CHAPTER -II

SYNTHESIS
AND
CHARACTERIZATION
CHAPTER - II

PART A : SYNTHESIS OF FERRITES

INTRODUCTION

The properties of ferrites greatly depend on their microstructure, which itself is much sensitive to the preparation conditions. Hilpert [1] laid the foundations of ceramic magnets by fabricating ferrites at the Bell Telephone Laboratories. Since then a lot of work has been done on the understanding of ferrite reactions. A number of novel methods have been developed since then for the preparation of homogeneous, fine particle, high density ferrites. The preparation methods have been broadly classified as

1. Ceramic method
2. Precursor method
3. Wet chemical method

2.A.1 CERAMIC METHOD

This is the conventional powder processing method which is commercially accepted since it is possible to maintain the stoichiometry of the final product even at large scale industrial production.
The appropriate metal oxides or their salts, which decompose to give metal oxides, are accurately weighed in the desired proportion and mixed thoroughly. The mixing is usually carried out in liquid suspension (water, acetone, alcohol or kerosene) in a steel ball mill or agate mortar. The slurry is dried or filtered depending upon the suspension medium and then transferred to ceramic crucibles and presintered in air or oxygen atmosphere.

The presintered powder contains nucleation centers that are mixed homogeneously using agate mortar or steel ball mill, which helps in the distribution of nucleation centers formed during presintering. The mixing at this stage determines the grain size as well as the grain size distribution. An organic binder like polyvinyl alcohol (PVA) is often added at this stage. The sample is then pressed in a suitable die at about 5 to 10 x 10^6 Kg/m^2. The pressed material is then fired in oxygen or air between 1000 °C-1300 °C depending upon the substitutions in the ferrite. The completion of solid state reaction gives rise to homogeneous ferrite.

The method involves high temperatures which results in large grain sized ferrites and evaporation of elements like Zn, Li above 1000 °C. The evolution and absorption of oxygen increases porosity, hence high density
ferrites can not be easily obtained. The flow chart of stages in the ferrite, preparation is given in Fig 2.1 for ceramic as well as chemical methods.

2.A.2 PRECURSOR METHOD

This method involves preparing a precursor, which is a solid solution or a compound containing metal ions, $M^{2+}$ and $Fe^{3+}$ in the desired ratio and the decomposition of precursor to yield the ferrite. Some of the precursor methods used are

1. Hydroxide precursor
2. Carbonate precursor
3. Oxalate precursor
4. Hydrazine carboxylate precursor

This method requires low sintering temperatures and hence it is possible to maintain proper stoichiometry and obtain fine particle ferrites. The disadvantage in this method is that the hydroxides are gelatinous and therefore it is difficult to handle, filter and wash them. Sometimes the losses of ions like Cu, Ni occur on complexing with ammonia. The incomplete precipitation may result in undesired composition.
2.A.3 WET CHEMICAL METHOD

Preparation of ferrites from solutions of water soluble salts of the corresponding metals falls in this category. This method includes -

1. Spray reaction
2. Freeze drying
3. Hydrothermal oxidation

There is molecular level homogeneity, small grain size, low porosity and large surface area in this case but it is difficult to use the process for industrial production.

2.A.4 SOLID STATE REACTION

The mechanism of formation of ferrite by solid state reaction between MO and Fe₂O₃ has been discussed by several authors [2-4] on the basis of simple diffusion couple involving divalent metal oxide and Fe₂O₃ as shown schematically in Fig. 2.2.

In the initial configuration there is only one phase boundary between the reactants. After the nucleation of ferrites, this boundary is replaced by two different phase boundaries between MO and ferrite i.e. MFe₂O₄ and other between Fe₂O₃ and MFe₂O₄. At this stage further progress of the
reaction takes place by transport of reactants through the ferrite phase. The three different ways in which it can occur is shown in Fig. 2.2 indicating ionic and electronic fluxes as well as the position of inert markers before and after the formation of ferrite layer.

Case a: In this mechanism called as counter diffusion mechanism, as suggested by Wagner [2], the cations migrate in opposite direction and the oxygen ions are essentially stationary. Under these conditions the position of inert markers does not change. As expected the ratio of the amount of ferrite formed on both sides of line of markers is 1:3. The reaction between MgO and Fe$_2$O$_3$ forming MgFe$_2$O$_4$ has been found to undergo through this mechanism [5].

Case b: Here the anions take part in the diffusion process. In an extreme case, we may have a reaction in which the diffusion of one cation (either Fe$^{2+}$ or Me$^{2+}$) is compensated by an associated flux of anions. If the diffusion rate of Fe$^{3+}$ ions is greater than that of the divalent metal ion, the inert markers should be displaced together with MFe$_2$O$_4$ / Fe$_2$O$_3$ boundary. A typical example for this type of reaction is between ZnO and Fe$_2$O$_3$ to form ZnFe$_2$O$_4$[6].
FIG. 2-1 - FLOW CHART OF STAGES IN THE FERRITE PREPARATION.
**Figure X2**: Schematic representation of possible reaction mechanism involved in ferrite formation.
Case c: In this case ion diffuses through the ferrite layer in a reduced state of Fe$^{2+}$ as indicated by Paulus [7], and oxygen is transported through the gas phase. Oxygen is evolved at $\text{MFe}_2\text{O}_3 / \text{Fe}_2\text{O}_3$ interface and reabsorbed. The inert marker’s position in this case is proportional to the amount of oxygen transported through the external phase. An example for this type of reaction is between NiO and Fe$_2$O$_3$ to form NiFe$_2$O$_4$.

