Chapter - 3

Experimental Details
3.1 Introduction

The usefulness of a ferrite as a microwave magnetic material is influenced by the physical and chemical properties of the material which in turn are dependent on the method of preparation. For obtaining the desired properties, selection of the composition and substituent ions is important besides firing temperatures and schedule. The desired properties can be obtained only by virtue of the presence of certain combinations of the chemical constituents. The valence states of substituent ions in the selected composition influences magnetic, electrical, structural and microstructural properties of the selected compounds.

In this chapter detailed descriptions of method of preparation of the materials under investigation and characterization of the samples are given. Various measurement techniques used for studying the ferrite samples are presented.

3.2 Materials preparation

Ferrites, mostly, as prepared as ceramic materials by the conventional methods [1,2] with very little modifications. The general method described by a typical flow chart for reparation of ferrites is shown in fig.3.1. The basic composition chosen for the present study can be written as Li$_{0.5}$Fe$_{2.5}$O$_4$. The choice of using this particular composition has already been outlined in chapter1. Samples of this composition were prepared by taking the reagent grade oxides of lithium and iron powders which were selected chiefly on the basis of purity and particle size. The initial ingredients were intimately mixed in correct proportions and ground for 12 hours using agate mortar and pestle in the presence of methanol to improve
homogeneity. The resulting mixture was air dried and then pre-sintered in air for 8 hours at 750°C. The pre-sintered ferrite was again ground for four hours in the presence of methanol, air dried and granulated by using 5% poly vinyl alcohol (PVA) as a binder. The granulated powder was then pressed into pellets, which were subsequently sintered in air atmosphere at the temperature of 1000°C for 6 hours. The cooling of the samples was carried out at an approximate rate of 200°C per hour from the respective peak temperature and subsequently the furnace was switched off and allowed to cool naturally by over night to 60°C roughly.

In order to avoid any iron pick-up during the course of milling, agate mortar with pestle was used instead of ball mill for the purpose of grinding. Slow heating especially at temperatures where considerable sintering and shrinkage takes place has been maintained so as to minimize the internal strains.

Followed by this, samples corresponding to the following structural formulae, designated as LNC series and LNM series respectively, have been chosen with a view to study the influence of chemical composition on various properties of the ferrites. The formulae of the two series are as follows:

**LNC series**: \( \text{Li}_{0.5-x}\text{Ni}_x\text{Cu}_x\text{Fe}_{2.5-x}\text{O}_4 \), with \( x \) values ranging from 0.00 to 0.25 in steps of 0.05.

**LNM series**: \( \text{Li}_{0.5-x}\text{Ni}_x\text{Mg}_x\text{Fe}_{2.5-x}\text{O}_4 \), with \( x \) values ranging from 0.00 to 0.25 in steps of 0.05.

The samples of these two series were prepared by using the same procedure discussed above. The starting materials were reagent grade lithium oxide, nickel
oxide, copper oxide, and magnesium oxide and iron oxide powders. Sintering of the toroids and pellets was carried out in air atmosphere for 6 hours at 1000°C. After the sintering process, the furnace was switched off and allowed to cool naturally by overnight to 60°C roughly. The choice behind the selection of sintering temperature, sintering time, and cooling schedule was described in chapter 1.

In order to remove any oxide layer formed to the surface of the samples during firing, necessary grinding of the pellets and toroids was done before carrying out any measurements.

### 3.3 Characterization

Before proceeding with the analysis of the prepared materials, it was felt necessary to ensure that the process adopted in the preparation of the samples was the correct one and that the samples prepared were exactly the ones intended to be studied. The basic composition chosen for the present study, namely Li$_{0.5}$Fe$_{2.5}$O$_4$ whose properties are well established and widely reported in the literature, has been put to the following characterization tests:

(i) X-ray powder diffraction studies,

(ii) Saturation Magnetization, and

(iii) Curie Temperature measurements.

