loop is a measure of magnetic losses that occurred in the cyclic magnetization process. The values of $M_s$, $M_r$ and $H_c$ are shown inside the Fig. 3.3 (a-c). From this figure it is concluded that the area included in the loop is very small i.e. magnetic loss is very small for the sample with $x=0$, $x=0.1$ and $x=0.5$ but as we increase the Cu-content magnetic losses decrease. The decrease in the value of saturation magnetization ($M_s$) and decrease in value of $H_c$ suggest that the synthesized powder can be used for the applications such as high density media, magnetic storage devices and memory cores etc. Since recording media requires high saturation magnetization values and enough coercivity [38]. The decrease in the remanent magnetization ($M_r$) and saturation magnetization ($M_s$) with Cu-content, suggests the decrease of strongly interacting magnetic state towards a paramagnetic state [39,40]. This can be confirmed by magnetic susceptibility measurements. It can be observed that the smaller particle sizes exhibit smaller values of $M_s$ as expected from the surface disorder and modified cationic distribution [41]. In other words, the decrease in $M_s$ at smaller sizes is attributed to the pronounced surface effect in these nanoparticles. The surface of the nanoparticles is considered as disordered spins that prevent the core spins for aligning along the field direction resulting in decrease of saturation magnetization of the small sized nanoparticles [42]. It shows that the system presents superparamagnetic behavior. Superparamagnetic nanocrystals are believed to be promising for wide engineering applications, such as drug delivery, bio separation and magnetic resonance imaging (MRI) [43]. From Table 3.1 the anisotropy constant $K$ is determined for each composition for present system. It is observed from Table 3.1 that the sample containing more Cu shows more superparamagnetic behavior. Therefore anisotropy constant ($K$) is lower for copper rich sample as compared with Ni rich ferrites. Similar results were obtained in case of Cu-substituted Mg ferrite nanoparticles and thin films. In light of above discussion it is concluded that anisotropy constant ($K$) is directly proportional to saturation magnetization ($M_s$) which is confirmed by the relation 3.4.
Section B : Permeability

3. B.1 Introduction

Soft ferrites are still of great interest to researchers due to their high initial permeability over a wide range of frequencies leading to wide spread applications as inductor in radio frequency systems, recording heads, microwave devices etc. [44] They have a wide range of applications [45] in microwave absorbance, electronic devices such as radio and TV sets, integrated nonreciprocal circuits, high frequency transformers, memory core devices, rod antennas, read-write heads for high-speed digital tape or disk recording, telecommunication applications, excellent catalysts for alkylation of aromatics and in gas sensing. The magnetization mechanism of polycrystalline ferrites results from spin domain rotation and domain wall motion. In polycrystalline ferrites, the larger grain size and higher sintering density result in the higher initial permeability [46]. Initial permeability ($\mu_i$) is a structure sensitive property which depends upon the method of preparation, grain size and porosity [47]. The initial permeability ($\mu_i$) is important magnetic parameter which decides the material’s utility for specialized applications. For multilayer chip inductor (MLCI) applications, the temperature dependence of ($\mu_i$) is very important. Ni-Cu-Zn ferrite is one of the most important magnetic materials for MLCI applications due to its high electrical resistivity, low sintering temperature and high permeability [48-51]. The study of ($\mu_i$) has been of great interest from both theoretical and practical point of view.

Initial permeability could arise from two mechanisms viz.

i) Domain wall displacement and

ii) Spin rotation

It is generally assumed that the initial permeability is caused by the reversible displacement of domain walls, the contribution of rotation of spin inside each domain being negligibly small on account of relatively high crystal anisotropy. In polycrystalline ferrites, due to sintering, some air pores are present. In such a structure, the domain walls will extend from pore to pore so that they are not free to move. These pores have a considerable demagnetizing effect, which leads to rather intrinsic pattern of Weiss domain. Hence, it is impossible to say in advance which kind of magnetization process will give the predominant contribution to the initial permeability. The basic definition of initial permeability can be given as,
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$$\mu_i = \left( \frac{1}{\mu_0} \right) \lim_{H \to 0} \left( \frac{H}{H} \right)$$  \hspace{1cm} 3.5

where, $\mu_i$ = permeability in vacuum and  
$B/H$ = slope of B-H curve at knee position.

