Chapter - 5

Magnetic Properties
5.1 Introduction

Lithium ferrites and substituted lithium ferrites are widely used in microwave devices, latching-type phase shifters and information storage elements. Their important features are high Curie temperature, low loss and superior temperature stability of saturation magnetization for different technological applications of lithium ferrites in particular. Since their saturation magnetization is greater than 2000 Gauss, spinel lithium ferrites are mostly employed for high frequency applications. Because at higher frequencies, the lithium ferrites exhibit good temperature stability of magnetic properties equivalent to that of the nickel ferrites and very low insertion losses that are comparable to the magnesium ferrites. Magnetization studies are useful in arrangements of spins and the distribution of magnetic ions in the sublattices. These arrangements would decide the other desirable magnetic properties of magnetic devices.

The substituted lithium ferrites are promising candidates for microwave applications and preferred to garnets in view of their cost and other improved electrical and magnetic properties [1]. In this work, it is aimed at investigating the properties of nickel-copper and nickel-magnesium substituted lithium ferrites for microwave applications. The variations in Curie temperature, saturation magnetization, initial permeability of nickel-copper and nickel-magnesium substituted lithium ferrites are discussed in this chapter. The hysteresis loops of all the samples are obtained and possible mechanisms for understanding the magnetic behaviour are thoroughly analyzed.
5.2 Saturation magnetization

As mentioned in the chapter-3, the nickel-copper and nickel-magnesium substituted lithium ferrites samples are named as LNC series and LNM series, respectively for easy representation. Hereafter, for presentation of the results and also in the discussions they are referred to as LNC and LNM only. The obtained hysteresis loops of both the LNC and LNM series of samples at room temperature are shown in Figures 5.1(a) and 1(b), respectively. Saturation magnetization and coercivity values are extracted from these loops for all the samples. The magnetization curves of all the samples exhibit soft magnetic nature with low coercivities. The observed variations of saturation magnetization with concentration (x) for all the samples in both the series Li$_{0.5-x}$Ni$_x$Cu$_x$Fe$_{2.5-X}$O$_4$ (LNC) and Li$_{0.5-x}$Ni$_x$Mg$_x$Fe$_{2.5-X}$O$_4$ (LNM) where x = 0.00 to 0.25 in steps of 0.05, are shown in Figure 5.2.

![Figure 5.1(a). Room temperature hysteresis loops of Li$_{0.5-x}$Ni$_x$Cu$_x$Fe$_{2.5-X}$O$_4$](image-url)
The saturation magnetization has been observed to decrease with the concentration $x$ in both the series up to $x = 0.10$. Further, the observed decrease is more in LNC than that of LNM series of samples. Thereafter, the saturation magnetization of LNC has been continuously increased whereas for LNM samples it showed an increase up to $x=0.15$ and then decreased for further concentrations.

![Figure 5.1(b). Room temperature hysteresis loops of Li$_{0.5-x}$Ni$_x$Mg$_x$Fe$_{2.5-x}$O$_4$](image)

The observed variations in saturation magnetization as a function of substituent concentration can be explained on the basis of the strength of the super exchange interactions among tetrahedral (A) and octahedral [B] site ions in the spinel lattice.

Generally, in ferrites, Neel considered three kinds of exchange interactions between unpaired electrons of the ions, lying (i) both at A-sites (A-A interaction), (ii) both at B-sites (B-B interaction) and (iii) one at A-site and another at B-site (A-B interaction). Out of these three interactions, A-B interaction is predominant over B-B and A-A interactions. These interactions tend to align all the magnetic spins at A-site
in one direction and those at B-site in the opposite direction. The net magnetic moment of the lattice is, as a whole, therefore the difference between the magnetic moments of B and A sub lattices, i.e. $M_B - M_A$. The exchange interactions in the spinel lattice can greatly be influenced by the nature of the ions and their valency states present at both A- and B-sublattices.