2.A.5 ACTUAL PREPARATION OF FERRITE SAMPLES

In the present case, ceramic method was used to prepare the ferrite samples with general formula $\text{Li}_{0.5-x/2} \text{Co}_x \text{Fe}_{2.5-x/2} \text{O}_4$ (where $x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7$). AR grade Li$_2$CO$_3$, Fe$_2$O$_3$ and CoO were used for the preparation of samples. Oxides and carbonates were accurately weighed using a microbalance, in the required molar proportions and were thoroughly mixed mechanically in an agate mortar in acetone medium. All samples were presintered at 600 °C for 12 hours. The samples were then cooled in the furnace at a rate of 60 °C/hr in air medium.

The presintered powders were hand milled in acetone medium and dried powders were sieved through a fine sieve (mesh 200) to eliminate large sized particles. The powders were pressed in the form of pellets (1 cm
diameter) and torroids (ID = 1 cm, OD = 2 cm) using hydraulic press, applying a pressure of about 10 Pa for five minutes. The pellets and torroids were subjected to final sintering at 1000 °C for 24 hours in air medium in the furnace. The samples were cooled in the furnace at the rate of 60 °C/hr. The samples were removed from the furnace and polished. The physical density of the samples was measured using xylene medium using Archimedes principle.
PART B: CHARACTERIZATION

2.B.1 CHARACTERIZATION BY X-RAY DIFFRACTION

INTRODUCTION

The interplaner distances in solids are comparable to the wavelength of x-rays, electrons and neutrons. Because of high penetrating power, x-rays can provide an important information about the internal structure of matter. The angle of diffraction and the intensity of diffracted beam together are characteristics of a particular crystal structure. Since no two atoms have exactly the same size and x-ray scattering ability, the intensities of diffracted beams, will be unique for every material. This uniqueness helps to identify the structure of material.

In polycrystalline materials like ferrites there will be a great number of crystallites in all possible orientation. Thus when sample in powder form is placed in x-ray beam all possible inter atomic planes will be seen by the beam but diffraction from each different type of plane will occur at its characteristic diffraction angle \( \theta \). Thus by changing the angle of the detector with the specimen it is possible to observe all the possible
diffraction peaks which can be produced from the differently oriented crystallites in the powder.

In the x-ray diffraction pattern, the diffraction maxima occur when the Bragg's law,

\[ 2d \sin \theta = n \lambda \]  

... 2.1

where,

\[ n = \text{order of diffraction} \]
\[ \lambda = \text{wavelength of the monochromatic x-rays} \]
\[ d = \text{interplaner distances} \]
\[ \theta = \text{glancing angle} \]

is satisfied.

There are three principal methods of analysis of crystal structure by x-ray diffraction i.e. Laue method, rotating crystal method and the powder method. The powder method is extensively used for structural analysis of polycrystalline materials like ferrites.

2.B.1.1 Powder method

In this method fine grained polycrystalline specimen enclosed in a capillary tube is kept in the beam of monochromatic x-rays and rotated. In
Figure 2.3  X-ray diffractometer (Schematic)
the recent automated powder diffractometers the para focusing principle is used. The x-ray source, the specimen and the receiving slit are kept on a common circle, called the focusing circle. To meet the Bragg's condition the sample is moved through an angle $\theta$ while the detector is scanned through an angle $2\theta$. Geiger counter is usually used as detector. The diffractograms show variation in intensity of diffraction lines with diffraction angle $2\theta$. Each peak observed in the pattern corresponds to a particular set of inter atomic planes. A schematic diagram for the x-ray diffractometer is shown in Fig. 2.3.

2. B.1.2 EXPERIMENTAL TECHNIQUE

The powder diffraction patterns of the sample in the present case were obtained from USIC, Shivaji University, Kolhapur using CuK$\alpha$ radiation, $\lambda = 1.5418$ Å. The diffractograms were taken within the range of $2\theta$ between $20^\circ$ and $80^\circ$.

In case of cubic system, the interplaner distance is given by

$$d = a / (h^2+k^2+l^2)^{1/2} \quad \cdots \quad 2.2$$

where $a = \text{lattice parameter}$
(hkl) = Miller indices

from equations 2.1 and 2.2 the lattice parameter can be expressed as

\[ a = \lambda / 2 \sin \theta (h^2+k^2+l^2)^{-\frac{1}{2}} \] … 2.3

The diffractograms were indexed in the light of the crystal structure of natural spinel, MgAl$_2$O$_4$. The ‘d’ values for different planes were calculated by using the usual procedure.

