Chapter - 1

Introduction
1.1 Introduction

Microwave magnetic materials and devices have been widely used in different radio frequency (RF)/microwave devices such as inductors, filters, circulators, isolators, and phase shifters. With the increasing level of integration of these devices into various applications, there is an enormous need for development of new microwave magnetic materials with desired characteristics. The ongoing demand for miniaturization in electronic devices used in telecommunication and recording industry has stimulated the increase of research in areas like materials development, device analysis, design and microlithography. Wider use of microwave devices in consumer, automotive and industrial radar systems will attract the scientific community to improve their properties.

Higher frequencies (up to 100 GHz) and higher bandwidths (mm wave range) are used in microwave technology. Non conducting materials are essential to ensure total penetration of electromagnetic fields. Ferrimagnetic oxides of iron combine the properties of a magnetic material with that of an electrical insulator. Ferrite elements are widely used in microwave devices, isolators, circulators, phase shifters. For applications, requiring nonreciprocal operation, as in circulators and isolators, there is no alternative to magnetic devices. Due to the very high specific resistance, remarkable flexibility in tailoring the magnetic properties, ease of preparation, and, last but not the least, price and performance considerations make ferrites the first choice materials for microwave applications. However, the frequency range of
operation, the power handling capacity and the temperature sensitivity of ferrite
devices should be improved.

Magnetic materials are used in a large variety of devices like passive circuit
elements, sensors, reading-writing heads, information storage media, etc. The
synthesis and understanding of their properties are essential requirements for their
integration in a certain industrial fabrication process. One class of magnetic materials
which is of great interest in recent years is that of ultra-soft magnetic materials [1].
These materials can be used to extend the operation frequency range of various
passive circuit elements into the GHz regime.

Electromagnetic devices operating in the microwave frequency range and
using ferrites as an essential ingredient can broadly be subdivided into two
categories. The first class of devices makes use of the nonreciprocal behavior
obtainable with ferrites, and the second is based on the fact that the microwave
behavior can be substantially modified by the application of a biasing field. The first
class comprises primarily isolators and circulators, and the second class belongs to
primarily switches, phase shifters, and tunable filters. For non-reciprocal devices the
use of ferrites appears inevitable for the foreseeable future, since no alternative
technology that could achieve similar circuit functions appears on the horizon. For
variable devices, however, an alternative solution (usually relying on
semiconductors) is available in many instances. Thus the future use of ferrites in
these applications will be governed by the details of the technical problem that needs
solution as well as by economic considerations.
The various current and potential applications of ferrites at microwave frequencies require a wide variety of different ferrites. It is the operating frequency, power level and similar considerations decides the choice of material. Nevertheless, it is possible to enumerate a few properties that are generally desirable for all microwave ferrites.

First among these desirable properties is low dielectric and magnetic loss. Dielectric loss tangents can usually be kept below approximately $3 \times 10^{-4}$ by careful control of the composition and the firing schedule. At that level, the dielectric loss in a typical device is negligible compared to magnetic loss and copper loss. For a given material, the magnetic loss, as characterized by the imaginary part of the permeability $\mu''$, depends quite strongly upon the biasing field. For certain materials the value of $\mu''$ relevant in device applications is related to the width of the ferromagnetic resonance line $\Delta H$. Since $\Delta H$ is much easier to measure than $\mu''$ at the appropriate biasing field (usually much less than the field required for resonance, just enough to magnetize the sample substantially to saturation) the available line width data has frequently been used to infer $\mu''$ assuming that the line profile is Lorentzian. This procedure is generally less relevant particularly for low loss materials.

A second desirable property of microwave ferrites is substantial power handling capability. It is generally necessary to distinguish between peak power requirements and average power requirements. The peak power capability of a given material in a given device structure is determined by the rf field strength ($h_{\text{crit}}$) at which spin wave instability sets in. At power levels exceeding the threshold the
material is much more lossy than at low power levels. The instability threshold in
general varies with the biasing field and can also be influenced by variation of the
composition and of the microstructure of the material.