![Figure 5.2. Variations of specific saturation magnetization with concentration(x) in Li_{0.5-x}Ni_xCu_{x}Fe_{2.5-x}O_4 and Li_{0.5-x}Ni_xMg_{x}Fe_{2.5-x}O_4 (x = 0.0 to 0.25) series.](image)

The Lithium, nickel, copper and magnesium ions have been reported to exist in $Li^{1+}$, $Ni^{2+}$, $Cu^{2+}$, $Mg^{2+}$ valence states and were known to occupy octahedral sites on the basis of their corresponding crystal field stabilization energies and replace $Fe^{3+}$ ions in B-sites [2]. It is thus the nickel and copper ions in LNC ferrite system are expected to replace lithium and iron ions at octahedral sites only as per their site preferences. On the application of these cationic preferences to the LNC ferrite
system, the B-sublattice magnetization should decrease continuously without affecting the A-sublattice magnetization, thus resulting in the net decrease of the saturation magnetization with increasing nickel and copper concentrations. The observed variation in saturation magnetization from the figure 2 suggests that this argument holds good up to $x=0.10$. However, the observed increase in the magnetization beyond this concentration can be explained with the proposal of a small quantity of copper ($y$) might be occupying A-sites as well apart from their major occupation in B-sites. Similar reports on the occupation of a small percentage of copper in A-sites were reported earlier as copper shows the tendency to reside in tetrahedral sites at larger concentrations [3]. Accordingly, it has been verified by placing a small but increasing (increased by 10% for each step from $x = 0.15$ onwards) percentage of copper in A-sites for each step of substitution in the series, while the nickel displaces lithium at octahedral sites only. In such case, an amount of iron equal to that of copper i.e. present in A-sites will be forced to migrate to B-sites. This transfer of copper to A-sites and forced migration of iron to B-sites is assumed to be proportional throughout concentrations beyond $x=0.15$. On the basis of this proposed picture, the cation distribution can be represented as:

\[
(Fe^{3+})[Li_{0.5-x}Ni_x^{2+}Cu_y^{2+}Fe_{1.5-x}^{3+}]O_4, \ x \leq 0.10
\]  
\[
(Cu_y^{2+}Fe_{1-y}^{3+})[Li_{0.5-x}Ni_x^{2+}Cu_{x-y}^{2+}Fe_{1.5+y-x}^{3+}]O_4, \ x \geq 0.10
\]

(5.1) (5.2)

With every step of substitution from $x=0.15$ onwards, the density of the nonmagnetic Li$^{1+}$ ions decreases and the higher magnetic moment Fe$^{3+}$ ions increases; thus resulting in a net increase in the B-sub lattice magnetization without any prominent decrease in the predominant A-B exchange interaction. Hence, the net
magnetization of the compound increases for these higher concentrations and justifies the observed increase in magnetization.

Similarly, an attempt has been made to explain the variation of magnetization behaviour in the LNM ferrite system. The observed decrease in saturation magnetization up to $x = 0.10$ can also be explained in LNM system as discussed above. Accordingly, the proposed cation distribution up to $x = 0.10$ for the ferrite system is

$$\left( Fe^{3+} \right) [ Li_{0.5-x} Ni_x^{2+} Mg_x^{2+} Fe^{3+}_{1.5-x} ] O_4, x \leq 0.10 \quad (5.3) $$

In order to explain the observed magnetization values at $x = 0.15$, it has been proposed that a maximum 30% of substituted magnesium($y$) would be transferred to tetrahedral site and an equal amount of iron forcibly migrated to octahedral site. This kind of an assignment holds good for the LNM samples up to $x = 0.15$ only. Thereafter, the transferred amount of magnesium ($y$) to tetrahedral sites might be decreasing by 10% for each step of substitution from $x = 0.15$ onwards.

$$\left( Mg_y^{2+} Fe^{3+}_{1-y} \right) [ Li_{0.5-x} Ni_x^{2+} Mg_x^{2+} Fe^{3+}_{1.5+y-x} ] O_4, x \geq 0.10 \quad (5.4) $$

Similar to the magnetization behaviour in LNC series, the observed magnetization in LNM series too is marked by a slow increase with every step of substitution from $x=0.15$ onwards. This is because the density of the nonmagnetic Li$^{1+}$ ions decreases and the higher magnetic moment Fe$^{3+}$ ions increases in B-sites leading to a net increase in the B-sub lattice magnetization without any prominent decrease in the predominant A-B exchange interaction. Hence, the net magnetization
of the compound increases for these higher concentrations and justifies the observed increase in magnetization.