The bond lengths $R_A$ and $R_B$ were calculated using the relations,

\[ R_A = a \sqrt{3} (\delta + 1/8) \] … 2.4
\[ R_B = a (3 \delta^2 + 1/16 - \delta /2)^{\frac{1}{6}} \] … 2.5

where \( \delta = u - 0.375 \)

\[ u \] = oxygen parameter

\[ u = (u_1+u_2) / 2 = 0.383 \text{ Å} \]

\[ u_1 = 0.385 \text{ Å} \] for LiFe$_2$O$_4$
\[ u_2 = 0.381 \text{ Å} \] for CoFe$_2$O$_4$
\[ u_{ideal} = 0.375 \text{ Å} \]

The site radii were calculated using the relations.

\[ r_A = a \sqrt{3} (u-1/4) - r_0 \] … 2.6
\[ r_B = a (5/8 - u) - r_0 \] … 2.7

where \( r_0 = 1.35 \text{ Å} \) (Radius of oxygen ion)
The actual density of the ferrite samples was calculated by the xylene method using Archimedes principle. The weight of the sample was taken in air. It was then suspended in xylene for 12 hrs. The loss of weight in xylene medium is measured.

The relation

\[ \rho = \frac{w \rho'}{(w - w')} \]  

where \( w \) = Weight of sample in air  
\( w' \) = Weight of sample in xylene  
\( \rho' \) = density of xylene

was used to calculate the density. Xylene is used as it is a non-reactive medium and does not evaporate easily like benzene, acetone etc.

The porosity was calculated using the relation.

\[ P = \left(\frac{(dx - da)}{dx}\right) \times 100 \% \]

where  
\( dx \) = X-ray density  
\( da \) = Actual density
2. B.1.3 RESULTS AND DISCUSSION

The x-ray diffraction patterns for the samples in the system Li$_{0.5-x/2}$Co$_x$Fe$_{2.5-x/2}$O$_4$ where $x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6$ and $0.7$ are shown in Figs. 2.4 to 2.10. The peaks on the XRD patterns were indexed in the light of natural spinel structure MgAl$_2$O$_4$. According to the spinel structure the planes that diffract x-rays are (220), (311), (400), (422), (333) or (511) and (440). For spinel ferrites the (311) line is the intense line. The observed reflections in the present case are also similar to these. All the samples exhibit cubic spinel structure. The absence of extra lines in the patterns confirms the single-phase formation of the ferrite by completing the solid state reaction with Li$^{1+}$ ion ordering at B site.

The interplaner distances ‘d’ were calculated for each line with respect to the line of maximum intensity. The observed and calculated ‘d’ values are tabulated in the Tables 2.1 to 2.7. The ‘d’ values are in good agreement with each other.

Table 2.8 contains data on composition, lattice parameter, bond lengths and site radii. The reported values of lattice parameter for lithium ferrite [8] and cobalt ferrite [9] are 8.330 Å$^0$ and 8.352 Å$^0$ respectively. The present values of lattice parameter are within the range of reported values.
The variation of lattice parameter 'a' with content of cobalt is shown in Fig 2.11. From the figure, it is seen that the lattice parameter increases linearly with the content of cobalt. Similar results have been obtained for Li-Co ferrites [10,11] and other substituted lithium ferrites [12,15]. The linear variation of lattice parameter indicates that the present system obeys Vegard's law. The linear increase in lattice parameter with content of cobalt can be explained on the basis of ionic size difference of the component ions viz. Li$^{1+}$ (0.69 Å), Fe$^{3+}$ (0.67 Å) and Co$^{2+}$ (0.82 Å). As the concentration of cobalt increases the concentration of Fe$^{3+}$ and Li$^{1+}$ decreases. When an ion with larger ionic radius replaces an ion with smaller ionic radius it results in increase in lattice parameter. The unit cell expands to accommodate the larger ions.

The x-ray diffraction data was further used to calculate the bond lengths $R_A$, $R_B$ and site radii $r_A$ and $r_B$. The values of bond lengths and site radii are given in Table 2.8.

Fig 2.12 shows the variation of $R_A$ and $R_B$ with content of cobalt. It can be seen that both $R_A$ and $R_B$ increase linearly with cobalt content, which can be attributed to the fact that the lattice parameter increases
Fig 2.4 X-ray diffraction pattern of $\text{Li}_{0.45} \text{Co}_{0.1} \text{Fe}_{2.45} \text{O}_4$ ferrite.
Fig 2.5  X-ray diffraction pattern of $\text{Li}_{0.4}\text{Co}_{0.2}\text{Fe}_{2.4}\text{O}_{4}$ ferrite.
Fig 2.6 X-ray diffraction pattern of Li$_{0.35}$Co$_{0.3}$Fe$_{2.35}$O$_4$ ferrite.
Fig 2.7 X-ray diffraction pattern of Li$_{0.3}$ Co$_{0.4}$ Fe$_{2.3}$ O$_4$ ferrite.
Fig 2.8 X-ray diffraction pattern of Li$_{0.25}$Co$_{0.5}$Fe$_{2.25}$O$_4$ ferrite.
Fig 2.9 X-ray diffraction pattern of Li$_{0.2}$Co$_{0.8}$Fe$_{2.2}$O$_4$ ferrite.
Fig 2.10 X-ray diffraction pattern of Li$_{0.15}$Co$_{0.7}$Fe$_{2.15}$O$_4$ ferrite.
Fig 2.11 VARIATION OF LATTICE PARAMETER WITH CONTENT OF COBALT
Fig 2.12 VARIATION OF BOND LENGTHS $R_A, R_B (\text{Å})$ WITH CONTENT OF COBALT
Fig. 2.13 VARIATION OF SITE RADII $r_A, r_B$ (Å) WITH CONTENT OF COBALT
linearly with content of cobalt. Similar results have been reported for substituted lithium ferrites [12,13]. The bond length $R_B$ is greater than $R_A$.

