CHAPTER - II
2.1 Introduction

Ferrites were first formed by nature. The naturally occurring material, magnetite, a ferrous ferrite, aroused considerable scientific curiosity among the Greeks, centuries before the Christian era. Magnetite can be altered by substituting and combining other constituents with it to produce improved ferrimagnetic spinels. Hilpert, one of the earliest experimentalists took out patents on magnetic core material in 1909 [1]. Forestier in 1928 prepared ferrites by precipitation from chloride solutions and subsequent heat treatment [2].

The usefulness of ferrites are determined by their physical and chemical properties which fall into two categories, intrinsic and extrinsic. The method of preparation needs heat treatment for the formation of crystal structure of the material. It influences the intrinsic properties, which are usually understood in terms of cation distribution. However, the details of the heat treatment like firing temperature and time, atmosphere and cooling rate etc. constitute the thermal history of the sample through the imprint on almost all the attendant. In addition to the method of preparation care has to be taken particularly regarding the homogeneity of the material, so that the chemical composition and phase relationship are not adversely
affected by the disproportionate non-equilibrium component of the heat treatment.

There are number of methods that are used for the preparation of ferrites. In general most widely accepted method is ceramic method. It makes possible to the preparation of complex chemical composition, desired microstructure and shape of the final products. It is much economical than other methods. The grain growth, densification and microstructural features develop during sintering process. Ceramics have sufficient mechanical strength to allow it to be formed in desired shape. Ceramics provide a way of avoiding undesired effects such as eddy current losses, which can be suppressed by internal lamination along grain boundary [3].

2.2 Methods of Preparation of Ferrites:

Ferrites are prepared for the use in magnetic devices, either in polycrystalline form or single crystal form. Different techniques have been developed for the preparation of practical ferrites in these two forms. In the preparation of ferrites, the starting materials are allowed to undergo the solid state reaction and therefore, it is usually called as ceramic process. Basically there are 4 steps in the preparation of the ferrite materials for any required application.

1. preparation of material to form an intimate mixture in the desired composition,
2. presintering and calcination,

3. converting the raw ferrite into powder and pressing the powder into the desired shape,

4. sintering to produce a highly densified product,

The general methods for the preparation of ferrite compositions are -

   a) oxide method

   b) Decomposition method

   c) Hydroxide perception method

   d) Oxalate precipitation method.

2.2.1 Oxide Method:

This is most extensively used in the commercial production of ferrites, which requires little chemical knowledge. High purity oxide materials are mixed together in the required proportions. They are either mixed manually or wet milled with steel balls for a few hours. After milling, the mixture is dried up and passed through the mesh screen. The mixture is calcinated at elevated temperature and powdered and dried. The powder is then pressed into a suitable shape with the help of hydraulic press and finally sintered. The purity of oxides, particles size and shapes are important for desired application [4]. They must possess high resistivity so that on mixing and after calcination the homogenous ferrite can be achieved.
2.2.2 Decomposition Method:

Instead of using the oxides, starting with carbonates, nitrates and oxalates, one can obtain oxides with required proportion by thermal decomposition. They are mixed in the required proportions and pre-heated usually in air producing oxides by thermal decomposition. The preheated oxides "In Situ" can more readily undergo solid state reaction [5]. Other details of this method are similar to oxide method.

2.2.3 Hydroxide Precipitation Method:

Attempts have been made to precipitate simultaneously the required hydroxide from a solution to avoid lengthy milling process involved in dry mixing. The precipitate contains the required metal ions in correct proportion already intimately mixed. Knowledge of solubility products of the substances is essential in order to determine the pH value of the complete precipitation. Economos [6] established this method for the preparation of ferrites. Ultrafine spinel ferrites and preparation of VIG [7] are possible by this method. Chemical process must be understood quantitatively in order to ensure the simultaneous precipitation of the hydroxides. Sato and his co-workers [8,9] prepared ultrafine spinel ferrites by this method and studied their properties.
2.2.4 Oxalate Precipitation Method:

If the salts of different cations have the same crystal structure form, the precipitate may consists of mixed crystals. This mixing on the molecular scale will lead to the formation of the ferrite at much lower temperatures than those for the usual oxide mixtures. Oxalate of Mg$^{2+}$, Mn$^{2+}$, Fe$^{2+}$, Co$^{2+}$, Ni$^{2+}$ and Zn$^{2+}$ give mixed crystals rather than crystal mixtures. X-ray diffraction studies have revealed that the precipitates are single phase.