5.2.1 Cation distribution based on magnetic moments

Further, in order to verify and confirm the proposed distribution of copper ions among A- and B- sites in the LNC series, the lattice constant and magnetic moment values have been calculated for all the samples. The net magnetic moment, \( M(x) \), of the \( \text{Li}_{1-x}\text{Ni}_x\text{Cu}_x\text{Fe}_{2.5-x}\text{O}_4 \) system, being the difference between the magnetic moments of the octahedral and tetrahedral sublattices, was estimated from the equations 5.1 and 5.2 by substituting the magnetic moments of the cations \( \text{Li}^+ (0 \, \mu_B) \), \( \text{Ni}^{2+} (2 \, \mu_B) \), \( \text{Cu}^{2+} (1 \, \mu_B) \) and \( \text{Fe}^{3+} (5 \, \mu_B) \) in the following equation [4]:

\[
M(x) = xM_{\text{Ni}} + (1.5 + y - x)M_{\text{Fe}} + (x - y)M_{\text{Cu}} - 5(1 - y)M_{\text{Fe}} - yM_{\text{Cu}} \\
= 2.5 - 2x + 8y
\]

The calculations of the net magnetic moment have been extended to the whole range of concentrations in the LNC ferrite system. As discussed in Chapter 4, the \( \text{Cu}^{2+} \) ions were assumed to occupy only B-sites (i.e., \( y=0 \)) at the lower substituent concentrations, and thereafter (for \( x \geq 0.15 \)) some of them are expected to occupy A-sites as well along with their preferential occupation of B-sites. Interestingly, with increasing concentration (\( x \)) of the nickel-copper substitution, the observed and calculated values of both the magnetic moments and the lattice constants follow the same trend; thus indirectly supports the occupation of copper ions in tetrahedral sites at higher concentrations. Based on the obtained results, cation distribution for the whole range of concentrations in LNC series was assigned and listed in the Table 5.1 against the respective concentration.
Table 5.1. The proposed cation distribution based on magnetic moments for the LNC series of samples

<table>
<thead>
<tr>
<th>x</th>
<th>A site</th>
<th>B site</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>Fe</td>
<td>Li_{0.5} Fe_{1.5}</td>
</tr>
<tr>
<td>0.05</td>
<td>Fe</td>
<td>Li_{0.45} Ni_{0.05} Cu_{0.05} Fe_{1.45}</td>
</tr>
<tr>
<td>0.10</td>
<td>Fe</td>
<td>Li_{0.4} Ni_{0.1} Cu_{0.1} Fe_{1.40}</td>
</tr>
<tr>
<td>0.15</td>
<td>Fe_{0.985} Cu_{0.015}</td>
<td>Li_{0.35} Ni_{0.15} Cu_{0.135} Fe_{1.365}</td>
</tr>
<tr>
<td>0.20</td>
<td>Fe_{0.925} Cu_{0.075}</td>
<td>Li_{0.25} Ni_{0.25} Cu_{0.175} Fe_{1.325}</td>
</tr>
<tr>
<td>0.25</td>
<td>Fe_{0.925} Cu_{0.075}</td>
<td>Li_{0.25} Ni_{0.25} Cu_{0.175} Fe_{1.325}</td>
</tr>
</tbody>
</table>

Similarly, an attempt has been made to verify and confirm the cation distribution in the LNM ferrite system. For this purpose, the net magnetic moment, \( M(x) \), of the Li_{1-x}Ni_{x}Mg_{x}Fe_{2.5-x}O_{4} system was estimated from the equations 5.3 and 5.4 by substituting the magnetic moments of the cations Li\(^{+}\) (0 \( \mu_{B} \)), Ni\(^{2+}\) (2 \( \mu_{B} \)), Mg\(^{2+}\) (0 \( \mu_{B} \)) and Fe\(^{3+}\) (5 \( \mu_{B} \)) in the following equation:

\[
M(x) = xM_{Ni} + (1.5 + y - x)M_{Fe} + 5(1 - y)M_{Fe} \\
= 2.5 - 3x + 10y
\]

In this system too, the observed and calculated net magnetic moments have been found to experience the same trends beyond \( x = 0.15 \) and thus supports very much the assigned cation distribution. Further, the proposed cation distribution has
also been verified by comparing the observed and calculated lattice constants (presented in the previous chapter), and they are found in agreement with each other; thus, confirming the proposed cation distribution for the whole range of concentrations in the LNM ferrite system.

Based on the obtained results and their analysis, the assigned cation distributions for the whole range of concentrations in LNM series is listed in Table 5.2 for the LNM series against the respective concentration.