Levine [16] has correlated the decrease in bond length to an increase in covalent character. In the present system the increase in $\text{Co}^{2+}$ content decreases $\text{Li}^{1+}$ and $\text{Fe}^{3+}$ content which results in decrease of covalent character of the ferrite. The bond lengths exhibit a sensitive dependence on covalancy and composition [17,18].

Fig 2.13 shows the variation of site radii $r_A$ and $r_B$ with composition. From the figure it can be observed that the site radii $r_A$ and $r_B$ also increase linearly with the content of cobalt. The increase is attributed to the ionic size difference between the cations. The site radius $r_B$ is greater than $r_A$.

Table 2.9 lists the data on x-ray density, physical density and porosity. The values of porosity lie in the range 10% to 16% for the present samples.
Table 2.1
x-ray diffraction data of Li_{0.45}Co_{0.1}Fe_{2.45}O_{4} ferrite
Lattice parameter = 8.314 Å

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<th>d_{cal}, Å</th>
<th>d_{obs}, Å</th>
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Table 2.2
x-ray diffraction data of Li_{0.4}Co_{0.2}Fe_{2.4}O_{4} ferrite
Lattice parameter = 8.317 Å

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<tr>
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Table 2.3
X-ray diffraction data of Li$_{0.35}$Co$_{0.3}$Fe$_{2.35}$O$_4$ ferrite

Lattice parameter $= 8.320$ Å

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Table 2.4
X-ray diffraction data of Li$_{0.3}$Co$_{0.4}$Fe$_{2.3}$O$_4$ ferrite.

Lattice parameter $= 8.328$ Å

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Table 2.5
x-ray diffraction data of Li$_{0.25}$Co$_{0.5}$Fe$_{2.25}$O$_4$ ferrite

Lattice parameter $= 8.333$ Å

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Table 2.6
x-ray diffraction data of Li$_{0.2}$Co$_{0.6}$Fe$_{2.2}$O$_4$ ferrite

Lattice parameter $= 8.358$ Å

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Table 2.7

x-ray diffraction data of Li$_{0.15}$Co$_{0.7}$Fe$_{2.15}$O$_4$ ferrite

Lattice parameter = 8.366 Å

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Table 2.8

Data on bond lengths (R$_A$, R$_B$), site radii (r$_A$, r$_B$) and lattice parameter (a) for Li$_{0.5-x/2}$Co$_x$Fe$_{2.5-x/2}$O$_4$ ferrites

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<th>x</th>
<th>'a' Å</th>
<th>R$_A$ Å</th>
<th>R$_B$ Å</th>
<th>r$_A$ Å</th>
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Table 2.9

Data on molecular weight (M), physical density (da), x-ray density (dx) and porosity (Po) for Li_{0.5-x/2}Co_{x}Fe_{2.5-x/2}O_{4} ferrite

<table>
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<th>da (gm/cc)</th>
<th>dx (gm/cc)</th>
<th>Po, %</th>
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<td>4.47</td>
<td>5.011</td>
<td>12</td>
</tr>
<tr>
<td>0.4</td>
<td>226.7</td>
<td>4.30</td>
<td>5.13</td>
<td>16</td>
</tr>
<tr>
<td>0.5</td>
<td>229.1</td>
<td>4.54</td>
<td>5.22</td>
<td>12</td>
</tr>
<tr>
<td>0.6</td>
<td>231.2</td>
<td>4.57</td>
<td>5.23</td>
<td>10</td>
</tr>
<tr>
<td>0.7</td>
<td>233.3</td>
<td>4.76</td>
<td>5.24</td>
<td>10</td>
</tr>
</tbody>
</table>
2.B.2 INFRARED SPECTRA OF FERRITES

INTRODUCTION

The infrared spectroscopy is a nondestructive and rapid method of characterization applicable to all phases. The method provides qualitative analysis of complex structures from the view of atomic groups, their linkage and identification of complex molecules. Lattice vibrations occur in the frequency range of 300 cm$^{-1}$ to 600 cm$^{-1}$. These vibrations are unique for specific crystalline compounds and very useful in identification of the sample. The heavy metal oxides and many organic compounds absorb radiation in the above-mentioned range. The lattice vibrational frequencies can be correlated with crystal structure. Frequencies are also found to be dependent on atomic mass and radius of cations or anions. Waldron [19] for the first time used the IR absorption spectra for the analysis of ferrites. He observed vibrational modes and IR active modes of metal oxygen polyhydra in oxides. He also gave the structural correlation to electrical and magnetic properties.