In particular doping a low-loss ferrite with small amounts of strong relaxers
(such as rare earths except Gd) raises the instability threshold significantly.
Improved high-power behavior is also obtained by fine-graining, i. e., processing the
material in such a way that the grain size remains less than approximately 1 µm.
Both methods of increasing $h_{\text{crit}}$ are apt to increase also $\mu''$, because the spin wave
damping (which largely determines $h_{\text{crit}}$) is closely related to the damping of the
uniform magnetization (which determines $\mu''$). Thus we face a rather basic dilemma
when trying to combine low loss with high peak power capability. The capability of
handling high average power levels is largely determined by the thermal
conductivity of the ferrite and its thermal contact with its environment. The prospect
of improving the thermal conductivity substantially is quite remote. It is also
important in this context to keep $\mu''$ and $\varepsilon''$ (imaginary part of the dielectric constant)
as low as possible.

Other desirable properties of microwave ferrites are: 1) insensitivity to
temperature variation; 2) high ratio of remanent magnetization to saturation
magnetization (important for latching phase shifters); 3) insensitivity to strain, and 4)
low magnetostriction [2].

It is well known that when a highly permeable soft magnetic material is
placed near a conductor carrying an electrical current, the inductance of the
conductor will increase. In the ideal case, if the conductor is enclosed in an infinite
magnetic medium, the inductance is increased by a factor of \( \mu_r \), the relative permeability of the medium. Additionally, the quality factor (Q) of such a structure increases if the magnetic losses are small. This means that if a highly permeable material is incorporated into an inductor without producing extra losses, a substantially higher inductance and Q value can be obtained without increasing the size of the device. Alternatively, for the same inductance a much smaller area is needed. Moreover, the cross-talk between inductors on the same chip would be reduced because the magnetic flux is confined within the magnetic core. These issues are particularly relevant for electronic circuits used in mobile communication systems where miniaturization and integration of the inductors used in LC (inductor-capacitor) filters and voltage controlled oscillators are of great interest.

1.2 Currently used materials

Most of the current applications of ferrites at microwave frequencies use polycrystals. The behavior of ferrites can be analyzed with regard to two characteristics, namely, extrinsic and intrinsic. Microstructure based properties such as initial permeability, resonance line width, hysteresis loss and coercive force are of extrinsic nature. Saturation magnetization, Curie temperature, crystalline anisotropy and stress sensitivity belong to the intrinsic category. The physical parameters that suit in an application depend on ferrite chemical composition and the method of preparation.

For applications in the range from several kHz to several MHz, the best choice of the ferrite magnetic material medium is NiZn ferrite. This is mainly because of its high resistivity coupled with useful magnetic properties. Mn-Zn
ferrites possesses high initial permeability and low hysteresis loss and are used in electronic and communication devices operating up to a maximum frequency of 1 MHz. With the development of modern electronic devices like compact power supplies Mn-Zn Ferrites were used at a high frequency i.e. 1 MHz [3]. However in late nineties the operating frequency in the switched mode power supply applications have increased up to 2 MHz [4], by decreasing its operating induction upto 50 mT from 200 mT.

Ni-Zn Ferrite has moderate initial permeability and high Curie temperature. These materials have high resistance compared to Mn-Zn Ferrites. Hence, low eddy current losses are observed. Hence, applications of Ni-Zn Ferrites are spread for frequencies well beyond 2 MHz but limited up to several MHz only.

Magnesium-Manganese ferrites were known as one of the most versatile microwave ferrites. Mg-Mn ferrites possess high resistivity of the order of $10^8$ Ohm-cm [5]. The discovery of magnetic garnets with resistivity in the range of $10^9$ Ohm-cm [6] has replaced the role of Mg-Mn Ferrites in a variety of microwave devices. Unfortunately, both garnets and Mg-Mn ferrites possess low Curie temperature and poor stability of magnetic properties with temperature. The loop squareness and remanence ratios in garnets were low in comparison with the values attainable in Mg-Mn ferrites. The Mg-Mn ferrites are suitable materials for isolators, switches, phase shifters and circulators while garnets are useful as permanent magnets.

Aulock [7] had published a comprehensive survey of microwave materials. These materials are useful in the high technology area of microwave devices [8]. Detailed theory of microwave devices and their historical development was
extensively dealt in the literature (Lax et al. [9], Sooho [10], Riches [11] and Wicker [12]).