(iv) FTIR Spectra studies

From the X-ray diffraction studies, the lattice constant of the basic composition Li$_{0.5}$Fe$_{2.5}$O$_4$ sintered under different conditions has been determined by using the procedure described in chapter 4. This study reveals that the lattice
constant does not change with the sintering conditions as is to be expected. The measured value of the lattice constant along with the values reported in the literature for the above composition are given in table 3.1 for comparison.

Table 3.1. Lattice constant values in Å for Li$_{0.5}$Fe$_{2.5}$O$_4$

<table>
<thead>
<tr>
<th>Present study</th>
<th>From the literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.287 ± 0.005</td>
<td>8.328 [3]</td>
</tr>
<tr>
<td></td>
<td>8.298 [4]</td>
</tr>
<tr>
<td></td>
<td>8.301 [5]</td>
</tr>
</tbody>
</table>

As is evident from the data that the values reported in the literature differ slightly with each other since the origin and method of preparation of the sample under test is different for different cases [8]. However, the observed value in the present study lies well within the reported range of lattice parameter values.

Table 3.2 Saturation Magnetisation (Ms) in emu/g and Curie temperature (Tc) in °C for the composition Li$_{0.5}$Fe$_{2.5}$O$_4$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Observed value</th>
<th>Reported in the literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ms</td>
<td>42 ± 5%</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>Refs. [3]</td>
<td></td>
</tr>
<tr>
<td>Tc</td>
<td>642 ± 5°C</td>
<td>645 °C</td>
</tr>
<tr>
<td></td>
<td>Refs. [6]</td>
<td></td>
</tr>
</tbody>
</table>
The observed values of room temperature saturation magnetization (Ms) and Curie temperature (Tc) along with the values reported in the literature for the \( \text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4 \) composition are given in table 3.2 for comparison.

Similarly, the observed values of room temperature vibrational frequency of two prominent absorption bands are listed in the Table 3.3 from the FTIR spectra.

Table 3.3. Vibrational frequency of two absorption bands of composition \( \text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4 \)

<table>
<thead>
<tr>
<th>Vibrational frequency</th>
<th>Observed (cm(^{-1}))</th>
<th>Reported (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahedral absorption band</td>
<td>579.39</td>
<td>580 [7]</td>
</tr>
<tr>
<td>Octahedral absorption band</td>
<td>395.24</td>
<td>390 [8]</td>
</tr>
</tbody>
</table>

From the close agreement between the values of various parameters as observed in the present study and those reported in the literature, it is evident that the preparation method of the above materials is satisfactory.

3.4 Energy dispersive spectroscopy

Energy-dispersive X-ray spectroscopy (EDS, EDX, or XEDS) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on the investigation of an interaction of some source of X-ray excitation and a sample. Phillips XL30 ESEM is used to obtain the elemental analysis of the selected composition.

It is observed from the EDS spectra, as shown in Figure 3.1, that the targeted compositions are synthesized as per the chemical equations.
$\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$

$\text{Li}_{0.45}\text{Ni}_{0.05}\text{Cu}_{0.05}\text{Fe}_{2.45}\text{O}_4$

$\text{Li}_{0.40}\text{Ni}_{0.10}\text{Cu}_{0.10}\text{Fe}_{2.4}\text{O}_4$

$\text{Li}_{0.35}\text{Ni}_{0.15}\text{Cu}_{0.15}\text{Fe}_{2.35}\text{O}_4$
$\text{Li}_{0.30}\text{Ni}_{0.20}\text{Cu}_{0.20}\text{Fe}_{2.30}\text{O}_4$

$\text{Li}_{0.25}\text{Ni}_{0.25}\text{Cu}_{0.25}\text{Fe}_{2.25}\text{O}_4$

$\text{Li}_{0.45}\text{Ni}_{0.05}\text{Mg}_{0.05}\text{Fe}_{2.45}\text{O}_4$

$\text{Li}_{0.40}\text{Ni}_{0.10}\text{Mg}_{0.10}\text{Fe}_{2.40}\text{O}_4$
Li$_{0.35}$Ni$_{0.15}$Mg$_{0.15}$Fe$_{2.35}$O$_4$