The IR spectra provide an important information about -

1. Completion of solid state reaction
2. Distribution of cations among non-equivalent sites and their valency

3. Nature of metal oxygen bonds

4. Calculation of force constant

5. Nature of electronic transitions and calculation of activation energy (ΔE)

Group theoretical considerations suggest four fundamental IR active modes in the spinel structure. An absorption band $v_1$ (around 550 cm$^{-1}$) is caused by stretching of tetrahedral metal oxygen bonds. The second absorption bond $v_2$ (around 400 cm$^{-1}$) is due to oxygen vibrations in a direction perpendicular to tetrahedral cation oxygen axis. The remaining bands $v_3$ and $v_4$ are associated with the vibrations of metal oxygen ions in the isotropic force field of the octahedral and tetrahedral environment respectively. These bands are located in the far IR region. Waldron and Hafner [19,20] have assigned $v_1$ band to intrinsic vibrations of tetrahedral complexes and the $v_2$ band to octahedral complexes. The IR absorption are being extensively used by many workers to characterize the ferrites[20-23].
2.B. 2.1 EXPERIMENTAL TECHNIQUE

The IR spectra of the samples in the present case were obtained from USIC, Shivaji University, Kolhapur using the Perkin Elmer IR spectrometer (model 783) in the range 200 cm\(^{-1}\) to 800 cm\(^{-1}\), in KBr medium. The force constants were calculated using Waldron’s formula.

2.B. 2.2 RESULTS AND DISCUSSION

The IR spectra of Li-Co ferrites under study are shown in Fig 2.14 and 2.15. The positions of bands is given in Table 2.10. The absorption bands observed in the present investigation are found to be in the range of 600 cm\(^{-1}\) to 580 cm\(^{-1}\) for the band \(v_1\) and 400 cm\(^{-1}\) to 385 cm\(^{-1}\) for band \(v_2\).

Bellad et al [23] have observed the \(v_1\) band in the range 600 to 550 cm\(^{-1}\) and \(v_2\) band in the range 472 to 380 cm\(^{-1}\) in case of Li-Cd ferrites. For Li-Ti ferrites the band \(v_1\) is found to be in the range 590 to 545 cm\(^{-1}\) and \(v_2\) in the range 400 to 370 cm\(^{-1}\) [24]. Shaikh et al [13] have reported \(v_1\) band in the range 610 -565 cm\(^{-1}\) and the lower band \(v_2\) in the range 430-420 cm\(^{-1}\). The absorption bands obtained in the present investigation are found to be consistent with these observations.
Fig 2.14 IR spectra of Li$_{0.5-x/2}$Co$_x$Fe$_{2.5-x/2}$O$_4$ ferrite.
Fig 2.15 IR spectra of Li_{0.5-x}Co_{x}Fe_{2.5-x}O_{4} ferrite.
FIG. 2.16 VARIATION OF FORCE CONSTANT ($K_i$) WITH BOND LENGTH ($R_A$)
FIG. 2.17 VARIATION OF FORCE CONSTANT \( K_0 \) WITH BOND LENGTH \( R_B \)
Table 2.10 Position of IR absorption bands in Li_{0.5-x/2} Co_x Fe_{2.5-x/2} O_4 ferrite

<table>
<thead>
<tr>
<th>( x )</th>
<th>( \nu_1 \text{ cm}^{-1} )</th>
<th>( \nu_2 \text{ cm}^{-1} )</th>
<th>( \nu_3 \text{ cm}^{-1} )</th>
<th>( \nu_4 \text{ cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>580</td>
<td>397</td>
<td>475</td>
<td>332</td>
</tr>
<tr>
<td>0.2</td>
<td>589</td>
<td>395</td>
<td>472</td>
<td>250</td>
</tr>
<tr>
<td>0.3</td>
<td>592</td>
<td>394</td>
<td>470</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>595</td>
<td>392</td>
<td>465</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>597</td>
<td>391</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>600</td>
<td>390</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.7</td>
<td>601</td>
<td>389</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.11 Data on force constants \((K_a, K_o)\), bond lengths\((R_A, R_B)\) for Li_{0.5-x/2} Co_x Fe_{2.5-x/2} O_4 ferrite

<table>
<thead>
<tr>
<th>( x )</th>
<th>( K_a \times 10^5 ) dynes/cm²</th>
<th>( K_o \times 10^5 ) dynes/cm²</th>
<th>( R_A ) Å</th>
<th>( R_B ) Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1.58</td>
<td>0.95</td>
<td>1.923</td>
<td>2.002</td>
</tr>
<tr>
<td>0.2</td>
<td>1.61</td>
<td>0.96</td>
<td>1.924</td>
<td>2.023</td>
</tr>
<tr>
<td>0.3</td>
<td>1.63</td>
<td>0.97</td>
<td>1.925</td>
<td>2.025</td>
</tr>
<tr>
<td>0.4</td>
<td>1.65</td>
<td>0.98</td>
<td>1.926</td>
<td>2.026</td>
</tr>
<tr>
<td>0.5</td>
<td>1.63</td>
<td>0.96</td>
<td>1.927</td>
<td>2.027</td>
</tr>
<tr>
<td>0.6</td>
<td>1.64</td>
<td>0.97</td>
<td>1.929</td>
<td>2.029</td>
</tr>
<tr>
<td>0.7</td>
<td>1.66</td>
<td>0.98</td>
<td>1.932</td>
<td>2.032</td>
</tr>
</tbody>
</table>
The ferrites crystallize in the natural spinel (MgAl$_2$O$_4$) form with the space group $Fd_{3m}$-($O_h^7$). On the basis of group theoretical calculations spinel ferrites exhibit four IR active fundamentals ($T_{lu}$) in the vibrational spectra of normal as well as inverse spinel ferrites. The first three IR bands are due to tetrahedral ($T_d$) and octahedral ($O_h$) coordination compounds, while the forth one is due to some type of lattice vibrations involving tetrahedral cations.