1.3 Importance of lithium ferrites

Recently, Lithium ferrites are considered to be one of the most versatile ferrites as it covers a large number of applications. Lithium ferrites are frequently used in the information storage, switching devices and phase shifters because of their excellent rectangular hysteresis loop characteristics [13]. It has a relative high curie temperature of about 640°C, which ensures its applicability over a wide range of technically useful temperatures. At room temperature lithium ferrite has permeability and saturation magnetization higher than those for Yittrium iron garnet. It has low cost when compare to the garnets.

Lithium and Magnesium ferrites are potential materials for applications from low frequency to microwave frequencies. The Li and Mg Ferrites with their high resistivity and low eddy current losses find themselves as useful materials for applications at microwave frequencies. They exhibit rectangular hysteresis loops, which makes them suitable for magnetic information storage devices. Moreover, these materials are cost effective with easy preparation techniques, excellent performance over a wide range of temperatures compared to garnets that have similar applications. This has attracted scientists and technologists for wide spread development of materials in different devices.

1.4 Historical background

The magnesium-manganese (Mg-Mn) and nickel (Ni) ferrite systems were used in early in the development of microwave devices. Substitution of nonmagnetic
ions, such as zinc (Zn), aluminum (Al), and gallium (Ga), into these systems resulted in obtaining a wide range of saturation magnetizations (from 500 to 5000 Gauss) and helped to cover a large segment of the microwave frequency spectrum. Both the Ni and Mg-Mn ferrite systems are characterized by high resistivity ( >10 ohm-cm), good dielectric loss tangents (0.00025 to 0.001), moderate anisotropy fields, and moderate to broad resonance line widths (100 to 800 Oe). However, the electromagnetic behavior of these two systems with respect to the temperature was not good enough to meet the required hysteresis loop properties.

The Mg-Mn ferrite system, which has long been in use in computers, has excellent square-loop properties, and has found applications in latching microwave devices such as switches, phase shifters, etc. However, the low Curie temperatures in this system result in excessive temperature variations in the saturation magnetization, remanence and coercive force. On the other hand, the Ni ferrite system provides adequate temperature performance, but the compositions with acceptable magnetic loss have had poor hysteresis loop properties, precluding their use in latching devices.

With the advent of the magnetic garnets, the Mg-Mn and Ni ferrite systems have been increasingly displaced in a variety of microwave applications. The garnets have provided excellent dielectric and magnetic loss tangents, high densities, low anisotropy, and consequently, a low resonance line width. (In dense materials with minimal levels of relaxing ions, the resonance line width is predominantly attributable to the anisotropy field.) Unfortunately, the Curie temperatures of the garnets are low (280°C). However, the substitution of rare earth ions such as
gadolinium (Gd for yttrium (Y)) provides good temperature compensation with a compromise in the magnetic loss. The loop squareness and remanence ratios in the garnet family, though they are not matchable with the values obtainable in the Mg-Mn system, are sufficient enough for utilization in latching devices. Moreover, the garnets have low coercive forces (< 1 Oe). The reason that the squareness and remanence ratios are not higher is attributable to the low anisotropy of the garnets.

A necessary condition for good squareness and remanence ratios is the dominance of the anisotropy energy over the magnetostrictive energy [14]. Failure to fulfill this condition also causes the garnets to be stress sensitive [15]. The addition of manganese (Mn) decreases the stress sensitivity [16, 17] but does not eliminate it completely. Innovative device designs [18], which minimize mechanical stresses on the ferrite part, can be expected to minimize the deleterious effects of magnetostriction. Despite the few deficiencies of the garnets, the desirable properties mentioned previously have caused the garnet materials to dominate in the microwave industry [19].

