CHAPTER I

General Introduction
Magnetite, Fe₃O₄, probably the first ever known magnetic material which was put into practical use by ingenious navigators in early days in the form of magnetic needle in compass as to get guided the direction of their voyages. Its saturation magnetization was measured in 1890 by Du Bois [1] and considered it as ferrous ferrite, FeO.Fe₂O₃. Manganese zinc ferrite is a naturally occurring mineral called franklinite discovered by Berthier in 1819. It has been found in only two places around Franklin, New Jersey. The mineral is slightly magnetic because of contamination and oxidation and it was Snoek [2] who synthesized it first and recognised its potential as a high frequency magnetic core material. Manganese zinc ferrite is an isomorph of magnetite and as such has the cubic spinel structure. A variety of synthetic ferrites were then prepared by Hilpert [3] who
suggested the basic formula for the ferrites as MO$_2$Fe$_2$O$_4$, where M is the divalent metal ion.

Ever since the realisation of the application of these natural magnetic materials, several magnetic materials of interesting compositions have been synthesized, characterized and put them in use for the benefit of humanity. Three basic types or classes of magnetic crystal structures have found wide applications in electronic industries and other industrial pursuits. Each of these types contains families of completely different compositions all of which possess unique properties and characteristic applications. These three classes of ferrimagnetic oxides are ferrites (spinels), garnets and hexagonal materials.

The ferrites are further classified as soft and hard, depending on their magnetic characteristics. During the early days (some 60 years ago) ferrites, especially soft ferrites, found use primarily in the communication areas. When television arrived, they were used as flyback transformers or as deflection yokes. In telephones, they were used as channel filters and in tone generators circuits ferrites find applications in touch-tone phones. Of ten million telephones that manufactured by Western Electric in early 1970's [4] about 3 million were touch-tone dials. At that time MnZn ferrite was the only material that met all the requirements that are important viz. High Q, good stability with time and temperature, small size, low cost.

In 1980’s a transistor switched power supplies created a need for ferrite material operating at much higher flux levels and frequencies than those encountered in telecommunications. MnZn ferrites were the materials that found use, that time, but then with the increase in switch-mode power supply market, requirement of magnetic characteristics also changed. Power ferrites are thus arrived. The power ferrites needed to be operated at higher frequencies. Frequency of operation kept increasing as the solid
state industry developed enabling to prepare newer ferrites. The need for small compact power supplies for computers, microprocessors and VCR's have further triggered a great demand for power ferrites. The new power ferrites have to have two new attributes [5] that not previously needed in other applications: 1) they have to possess high saturation, $B_s$ and 2) they should have low core loss at higher flux densities (near the position of $\mu_{\text{max}}$) and at fairly high frequencies.

MnZn ferrites are materials of low resistivity which impedes their use in high frequency applications due to several losses like eddy current etc. A higher resistivity materials, MgZn ferrites are now replacing MnZn ferrites in certain applications. A comparison of important properties between MgZn and MnZn ferrites reveals that, although permeability and saturation reduced from 900 – 1000 and 3000 – 4000 Gauss in MnZn ferrites to 350 – 500 and 2400 – 2700 Gauss in MgZn ferrites, the loss factor remained almost constant at $10^{-5}$. But, there is tremendous increase in resistivity observed in MgZn ferrites of $10^7 - 10^8 \, \Omega \, \text{cm}$, while MnZn ferrites show low resistivity, $10^2 \, \Omega \, \text{cm}$.

Infact, Mg ferrites and allied compounds have found widespread applications in microwave devices. They are considered as the most versatile ferrites in electronic industry [6] because of their comparatively low magnetic and dielectric losses obtainable. In particular, these possess high resistivities which can be obtained by the selection of suitable minor additives and using appropriate firing procedures. Among the various magnesium ferrites, MgZn ferrites have been most thoroughly examined. MgAl ferrites are the other examples which have been widely studied when useful frequency ranges of microwave devices have to be extended for low microwave bands and ultra high frequency devices. These materials of MgFe$_2$O$_4$ group are of much interest because they
exhibit low saturation magnetization, high resistivity and uniform and reproducible characteristics needed for microwave device applications.

Spinel, thus, of general formula $\text{MFe}_2\text{O}_4$ find applications when additives are present in divalent form. MnZn ferrite is achieved on substituting $\text{Zn}^{2+}$ from $\text{ZnFe}_2\text{O}_4$ by $\text{Mn}^{2+}$ or $\text{Mn}^{2+}$ from $\text{MnFe}_2\text{O}_4$ by $\text{Zn}^{2+}$. A 50% substitution of $\text{Zn}^{2+}$ from $\text{ZnFe}_2\text{C}_1$ leads to $\text{Mn}_x\text{Zn}_y\text{Fe}_2\text{O}_4$. A solid solution of $\text{MnFe}_2\text{O}_4$ and $\text{ZnFe}_2\text{O}_4$ is thus achieved: $\text{Mn}_x\text{Zn}_y\text{Fe}_2\text{O}_4$, where $x = 0.5$. Similarly a solid solution of $\text{MgFe}_2\text{O}_4$ and $\text{ZnFe}_2\text{O}_4$ may be written as $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$, where $x = 0.5$. However, a complete range of solid solutions can be obtained by varying $x$ from 0.00 to 1.00 in many spinels. Such a wide range of solid solutions show interesting properties, as literature survey reveals many different spinels of different additives. Last seven to eight decades ferrites researchers realised many interesting properties of these from both academic and application point of view by using more than one additives in the spinel structure. If ferrites are considered as materials containing mostly iron which are derived from magnetite $\text{Fe}_3\text{O}_4$, $(\text{Fe}^{2+}\text{O} \cdot \text{Fe}^{3+}_2\text{O}_3)$ by substituting $\text{Fe}^{2+}$ by divalent metals, $\text{M}^{2+}$, a wide range of ferrites can be produced. The more common divalent metal ions that are being used are Mn, Fe, Co, Ni, Cu, Zn, Mg, Cd, and Ge. Trivalent metal $\text{Fe}^{3+}$ from $\text{Fe}_3\text{O}_4$ is also substituted by trivalent metals such as, Al, Cr, Ga, Mn. Monovalent Li and tetravalent Ti and Sn are even incorporated into the lattice of the spinel by the respective decrease or increase in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio. When such additives are introduced, it becomes quite involved research as far as their synthesis is concerned, as single phase ferrite is needed to be formed to achieve desired properties. And, hence, the synthesis of the ferrites becomes main objective of any researcher who enters this field.