Table 5.2. The proposed cation distribution based on magnetic moments for the LNM series of samples

<table>
<thead>
<tr>
<th>x</th>
<th>A site</th>
<th>B site</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>Fe</td>
<td>Li$<em>{0.5}$ Fe$</em>{1.5}$</td>
</tr>
<tr>
<td>0.05</td>
<td>Fe</td>
<td>Li$<em>{0.45}$ Ni$</em>{0.05}$ Mg$<em>{0.05}$ Fe$</em>{1.45}$</td>
</tr>
<tr>
<td>0.10</td>
<td>Fe</td>
<td>Li$<em>{0.40}$ Ni$</em>{0.10}$ Mg$<em>{0.10}$ Fe$</em>{1.40}$</td>
</tr>
<tr>
<td>0.15</td>
<td>Fe$<em>{0.955}$ Mg$</em>{0.045}$</td>
<td>Li$<em>{0.35}$ Ni$</em>{0.15}$ Mg$<em>{0.105}$ Fe$</em>{1.395}$</td>
</tr>
<tr>
<td>0.20</td>
<td>Fe$<em>{0.960}$ Mg$</em>{0.040}$</td>
<td>Li$<em>{0.30}$ Ni$</em>{0.20}$ Mg$<em>{0.160}$ Fe$</em>{1.340}$</td>
</tr>
<tr>
<td>0.25</td>
<td>Fe$<em>{0.975}$ Mg$</em>{0.025}$</td>
<td>Li$<em>{0.25}$ Ni$</em>{0.25}$ Mg$<em>{0.225}$ Fe$</em>{1.275}$</td>
</tr>
</tbody>
</table>

For more clarity, the trends of the observed and calculated net magnetic moments for both LNC and LNM ferrite systems for the whole range of substituent concentrations have been shown graphically in Fig. 5.3. The calculated net magnetic moment in each of the series is found in good agreement with that of the experimentally derived magnetic moment.
Figure 5.3. Comparison of variations of observed and calculated magnetic moments with concentration (x) in LNC and LNM series.

5.3 Curie temperature

Variations in Curie temperature with concentration (x) for both LNC and LNM ferrite systems are shown in Figure 5.4. The Curie temperature has been
observed to decrease continuously throughout the concentration in both the LNC and LNM ferrite systems. The observed decrease is more in LNM series than that of the LNC series. However, the observed variations of Curie temperature are in opposite trend to the observed variations of saturation magnetization values in both the series.

The variations in the Curie temperature can be explained on the basis of exchange interactions. As discussed, according to the Neel’s molecular field theory [5], there exist three kinds of exchange interactions in ferrites (A-A, B-B and A-B interactions); and the AB interaction predominates over the other two. As the exchange interaction between magnetic ions would increase with both the density and magnetic moment of the magnetic ions, greater amount of thermal energy will be required to offset the effects of exchange interactions in case of materials having large number of magnetic ions and larger magnetic moments.

The observed variations of Curie temperature are explained on the basis of density of magnetic ions, their magnetic moments and the strength of the exchange interactions between the magnetic cations. It has been mentioned that the decrease in density of magnetic ions and the net magnetic moment is larger in LNM series than that of LNC series of samples. This explains the Curie temperatures in the LNC ferrite system are less than those of LNM ferrite system throughout the concentrations.

The substitution of copper (1μB) and nickel (2μB) ions in place of Fe (5μB) and diamagnetic lithium (0μB) ions would decrease the net magnetic moment by 2μB in LNC series where as the substitution of diamagnetic magnesium (0μB) and nickel (2μB) ions would decrease by 3μB in LNM series. Moreover, the strength of the A-B exchange interaction would also be decreased more in LNM series than in LNC series
as per the cation distribution discussed in the previous section. Since the transfer of large amount (30%) of diamagnetic magnesium ions to A-sites and corresponding migration of Fe ions to B-sites up from x = 0.15 concentration onwards leads to a larger decrease in the strength of the A-B exchange interaction, and thus explains the observed larger decrease in the Curie temperature for the LNM samples. However, since the transferred amount of magnesium in these concentrations is decreased by 10% for every increased step of substitution, a corresponding smaller decrease in Curie temperature is observed.

Figure 5.4. Variations of Curie temperature with concentration (x) in Li_{0.5-x}Ni_{x}Cu_{x}Fe_{2.5-x}O_{4} (LNC series) and Li_{0.5-x}Ni_{x}Mg_{x}Fe_{2.5-x}O_{4} (LNM series).