The high cost of garnet raw materials (i.e., yttrium oxide and other rare earth oxides) has led to efforts to evolve lower cost systems. One approach has been to replace yttrium with cheaper materials such as calcium [20]. Although this scheme has advantages and the resulting materials could be useful replacements for the more costly garnets in some devices, the success up to this point has been limited, and more exploration is necessary. The two major problems to overcome are remanence ratios which are too low for latching device application and poor temperature performance.
Another approach to finding low cost replacements for garnets has been the development of microwave lithium ferrite compositions, which are the subject of this report. Lithium ferrites have been of interest to microwave device designers for some years. Lithium ferrite, Li$_{0.5}$Fe$_{2.5}$O$_4$, has the highest Curie temperature (670°C) among the ferrimagnetic oxides [21]. This factor, coupled with excellent squareloop properties, has resulted in a domination of the computer core industry by lithium ferrite compositions [22], a situation analogous to the present position of garnets in the microwave industry. These same properties are also important for microwave devices such as high squareness and remanence ratios for latching devices and wide temperature performance for most microwave devices. The high ratios of anisotropy to magnetostriction in lithium ferrites result in low stress-sensitivity of the remanence. Furthermore, lithium ferrites do not contain costly ingredients. Therefore, there exists a scope for sizeable reductions in the costs of manufacturing microwave devices. A number of problems, characteristic of a variety of lithium ferrite compositions, have prevented broad utilization of these materials. Probably the most important have been high dielectric and magnetic loss tangents. High anisotropy, high coercive forces, and low densities have also been instrumental in preventing these materials from reaching their potential.

1.5 Review of the past work on Li based ferrites

In one of the landmark investigations aimed at producing useful microwave materials, Jefferson and West [23] fabricated a series of lithium ferrites containing titanium and aluminum substitutions to provide a range of saturation magnetizations. Manganese, zinc, and nickel were among the other constituents which were
explored. The resulting materials produced desirable phase-shift properties. However, the dielectric loss tangents were high (greater than or equal to 0.004), and no data were given for low-field magnetic loss, coercive force, or density.

Some years later, Vassiliev and Lagrange [24] reported the development of a group of lithium ferrites which were doped with aluminum and manganese. These materials covered a range of magnetizations from 1340 - 3770 Gauss and had satisfactory squareness and remanence ratios for materials fired at 1200°C, and the corresponding coercive forces were varied from 1.7 to 2.5 Oe. And, lower coercive forces (1.1 to 1.9 Oe) were obtained when these compositions were fired at 1250°C, but squareness and remanence ratios were low. Further, the resonance line widths were all greater than 489 Oe, and dielectric loss tangents were all in excess of 0.004. Of course, no low-field loss data was given.

Baba and Banerjee [25] explored a variety of lithium-aluminum and lithium-titanium ferrites. These materials exhibit high losses. Efforts were then concentrated on further investigating lithium-titanium compositions, which were easier to sinter and produced better microstructures. They also studied compositions based on substitutions of copper and manganese, which had resulted promising phase-shift properties. Preliminary magnetic loss measurements in a helical phase shifter indicated loss levels are approaching those of some garnets. However, dielectric loss tangents, coercive forces, and densities were in need of improvement.

Later, Collins and Brown [26] also studied lithium-titanium ferrites and whose compositions covered magnetizations in the range from 2600 to 3600 Gauss. Manganese substitutions were also used to achieve low dielectric losses, but oxygen
Annealing was felt necessary for these materials after firing to yield dielectric loss tangents less than 0.0005.

An investigation by Bunina et al. [27] was concerned with the effect of cobalt additions on the spin wave linewidths ($\Delta H_k$) of a group of lithium-titanium ferrites. It was demonstrated that small quantities of cobalt dramatically increases $\Delta H$, in lithium-titanium ferrites. Bunina et al. further found that the $\Delta H_k$ of the cobalt-doped materials was strongly influenced by the presence of zinc.

Majority of the physical and structural properties of ferrites depend on sintering conditions, preparation methodology [29], microstructure, [30] and types of impurities present in the ferrite. Wu et al. [31] studied the electrical resistivity of different ferrites (Ni, Co, Zn, Mn, Mg) as function of sintering temperature and concluded that resistivity reaches a maximum at a temperature of 1300 °C, and beyond this temperature the resistivity decreases. In another study in which the effect of the substitution of Li$^{1+}$ ions is explored in $\text{Ni}_{0.4}\text{Zn}_{0.6-2x}\text{Li}_x\text{Fe}_{2+x}\text{O}_4$, the Curie temperature increased with increase of Li$^{1+}$ ions concentration while initial permeability decreased [32]. And, the saturation magnetization increased initially for Li$^{1+}$ ions concentration up to $x = 0.15$ and decreased thereafter for higher concentrations. The observed variations were explained on the basis of preferential site occupancies of different ions and their magnetic interactions [33].