Synthesis of Ferrites

Ferrites synthesis needs a thorough understanding of chemistry aspects. Since
Ferrites are oxide solid ceramic materials, high temperatures are needed to prepare them. As solid state reactions are sluggish, reactivity of starting materials requires to be increased. Fine grained starting materials are therefore used. A homogeneous mixing ensures close proximity of individual reactants with each other. Instead of heating directly the ground mixtures to high temperatures, preheating is done to initiate the reactions. This preheating is normally done in pelletised powders to ensure better reactions. The preheated samples are then cooled, ground and repelletised then further heat treatment is done at much high temperatures. Many a times, one more grinding and pelletising is carried to go for final sintering at the desired temperatures to get well dense, fully grown microstructures. Ferrites preparation is laborious, as one has to make a compromise between their intrinsic and extrinsic properties to realise a material of optimum characteristics.

Intrinsic and Extrinsic properties

The intrinsic properties of ferrites are saturation magnetization, magnetostiction, anisotropy, permeability and Curie temperatures whereas the extrinsic properties are hysteresis, resistivity, dielectric constants etc. The parameters such as porosity, grain size, impurities, etc. affect the extrinsic properties. The extrinsic properties are also referred to as structure sensitive properties. Single phase ferrites of the desired compositions are must to achieve the required magnetization and Curie temperature values.

Importance of extrinsic properties

Ferrites of optimum properties are difficult to achieve and hence the preparation of polycrystalline magnetic materials is considered to be difficult and complex. It is now well understood that the control of extrinsic properties is most desired to achieve the
required properties for device applications. Hence, the knowledge of the parameters of microstructure such as density, grain size and porosity and their intra and intergranular distribution are important in controlling the extrinsic properties. The knowledge of chemistry and crystal structure along with the microstructural aspects become the important criteria in the study of ferrites.

Chemistry, crystal structure and microstructure of ferrites

Ferrites of general formula MFe$_2$O$_4$, where M is a divalent metal, are structurally similar to the mineral spinel MgAl$_2$O$_4$. Conventionally they are written as $(M^{2+})_{tet}[Fe^{3+}]_{oct}$O$_4$, where tet = tetrahedral site and oct = octahedral site. Spinel has a close packed cubic structure of oxygen atoms with 8 formula units per unit cell and the unit cell structural formula is written as, $(M^{2+})_{A tet}[Fe^{3+}]_{B oct}$O$_{32}$, where ( ) = A site and [ ] = B site. The unit cell consists of all 64 tetrahedral sites and 32 octahedral sites of which $\frac{1}{8}$ tetrahedral sites and $\frac{1}{2}$ octahedral sites are occupied.

Normal spinel

All divalent metal ions, M$^{2+}$, when occupy the tetrahedral sites a normal spinel is arrived. ZnFe$_2$O$_4$ is an example of such a spinel with formula, Zn$^{2+}[Fe^{3+}]_2$O$_4$. The ( ) bracket can be omitted.

Inverse spinel

Divalent metals here enter the octahedral sites replacing the trivalent metals which then go to tetrahedral sites as in Fe$_3$O$_4$, Fe$^{3+}[Fe^{2+}Fe^{3+}]$O$_4$. Nickel ferrite is another example, NiFe$_2$O$_4$, Fe$^{3+}[Ni^{2+}Fe^{3+}]$O$_4$.

Random spinel

An intermediate between normal and inverse spinels are observed when divalent
metals occupy both A and B sites. Examples are many, depending on number of such distributions. In MgFe$_2$O$_4$ the divalent cation distribution is Fe$^{3+}_{0.9}$Mg$^{2+}_{0.1}[Mg^{2+}_{0.9}Fe^{3+}_{1.1}]O_4$. The other member of this class is Mn$_2$Fe$_2$O$_4$, Mn$^{2+}_{0.8}Fe^{3+}_{0.2}[Mn^{2+}_{0.8}Fe^{3+}_{1.2}]O_4$.

**Vacancy spinel**

Although all 8 tetrahedral and 16 octahedral sites are occupied by metal ions as in normal and inverse spinels, there are instances wherein few vacancies are observed in spinel structure. The vacancies are due to non-occupation of few of 8 tetrahedral or 16 octahedral sites of the spinel structure. A good example is the oxidation product of magnetite itself. Fe$_3$O$_4$, Fe$^{3+}[Fe^{2+}Fe^{3+}]O_4$ on oxidation, all Fe$^{2+}$ on octahedral sites convert into Fe$^{3+}$ and results into gamma ferric oxide, $\gamma$-Fe$_2$O$_3$, Fe$^{3+}[Fe^{3+}\square_{1/3}]O_4$, where $\square$ represents vacancy. The spinel lattice can tolerate a high concentration of cation vacancies.

This tendency to form cation vacancies increases in spinels [7] of practical application, (M$_{A}$+$M_{B}$)$_{1-x}$Fe$_{2+x}$O$_4$, when there are two or more metals besides iron and when $x$ varies between -0.3 to 0.3. The ferrite is considered to be stoichiometric from formula standpoint when $x = 0$ (or Fe$_2$O$_3$ = 50 mole %). In contrast to this formula stoichiometry, there can exist an atomic stoichiometry where there are exactly 3 metal atoms for every 4 oxygen atoms.

The tendency to form cation vacancies increases as $x$ increases from 0 to a more positive value by the combination of excess $\alpha$-Fe$_2$O$_3$ with rhombohedral structure dissolving into a ferrite spinel structure,

$$4Fe^{3+}_{2}O_3(\text{rh}) \rightarrow 3Fe^{3+}_{6/3}\square_{1/3}O_4(\text{sp})$$

and the equilibration of the dissolved species with temperature and atmosphere,
Increased temperature and decreased atmospheric oxygen tend to reduce the cation vacancy content. From this analysis, atomic stoichiometry can exist without having formula stoichiometry. Cation vacancies play an extremely important role in the ferrite's sintering kinetics and magnetic properties.

Chemistry

Ferrites of spinel structure exhibit magnetism, ferro-, ferri- and antiferro- due to i) unpaired 3d electrons ii) super exchange between adjacent metal ions and iii) non equivalence in number of A and B sites. Magnetic moment of free state magnetic atom is the sum of the electron spin and orbital moments, while the atoms in spinel exhibit only spin magnetic moments as quenching of orbitals takes place due to the electronic fields caused by the surrounding oxygen about the metal ion. Therefore, atomic magnetic moment ($m$) is simply its electronic spin moment and is equivalent to $m = \mu_B n$ where $\mu_B$ is a Bohr magnetone unit and $n$ is the number of unpaired electrons.