From the elaborate discussions made in saturation magnetization section, in LNC series, it has been proposed that the transfer of the amount of copper to A-sites is increased by 10% while ensuring a corresponding migration of Fe ions to B-sites.
for every increased step of substitution from $x = 0.15$ onwards. This transfer of copper and corresponding migration of iron in LNC ferrite system are less in magnitude compared to the transfer of magnesium and the corresponding migration iron in LNM system, and thus strength of the A-B exchange interactions in LNC series is more and obviously larger values of Curie temperature can be expected for this system. The observed variations of the Curie temperatures for both the ferrite systems are in accordance with arguments made above and thus further confirm the cation distributions assigned for both the systems.

Nevertheless, it can be seen from the figure that the decrease of Curie temperature at lower concentrations is sharper and linear whereas the decrease is a bit slower and deviated from linearity at higher concentrations in both the ferrite systems. This has been attributed to the non migration of either copper or magnesium to A-sites in each of the series for these concentrations and to a corresponding larger drop in the strength of the A-B exchange interactions due to rapid dilution of octahedral Fe$^{3+}$ ions by Cu$^{2+}$ ions and Mg$^{2+}$ ions, respectively [6,7]. This behaviour is in complete agreement with the assignment of cations in the respective lattice sites for both the systems and confirm the proposed cation distributions made above.

5.4 Coercivity

The observed variations of coercivity with concentration ($x$) for both the LNC and LNM ferrite systems ($x = 0.0$ to 0.25) are shown in Figure 5.5. The coercivity has been observed to increase up to $x = 0.15$ and thereafter decreased sharply for the higher concentrations in the LNC system, whereas a continuous increase and also
higher values of coercivity are observed in the LNM system. However, it should be
pointed out that the increase of Tc in LNM series in the lower concentrations has
been sharp and it has a bit slowed down at higher concentrations indicating that such
a deviation might be associated with a change in the cation distribution among the
lattice sites.

Figure 5.5. Variations of coercivity with concentration(x) in Li_{0.5-x}Ni_{x}Cu_{x}Fe_{2.5-x}O_{4}
and Li_{0.5-x}Ni_{x}Mg_{x}Fe_{2.5-x}O_{4} series

It is clearly evident from the hysteresis curves shown in the previous section
as well as from the present figure that the samples of both LNC and LNM ferrite
systems exhibit low coercivities indicating that all the samples belong to the family
of soft ferrites. The coercivity of magnetic material is the opposing magnetic field
strength required to reduce remanence to zero. Coercivity in a ferrite system is
known to depend on various parameters like magneto crystalline anisotropy, lattice imperfections, dislocations, internal strains, particle size [8] and secondary phases [9]. In the present samples when sintered at elevated temperatures, the lithium ions may get slightly volatilized and as a result there is a possibility of formation of a small quantity of Fe\(^{2+}\) ions in each of the systems. The observed continuous increase and higher values of coercivity in the LNM system has been attributed to additional crystalline anisotropy associated with the presence of such minor quantity of Fe\(^{2+}\) ions [10]. However, in the LNC ferrite system the possible existence of copper ions in multivalent state might be counter balancing the anisotropy contributions caused by the Fe\(^{2+}\) ions, and thus observed relatively lower values of coercivity. Further, the observed deviations in the trends of coercivity variations at higher concentrations in both the ferrite systems may be seen as consequences of occupation of some of the copper or magnesium ions in A-sites apart from their major occupation in B-sites.

### 5.4.1 Dependence of coercivity on grain size

It is well known that the coercivity varies inversely with the grain size. The samples with larger grain size would have greater number of domain walls. In the process of magnetization or demagnetization, the domain wall movement increases with the number of domain walls. The domain wall movement requires less energy than that required by domain rotation [11]. Hence, samples with larger grain size are expected to have low coercivity values.

The observed variations of coercivity and grain size as a function of concentration (x) for both LNC and LNM ferrite systems are shown in Figures 5.6.
Figure 5.6. Variations of coercivity (Oe) and grain size ($\mu m$) with concentration (x) in LNC and LNM series
In the LNM series, the observed variations are completely in agreement with the arguments made above for the whole range of concentrations, whereas in the LNC series there is an exception for this trend in the regions of \( x = 0.05 \) and 0.25. This could be attributed to the structural imperfection with discontinuous grain growth for these samples as discussed in the microstructural properties of LNC ferrite samples in the earlier, in chapter 4. Besides, the transfer of maximum amount of copper ions at \( x = 0.25 \) to the A-sites and the corresponding migration of Fe ions to the B-sites is also contributed to alter the microstructure of that sample remarkably, which in turn seems to dominate the coercivity decrease significantly.