The studies of addition of a variety of metal ions in the formula unit in polycrystalline lithium ferrites would give useful information not only to understand the basic mechanisms involved in influencing their structural, magnetic and electrical properties but also to find their utility for microwave application systems.
Accordingly, substituted lithium ferrites have been studied by many investigators by making substitutions of different ions to modify their electric and magnetic properties [34-37].

Ruiyun He et al. [38] discovered the application of titanium substituted lithium ferrites in circulators at 11GHz operating between the temperatures from 20K to 300K. The saturation magnetization and Curie temperature decrease with the increased Ti content. Reddy et al. [39] studied the lithium titanium mixed ferrites. The saturation magnetization decreased with titanium concentration. Kuar et al. [40] reported that in Co substituted Li-Ti ferrite, \( \text{Li}_{0.68-x/2}\text{Zn}_{0.1}\text{Mn}_{0.1}\text{Ti}_{0.46}\text{Co}_{x}\text{Fe}_{1.66-x/2}\text{O}_4 \), dielectric permittivity decreases with the cobalt concentration at low frequency and the value of dielectric permittivity is frequency independent at higher frequencies.

It was found that the Zn addition to lithium ferrite [41] promotes the grain growth and causes densification but it decreases the Curie temperature, loop squareness and remanence ratio. The addition of zinc to the lithium ferrite produces a marked increase in resistivity up to 0.4 atom/formula unit, reported by Pran Krishan et al[42]. However, they found that such an addition decreases the resistivity at higher concentrations. It was also found that the dielectric constant (\( \varepsilon \)) and loss (\( \tan \delta \)) for mixed Li-Zn ferrites decreased with increasing concentration of Fe\(^{2+} \) ions for zinc concentrations of \( x \leq 0.6 \) mole\%. Above 0.6 mole\% of zinc concentration, there was an increase in \( \varepsilon \) and \( \tan \delta \) [43]. The squarness and remanence ratio of lithium ferrites is increased by adding small amount of Ni [44]. The electrical properties of Li-Ni ferrites were studied by Reddy et al.[45]. It was found that the conductivity and dielectric constant decreased with decreasing concentration of ferrous ions in the
ferrite. Khan et al [46] investigated gallium doped lithium ferrite and observed that the lattice constant increased with decreasing gallium concentration. In Al substituted lithium ferrites, the magnetization was found decreased [47].

Lithium ferrite with substitution of different cations and different valences such as Al$^{3+}$, Ti$^{4+}$, Ni$^{2+}$, Co$^{2+}$, etc. was studied extensively [48]. These materials were used in number of applications because of their high Curie temperature, rectangular hysteresis loop characteristics, high saturation magnetization, high dielectric constant and low values of resonance line width and magnetostriction to magnetocrystalline anisotropy ratio.

Conductivity studies as a function of temperature on magnesium ferrite were carried out by Gillaud et al [49] and Bradburn et al [50]. Studies on magnetic properties of magnesium ferrite in association with substituents like zinc and copper were reported [51]. Studies on Lithium-Magnesium ferrites with substitution of tetravalent cations such as Si$^{4+}$, Ti$^{4+}$, Sn$^{4+}$ were performed to understand their influence on magnetic and electrical properties [51].

Nevertheless, the effects of some of the most substituted individual ions with different valences (constituents) on lithium ferrite or mixed lithium ferrites are summarized below in terms of their usefulness (please see Table 1.1) and the actual requirement (please see Table 1.2) for them to be used in application systems:

_Tetravalent ions – Titanium:

The primary function of the titanium is to lower saturation magnetization. Stoichiometric lithium ferrite, Li$_{0.5}$Fe$_{2.5}$O$_4$, had been reported to produce an $M_s$ of approximately 3730 Gauss [52]. As in all ferrites, the magnetization may be reduced
by the substitution of various nonmagnetic ions for iron ions in the octahedral sublattice [53]. Titanium, which was explored by a galaxy of investigators [54-56], also yielded the best combination of properties. Titanium gave better microstructures, resulting in lower coercive forces and line widths than were obtainable in the aluminum-substituted materials. The principal drawback in using titanium is the requirement for compensation of its high valence state; i.e., 4+ compared with 3+ for aluminum. If not properly compensated, the titanium causes iron to become divalent, with an associated sharp increase in losses. In the above studies, the titanium was compensated in part by divalent ions and by additional monovalent lithium. Since lithium ions in excess of approximately 0.5 ions/formula unit preferentially populate tetrahedral sites [57], the net result of such compensation is substantial lowering of the Curie temperature and a greater temperature coefficient.