It is observed that $\nu_1 > \nu_2$ for all Li-Co ferrites similar to other spinel ferrites. This may be because there are two types of metal ions in the majority of $T_d$ and $O_h$ sites ($Me^{2+}$ and $Fe^{3+}$). In such samples, we have four types of phonon modes $E^0$, $E^t$, $T_{2}^0$, $T_{2}^t$ where the subscripts O and T indicate the E and T2 symmetry of atomic displacements around Oh and Td metal ions in a normal ferrite[25].

From Figs. 2.14 and 2.15 it can be seen that the IR spectra of the samples under study exhibit four principle bands. After the addition of cobalt the intensity of all the bands decreases continuously up to $x = 0.4$. For the samples with $x > 0.4$ no such variation in observed in the intensity. The decrease in intensity is accompanied by the broadening of bands.
The broadening of bands has been reported earlier by many workers. Patil et al [26] have observed more and more broadening for higher content of cobalt in case of Cd-Co ferrites. They have reported that such broadening is commonly observed in inverse spinel ferrites and has been attributed to statistical distribution of $\text{Fe}^{3+}$ ions on A and B sites. Mohan et al [25] have observed a continuous decrease in intensity with addition of cobalt for all the bands in Li-Co ferrites. They have attributed the decrease to the stretching of tetrahedral metal complex ($T_d$). Mazen et al [24] have observed a similar variation in case of Li-Ti ferrites. They have attributed the broadening to transformation of long-range order into more and more short-range order. They have correlated the transformation to the lowering of crystal symmetry, which reflects in magnetization and Curie temperature, where these properties decrease with decrease in long-range ordering. The decrease in intensity of the bands has been attributed to the decrease in 1:3 ratio of $\text{Li}^{1+}$ and $\text{Fe}^{3+}$ ions on B site with the increase in content of cadmium in Li-Cd ferrites by Bellad et al [23].

The shift in band positions is also observed in the present case. Such a shift in band positions is expected because of the difference in the $\text{Fe}^{3+}$-$\text{O}^{2-}$ distances for the octahedral and tetrahedral coordination compounds.
The center frequency of the bands $v_1$ and $v_2$ show a slight variation with the increase in cobalt content. The band $v_1$ shifts slightly towards higher frequency side and $v_2$ towards lower frequency side. It is known that increase in bond length reduces the fundamental frequency and therefore the center frequency should shift towards lower frequency side. The small shift in $v_1$ towards higher frequency may be attributed to the shifting of Fe$^{3+}$ ions towards oxygen ion on occupation of tetrahedral site by Co$^{2+}$ ions with larger ionic radii, which decreases Fe$^{3+}$-O$^{2-}$ distance even though the average bond length increases [26]. The shift of $v_2$ band towards lower frequency side can be anticipated as bond length $R_B$ increases with $x$.

The third absorption band $v_3$ is attributed to the Li$^{1+}$-O$^{2-}$ complexes at octahedral site [27]. The intensity of $v_3$ band is found to decrease with increase in concentration of cobalt as the content of Li$^{1+}$ decreases with increase in cobalt concentration. The band $v_3$ is observed only up to $x = 0.4$. The $v_4$ band is observed clearly only up to $x = 0.2$ and then it merges with band $v_2$. The $v_4$ band is attributed to the lattice vibrations involving tetrahedral cations.

The force constant is a second order derivative of potential energy with respect to the bond length, the other independent parameters being
kept constant. The force constants were calculated using the standard formulae given in the literature[28].

The variation of force constants with bond lengths is shown in Figs. 2.16 and 2.17. Table 2.11 lists the values of bond lengths $R_A$, $R_B$ and force constants $K_t$ and $K_o$. The force constants are found to increase with bond lengths as shown in Figs. 2.16 and 2.17. Normally increase in bond length leads to decrease in force constants. But Srivastava et al [29] have stated that the bond stretching for tetrahedral site would lead to higher force constants than that for octahedral site. Patil et al [26] have observed some unexpected results for Co-Cd ferrites. They have attributed the results to the fact that oxygen can form under favourable conditions stronger bonds with metal ions even at larger inter nuclear separations. Similar behaviour has been reported for transition metal oxides with atomic numbers in the range 26 to 29 [30] and by Bhise [17], Sasmile [31] and Shaikh [32] in case of Cu-Mg-Zn, Y-Mg-Zn and Li-Mg-Zn ferrites.
2.B.3 SCANNING ELECTRON MICROSCOPY

INTRODUCTION

The scanning electron microscope (SEM) is the most widely used form of electron microscope in the field of materials science. Two electron beams are used simultaneously. One strikes the specimen and other strikes the CRT viewed by the operator. The resultant of the impact of the incident beam is that variety of electrons and photoemissions are produced. These signals are scanned after collection to obtain the resultant on the CRT.