Precipitation of metallic oxalates is preferable for two reasons. The first reason is that precipitation can be carried out using ammonium oxalates, which will not leave any residue after heating. Secondly, most of the metal oxalates have very similar crystal structure so that precipitation tends to produce mixed crystals, which contain the metallic cations in exactly the same proportions in which they were present in the solution. Hence mixing in the correct ratios can be achieved on a molecular scale [6]. If the precipitation occurs at widely different rates, mixed crystals do not form uniformly.

2.3 Sintering:

This is the most important heat treatment process by which a mass of compact powder is transformed into a dense object. There are two steps of sintering one is pre-sintering and the other is final sintering.
2.3.1 Pre-Sintering:

Pre-sintering is to be carried out, to decompose higher oxides and carbonates which reduces the evolution of gas in the final sintering process. This process also helps to homogenize the material and to reduce the effect of variation in the composition of the initial raw materials and to control the shrinkage of the material that occurs during the final sintering process. The raw material partly react to form final product during pre-sintering and the amount of reaction depends on the reactivity of the components and on pre-sintering temperature [10]. The ferrite is formed essentially in pre-sintering but raw ferrite thus formed has poor qualities in two respects. First, its decomposition is not expected to be homogenous and second, it contains pores as a result of the evolution of oxygen. Wagner [11] reports the use of high temperature furnace for pre-sintering purpose.

2.3.2 Final Sintering:

This is the most common process of integrating and preparing solid state materials. Final sintering of ferrite product must fulfil following three requirements -

i) to bond the particles together so as to impact sufficient strength to the products.

ii) to densify the grain compacts by eliminating the pores and
iii) to homogenise the materials by completing the reactions left unfinished in the pre-sintering stage.

The first two requirements are closely related as far as their mechanism are concerned. We assume that the cations are present in correct proportions, but they are affected by the time and temperature of sintering, the partial pressure of oxygen or any other sintering atmosphere and the cooling rate. Predujin and Peloshek [12] have commented "A quantitative study of the contribution of each parameter to the magnetic properties should take years of work or be perhaps impossible. However by qualitative considerations good results can be obtained and improvement can be achieved. Extensive reviews on grain growth and sintering are available [13,14]. During sintering densification and grain growth occur, and at the same time to lead variety of microstructure.

Volume diffusion is the main transport mechanism in an ionic solid such as spinels. Nabarrao [15], Herring [16] theory for diffusional microcreep is considered to be main mechanism for densification. The surface of the pores acts as a source of vacancies. Migration of vacancies occur as a result of concentration gradient between the curved surface of the pores and equilibrium vacancy concentration under the flat surface (C₀). The vacancy concentration (Cᵣ) under the surface of radius of curvature (r) is given by Kelvin's equation

\[
\frac{2r \pi a^3}{r.KT} Cᵣ = C₀ \exp \left( \frac{2r \pi a^3}{r.KT} \right) \quad \text{...... 2.1}
\]
Where, $a^3$ is the vacancy volume. As the concentration of grain boundary is equal to $(C_0)$, vacancy migrates at a temperature where the mobility is sufficiently high from the pore surface to the grain boundaries.

In grain growth the grain boundary energy is decreased when the boundaries move to their centre of curvature. The rate of grain growth is given by [17]

$$D - D_o = Kt^n$$  \[2.2\]

Where, $D_o$ is the original particle size, $K$ is the temperature dependent factor and $t$ is time. The expected rate of grain growth is proportional to $t^\alpha$. However, in practice it is proportional to $t^{1/3}$, due to the presence of impurities and inclusions in the grain boundaries. Zener [18] has given a purely empirical relationship for discontinuous grain growth

$$D_{cr} = \frac{d_i}{f_i}$$  \[2.3\]

Where, $d_i$ is the diameter of inclusion and $f_i$ is the volume fraction. The discontinuous grain growth may lead to a ‘duplex’ structure of giant grains in a matrix of small grains. This appears to be quite common in technical ferrites leading to a characteristically porous structure. It is because the rapid growth entraps pores in the grains, which is scarcely possible to eliminate due to their great distance from the grain boundaries.
2.4 Sintering Atmosphere:

Careful control of sintering atmosphere is very important as it affects the exact proportions of metal ions and also the correct valency in the final product. Fe, Mn, Cu and Co have variable valance states and while preparing ferrites containing such metal ions, care should be taken of sintering atmosphere. Strict control of the furnace temperature and sintering atmosphere are being considered to be important because these variables have very prominent effects on the magnetic properties of the product. The partial pressure of oxygen atmosphere in the furnace must be equal to the equilibrium in order to maintain the stoichiometry and the desired Valance State. It is found that the oxygen deficiency causes iron and some other ions to exist in more than one-valence states. Excess of oxygen will result in the formation of cation vacancies. An oxygen deficient ferrite corresponding to the formation of excess ferrous ions will result in the co-existence of ferric and ferrous ions. This gives rise to an electrical conductivity mechanism ($\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$) with low activation energy. To maintain the high resistivity, a slightly oxidising atmosphere appears to be desirable. Investigations of the effects of the firing atmospheres have been reported by Darken and Gurry [19], Smiltens [20], Woodhouse and White [21], Paladino and Economos [22].
2.5 Hot Pressing:

Sintering with simultaneous application of an external pressure is called hot pressing. A mechanical pressure can increase the driving force for densification by acting against the internal pore pressure, without increasing the driving force for grain growth [23]. The hot pressing process has been increasingly used on an experimental scale during the last few years. In this process both high pressure and high temperature are applied simultaneously [24]. In this method, the powder is enclosed in a flexible evacuated container made up of rubber or plastic. The container is immersed into a hot oil bath, to which high pressure is applied. The effect is to give much more uniformity and high density than conventional methods. It also encourages continuous grain growth and favours to obtain low porosity and grain size. It seems apparent that pressure should lead to a high degree of compaction and enhance contact between grains during sintering. At 1000°C ferrites have sufficient plasticity to flow to a considerable extent at high pressures. It is favourable to produce high-density compacts in which the original grain size is maintained. The process of hot pressing is benefitted when the compositions contain the volatile elements.

2.6 Mechanism of Solid State Reaction:

According to Wagner [25] the spinel phase $\text{Mg}^{2+}\text{Fe}^{3+}\text{O}_4$ is formed at the interface of $\text{MgO}^{2+}$ and $\text{Fe}_2^{3+}\text{O}_3$. The reaction proceeds by the counter diffusion of the cations $\text{Mg}^{2+}$ and $\text{Fe}^{3+}$ in the ratio 3:2 through the practically
rigid lattice of oxygen anions. (Fig. 2.1Q). If we provide the interface with the markers, the spinel should have formed an either side of markers in the ratio 1:3. The markers should undergo no shift during the reaction. The ratio for MgAl₂O₄ is found to be 1:3 whereas it is 1:2:7 for MgFe₂O₄ – Fe₃O₄ [26].

According to Wagner model in case of the MgFe₂O₄ formation the Fe₂O₃ at MgFe₂O₄ – Fe₂O₃ phase boundary dissolves into the spinel phase without any loss of oxygen i.e. iron remains in the trivalent state. The dissolution of Fe₂O₃ into spinel is accompanied by the loss of oxygen. Assuming counter diffusion model with Mg²⁺ and Fe³⁺ instead of Mg²⁺ and Fe³⁺ and with oxygen transport through the gas phase. The volume ratio of MgFe₂O₄ phase formed on both sides of the markers should be 1:2 and there should be smaller displacement of the markers. The effect is also called as Kirkendall effect [Fig. 2.1b]. This mechanism has the important consequences that the reaction becomes dependent on the oxygen partial pressure. The reaction rate will increase by reducing conditions, because large concentration gradients are set up over the reaction layer and more Fe₂O₃ can dissolve into the spinel phase [27]. It is proved earlier [28] that formation of MgFe₂O₄ takes place due to Kirkendall effect. It is also reported that the similar phenomenon occurs during the formation of NiFe₂O₄ ferrites [29]. The completion of solid state reaction can be confirmed by X-ray diffraction technique.
Fig. 2.1 – MECHANISMS OF THE FORMATION OF
a) MgAl₂O₄ AND b) MgFe₂O₄.

\[ \text{Marker} \]

\[
\begin{array}{c}
\text{MgO} \\
\text{Al}_2\text{O}_3 \\
\hline
\text{MgAl}_2\text{O}_4 \\
\text{MgO} \\
\text{Fe}_2\text{O}_3 \\
\hline
\text{MgFe}_2\text{O}_4 \\
\text{MgO} \\
\text{Fe}_2\text{O}_3 \\
\hline
\end{array}
\]

\[
\begin{align*}
\text{a)} & \quad \text{Counter diffusion of Mg}^{2+} \text{and Al}^{3+} \text{cations, no anion diffusion (Wagner mechanism).} \\
\text{b)} & \quad \text{Counter diffusion of Mg}^{2+} \text{and Fe}^{2+} \text{cations, no O}^{2-} \text{anion diffusion but reduction and oxidation of Fe ions at the respective phase boundaries which is equivalent to an oxygen transport through the gas phase.}
\end{align*}
\]
2.7 Actual Method For Preparation of Ferrite Sample:

The simplest and widely accepted method for the preparation of ferrite is the ceramic method. This is economical hence it is preferred in the present work. A flow chart of the preparation process of polycrystalline ferrite is as shown in fig. 2.2. A. R. Grade Ferric oxide, Copper oxide, and Magnesium oxide are used as raw materials. The chemical formula and other details are given below. These raw materials are weighted accurately to required molar proportions using single pan semi-micro balance for the preparation of following systems.

\[ \text{Cu}_{x,0.5}\text{Mg}_{x}\text{Fe}_2\text{O}_4 \text{ where } x = 0, 0.15, 0.3, 0.45, 0.6, 0.75, 0.9 \text{ and } 1 \]

\[ \text{Cu}_x\text{Fe}_{3-x}\text{O}_4 \text{ where } x = 1, 0.8, 0.6, 0.4, \text{ and } 0.2 \]

\[ \text{Mg}_x\text{Fe}_{3-x}\text{O}_4 \text{ where } x = 1, 0.8, 0.6, 0.4 \text{ and } 0.2 \]

The weighed oxides of a particular sample of a series are mixed together thoroughly in an agate motar with acetone. This mechanical blending is carried out in acetone medium carefully without any loss of powder. The mixture was dried at a temperature of about 100°C. The dry mixtures were then transferred into platinum crucibles and were pre-sintered at 800°C for 10 hours in air in a glover furnace. Then the furnace was cooled slowly. The temperature of the furnace was measured with the help of Cr-Al thermocouple, which was calibrated by usual method before measuring the temperature of the furnace. The pre-sintered powder was
Flowchart of the stages in the ferrite preparation.

Preparation of Ferrite composition
(Dry process) (Wet process)

Weigh and mix the starting material
Oxides
Carbonates, oxalates, nitrates etc.

Decompose by heat

Mix, usually by mill.

Weigh and dissolve the starting material

Precipitation

Filter, dry and powder as necessary

Pre-Sinter

Mill

Sinter

Mill→add, binder and lubricate if necessary

Press, Final sinter and Finish

Fig 22.
ground in an agate mortar in a acetone medium for two hours and powder was collected in a clean glass tube.

2.7.1 Pellet Formation:

About two grams of pre-sintered dry powder was taken in an agate mortar and milled to have fine particles. This dry powder was then transferred into a die having 1.5 cm diameter and pressed in a hydraulic press with the pressure of the order of 8 to 10 tonnes per square inch about 5 minutes. After removing the load, pellet was taken out from the die. Several pellets of different compositions were prepared using the same technique. Toroids were also prepared with the help of toroid die.

2.7.2 Final Sintering:

The pellets and toroids thus prepared were placed on a platinum foil and kept in a glow-bar furnace at a temperature of 1150°C about 24 hours in an air medium for the completion of solid state reaction. Then the furnace was cooled at the rate of 80°C/hr.

2.8 Density Measurements:

The density of ferrite samples can be determined by measuring both the weight and volume of the samples but it gives some error, because part of the uncertainty is being due to the inhomogenities and shape in the materials. Hendricks and Jefferson [30] have developed a method to measure the density accurately. This method depends on immersing the
solid in some liquid of known density in which the solid is completely insoluble. For this measurement, liquid pyknometer was used. It was designed by Johnston and Adams [31]. In the pyknometric method, the volume of the solid was more accurately found by determining the changes in weight. The basic equation for the calculation of density ($d_s$) of solid is

$$d_s = \frac{W_s}{V_{DL}}$$ ........2.4

Where, $V_{DL}$ is the volume corresponding to ‘$W_s$’ grams of solid. $V_{DL}$ can be regarded as the amount of liquid ($V_{DL}$ grams of density $d_L$) which would be displaced if a $W_s$ gram of solid was put into a completely liquid filled vessel.