As for the other required parameters listed in Table 1.2, the effects of titanium are less important. The beneficial decrease of tanδm is mainly attributable to the decrease of $4\pi M_s$. The deleterious effects on $H_c$, $R$, $S$, and porosity are not serious.

*Trivalent ions – Aluminum:*

Because aluminum ions are known to have a strong affinity for octahedral sites, aluminum is often employed in ferrites to lower the magnetization. It was found that aluminum substitutions in lithium ferrite decreases the magnetization to a greater extent but not the anisotropy. Thus, the anisotropy field was often reported to increase with the addition of aluminum.

*Trivalent ions – Manganese:*


Manganese is added for two reasons. Because of the buffering reactions discussed earlier, $\tan \delta$ is diminished with the addition of manganese in lithium ferrite. Moreover, it has been shown that manganese ions can reduce the magnetostriction constants in lithium ferrite [16]. As a result, the stress-sensitivity is lowered, and as a by-product, squareness and remanence ratio are improved. Manganese is also somewhat beneficial as a sintering aid, thereby diminishing porosity and $H_c$. A decrease in the Curie temperature is thus the major negative factor associated with the addition of manganese.

**Trivalent ions – Bismuth:**

The key to the low $\tan \delta_c$, $H_c$, and porosities is the addition of minute quantities of bismuth. Bismuth oxide becomes liquid above 825 °C and forms low-melting eutectics in a variety of oxide systems. By means of this additive, densities > 99% are obtainable at firing temperatures near 1000 °C. Avoidance of high firing temperatures minimizes the oxygen loss and lithium volatility, thereby reducing the occurrence of divalent iron and allowing low values of $\tan \delta$.

**Divalent ions – Zinc:**

Zinc performs a number of beneficial functions. One of the most important is the lowering of the anisotropy field. Therefore, zinc aids in meeting the Polder-Smit magnetic loss criterion [58], and it thus decreases the resonance linewidth. It also provides a two-fold effect in controlling $H_c$. Besides decreasing the anisotropy, zinc had long been known as a fluxing agent in ceramic systems. It thereby promotes densification and grain growth, both of which decrease $H_c$. Zinc also increases $\Delta H_k$, in cobalt-doped systems as shown by Bunina et al [59]. The effect on $\Delta H_k$ is
minimal when cobalt is not present. Some deleterious effects of zinc arise as a consequence of the preferential tetrahedral site occupancy. Such occupancy by nonmagnetic ions increases $M_s$, offsetting the effect of the titanium, and causes a large drop in the Curie temperature. Zinc also decreases the squareness and remanence ratio.

**Divalent ions – Cobalt:**

Divalent cobalt ions on octahedral sites in lithium ferrite lattice are relaxing ions, and very small quantities broaden the spin wave linewidth. At the same time, it causes an increase in $\tan \delta$ and such an increase must be tolerated. Other effects of cobalt substitutions are an increased $H_c$ and a slight degradation of squareness and remanence ratio, which could perhaps be as a result of increased magnetostriction. Interestingly, cobalt does not produce a minimum in anisotropy or resonance linewidth in the lithium-titanium ferrite system. This effect has been noticed and reported by Jefferson and West [54] and has further been explained by Banerjee *et al* [60].

**Divalent ions – Nickel:**

Small quantities of nickel enhance the squareness and remanence ratio of lithium ferrite as reported by West [54]. Other properties are minimally affected.

**Divalent ions – Copper:**

Copper ion could create John Teller distortion and effects the crystal field and acts as a relaxator, and would decrease the dielectric losses [61].

**Divalent ions – Magnesium:**
Small quantities of magnesium would enhance the resistivity values and would increase the relaxation critical frequency [62].