The magnification achieved is purely geometrical. The preparation of samples for SEM is relatively straightforward. If the specimen is not a good electrical conductor i.e. like the ferrites then evaporating a thin metal layer on the surface and electrically grounding it must provide conductivity.

2.B.3.1 ASPECTS OF MICROSTRUCTURE

The most apparent features of ferrite microstructure are grain size, grain boundaries, pores, inclusions, regions of inhomogeneity and crystal defects. The porosity and grain boundaries are inherent features of the ceramic structure. The presence of porosity decreases the physical density. The increased grain growth increases physical density. The properties such
as permeability and coercive force depend upon the porosity. The grain boundaries are related to grain growth. Small grains have more grain to grain contact boundaries and larger will be the hindrance to the motion of Bloch Walls that increases electrical resistance and coercive force.

The important microstructural aspects of ceramics are porosity and temperature –

a. Porosity - Porosity is an inherent phase of sintered ceramics. If the powder sample is compacted and sintered it generates pore structure in which the interstitial voids act as pore volume. The pore volume depends upon particle size and average co-ordination number. The pore structure is very much sensitive to temperature and pressure.

b. Temperature - The microstructure develops during sintering. As the temperature increases three stages are observed.

1. Smoothening - elimination of internal porosity of the discrete particles.

2. Adhesion - The discrete particles develop point to point contact with sufficient strength as the temperature
increases. The temperature at which this occurs is at 2/3 of melting temperature of the material. The solid mass in this stage constitutes mesopores and micropores.

3. Shrinkage: At this stage the entire body shrinks and the isolated voids are eliminated by diffusion of vacancies, which occur at the grain boundaries. In ferrites sintering rate is limited by diffusion rate of oxygen ions. The optimum sintering rate is given by

\[ D_c C_c = D_0 C_o \]  \hspace{1cm} \text{... 2.10}

- \( D_c \) = Diffusion constant of cation vacancies
- \( D_0 \) = Diffusion constant of oxygen vacancies
- \( C_c \) = Bulk concentration of cation vacancies
- \( C_o \) = Bulk concentration of oxygen vacancies

At lower sintering rates the pore growth is less but it may promote discontinuous grain growth. The external variables such as sintering temperature, sintering time, heating and cooling rate, sintering atmosphere influence the grain growth. The internal factors such as nucleation sites also affects the grain growth.
c. Normal Grain Growth

At the time of grain growth grain boundaries move towards their center of curvature. The presence of impurities in the grain boundaries hinders grain growth as the impurities have to be dragged along with grain boundaries when pores or inclusions disappear during heating or somewhat larger grain it formed in the matrix of finer grains.

The grain growth occurs when the following condition is satisfied

\[ D_{cr} = \frac{d_i}{d_{fi}} \]  \hspace{1cm} (2.11)

\( D_{cr} \) = Critical diameter of the grain

\( d_i \) = Diameter of inclusion

\( d_{fi} \) = Volume fraction of inclusion.

When the grain size reaches these critical dimensions the normal grain growth is observed.

d. Exaggerated grain growth

If rapid growth of few grains at the expense of the neighbours takes place on account of lack of homogeneity, we observe the exaggerated grain growth. Presence of impurities and lack of homogeneity favours exaggerated grain growth.
2.B.3.2 MICROSTRUCTURE AND PROPERTIES OF FERRITES

1. Electrical Properties

In polycrystalline ferrites the microstructure plays an important role. Guillaud et.al.[33] have studied the resistivity of Mn-Zn ferrites and have stated that the grain boundaries act as source of resistance. Long Kla et.al. [34] have reported on the effect of grain boundary and structure distortion on resistivity of ferrites. The presence of air gaps results in the formation of inhomogeneous structure, which affects the electrical conductivity. Therefore one of the important factors for resistivity is the grain size. Naik et.al. [35] and Joysulu et.al. [36] have stressed the importance of microstructure in controlling the resistivity of ferrites which depends upon sintering conditions. Heister [37] has emphasized the importance of uniform grain size in minimizing the eddy current losses.

Kramer et.al.[38] have studied the dielectric properties of ferrites and have explained the properties on the basis of grain size, as the dielectric polarization is dependent on the grain size and grain size distribution. Iwauchi [39] has observed the dependence of dielectric properties on
preparation technique. Largenteau et al. [40] have also reported on the grain size dependence of dielectric behaviour of Ni-Zn ferrites.

The grain size depends upon sintering conditions. The higher sintering temperature gives larger grain size and lower porosity. The porous nature of ferrites affects the dielectric properties. The Hall mobility and Seebeck coefficient are also found to depend upon microstructure. Na et al. [41] have studied the dependence of properties like resistivity, charge carrier mobility etc. on sintering conditions in case of cobalt ferrite. Heister [37] has observed fracture at grain boundaries of Mn-Zn ferrite sintered at 1000 °C. He has stated the importance of uniform grain size to minimize eddy current losses.