The densities of the present samples were determined by liquid immersion method described above. For this measurement toluene is used as a liquid. The measured densities for all the compositions are listed in Tables 2.1 to 2.3. The porosity of the samples was calculated by using the formula,

$$P = \frac{dx - ds}{dx} \times 100$$

and

$$dx = \frac{8M}{Na^3}$$
where, $d_s$ is the actual density calculated by liquid immersion method. $M$ is the molecular weight, $a$ is the lattice constant and $N$ is the Avagadro's number. The values of porosity and x-ray densities are also listed in the corresponding Tables. It is observed that the porosity of these samples is - 15-22%. However no systematic variation is observed with composition. This is because of the ceramic nature of the materials.
### Table 2.1 Physical Constants of Cu$_{1-x}$Mg$_x$Fe$_2$O$_4$ system

<table>
<thead>
<tr>
<th>Composition</th>
<th>Molecular weight M gms</th>
<th>Packing Density $D_s$ gms/cm$^3$</th>
<th>X-ray Density $D_x$ gms/cm$^3$</th>
<th>Porosity $P_o$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuFe$_2$O$_4$</td>
<td>239.23</td>
<td>4.273</td>
<td>5.49</td>
<td>22.16</td>
</tr>
<tr>
<td>Cu$<em>{0.85}$Mg$</em>{0.15}$Fe$_2$O$_4$</td>
<td>233.33</td>
<td>4.123</td>
<td>5.27</td>
<td>21.85</td>
</tr>
<tr>
<td>Cu$<em>{0.7}$Mg$</em>{0.3}$Fe$_2$O$_4$</td>
<td>227.45</td>
<td>3.947</td>
<td>5</td>
<td>21</td>
</tr>
<tr>
<td>Cu$<em>{0.55}$Mg$</em>{0.45}$Fe$_2$O$_4$</td>
<td>221.57</td>
<td>3.968</td>
<td>5</td>
<td>20.64</td>
</tr>
<tr>
<td>Cu$<em>{0.4}$Mg$</em>{0.75}$Fe$_2$O$_4$</td>
<td>209.98</td>
<td>3.79</td>
<td>4.7</td>
<td>19.36</td>
</tr>
<tr>
<td>Cu$<em>{0.1}$Mg$</em>{0.9}$Fe$_2$O$_4$</td>
<td>203.92</td>
<td>3.74</td>
<td>4.6</td>
<td>18.69</td>
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<tr>
<td>MgFe$_2$O$_4$</td>
<td>200.00</td>
<td>3.70</td>
<td>4.5</td>
<td>17.77</td>
</tr>
</tbody>
</table>

### Table 2.2 Physical Constants of Cu$_x$Fe$_{3-x}$O$_4$ system

<table>
<thead>
<tr>
<th>Composition</th>
<th>Molecular weight M gms</th>
<th>Packing Density $D_s$ gms/cm$^3$</th>
<th>X-ray Density $D_x$ gms/cm$^3$</th>
<th>Porosity $P_o$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuFe$_2$O$_4$</td>
<td>239.23</td>
<td>4.273</td>
<td>5.49</td>
<td>22.16</td>
</tr>
<tr>
<td>Cu$<em>{0.8}$Fe$</em>{2.2}$O$_4$</td>
<td>237.69</td>
<td>4.409</td>
<td>5.037</td>
<td>17.89</td>
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<tr>
<td>Cu$<em>{0.6}$Fe$</em>{2.4}$O$_4$</td>
<td>236.15</td>
<td>4.300</td>
<td>5.34</td>
<td>19.47</td>
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<tr>
<td>Cu$<em>{0.4}$Fe$</em>{2.6}$O$_4$</td>
<td>234.60</td>
<td>4.209</td>
<td>5.29</td>
<td>20.43</td>
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<tr>
<td>Cu$<em>{0.2}$Fe$</em>{2.8}$O$_4$</td>
<td>233.06</td>
<td>4.312</td>
<td>5.51</td>
<td>21.60</td>
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### Table 2.3 Physical Constant of Mg$_x$Fe$_{3-x}$O$_4$ system

<table>
<thead>
<tr>
<th>Composition</th>
<th>Molecular weight M gms</th>
<th>Packing Density $D_s$ gms/cm$^3$</th>
<th>X-ray Density $D_x$ gms/cm$^3$</th>
<th>Porosity $P_o$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgFe$_2$O$_4$</td>
<td>200.00</td>
<td>3.70</td>
<td>4.5</td>
<td>17.77</td>
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<tr>
<td>Mg$<em>{0.8}$Fe$</em>{2.2}$O$_4$</td>
<td>206.30</td>
<td>3.952</td>
<td>4.7</td>
<td>15.91</td>
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<td>Mg$<em>{0.6}$Fe$</em>{2.4}$O$_4$</td>
<td>212.61</td>
<td>4.012</td>
<td>4.8</td>
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<td>Mg$<em>{0.4}$Fe$</em>{2.6}$O$_4$</td>
<td>218.91</td>
<td>4.180</td>
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<td>Mg$<em>{0.2}$Fe$</em>{2.8}$O$_4$</td>
<td>225.22</td>
<td>4.213</td>
<td>5.2</td>
<td>18.98</td>
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REFERENCES