Table 1.1 Effect of constituent metal ions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Tetravalent ion</th>
<th>Trivalent ions</th>
<th>Divalent ions</th>
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<tbody>
<tr>
<td>Ti</td>
<td>B</td>
<td>M</td>
<td>M</td>
</tr>
<tr>
<td>Bi</td>
<td>M</td>
<td>M</td>
<td>B</td>
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<tr>
<td>Mn</td>
<td>B</td>
<td>M</td>
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<tr>
<td>Zn</td>
<td>B</td>
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<td>M</td>
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<tr>
<td>Co</td>
<td>D</td>
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<tr>
<td>Mn</td>
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</tr>
<tr>
<td>Ni</td>
<td>M</td>
<td>M</td>
<td>M</td>
</tr>
<tr>
<td>Cu</td>
<td>M</td>
<td>M</td>
<td>M</td>
</tr>
<tr>
<td>Mg</td>
<td>M</td>
<td>M</td>
<td>M</td>
</tr>
<tr>
<td>$\tan \delta_m$</td>
<td>B</td>
<td>M</td>
<td>M</td>
</tr>
<tr>
<td>$\tan \delta_c$</td>
<td>M</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td>$4\pi M_s$</td>
<td>B</td>
<td>M</td>
<td>M</td>
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<tr>
<td>$\Delta H_k$</td>
<td>M</td>
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<td>M</td>
</tr>
<tr>
<td>$H_c$</td>
<td>D</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td>Squareness ratio</td>
<td>D</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td>Stress sensitivity</td>
<td>M</td>
<td>M</td>
<td>B</td>
</tr>
<tr>
<td>Porosity</td>
<td>D</td>
<td>B</td>
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<td></td>
<td>B</td>
<td>M</td>
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<td></td>
<td>M</td>
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</table>

B= Beneficial       M= Minimal       D= Deleterious

The effects of tetravalent, trivalent and divalent ions on electromagnetic properties are summarized in Table 1.1. The notations of Beneficial, Minimal Effect, and Deleterious are introduced based on our critical review, but shall not be considered as a generally applicable notation. Some of the constituents may behave differently in other ferrite systems. Furthermore, the effects listed in Table 1.1 are pertinent only for the quantities in which they were incorporated into the formulations in the present investigation. For example, a constituent may be beneficial to the remanence ratio when used in small quantities, but may degrade it
in large quantities. Also, the desirable characteristics of microwave materials are listed in Table 1.2.

The primary source of dielectric loss in ferrites at microwave frequencies is generally ascribed to conduction by means of electrons jumping from divalent iron ions on octahedral sites to neighboring trivalent iron ions on octahedral sites. In the practice of sintering lithium ferrites, temperatures well above 1000°C are employed. Considering the fact that lithium ferrites are typically fired at or above the temperatures of 1150 to 1250°C to achieve porosities below 10%, oxygen dissociation and, additionally, lithium volatility are the main factors. As a result, divalent iron ions are generated [63]. The dielectric loss of lithium ferrites can be a few orders of magnitude greater than the value of 0.0002, as shown in Table 1.2. One way to lower the loss is to decrease the number of divalent iron ions present by the well-known buffering reaction [64, 65]. A high degree of porosity in a microwave material is undesirable from several standpoints. Where hysteresis loop properties are important, such as in latching devices, porosity has a deleterious effect on both squareness ratio [66] and $H_c$ [67]. The porosity also has a negative influence on tan $\delta$ [68] and allows moisture absorption, which increases tan $\delta_m$. Lithium ferrites have traditionally been difficult to densify sufficiently. Oxygen dissociation, lithium volatility, and discontinuous grain growth have placed a limitation on the sintering temperatures that could be employed. At the 1150 - 1250°C sintering range which is typical for these materials, porosities are generally about 5 to 10%.
Table 1.2. Desirable characteristics of microwave materials

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Desirable value</th>
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<tbody>
<tr>
<td>$4\pi M_s$</td>
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<tr>
<td>$\tan \delta_m$</td>
<td>$\leq 0.001$</td>
</tr>
<tr>
<td>$\tan \delta_e$</td>
<td>$\leq 0.0002$</td>
</tr>
<tr>
<td>$\Delta H_k$</td>
<td>1-10 Oe</td>
</tr>
<tr>
<td>$H_c$</td>
<td>$\leq 1$ Oe</td>
</tr>
<tr>
<td>Squareness ratio</td>
<td>$\geq 0.75$</td>
</tr>
<tr>
<td>Stress sensitivity</td>
<td>As low as possible</td>
</tr>
<tr>
<td>Porosity</td>
<td>$\leq 1%$</td>
</tr>
</tbody>
</table>

Nevertheless, in spite of the extensive research efforts by many groups all over the world, the above survey of literature abundantly made us clear to realize that the lithium ferrite and mixed lithium ferrites have become important materials for microwave applications because of their low costs, high Curie temperature and low dielectric losses, and their vast scope for explorability.