For reversible rotational process Chikazumi has expressed permeability as,

$$\mu - 1 = \text{constant} \frac{(M_s)^2 \sin^2 \theta}{K_1}$$  \hspace{1cm} 3.6

where, $0$ is the angle between $M_s$ and $\mu$.

For reversible wall process permeability can be given by,

$$\mu - 1 = \text{constant} \frac{(M_s)^2}{a}$$  \hspace{1cm} 3.7

where, $S$ = wall surface area  
$a$ = second order derivative of wall energy with respect to wall displacement.

At lower frequencies domain wall motion is a dominant mechanism. The second source of initial permeability viz. domain rotation is largely responsible for high frequency permeability. Frequency dispersion in ferrite has attributed to domain wall displacement. The absence of low frequency resonance indicates the absence of domain wall movements. Pores hinder walls and also give rise to a local demagnetizing field, which is expected to modify the domain pattern near boundary. The hindrance to the domain wall motion results in low value of it. The permeability of polycrystalline spinels is given by the relation.

$$\mu_i^{-1} = \frac{(M_s)^2}{K_1}$$  \hspace{1cm} 3.8

where, $K_1$ = Magnetocrystalline anisotropy constant  
$M_s$ = Saturation magnetization

From the above relation, it is seen that $\mu_i$ is proportional to square of $M_s$ Initial permeability can arise either due to the contribution from spin rotation or from domain walls. The contribution from spin rotation is smaller than that of domain wall motion. The permeability due to domain wall motion is given by the relation.

$$\mu_i - 1 = \frac{3\pi (M_s)^2 D}{4\gamma}$$  \hspace{1cm} 3.9
where, \( Ms \) = the saturation magnetization
\( D \) = the mean grain size
\( \gamma \) = magnetic domain wall energy

3. B.2 Experimental

Inductance and magnetic loss are basic properties of any ferrite. The inductance of ferrite core depends on the number of turns, diameter of coil and nature of ferrite compositions. For the determination of permeability the samples in the form of toroids with inner diameter (ID = 1cm) and outer diameter (OD=2cm) were used. Enameled copper wire of 100 turns was wound on toroid so as to form the core. By using LCR meter HIOKI 3532-50 LCR HiTESTER, the values of inductance (L) and quality factor (Q-factor) were noted at room temperature. The permeability was calculated by using the relation,

\[
\mu_i = \frac{L}{0.0046N^2h\log\left(\frac{OD}{ID}\right)}
\]

where, \( L \) = inductance in \( \mu \) H
\( N \) = number of turns of copper wire on toroid
\( h \) = height of the core in inches
\( OD \) = outer diameter of toroid
\( ID \) = inner diameter of toroid

Fig. 3.4 Ferrite core with 100 turn.
3. B.3 Results and discussion

B.3.1 Frequency dependence of initial permeability

Variation of initial permeability with frequency of Ni$_{0.5-x}$Cu$_x$Zn$_{0.3}$Mg$_{0.2}$Fe$_2$O$_4$ ferrites for x=0, x=0.1, x=0.3 and x=0.5 is shown in Fig. 3.5

![Permeability vs Frequency Graph](image)

**Fig. 3.5 Variation of initial permeability with frequency of Ni$_{0.5-x}$Cu$_x$Zn$_{0.3}$Mg$_{0.2}$Fe$_2$O$_4$ ferrites**