In spinel both A and B sites are capable of accommodating variety of metal ions, magnetic and non magnetic. Since these two sites have two different environments: one has tetrahedral and the other octahedral, magnetic interaction between atoms on these sites: AB interaction via oxygen ions (super exchange) occurs and it decreases as the distance between the metals increases and as the angle of $\text{M-O-M}$ decreases from 180 to 90°.

In spinel both A and B sites are equally capable of accommodating magnetic ions. Thus, magnetic ions are distributed throughout the crystal lattice which tend to interact through oxygen (super exchange) magnetically and hence exhibit magnetism. Interaction is maximum when $\text{M-O-M}$ angle is 180° and distance between the metals is small. A look at the spinel structure (Fig 1.1) indicates an angle $\text{M}_A\text{-O-M}_B \sim 125°$ where $\text{M}_A$ and
FIG. 1.1  Crystal structure of spinel ferrites showing tetrahedral and octahedral co-ordination
MB are metals on A and B sites, respectively. On the other hand, M_b-O-M_b is 90° and interaction is minimum or negligible. The strength of interaction depends on the degree of orbital overlap of oxygen p orbits and the metal (mostly transition) d orbitals.

Based on these interaction knowledge [8-13] and the nature of metal ions possibly present on two sites, magnetic moments can be calculated and experimentally observed. Thus, Fe_3O_4, Fe^{3+}[Fe^{2+}Fe^{3+}]O_4 having 3d^5 (Fe^{2+}) and 3d^5 (Fe^{3+}) electrons contributing to magnetism gives experimentally magnetic moment, \( \eta_B = 4.1 \) which is close to the theoretical value of 4.0. Since B-B interaction is negligible and zero, the only significant interaction is A-B. If Fe^{3+} on A site (of \( \mu_B = 5 \)) is considered to interact with Fe^{5+} of B site, then magnetic moment cancel as they are antiparallel to each other. And, hence, the magnetic moment is only due to Fe^{2+} (\( \mu_B = 4 \)). This confirms the cation distribution. Then, if MgFe_2O_4 is considered to be normal spinel, Mg^{2+}[Fe^{3+}Fe^{3+}]O_4, Mg on A site with no d-electrons, will not have interaction with B site Fe^{3+} ions. And, since B-B interaction is zero, the spinel should show no magnetic moment. However, it does show magnetic moment, \( \eta_B = 1.1 \). From the experimental value a cation distribution for MgFe_2O_4 is written and confirmed as Fe_{0.9}Mg_{0.1}[Mg_{0.9}Fe_{1.1}]O_4 and the calculated \( \eta_3 = 1.0 \) is thus very close to the experimental findings.

Experimental and calculated values of magnetic moments in ferrite may not necessarily guide one to the distribution of cations on A and B sites. For example, cobalt ferrite is known inverse spinel, CoFe_2O_4, Fe^{3+}[Co^{2+}Fe^{3+}]O_4. The 3d^7 electrons (\( \mu_3 = 3 \)) on octahedral sites make this spinel to possess magnetic moment of 3 Bohr magnetone but experiment indicates it to have 3.7 at 0 K. The higher value is due to orbital contribution of Co to the magnetic moment.

Thus, one can with some efforts make sure about the cation distributions in ferrites and confirm by other supporting experiments such as Mössbauer effect studies.
And, if cation distributions are thus confirmed, then there is no much difficulty in preparing such ferrites by chemical knowledge. Although preparation of ferrites is laborious, one is certain of the preparation. The synthesized material may be expected to give the desired properties like magnetization, Ms and Curie temperatures which are the intrinsic properties of ferrites. But they may not assure of the other properties considered to be extrinsic one.

Properties dependence on microstructure

Ferrites find applications in wide range of electronic appliances. MnZn ferrites are used \([14-20]\) in devices, such as inductor, transformer, loading coil, flyback transformer, deflection yokes, recorder heads, power transformers. The desired properties for such device functions are permeability, \(\mu\), high stability of \(\mu\) with temperature and time. But for transformer purpose a high \(\mu\) and low hysteresis loss is needed. In loading coil applications high \(\mu\), high saturation \(B_s\), high stability of \(\mu\) with temperature are the requirements.

Ferrites for application at frequencies below 1 MHz the core materials should have high permeability but for high frequency signals to achieve, a high value of saturation magnetization is desired.

Ferrites designed for frequencies above 1 MHz should possess high resistivities to avoid eddy current losses. Dielectric losses are minimised by choosing ferrites with resistivities \(> 10^6 \Omega \text{ cm}\). Ferrites useful for storing information, cores should show square loop hysteresis having two equally stable magnetic states by \(+B_r\) and \(-B_r\), the two remanent flux density states. Magnesium manganese ferrites, \(\text{Mg}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4\) find use in such applications. Manganese ferrite, \(\text{MnFe}_2\text{O}_4\) with saturation induction \(B_s = 5000\) Gauss at room temperature and \(\text{MgFe}_2\text{O}_4\) of \(B_s = 1800\) Gauss are used to prepare a solid solution of these two to get induction values of desired level by careful choice of \(x\).
Switch cores need ferrites of high flux density and is achieved by using a composition with high percentage of MnFe₂O₄.

Microwave devices for ultra high frequency applications demand ferrites exhibiting small saturation magnetization between 300-1900 G. Yttrium iron garnet (YIG), Y₃Fe₅O₁₂ (4πJₛ = 1790 G) and yttrium substituted YIG are most suitable for such applications [21] as depending on the required magnetization value the substitution may be effected without bringing any change in Curie temperature. Magnesium ferrite and substituted magnesium ferrites are also studied widely as they do find widespread applications in microwave devices.

Thus, it can be inferred that important properties of ferrites that make them useful for device applications are permeability, saturation magnetization, remanent flux, Curie temperature, resistivity, dielectric properties etc. But losses like eddy current, hysteresis loss, dielectric loss etc. required to be checked if ferrites are considered for device applications. For example, ferrites useful in radio frequency ranges the eddy current losses can be minimised by increasing resistivity, \( \rho \). But the increase in frequency \( f \), too enhances the loss, however, one can check this loss by decreasing the thickness of the ferrite core [22] as

\[
\text{Eddy current loss} \propto \frac{D^2f}{\rho} \tag{3}
\]

where \( D \) is the thickness of the core, \( f \) is the frequency of the a.c. field.