2. Magnetic Properties

The intrinsic properties such as permeability, ac susceptibility etc. are very much dependent upon grain size. The pinning of domain walls due to porous nature of ferrites affects the permeability.

The linear relationship between initial permeability and grain diameter is demonstrated by Globus and Duplex [42] in YIG. It has been reported that the domain wall relaxation frequency and maximum losses
shift to lower values with increasing grain diameter [43]. As the grain size increases domain wall increases and the domain wall oscillations are more easy while remaining pinned at the grain boundaries. The pinning effect is due to the magnetostatic effect associated with inter granular pores or discontinuity in the direction of magnetization. The coercivity is found to be dependent on pore size and distance between the pores. For low Hc the distance between the pores and pore diameter should be large. Thus Hc depends upon the sintering conditions which determine the microstructure.

The presence of pores breaks the magnetic circuits among the grains and results in the net reduction of magnetization with increased pore concentration. There is also a possibility of formation of closed pore chains at low firing temperatures, leading to the decrease in magnetization. Rikukawa while proposing the diamagnetic field caused by pores has supported such an idea [43].

The importance of fine grained ceramics can be realized since the fine grains can only reverse magnetization by rotation as the domain wall motion is energetically unfavourable in fine grains. Small grain size is favourable since it leads to small domain spacing and reduction of distance through which the wall must move to reverse the magnetization. The
duplex structure is another undesirable type of structure since it lowers the permeability. The segregation of particular impurity produces rapid growth locally while the other undoped area remains unaffected.

2.B.3.3 EXPERIMENTAL TECHNIQUE

The SEM micrographs of the samples in the present case were obtained from National Chemical Laboratory, Pune using scanning electron microscope (Model LICER stereoscan 440).

2.B.3.4 RESULTS AND DISCUSSION

The SEM micrographs of the samples are presented in Figs 2.18 and 2.19. The average grain diameter was measured by counting the number of grain boundaries intercepted by a measured length of a random straight line drawn on the micrograph [44].

The compositional variation of average grain diameter along with porosity is given in Table 2.12. The variation of grain size with cobalt content is shown in Fig 2.20.

The studies from the micrographs reveal the following features
1. The samples show fine grains with smaller sized inclusions spread between them.

2. The porosity varies from samples to sample.

3. The average grain diameter initially decreases up to $x = 0.4$ and an increase in grain diameter is observed for $x > 0.4$. The average grain size for the samples with $x = 0.1$ and $x = 0.7$ are $6.7 \mu m$ and $5.9 \mu m$ respectively, while the sample with $x = 0.4$ has the average grain size of $2.06 \mu m$.

4. Segregation of impurity phase is not observed.

The grain growth mechanism is compromised between driving force for grain boundary movement and retarding force of pores and inclusions during the sintering process. The strength of the driving force, generated due to thermal energy, depends upon sintering temperature and diffusivity of constituent ions.

The mechanism of neck growth as a consequence of migration of vacancies from pore to neck to grain boundary is observed in the micrograph. The samples show fine grains with small sized inclusions spread between them. The NPL group [45-47] has developed the grain growth kinetics of Mg-Zn ferrites. They concluded that impurities and
Fig 2.18  SEM micrographs of Li_{0.5-x/2} Co_x Fe_{2.5-x/2} O_4 ferrite.
Fig 2.19 SEM micrographs of $\text{Li}_{0.5-x/2} \text{Co}_x \text{Fe}_{2.5-x/2} \text{O}_4$ ferrite.
FIG. 2.20 VARIATION OF AVERAGE GRAIN DIAMETER WITH CONTENT OF COBALT
Table 2.12 Data on grain size and porosity for Li_{0.5-x/2} Co_x Fe_{2.5-x/2} O_4 ferrite

<table>
<thead>
<tr>
<th>x</th>
<th>Grain size, (µm)</th>
<th>Po, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>6.7</td>
<td>10</td>
</tr>
<tr>
<td>0.2</td>
<td>4.7</td>
<td>11</td>
</tr>
<tr>
<td>0.3</td>
<td>3.1</td>
<td>12</td>
</tr>
<tr>
<td>0.4</td>
<td>2.06</td>
<td>16</td>
</tr>
<tr>
<td>0.5</td>
<td>2.9</td>
<td>12</td>
</tr>
<tr>
<td>0.6</td>
<td>4.6</td>
<td>10</td>
</tr>
<tr>
<td>0.7</td>
<td>5.9</td>
<td>10</td>
</tr>
</tbody>
</table>
porous nature of sintering material hinder the normal grain growth. Kadam [48] has observed a decrease in grain size with content of cobalt in Co-Mg ferrites and has attributed the behaviour to the SD nature of these ferrites.

The grain size in Cd-Ni-Mn ferrite is found to decrease with Mn content and then an increase for higher concentration of Mn [49]. It seems that Co$^{2+}$ ions do not promote the grain growth if present in smaller proportion. However it can be concluded that the cobalt enhances the grain growth mechanism due to greater solubility in the solid state reaction, higher diffusion coefficients etc. at higher concentrations[50].
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