Li$_{0.30}$Ni$_{0.20}$Mg$_{0.20}$Fe$_{2.30}$O$_4$

Li$_{0.25}$Ni$_{0.25}$Mg$_{0.25}$Fe$_{2.25}$O$_4$

Figure 3.1. EDS spectra of LNC and LNM series of samples

The EDS patterns quantitatively describe the presence of Ni, Cu, Mg, Fe and O elements in the respective sample used in the measurements. The EDS analysis of all the patterns accurately provided estimation of the elemental concentrations as per the specifications mixed at the time of preparation; thus confirming the compositions
of the Ni-Cu and Ni-Mg substituted lithium ferrite samples in correct proportions in the final products.

3.5 SEM studies

JEOL JSM 5600 scanning electron microscope (SEM) was employed to examine the surface microstructures of all the samples of LNC and LNM series of samples. The surfaces of the ferrite materials investigated in the present study are covered by microstructural grains and grain boundaries with the evidences of inter and intragranular pores. The atomic arrangements are governed by the inter atomic forces and chemical bonds. The SEM can be effectively used to test the amorphous or crystalline texture of materials. This is also an effective tool to check the porosity and the presence of physically absorbed and chemically bound water in the form of traces or segregations at the grain boundaries.

3.6 Measuring Techniques

3.6.1 DC resistivity

DC resistivity measurements on the samples were made by using two-terminal method. The samples were kept in between the two electrodes of a measurement cell. For better ohmic contact, silver paste was applied on to freshly ground and cleaned surfaces of the ferrite samples. The current in the samples was measured by using a keithley digital electrometer 614. For temperature variation of resistivity, the cell containing the sample was kept in a furnace and maintained at the desired temperature. Measurements were conducted in such a manner that at each temperature sufficient time was allowed for the sample to attain thermal equilibrium. The dimensions of the samples were approximately 5mm x 3mm.
3.6.2 Dielectric properties

The capacitance C and the dissipation D (dielectric loss tangent, tan δ) of the ferrite samples were measured as a function of frequency in the range 1 KHz to 13 MHz by using HP4192A LF Impedance Analyzer. From the values of C and D, dielectric constant (\( \varepsilon' \)) and AC resistivity (\( \rho_{AC} \)) were calculated according to the formulae [9]

\[
\varepsilon' = \frac{d}{\varepsilon_0 A} \times C \quad \ldots \quad 3.1
\]

and

\[
\rho_{AC} = \frac{1}{W \varepsilon_0 \varepsilon''} \quad \ldots \quad 3.2
\]

where \( \varepsilon_0 \) is the free space permittivity,

\( \varepsilon'' = \varepsilon' \tan \delta \) is the imaginary value of the dielectric constant,

\( W \) is the angular frequency,

\( A \) is the area of cross section of the sample, and

\( d \) is the thickness of the sample.

3.6.3 Curie temperature

Curie temperature measurements were made by a simple technique [10] of attaching a small piece of ferrite material to the lower end of an iron rod attached to an electro-magnet, as described in reference [10]. The iron rod with the ferrite material attached to it was kept in an electric furnace. The temperature of the furnace was slowly raised till the material transformed from ferromagnetic to
paramagnetic. At that particular temperature, the samples loses its magnetic property and left the magnetized iron rod so as to fall under gravity. Clearly, the temperature at which this happened was the curie temperature of the respective sample. The temperature was measured by using a Cr-Al thermocouple. The accuracy of the method was found to be $\pm 5^\circ C$.