Permeability is an important property to be considered in ferrite applications. Permeability is governed by two mechanisms, namely, spin rotation in the magnetic domain and wall displacement. Although two mechanisms are well understood theoretically, when it comes interpreting the property from the experimental results, many difficulties arise. And, it has been described [7] that the intrinsic rotational permeability,
and 180° wall permeability, $\mu^W$ depend, no doubt, on saturation magnetization but also on anisotropy, wall energy and diameter of the grains of the ferrite compacts,

$$\mu^R = 1 + 2\pi Ms^2/K$$
$$\mu^W = 1 + \frac{3}{4} \pi Ms^2 D/\gamma$$

(4)

where $Ms =$ saturation magnetization

$D =$ grain size

$K =$ total anisotropy $= K_1 + \lambda_s \sigma$

$K_1 =$ first order magnetocrystalline anisotropy

$\lambda_s =$ magnetostriction or deformation with the field

$\sigma =$ internal stress

$\gamma =$ wall energy $= KSu$

$Su =$ wall thickness

The wall permeability, $\mu^W$, may be written as:

$$\mu^W = 1 + (3\pi/4Su)(Ms^2/K)D$$

Thus, wall permeability is dependent on intrinsic properties, $Ms$, $K_1$, $\lambda_s$ and grain dependent properties (extrinsic). The rotational permeability, $\mu^R$, on the other hand, is dependent only on the intrinsic properties such as $Ms$, $K_1$, $\lambda_s$. Hence, the technologically important permeability property of magnetic materials if required to be adjusted, one has to have the knowledge of several above parameters.

The intrinsic properties such as $Ms$, $K_1$, $\lambda_s$ are controlled by chemistry. The permeability properties then depend, apart from these intrinsic properties, or grain dependent parameters such as grain size and intergranular defects such as porosity, second phase inclusions and dislocations that affecting the wall energy. Thus, microstructural aspects of ferrites compacts are required to be understood thoroughly while establishing the required permeability values.
To obtain high permeability the ferrite core should possess small pores and pores must occur only between the grains and not inside the grain. A high purity starting materials that yield quite homogeneous single phase ferrite may attain high permeability. A linear increase in permeability with the grain size has been realised technologically and a maximum permeability of ~ 40,000 is also reported [23] in MnZn ferrites by modifying sintering conditions.

The pores, impurities, inhomogeneity, inclusions, grain boundary all together act as an obstacle to rotation of the magnetization and hence permeability ($\mu_R$) is hindered. Pores inside the grain, on the other hand, effectively trap the walls of the domain and thus permeability due to wall movement is also hampered.

Hysteresis loss make ferrites unsuitable for many applications, especially in power ferrites. The factors that govern the hysteresis loss are

1. Magneto crystalline anisotropy ($K_1$)
2. Magnetostriction ($\lambda$)
3. Internal and external stress ($\sigma$)
4. Volume fraction of inclusions (include pores, dislocations, cavities and impurities)
5. Saturation magnetization ($M_s$)

To reduce hysteresis loss $K_1$, $\lambda$, $\sigma$ and volume fraction of inclusions should be small and $M_s$ should be large. $K_1$, $\lambda$ and $M_s$ are primarily dependent upon chemical composition (intrinsic properties). Internal stress and volume fraction of inclusions are determined by microstructure. It is, therefore, the microstructure of the ferrite is important in controlling the hysteresis loss as the intrinsic properties are easy to manage by chemistry.

Resistivity ($\rho$) determines eddy currents loss (equation 3). Because microstructure controls resistivity, it can be expected that microstructure also controls the eddy current
loss.

There are always efforts in ferrites industry to find best method to minimise the above obstacles by adopting processes to obtain well compact ferrites. Hence, not only chemistry but also microstructural aspects are required to be thoroughly studied while looking for newer methods of synthesis of ferrites. Both intrinsic and extrinsic properties need to be carefully considered in any ferrite studies.

Ferrite raw materials

Ferrites of general formula MO.\text{Fe}_2\text{O}_3, \text{where M} = \text{divalent metals, Mg, Mn, Ni, Fe, Cu, Co} \text{are derived from the ferrite when M} = \text{Fe}^{2+} \text{and hence, in ferrites preparation it is iron oxide which is the major raw material. The iron oxide sources (Table 1.2) for the preparation of ferrites are mainly [24]: upgraded magnetite, upgraded hematite, oil free mill scale, fluidized bed regenerated granules, spray roasted ferric oxide with high, medium and little impurities, sulphate processed medium and little impurities and carbonyl. In table 1.1 the world ferrite production projected [24] for year 1990, 1995 and 2000 indicates enormous requirement of iron oxides that are obtained from above sources.}

Table 1.1 Future utilisation of iron oxide raw materials for world ferrite production [24]

<table>
<thead>
<tr>
<th>Year</th>
<th>1990</th>
<th>1995</th>
<th>2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estimated total world ferrite production in MTPY</td>
<td>516,000</td>
<td>665,500</td>
<td>974,000</td>
</tr>
<tr>
<td>Total ferric oxide consumption in MTPY</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hard ferrites (x 0.87)</td>
<td>318,000</td>
<td>420,000</td>
<td>550,000</td>
</tr>
<tr>
<td>Soft ferrites (x 0.70)</td>
<td>105,000</td>
<td>130,000</td>
<td>155,000</td>
</tr>
<tr>
<td>Sub total ferric oxide</td>
<td>423,000</td>
<td>550,000</td>
<td>705,000</td>
</tr>
</tbody>
</table>
Table 1.2 Iron oxide sources for ferrite preparation [24]