It is seen from Fig. 3.5 that all the samples show a flat profile in the frequency range 100 Hz to 1 MHz for x=0, x=0.1, x=0.3 and x=0.5 then the dispersion occurs. In general it is observed that the initial permeability remains almost constant up to a certain frequency after which it increases to a maximum value and then decreases rapidly to the lower value. This phenomenon is known as dispersion of initial permeability. It is attributed to either domain wall displacement or domain rotation or both of these. Initial permeability is reported to be due to the domain wall displacement and remains constant with frequency as long as there is no phase lag between the applied field and domain wall displacement. It is also observed for the sample (x=0.5) that in the low frequency range 100 KHz–1MHz, domain wall motion plays a predominant role in the magnetizing process and loss mechanism. For the sample x=0.5 wall relaxation occurs at 3 MHz while for the sample x=0 and x=0.1 relaxation occur at 1MHz. The rapid decrease in initial permeability at higher frequencies indicates the onset of ferromagnetic resonance [32,52]. In the present case
addition of Cu lowers the value of anisotropy constant [Table 3.1] and reduces the natural frequency of precession, which leads to onset resonance at lower frequency [20]. When the frequency of the applied magnetic field is equal to the Larmor precession frequency of the electron spin, the resonance occurs and the energy is transferred from the field to the system in orienting magnetic dipoles. Normally two resonance peaks are observed in ferrites, one at lower frequencies due to domain wall oscillations [53, 54] and other due to Larmour precession of electron-spin at higher frequencies. The fairly constant initial permeability ($\mu_i$) value over a large frequency range shows the compositional stability and quality of the ferrites prepared by the auto-combustion method. This is a desirable characteristic for various applications such as broadband pulse transformer and wide band read-write heads for video recording [32]. Similar behaviour was observed in the case of Cu-substituted Mg-Zn ferrite, Mg-substituted Ni-Cu-Zn ferrite, Samarium-substituted Ni-Cu-Zn ferrite, Zn-substituted Mg-Cu ferrite, Ni-Zn ferrite, vanadium-substituted Lithium-Zinc-Titanium ferrite and Mg-Cu-Zn ferrite [55-61].

It is well known that the initial permeability of ferrite is strongly affected by saturation magnetization, crystal magnetization anisotropy, magnetostriction constant and internal stress [52]. The permeability of polycrystalline ferrites can be due to the superposition of domain wall motion and spin rotational component. In general the permeability is related to two different magnetizing mechanisms the spin rotational magnetization and the domain wall motion [62]. The spin rotational component is relaxation type and its dispersion is inversely proportional to the frequency. The domain wall component is of resonance type and depends on the square of the frequency. Spin rotational component is dominated by the chemical composition, while domain wall component is affected by both the composition and the microstructure.
B.3.2 Magnetic loss (tan δ_µ) with frequency

The variation of tan (δ_µ) with frequency is shown in Fig 3.6 for the sample s x=0, x=0.1, x=0.3 and x=0.5. From Fig 3.6 it seems that the tan (δ_µ) has high value at lower frequency and it decreases with increase in frequency ~ 2MHz, afterwards tan (δ_µ) increases rapidly showing a tendency for a resonance loss peak. The resonance frequency indicates the limit of operational frequency of the sample. At resonance frequency, maximum energy is transferred from the applied field to the lattice resulting in the rise of tan (δ_µ) [63]. It is also observed that maximum energy is transferred when Cu-content is increased.

Fig. 3.6 Variation of tan (δ_µ) with frequency (f) of Ni_{0.5-x} Cu_x Zn_{0.3} Mg_{0.2} Fe_{2} O_{4} ferrites for x=0, x=0.1, x=0.3 and x=0.5
B.3.3 Relative loss factor (\(\tan \delta \mu/\mu_i\)) with frequency

The variation of relative loss factor (RLF) with frequency is shown in Fig 3.7. RLF is the ratio of the magnetic loss tangent (\(\delta \mu\)) to initial permeability (\(\mu_i\)). For high initial permeability (\(\mu_i\)) and low magnetic loss (\(\delta \mu\)), low RLF values are required. The RLF should be as low as possible for some high frequency application. In the present case RLF is practically independent of frequency from 1KHZ to 5MHz and shows an increase at higher frequencies from 5MHz. This increase is an indication of the presence of resonance at higher frequencies [53] the value of RLF observed in the present work is in the range \(10^{-2}\) to \(10^{-1}\).

It is clear from literature that [59] RLF is directly proportional to magnetic loss (\(\tan \delta\)). At low frequency region magnetic loss is higher indicating that domain wall gets enough time to move. High domain wall motion generates high eddy current which increases the magnetic loss. This behavior is observed in the present samples as shown in figure 3.7. In the same content at higher frequency domain wall motion get
restricted, as a result value of magnetic loss is lower in the high frequency. Hence variation of RLF follows the similar behavior of magnetic loss with frequency.

The higher RLF of un-substituted ferrites may be due to higher hysteresis loss of the specimen and higher saturation magnetization which may arise due to its porous (porosity ~30 %) structure. The RLF values in the present work are comparable with the values reported earlier [54, 55].