Further, higher values of coercivity, as observed in LNM series, are also influenced by the microstructures of those samples. It has been proposed that the substituted diamagnetic magnesium is segregated partially at the grain boundaries. This might be the major cause for the observed higher values of coercivity in the LNM ferrite system. This proposal has been supported by the lower values of initial permeability (to be discussed in a later section) than LNC series of samples, as the inhomogenieties would act as pinning centers for domain bulging. This kind of segregation at the grain boundaries leading to higher resistivity values is further supported by the resistivity behaviour of these samples (to be discussed in the next chapter) of LNM ferrite system.

5.4.2 Dependence of coercivity on porosity

The variations of coercive field and the percent porosity with concentration \( x \) in both the LNC and LNM ferrite systems are shown in Figure 5.7. The variations of coercive field and porosity follow the same trend at higher
concentrations while they follow the opposite trend at lower concentrations in LNC ferrite system. Whereas, the coercive field and porosity of the LNM ferrite samples behave completely opposite to each other throughout the whole range of concentrations.

Figure 5.7. Variations of coercivity and percent porosity with concentration(x) in LNC and LNM ferrite systems
Similar results of coercive field and percent porosity with opposite trends have been reported in the literature [12]. If the grains of the samples are characterized by intragranular pores with number of pinning points, then there would be scope for increased coercive field when there is an increase in the porosity. But in the present samples, the microstructures indicate that the porosity comes mostly from the intergranular pores only and thus it is obvious that the field required for rotating the spins or bulge the domain walls is opposite to the amount of porosity present. The observed results are in accordance with the above arguments.

5.4.3 Dependence of squareness ratio on porosity

The squareness ratio is essentially a measure of $M_r/M_s$ of the hysteresis loop. If the squareness ratio takes the value of about 0.5, it implies that the sample is produced of single magnetic domains [12]. The present samples display the squareness ratio values in the range from 0.18 to 0.26, which are typical of multidomain magnetic grains composed in the structure. This ratio is also in direct proportion with the coercivity values as well as the percent porosity data.

The variations of squareness ratio ($M_r/M_s$) and the porosity with concentration (x) for both the LNC and LNM ferrite systems are shown in Figure 5.8. Similar to the coercive field-porosity behaviour, the variation of squareness ratio shows a quite contrasting behaviour between lower and higher concentrations of copper in LNC samples. This is attributed to change in site preferences of Cu ions at higher concentrations as discussed in the assigned cation distribution for this system.
Figure 5.8. Variations of squareness ratio, coercivity and porosity with concentration(x) in LNC and LNM series.
The value of intrinsic coercivity in case of Ni-Mg substituted ferrite is more than Ni-Cu substituted is due to the decrease in grain size in Cu ferrite, this resembles with literature report about inverse nature of coercivity with grain size.

5.5 Compositional variations of initial permeability

The observed variations of initial permeability as well as grain size with concentration(x) for all the samples in both LNC and LNM ferrite systems (x = 0.0 to 0.25) are shown in Figure 5.9a and b. The initial permeability in LNC series has been observed to increase initially for the concentration x = 0.05 and the decreased marginally up to 0.15 followed by a slight increase for further concentrations in that system. Whereas for LNM series of samples, a sharp decrease of initial permeability is observed up to x= 0.10 and then it decreased marginally for remaining concentrations. Further, the nickel-copper substitutions in LNC series however resulted relatively higher permeabilities while the nickel –magnesium substitutions in LNM series degraded the permeability compared to the basic composition.

Initial permeability of polycrystalline ferrites is dependent on many factors like grain structure, stoichiometry, composition, impurity contents, saturation magnetization, coercivity, magnetostriction, magneto crystalline anisotropy and porosity [13]. Thus, all these aspects shall be taken into consideration before drawing a specific conclusion for the variation of initial permeability with dopant concentration.
Figure 5.9a. Variations of initial permeability with concentration(\(x\)) in LNC and LNM series samples

In the present work, the variations can be best explained on the basis of average grain size of the samples, which showed a similar variation to the permeability. It is well known from the Globus-Duplex relation for domain wall motion [14] that the initial permeability directly depends on the grain size. The initial permeability has been found to increase with increase of grain size [15]. This is because bigger grains tend to contain more number of domain walls, and the initial permeability being a result of the reversal of domain wall displacements, the greater the number of domain walls the higher is the initial permeability.