<table>
<thead>
<tr>
<th>Iron oxide source</th>
<th>Year 1990</th>
<th>Year 1995</th>
<th>Year 2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. *Upgraded Magnetite</td>
<td>*5%</td>
<td>*5%</td>
<td>*5%</td>
</tr>
<tr>
<td>2. *Upgraded Hematite</td>
<td>*30%</td>
<td>*50%</td>
<td>*65%</td>
</tr>
<tr>
<td>3. *Oil free Mill Scale</td>
<td>*15%</td>
<td>*10%</td>
<td>*10%</td>
</tr>
<tr>
<td>4. *Fluidized bed regenerated granules</td>
<td>*50%</td>
<td>*35%</td>
<td>*20%</td>
</tr>
<tr>
<td>*Subtotal 1-4 (MTPY)</td>
<td>127,000</td>
<td>192,500</td>
<td>242,000</td>
</tr>
<tr>
<td>5. Spray roasted ferric oxide, high content of impurities</td>
<td>20%</td>
<td>15%</td>
<td>10%</td>
</tr>
<tr>
<td>6. Spray roasted ferric oxide, medium content of impurities</td>
<td>70%</td>
<td>65%</td>
<td>60%</td>
</tr>
<tr>
<td>7. Spray roasted ferric oxide, little impurities (~200 ppm SiO2)</td>
<td>10%</td>
<td>20%</td>
<td>30%</td>
</tr>
<tr>
<td>*Subtotal 5-7 (MTPY)</td>
<td>275,000</td>
<td>330,000</td>
<td>337,000</td>
</tr>
<tr>
<td>8. *Sulfate processed medium impurity</td>
<td>*16%</td>
<td>*16%</td>
<td>*16%</td>
</tr>
<tr>
<td>9. *Sulfate processed little impurities</td>
<td>*80%</td>
<td>*80%</td>
<td>*80%</td>
</tr>
<tr>
<td>10. *Carbonyl</td>
<td>*4%</td>
<td>*4%</td>
<td>*4%</td>
</tr>
<tr>
<td>*Subtotal 8-10 (MTPY)</td>
<td>21,000</td>
<td>27,500</td>
<td>36,000</td>
</tr>
</tbody>
</table>

From Table 1.2 one can infer that in the coming years ferrite industry has to depend mainly on upgraded hematite ore and spray roasted ferric oxide for meeting the ever expanding ferrite industries requirement of the raw material. Ferrite industry itself is expected to increase its production to 974,000 metric tonnes per year (MTPY), by the turn of this century. And, the iron oxide required for such production is ~ 705,000 MT/ Y.

Indian ferrite production

Indian contribution in the world ferrite production (Table 1.3) [24] is insignificant. Comparing the world leaders in ferrite manufacturers from Table 1.3, India lags behind many developed and developing countries, as shown below.

Although, India is one amongst very few countries to have one of the best iron oxide sources in the world, yet there are no much improvement in the ferrite production capacity in India.
USA    1,40,000 (1979)  85,000 (1989) MTPY
G. Britain  17,000    12,000
France    21,500    2,21,500
Germany   21,500    20,500
Italy     21,500    18,200
USSR      45,000    45,000
China     35,000    37,000
Japan     1,35,000  1,80,000
India     9,000     9,000

India is dependent on the import of iron oxides of ferrite grade. In fact, Indian annual demand for the iron oxide to manufacture ferrites (both soft and hard) in 1977 was ~25 metric tonnes (MT) and was met through import [25]. Year 1988 was no better than year 1977 and the ferrite grade iron oxide import remained the same (Business India 11-24 July 1988).

Recently, India has begun in a small way to produce ferrite grade iron oxide and a pilot plant of capacity ~50,000 tonnes per year is already setup (The Economics Times, Bombay, India, 27 August 1990). A plant to manufacture very high-grade iron oxide required for quality ferrites manufacturer is also installed, of capacity 10,000 tonnes year ferrite grade iron oxides.

Iron oxides required for ferrites (soft and hard) are mostly spray roasted iron chloride from acid (HCl) pickling solution in steel industries (Table 1.2). This is the synthetic ferric oxide, called as spray roasted iron oxide. Natural iron oxides of magnetic origin are also used in ferrites synthesis, after upgradation and this beneficiated ore along with the upgraded hematite are also used as raw material in ferrite industry.
### Table 1.3 Estimated world ferrite production for 1990 in metric tonnes per year [24]

<table>
<thead>
<tr>
<th>Country</th>
<th>Hard Ferrite</th>
<th>Soft Ferrite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canada</td>
<td>4,000</td>
<td>4,000</td>
</tr>
<tr>
<td>USA</td>
<td>95,000</td>
<td>75,000</td>
</tr>
<tr>
<td>Mexico</td>
<td>3,500</td>
<td>2,500</td>
</tr>
<tr>
<td>Venezuela</td>
<td>2,500</td>
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<td>World ferrite production</td>
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Both the natural iron oxides and synthetic spray roasted iron oxides have inherent impurities which hinder them to use in high tech ferrites manufacture, however, routine ferrites are made by these.

Purity of any raw material is an important criterion in the synthesis of raw material of technological importance. There is no such thing as high purity or low purity when it comes to synthesizing any ferrite of optimum intrinsic or extrinsic properties. Without any reservation one can safely say that impurity free raw materials lead to high quality end products. Then it is difficult to always adhere to such specifications. One has to make some attempt, as far as possible, to free the impurities, as it is difficult to obtain nil impurity material.

Spray-roasted iron oxide

In ferrite synthesis, natural raw material (upgraded) as well as synthetic spray roasted iron oxides are bound to have impurities. The spray roasting of acid (HCl) pickle solution of steel industry into iron oxide normally retains all additive metals that are used in the steel making in the form of their respective oxides, along with the main constituent iron oxide. The technique of spray roasting is well developed by Ruthner [26-29] and put into large scale production by different countries in the name 'Ruthner Process'. In the spray roasting the pickle solution consist of the chlorides of metals.

Spray roasting process which was earlier recognized as pyrohydrolysis process [30] had been originally used to completely regenerate hydrochloric acid from the waste pickle acids produced by the steel industry. The process then underwent considerable development and not only the acid is being regenerated effectively but also a lot emphasis is put on the oxides that are the end product of the roasting. Many ceramic oxides such as \( \text{Al}_2\text{O}_3, \text{MgO, Mn}_2\text{O}_3, \text{NiO, Fe}_2\text{O}_3 \) have been synthesized in single step using pickle solution of steel industry and acid solution of mixed metals have further given scope to
prepare mixed metal oxides and by such spray roasting technique many industrially important ferrites, NiFe$_2$O$_4$, MnFe$_2$O$_4$, MnZn ferrite etc. have been manufactured.

In spray roasting the metal chlorides are sprayed through ceramic spray nozzle at a pressure of 3 to 5 bars ($3 \times 10^5$ to $5 \times 10^3$ Pa) in the upper portion of the reactor (oil or gas fired cylindrical tower furnace). The droplets produced by the nozzle finally fall at the bottom in the form of oxide particles of an average particle size between 0.10 to 0.25 μ.