B.3.4 Variation of quality factor (Q) with frequency

![Graph showing variation of quality factor (Q) with frequency](image)

**Fig3.8 Variation of Quality factor (Q) with frequency (f) of Ni\(_{0.5-x}\) Cu\(_x\) Zn\(_{0.3}\) Mg\(_{0.2}\) Fe\(_2\)O\(_4\) ferrites for x=0 x=0.1 x=0.3 and x= 0.5**

The Quality factor (Q) was calculated from the magnetic loss moment on the coil wound on toroidal sample. The variation of quality factor (Q) as a function of frequency for the samples with x=0 x=0.1 x=0.3 and x= 0.5 is shown in Fig. 3.8. From this figure, it can be seen that quality factor (Q) of the samples is significantly improved and shows resonating behavior. Moreover, as we increase Cu-content the resonance curve becomes sharp and also the value of Q-factor increases. Hu et al. [64] have reported significant improvement in Q-factor over the frequency range of 10
kHz–1 MHz for calcined and uncalcined samples in case of Ni-Cu-Zn ferrites. Similar effect was observed in case of [61,65].

**B.3.5 Temperature dependence AC magnetic susceptibility \( (\chi_m) \)**

![Graph showing temperature dependence of AC magnetic susceptibility](image)

**Fig. 3.9 Temperature dependence of AC magnetic susceptibility \( (\chi_m) \) for \( \text{Ni}_{0.5-x} \text{Cu}_x \text{Zn}_{0.3} \text{Mg}_{0.2} \text{Fe}_2 \text{O}_4 \) ferrite for \( x=0 \) and \( x=0.5 \)**

The variation of AC magnetic susceptibility \( (\chi_m) \) with temperature is shown in Fig. 3.9. The Curie temperature is another important property of nanocrystalline ferrites. It is an intrinsic property of spinal ferrites, which can be controlled by preparation conditions and substitution of different metal ions. The synthesis technique, microstructure, and grain size play a dominant role in deciding AC magnetic susceptibility [66]. The temperature dependence AC magnetic susceptibility \( (\chi_m) \) measurements for the samples \( x=0 \) and \( x=0.5 \) were carried out in the temperature range from 300 to 900 K. Fig. 3.9 represents temperature dependence of the AC magnetic susceptibility \( (\chi_m) \). From the Fig 3.9 it is clear that \( (\chi_m) \) decreases with increasing temperature and falls sharply when magnetic state of sample changes from ferrimagnetic to paramagnetic. Curie temperatures are indicated by the x-intercepts of straight line. The change in Curie temperature is due to the influence of cations stoichiometry and their occupancy in specific sites as explained by Rath et al. [3]. In the present work observed magnetic transition temperature \( T_C \) for the sample \( (x = 0) \) is 802 K and for the sample \( (x=0.5) \) is 668 K. Transition temperature \( (T_C) \) reported
from dielectric measurements and magnetic measurements for the sample $x=0$ and $x=0.5$ are in good agreement [67]. The sample can be considered to be in a pure ferrimagnetic phase in which the thermal energy is not quite sufficient to disturb the aligned moments of the spins. After the transition temperature ($T_C$), the thermal energy is high enough to disturb all the aligned spins and a paramagnetic region appears. For the sample $x=0.5$ the decrease in ($\chi_m$) with increasing field intensity can be considered as a normal magnetic behavior, which can be attributed to the saturation of the ferrimagnetic domains at such a high field [68]. The obvious decrease in the $T_C$ value with increasing Cu-content can be attributed to the increase in the paramagnetic region at the expense of the ferrimagnetic region, which indicates that the ferrimagnetic grains are widely separated by the less magnetic copper ions. The Curie temperature of the ferrites is determined by the overall strength of the A–B interactions, but sometimes the intra-sublattice A–A and B–B interactions may become important [69]. The occupancy of the copper ion on a B-site instead of nickel ions weakens the A–B exchange interaction, resulting in a decrease in the magnetic interaction ($J_{AB}$). The internal energy required to offset the spin alignment will decrease and the Curie temperature is then expected to fall [70]. Similar results were obtained for Co-Zn ferrites, [71].
References

Chapter-III Magnetic Properties