The observed variations of initial permeability follow the same trend of grain size in both the series except at \(x = 0.25\) in LNC series as shown in Figure 5.9b. The deviation at \(x=0.25\) may be attributed to the presence of higher concentration of non magnetic copper in the compound and higher porosity.
Figure 5.9b. Variations of initial permeability and grain size with concentration(x) in both the series LNC and LNM.

Higher values of initial permeability for the LNC samples compared to the LNM samples may be attributed to the larger grain size of the samples in that series, and also due to the smaller crystalline anisotropic nature arising out of smaller coercivities for those samples.
5.6 Frequency dependence of permeability

The complex permeability was measured as a function of frequency for all the samples in both the LNC and LNM ferrite systems (x = 0.0 to 0.25) and the dispersion spectra are shown in Figure 5.10. All the substituted LNC series of samples exhibits larger real permeability values than LNM series of samples. Real permeability values ($\mu'$) are found to increase from 20 to 32 with concentration Ni-Cu (x) in LNC series while it is observed to decrease to 6 with the concentration Ni-Mg (x) in LNM series in the (low) frequency region below 50 MHz. In the LNC series, maximum permeability value is obtained for the x = 0.05 sample. The real part of the permeability $\mu'$ remained almost constant up to 10 MHz in LNC series and nearly up to 1 GHz in LNM series, and then began to decrease as the frequency further increases. The imaginary permeability $\mu''$ gradually increased with the frequency, and took a broad maximum at a certain frequency, where the real permeability rapidly decreased. This feature is well known as the natural ferromagnetic resonance. The curve of $\mu''$ exhibits a peak at 50-80 MHz for basic lithium ferrite, which is slightly more than that reported by Smit and Wijn as the natural resonance frequency (50 MHz) for Li$_{0.5}$Fe$_{2.5}$O$_4$ ferrite prepared by conventional ceramic method [16]. The natural resonance frequency has been observed to shift from 106 to 367 MHz for the substituted samples in the LNC series whereas it is 1GHz for the concentration of x = 0.15 in the LNM series. The imaginary permeability $\mu''$ had a maximum value at this frequency for this sample. This enhancement in the imaginary part of permeability will improve the electromagnetic interference shielding effect by transferring magnetic energy into
heat energy. Based on literature [17, 18] a large Snoek's product leads to a large $\mu''$ value in the high-frequency region. Thus, though there observed an increase in the imaginary permeability of substituted lithium ferrites in the LNC series and a decrease in the LNM series, these materials have shown good magnetic behaviour even up to X-band microwave frequencies.

Figure 5.10a. Frequency variations of real and imaginary parts of initial permeability in the LNC series

The frequency response of permeability shows a typical relaxation character. This behavior may be defined by the phenomenon of reversible displacement of domain walls and also due to the rotation of magnetization dipole inside the domain. The permeability response at higher frequency is mainly determined by domain wall displacement resonance and spin rotation resonance [19, 20]. It is also well known that the spin rotation resonance frequency is higher than the domain wall
displacement resonance frequency [20-22]. The spin rotational component is of relaxation type, in which damping friction is thought to be large enough, and its dispersion is inversely proportional to the frequency. The imaginary part of the permeability ($\mu''$) is treated as magnetic loss, arises due to lag between the magnetization and applied alternating field.

Figure 5.10b. Frequency variations of real and imaginary parts of initial permeability in LNM series

The relations between the components magnetizing mechanisms of spin rotational magnetization and domain wall motion in the complex permeability can be described as under:

$$\mu(\sigma) = 1 + \chi_{sp}(\sigma) + \chi_{dw}(\sigma) \quad (1)$$

$$\chi_{sp}(\sigma) = K_{sp} /[1 + j(\sigma / \sigma_{sp})] \quad (2)$$
\[ \chi_{dw}(\sigma) = K_{dw} \sigma_{dw}^2 / [\sigma_{dw}^2 - \sigma^2 + j \beta \sigma] \quad (3) \]

where \( \sigma \) is the RF magnetic field frequency, \( K_{sp} \) is the static spin susceptibility, \( \sigma_{sp} \) the spin resonance frequency, \( \sigma_{dw} \) the static susceptibility of the domain wall motion, \( \sigma_{dw} \) the domain wall motion resonance frequency, and \( \beta \) the frictional damping factor of the domain wall motion.