Impurities in spray roasted iron oxides originate from high temperature steel manufacturing process. Among the most significant impurities in these oxides are Mn, Al, Cr, Ni and Si.

Control of impurities in ferrite grade iron oxide

Both upgraded iron ores, hematite and magnetite, do retain minor impurities, depending upon ore sources and the use of beneficiation processes. The spray roasted iron oxide also contains impurities, as mentioned earlier. The upgradation of iron ores is a physical beneficiation process and hence depending on the mineralogy of the ore deposits, the techniques [31-35] of oil agglomeration, froath flotation, selective flocculation have been adopted to considerably increase the mineral content in the ore. In one such a study [31] the flotation beneficiation of low grade hematite ore (cf M/s Sallitho iron ores limited, Goa from the Pale mines) enabled to increase the iron content from 43 (%) to 68-70 (%). The Si content was decreased from 9 (%) to 1.4 (%), while aluminium could be brought down to 1.1 (%) from 13.5 (%) present in the ore. But the ferrite industry needs still better improvement in the major impurities: Al and Si.

The pickle solution before spray roasting can also be purified by precipitation or coprecipitation of the impurities, by solvent extraction, by ion exchange or by crystallization. The solvent extraction or ion exchange processes allow one to obt
desired metal chloride (iron chloride) in the concentrated form enabling the roasting process to yield pure oxide.

A new production method using solvent extraction technique to prepare iron oxide of high purity from waste acids from pickling plants has been described [36]. The extraction of iron (III) is effected by methyl isobutyl ketone (MIBK) and the iron precipitated subsequently from ammonia or heat yielded iron oxide of impurities (in ppm): Mn – 10, SiO₂ – 16, CaO – 10, Al₂O₃ – 10 and Cr – 10.

Use of γ-Fe₂O₃ in ferrite synthesis

In ferrites synthesis the iron oxide obtained, whether it is from spray roasted (Table 1.2) technique or sulphate processed method, is of alpha form, α-Fe₂O₃, with corundum structure having hexagonal close packing (hcp) of oxide ions. And Fe⁺⁺ ions occupy the octahedral sites of the hcp arrangement. The upgraded magnetite, on the other hand, is the magnetic oxide of iron, Fe₃O₄, the ferrous-ferric oxide, FeO.Fe₂O₃, which has spinel structure. In the cubic close packed (ccp) arrangement of oxide ions of Fe₃O₄, the Fe²⁺ occupy the octahedral sites and the Fe³⁺ ions get accommodated on both tetrahedral and octahedral sites.

Sluggish reaction between α-Fe₂O₃ + MO

The method used in the most of the ferrite industries is a conventional ceramic technique which requires very high temperature to complete usually the sluggish solid-solid reactions. The raw materials iron oxide and oxides of divalent metals (or carbonates, nitrates, hydroxides of M²⁺) are ground and heated to high temperatures.

The reaction between Fe₂O₃ and MO is sluggish. Causes for the sluggishness are many and one important factor for such delayed formation of a product can be considered based on the structure of the reactants and the product. The divalent oxides, MO, say
NiO, MnO, etc. are cubic with rock salt structure while Fe₂O₃ (α-Fe₂O₃) is rhombohedral of hexagonal close packing. The product is MFe₂O₄, a spinel of ccp. Therefore, the main raw material α-Fe₂O₃ of corundum structure has to rearrange itself to react with cubic MO to form cubic spinel.

It is considered [37] that first α-Fe₂O₃ transforms at high temperatures into cubic spinel Fe₃O₄ as shown in equations 1 and 2. According to Richards and White [36] pure Fe₂O₃ dissociates into Fe₃O₄ evolving oxygen at 1385°C. But, in the presence of the other metal oxides like MgO, the dissociation occurs at lower temperature. The spinel Fe₃O₄ formation from α-Fe₂O₃ through a cation vacancy intermediate is dependent on

\[
\begin{align*}
4 \text{Fe}_2\text{O}_3\text{(th)} & \rightarrow 3 \text{Fe}^{3+}\text{O}_6\text{O}_8^3 \rightarrow 8/3 \text{Fe}^{2+}\text{Fe}_2^{3+}\text{O}_4 + \text{O}_2 \\
& \text{temperature and oxygen partial pressure as the cation vacancies decrease with the increase in temperature and the decrease in atmospheric oxygen.}
\end{align*}
\]

At this high temperature the cubic spinel Fe₃O₄ formed easily reacts with the cubic MO present in the vicinity, thereby, completing the ferrite formation.

Upgraded magnetite if used, therefore, is expected to give easily ferrites, may be at lower temperature than the upgraded hematite when used, in ferrites synthesis. Natural magnetite Fe₃O₄ has been used [39] to make the high quality ferrite magnets and the large reserves of this mineral in Vietnam is being successfully exploited in ferrite synthesis. In the synthesis of barium ferrite from natural Fe₃O₄ and barium carbonate, the magnetite undergoes its usual phase transition from Fe₃O₄ to Fe₂O₃ in the heating process and the reactive Fe₂O₃ that formed now reacts with the reactive BaO that also formed in situ by the thermal decomposition of the carbonate. Thus, reactive Fe₂O₃ and BaO immediately form ferrite. Hence, it is considered that the ferritization is occurred well and even finished sooner when Fe₃O₄ is used [40] as a raw material than using the chemical oxide Fe₂O₃.
A systematic study is being done [41] to evaluate the processes of the formation of nickel ferrite NiFe$_2$O$_4$ from hematite, magnetite and magnetite like spinel iron sand found on the west coast of the North Island of New Zealand. From Differential thermal analysis (DTA) and evolved gas analysis (EGA) carried out on the reactants (and NiO) and their mixtures in different atmospheres, it was found that magnetite like iron sand, prior to their reaction with NiO, undergoes oxidation reaction $\sim 220^\circ$C, while no such oxidation process is observed with hematite + NiO mixture. And, high reactivity found in magnetite + NiO and iron sand + NiO was attributed to the formation of reactive hematite in situ in the oxidation of the magnetite $\sim 220^\circ$, which immediately reacts with the NiO, yielding NiFe$_2$O$_4$.