3.6.4 Saturation magnetization

Saturation magnetization of the samples was measured by Lakeshore 7400 Vibration Sample Magnetometer (VSM). First, the magnetic moment is measured for a given sample with an accuracy $1 \times 10^{-7}$ emu (0.1 $\mu$emu). From this, we have measured the saturation magnetization, i.e., magnetic moment per unit mass from the Hysteresis loops.

When a sample material is placed in a uniform magnetic field, a dipole moment proportional to the product of the sample susceptibility times the applied field is induced in the sample. If the sample is made to undergo sinusoidal motion, an electrical signal can as well be induced in suitably located stationary pick up coils. This signal, which is at the vibration frequency, is proportional to the magnetic moment, vibration, amplitude and vibration frequency. The material under study is contained in a sample holder; which is centered in the region between the pole pieces of an electromagnet. A slender vertical coil connects the sample holder with a transducer assembly located above the magnet. This in turn, supports the transducer assembly by means of study adjustable support rods. The transducer converts a sinusoidal ac drive signal provided by a circuit located in the console into a sinusoidal vertical vibration of the sample rod and the sample is thus made to
undergo a sinusoidal motion in a uniform magnetic field. Coils mounted on the pole pieces of the magnet pick up the signal resulting from the sample motion. This ac signal at the vibrating frequency is proportional to the magnitude of the moment induced in the sample. However, it is also proportional to the vibration amplitude and frequency. A servo system maintains constancy in the drive amplitude and frequency, so that, the output accurately tracks the moment level without degradation due to variation in the amplitude and frequency of vibration.

This technique depends on the ability of a vibrating capacitor located beneath the transducer to generate an ac control signal, which varies solely with the vibration amplitude and frequency. This signal, which is at the vibration frequency, is fed back to the oscillator where it is compared with the drive signal so as to maintain a constant drive output. It is also phase adjusted and routed to the signal demodulator where it functions as the reference drive signal. The signal originating from the sample in the pick up coils is then buffered, amplified and applied to the demodulator. Then it is synchronously demodulated with respect to the reference signal derived from the moving capacitor assembly. The resulting dc output is an analog of the moment magnitude alone, uninfluenced by vibration amplitude changes and frequency drifts. The magnetic moment (emu) of the sample at different fields can be easily stored and transferred to other plotting software.

3.6.5 Initial permeability

Inductance (L) measurements on the 10 turns, 29 SWG enamed copper wire wound sintered toroidal samples were carried out by using a Hewlett-Packard 4192A LF impedance Analyzer/Agilent Network Analyzer. The average dimensions of the
toroidal samples used in this study were as follows: Outer diameter (OD) = 14mm, Inner diameter (ID) = 10, and Thickness (H) = 3.5mm. Using the value of L, initial magnetic permeability at different frequencies was computed as

\[ \mu_i = \frac{L}{L_0} \quad \ldots \quad (3.5) \]

where \( L_0 = 4.606 \times N \times \log(OD/ID) \times h \times 10^{-10} \) henry is the air core inductance, and \( N \) is the number of turns.

In order to study the variation of initial permeability and loss factor (\( \tan \delta_m \)) as a function of frequency, measurements of L were made at room temperature by using the same setup in the frequency range, 10 KHz to 2 GHz.

3.6.6 FTIR spectra

Room temperature FTIR spectra for all the samples of LNC series and LNM series were recorded on a Bruker FTIR Spectrometer. KBr beam splitter coated with Ge is used for measurements in the mid infrared region (300-750 cm\(^{-1}\)). The FTIR absorption spectra are obtained for all the samples.

When an infrared light interacts with the matter, chemical bonds will stretch, contract and bend. As a result, a chemical functional group tends to adsorb infrared radiation in a specific wavenumber range regardless of the structure of the rest of the molecule. The correlation of the band wavenumber position with the chemical structure is used to identify a functional group in a sample. In the present work, the metal-oxygen covalent bonds are to describe the spinel structures of our samples.
REFERENCES