Further, though there are many efforts to improve the properties of lithium ferrites by way of substitutions of different valent ions, there is not much data in the literature on Ni-Cu and Ni-Mg substituted Li-ferrites. Thus, the above literature survey prompted us to consider the substitution of Ni-Cu and Ni-Mg in Li$_{0.5}$Fe$_{2.5}$O$_4$ to obtain the desired characteristics for materials suitable for microwave applications.
Hence, in the present study, a systematic attempt has been made to explore two series of \( \text{Li}_{0.5-x}\text{Ni}_x\text{Cu}_x\text{Fe}_{2.5-x}\text{O}_4 \) and \( \text{Li}_{0.5-x}\text{Ni}_x\text{Mg}_x\text{Fe}_{2.5-x}\text{O}_4 \) compositions, which were prepared using the conventional solid state reaction method and investigated for their structural, magnetic and electrical properties to find their suitability for microwave applications.

1.6 Aim of the problem

Studies on independent substitutions of nickel, copper and magnesium for iron/lithium have been found to some extent in literature, but to our knowledge no reports have been so far on the co-substitutions of nickel and copper together, and nickel and magnesium together for lithium and iron in lithium ferrite. The study of solubility of Ni-Cu and Ni-Mg in lithium ferrite is interesting not only from the academic point of view related to its influence on electromagnetic properties but also for their technological applications considering the vast potential of applicability of lithium ferrite in the microwave region. Moreover, since the independent substitution of these ions for Li/Fe brings improvement in some of the magnetic and dielectric properties, the co-substitutions of Ni-Cu/Ni-Mg for Li and Fe in lithium ferrite would be expected to throw more light in determining compositions for low dielectric losses and increased Snoek products within the dynamical range of operation (GHz).

In the light of above, it is aimed at carrying out a systematic study on nickel-copper and nickel-magnesium substituted lithium ferrites for improvements in their structural, magnetic and electrical properties. For this purpose, two series of
substituted lithium ferrite systems $\text{Li}_{0.5-x}\text{Ni}_x\text{Cu}_x\text{Fe}_{2.5-x}\text{O}_4$, and $\text{Li}_{0.5-x}\text{Ni}_x\text{Mg}_x\text{Fe}_{2.5-x}\text{O}_4$ ($x = 0.00$ to 0.25 in steps of 0.05) have been investigated.

This thesis attempts to bring out a better understanding of physics involved in the observed variations of various structural and electromagnetic properties of substituted lithium ferrites and suggests the kind of substitute and its level of concentration suitable for microwave applications.

1.7 Thesis organization

The objective of this thesis is to contribute to the understanding of physics on the correlation between the chemical compositions, processing, structure and electromagnetic properties of substituted lithium ferrites for microwave frequency applications. Since our approach is primarily based on an academic pursuit, a substantial effort was made in the area of synthesis and characterization techniques. Followed by the above specific review and description of the problem, the necessary theoretical background relevant for measurements of various parameters are given in Chapter 2.

Chapter 3 provides details of the various experimental methods used in this work. Structural properties and the associated information for cation distribution are presented in chapter 4. The results of various magnetic parameters such as magnetization, coercivity, permeability of substituted lithium ferrites in relation to their crystal and microstructures are discussed in chapter 5. The idea was to investigate the possibility of obtaining good material suitable for microwave applications. The study of electrical properties was presented in chapter 6. The parameters that were systematically discussed include the resistivity, dielectric
constant and dielectric loss in relation to the composition, grain size and critical frequency.

We observed that the magnetization dynamics are strongly influenced by the structural parameters. A positive shift of the resonant frequency with substituent concentration is observed in Ni-Mg substituted series at higher concentrations and the same behaviour was observed at lower concentrations in Ni-Cu substituted series.

A brief summary, major conclusions of the work and future research plans are provided in chapter 7. Part of the work presented/communicated in the form of scientific publications is given at the end of the thesis.
References


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