**Mechanism of the solid state reactions**

It is generally considered that the sluggish solid state reaction can be made reactive by rendering the reactants active. This can be done by increasing the surface area of the reactants by grinding them to the finer size or the best way is to use the starting material not in oxide form, but in the easily decomposable compound form, say carbonates, hydroxides. During the heat treatment these decompose to give oxides with particles showing high surface area and surface energy. On the basis of a considerable amount of experimental work Gregg [42] has postulated some general rules which can be applied in most of the cases where an active solid is prepared by the thermal decomposition of the precursors of any oxide. Therefore, the Fe$_2$O$_3$ formed from its precursors, Fe$_3$O$_4$, is reactive and such particles of Fe$_2$O$_3$ then interact with NiO to yield easily NiFe$_2$O$_4$. If NiO is also made to form in situ, by choosing a conventional precursor of it, say NiCO$_3$, then the formed NiO is active and reacts more easily with the active Fe$_2$O$_3$ formed from Fe$_3$O$_4$. Finally the spinelization takes place effectively, may be at lower temperature.
The formation of any product in solid state reaction involves two stages which are usually identified as,

i. Nucleation of the product

ii. Subsequent growth of the product.

Nucleation is facilitated if there is a structural similarity between the product and one or both of the reactants because this reduces the amount of energy required for structural reorganization that is necessary for the nucleation to occur. In the reaction of cubic MgO and hexagonal close packed Al$_2$O$_3$ to form MgAl$_2$O$_4$, for instance, the spinel product has a similar oxide ion arrangement to that in MgO. Spinel nuclei may therefore form at or on the surface of the MgO crystals such that the oxide arrangement is essentially continuous across the MgO-spinel interface,

\[
\begin{array}{c|c}
\text{MgO} & \text{Al}_2\text{O}_3 \\
\end{array}
\]

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

The nucleation product, spinel phase, makes use of a matching or partially matching of its own structure to that of existing phase, MgO, in the reaction mixture and the nucleation step is easier as a consequence.

High temperature makes possible this nucleation process easy because the heat helps the structural recognition involving breaking up and reformation of bond by allowing the atoms to migrate (perhaps over considerable distance on an atomic scale).

The nucleation of the product phase thus leads to the growth of the product layer. Counter diffusion of Mg$^{2+}$ and Al$^{3+}$ through the product layer enables these ions to reach reaction interfaces.
In essence, the solid state reaction is an involved process wherein the crystal structure of the reactants and products, surface area or reactivity of the reactants, heat energy, breaking and forming of bonds, diffusion (or counter diffusion) of ions are all need to be understood.

However, high temperatures are usually adopted in ensuring the completion of the solid state reaction to form solid product, but, the solid product formed may not have an adequate stoichiometric composition as desired to obtain a uniform single phase spinel. Single phase products are difficult to achieve as there is every possibility of variation in the constitution elements concentration, say Mg rich phase of MgAl$_2$O$_4$ on MgO side and Mg deficient phase on the Al$_2$O$_3$ side are usually attained. This is due to the fact that the product of MgO + Al$_2$O$_3$ varies from MgAl$_2$O$_4$ to Mg$_{0.73}$Al$_{2.304}$. And, therefore to achieve a single phase product further complications are encountered.

Rate of Reaction

Thus, in the solid state technique many factors are to be considered to achieve the desired product. The important factors that influence the rate of reaction between solids are i) the area of contact between the reacting solids and hence their surface areas ii) the rate of diffusion of ions through the various phases iii) the rate of nucleation of the product phases. The area of contact between the reactants can be increased by increasing the surface area. Grinding of the reactants into fine powder makes surface area high. But, very important factor is the structural aspects; at least one of the reactants should have similarity in the structure with the product to be formed. If both the reactants are chosen having similar structure with that of the product, then the rate of reaction can be further enhanced.

In zinc and barium ferrites synthesis Hunh [44] used iron oxide consisting of a large percentage of gamma ferric oxide, γ-Fe$_2$O$_3$, instead of the usual raw material alpha
ferric oxide, $\alpha$-Fe$_2$O$_3$. And, it was observed that the rate of reaction is enhanced and ferrites occurred at lower temperatures than that indicated by using $\alpha$-Fe$_2$O$_3$ as a starting material in the ferrite synthesis. In nickel-zinc ferrite preparation it has been noticed [45] that the magnetic performance parameter and resistivity values increased when cubic spinel $\gamma$-Fe$_2$O$_3$ is used as a starting material instead of $\alpha$-Fe$_2$O$_3$. Although no explanations are given for such enhanced reaction rate between the reactants in zinc and barium ferrites formation, reason for the improved behaviour of $\gamma$-Fe$_2$O$_3$ as a starting material becomes quite obvious by considering different factors that influence the solid state reaction, as described in previous paragraphs, especially, the structural aspects may be considered as a main factor in influencing the solid state reactions, because high temperatures take care of all other factors if reactive reactants are used.

As it was mentioned, the nucleation of the reaction product is facilitated if there is a structural similarity between the product and one or both of the reactants, because this reduces the amount of energy that required for structural reorganisation that is necessary for the nucleation to occur. $\alpha$-Fe$_2$O$_3$ is rhombohedral with hexagonal close packed oxide ions arrangement is not similar in structure with cubic close packed spinel product, although MO (the divalent metal oxide used in ferrites synthesis) may or may not be cubic, say NiO and MnO are cubic. Instead of $\alpha$-Fe$_2$O$_3$ if cubic $\gamma$-Fe$_2$O$_3$ (vacancy ordered spinel) is used in the ferrite synthesis, say NiFe$_2$O$_4$, then both the reactants are now in cubic form ($\gamma$-Fe$_2$O$_3$ and NiO) which are similar in structure to that of the product spinel. And, hence, the rate of reaction is expected to be enhanced in the ferrite preparation when $\gamma$-Fe$_2$O$_3$ is used instead of $\alpha$-Fe$_2$O$_3$, as a starting material.

It may be argued similarly as above the enhancement of reaction rate and improvement of ferrite character when magnetite is used as a starting material [39 41] in ferrite synthesis. Here Fe$_3$O$_4$ and NiO both are cubic so also their product NiFe$_2$O$_4$ [41].
The structural similarities, thus, influence the rate of reaction. However, although the starting material is Fe$_3$O$_4$, there is a phase transition to Fe$_2$O$_3$ is observed which is hexagonal close packed one. But, then, the formed oxide is reactive and thereby increases its activity with the NiO.