The static spin susceptibility \( K_{sp} \) is given approximately by [23]

\[ K_{sp} = 2\pi M_s^2 / K_1 \quad (4) \]

and the spin resonance frequency \( \sigma_{sp} \) is proportional to the anisotropy field and given by [24]

\[ \sigma_{sp} = C\gamma(2K_1 / M_s) \quad (5) \]

where \( M_s \) is the saturation magnetization of polycrystalline ferrite, \( K_1 \) is the crystalline anisotropy, and \( \gamma \) is the gyro magnetic ratio. Roughly speaking, it is assumed that the damping constant does not depend seriously on the chemical composition, and \( C \) is thought to be the proportional constant. Therefore, the compositional variations of \( K_{sp} \) and \( \sigma_{sp} \) are attributed to the changes in both the anisotropy value \( K_1 \) and the magnetization value \( M_s \).

As discussed in saturation magnetization studies, the magnetization \( M_s \) is observed to decrease with \( x \) up 0.10 for both LNC and LNM series and took a maximum at \( x = 0.25 \) for LNC and \( x = 0.15 \) for LNM series. It is observed to decrease for further concentrations beyond \( x = 0.15 \) for LNM series. It is expected, from equation (4) that \( K_{sp} \) decreases with the increase in \( x \), and from equation (5)
that $\sigma_{sp}$ shifts higher where $M_s$ decreases. The $\sigma_{sp}$ shifts to higher values in both LNC and LNM series up to the concentration $x = 0.10$. They agree well with the experimental observations. Therefore, the compositional variations of $K_{sp}$ and $\sigma_{sp}$ are attributed mainly to the compositional variation of the magnetization. Additionally, the product of the static spin susceptibility and the spin resonance frequency is

$$K_{sp} \sigma_{sp} = 4\pi C \gamma M_s$$  \hspace{1cm} (6)

This value corresponds to Snoek’s product, which provides a limitation on the permeability spectrum in ferrite [25]. We calculated the values of Snoek’s product for both LNC and LNM series of ferrites, and they are plotted in Figure 5.11, and are listed along with saturation magnetization as a function of the chemical composition in Table 5.3. These variations are similar to those of the saturation magnetization values in the range $x = 0.05$ to 0.15, as was expected from equation (6). The compositional variations of $\sigma_{sp}$ are attributed mainly to the variations of saturation magnetization.
Figure 5.11. Variations of saturation magnetization and Snoek Product with concentration(x)
Table 5.3. Variations of Snoek product and saturation magnetization with concentration (x)

<table>
<thead>
<tr>
<th>x</th>
<th>LNC series</th>
<th>LNM series</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Snoek product GHz</td>
<td>Mₜ (emu/g)</td>
</tr>
<tr>
<td>0.00</td>
<td>0.8</td>
<td>41.6</td>
</tr>
<tr>
<td>0.05</td>
<td>1.1</td>
<td>36.1</td>
</tr>
<tr>
<td>0.01</td>
<td>0.9</td>
<td>25.6</td>
</tr>
<tr>
<td>0.15</td>
<td>3.1</td>
<td>32.0</td>
</tr>
<tr>
<td>0.20</td>
<td>0.7</td>
<td>34.9</td>
</tr>
<tr>
<td>0.25</td>
<td>0.8</td>
<td>45.9</td>
</tr>
</tbody>
</table>

At the beginning of the Ni-Cu substitution, x = 0.05 and for higher concentrations, x = 0.20 and 0.25, K₁ decreases (from where Copper ions migration is proposed from octahedral site to tetrahedral site). Copper ion is a John-Teller ion it is expected that the anisotropic contribution of copper ions would be decreased with the increasing migration of copper ions to tetrahedral site. Therefore, the Snoek product decreases even though the saturation magnetization is decreased at higher concentrations(x).
In LNM series also, the crystalline anisotropy is expected to decrease more rapidly than magnetization $M_s$. This rapid decrease of anisotropy may be due to the increased presence of non magnetic magnesium ions at A- and B- crystallographic lattice sites of LNM compound. Further, the resonant frequency has not been observed for higher concentrations ($x = 0.2$ and $0.25$) due to instrument limitation (limited to 2GHz). As discussed in magnetization studies, the magnesium is proposed to migrate from octahedral site to tetrahedral site from $x = 0.15$ onwards, the decreased presence of diamagnetic magnesium slightly increases the magnetic interactions, increases the anisotropy which in turn increases the resonant frequency. These larger values of resonant frequencies further corroborate the proposed magnesium migration from octahedral site to tetrahedral site.

From the above discussion, it can be concluded that the LNC series of ferrite samples at $x= 0.05$ and the LNM series of ferrite samples at the concentrations beyond $x =0.15$ are promising candidate materials for microwave applications.
References