The phase transformation of Fe$_3$O$_4$ to Fe$_2$O$_3$ ($\alpha$-Fe$_2$O$_3$) may also be considered to be through $\gamma$-Fe$_2$O$_3$ as,

$$\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_2\text{O}_3$$

Hence, when magnetite is used as a starting material in ferrite synthesis, say NiFe$_2$O$_4$, the reaction of cubic Fe$_3$O$_4$ with cubic NiO, no doubt, is increased but further enhancement in the rate occurs as Fe$_3$O$_4$ transforms not only into yet another cubic form, $\gamma$-Fe$_2$O$_3$ but also a much more reactive oxide, $\gamma$-Fe$_2$O$_3$, as it is formed in situ. Thus, Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ are found to be better starting materials in ferrite synthesis.

Since the preparation of ferrites by solid state technique is normally carried out in air with $\alpha$-Fe$_2$O$_3$ as the starting material, little is known of the reaction or the properties of the products obtained using magnetite or $\gamma$-Fe$_2$O$_3$ when used as a raw material. In literature few studies are being made [39-41, 46] about such synthesis using $\gamma$-Fe$_2$O$_3$ and Fe$_3$O$_4$, however, nothing beyond that is explained excepting a statement that the phase transformation of Fe$_3$O$_4$ to hematite, $\alpha$-Fe$_2$O$_3$, during heat process may be reactive and hence the reaction is speeded up giving ferrites well and even at lower temperatures.

Other than structural aspects that are being considered in the easy formation of spinel product, when one or both the reactants have similar structures to that of the nucleating product, there appears to be no very apt explanations for such enhanced rate of reaction that take place when $\gamma$-Fe$_2$O$_3$ and Fe$_3$O$_4$ are used as a starting material instead of $\alpha$-Fe$_2$O$_3$. 
Aim of the present studies

Solid state reactions between hematite, $\alpha$-$Fe_2O_3$, the usual starting material in ferrite synthesis and metal oxides leading to normal, inverse and random spinels of academic and industrial interest have been widely studied. However, a literature survey indicates that ferrites of better characteristics can be obtained by using magnetic iron oxides, magnetite ($Fe_3O_4$) and maghemite ($\gamma$-$Fe_2O_3$) instead of $\alpha$-$Fe_2O_3$ as a starting material.

Since, literature is quite exhaustive about the preparation, characterization and correlation of electromagnetic properties of ferrites with their structural and microstructural aspects which depends on their preparative conditions and nature of starting materials, the studies of ferrites using $\alpha$-$Fe_2O_3$ as a starting material do not require any further exploration. But, the investigation on ferrites prepared from $\gamma$-$Fe_2O_3$ / $Fe_3O_4$ need some attention of researchers to get to know whether ferrites can be produced with still better electromagnetic characteristics than those observed from ferrites obtained from routine raw materials, $\alpha$-$Fe_2O_3$. And, we are aiming at this aspect of knowing how far the magnetic spinel iron oxide, $\gamma$-$Fe_2O_3$, is superior in their behaviour to $\alpha$-$Fe_2O_3$ in yielding ferrites of better characteristics and that too at lower temperatures. A systematic study is, therefore, planned and the results of such investigations are presented in this thesis. These studies are not only aimed at knowing the superiority if at all of $\gamma$-$Fe_2O_3$ (or $Fe_3O_4$) in ferrites synthesis but also to see whether the knowledge thus acquired can be made applicable.

Scope

A preliminary studies done in our lab with $\gamma$-$Fe_2O_3$ and MgCO$_3$ as starting materials indicates a single phase MgFe$_2$O$_4$ formation $\sim$1000°C, while
\( \alpha\)-Fe\(_2\)O\(_3\) (hematite) + MgCO\(_3\) at that temperature showed a mixture of MgFe\(_2\)O\(_4\) (mainly) and \( \alpha\)-Fe\(_2\)O\(_3\) suggests that an incomplete reaction has taken place between hematite and the carbonate. The MgFe\(_2\)O\(_4\) obtained from \( \alpha\)-Fe\(_2\)O\(_3\) showed many properties different from that of the ferrite synthesized from \( \gamma\)-Fe\(_2\)O\(_3\). A variation in some properties are attributed not only to the non completion of the ferrite phase but also to non uniform particle size distribution in the ferrite prepared from \( \alpha\)-Fe\(_2\)O\(_3\). Although, the variation in properties could not be considered due to the only difference in the nature of reactants involved, but also to inadequate temperature adopted for the synthesis. Hence, many other different aspects are required to be ascertained. Only important outcome of these preliminary studies is that the \( \gamma\)-Fe\(_2\)O\(_3\) and mixture of \( \gamma\)-Fe\(_2\)O\(_3\) + \( \alpha\)-Fe\(_2\)O\(_3\) obtained from different sources gave ferrites of almost identical results which were distinctly different from the ferrite prepared from commercial \( \alpha\)-Fe\(_2\)O\(_3\). Though results in these studies could not give any inference, the ferrite synthesized from \( \gamma\)-Fe\(_2\)O\(_3\) seemed to be formed \( \sim\)1000°C, whereas, higher than this temperature is needed to achieve single phase ferrite from \( \alpha\)-Fe\(_2\)O\(_3\). But, most important results of these studies is that \( \gamma\)-Fe\(_2\)O\(_3\) useful in ferrite synthesis could be prepared easily from iron ore rejects from chemical beneficiation route using hydrazine method to prepare easily decomposable precursors from acid extract of the ores.

Iron ore rejects are the main iron oxide sources for the synthesis of ferrites in our current research activities. From Table 1.3 it is seen that Indian contribution in the world ferrite production is insignificant. Considering the significant projected world ferrites production, by the turn of this century (Table 1.1), India can play an important role in world ferrites market as upgraded hematite (Table 1.2) expected to meet the huge iron oxide requirement needed for the manufacture of the ferrites (both soft and hard). This is due to the fact that India has rich iron ore reserves [43] of about 15265 million tonnes.
(mt) which will last for another 250 years with the present rate of mining of ~ 60 mt per year. And Goa, a tiny state of India, was blessed with such rich iron source. But, because of rampant high grade iron ore exports, since 1950, amounting to about 300 mt, Goa now has an estimated reserves of ~ 400 mt which is expected to last another 20 - 25 years with the present rate of production of 15 - 17 mt per year.

Iron ore mining industry in Goa is mostly export oriented. Considering the high grade iron of > 58(%) Fe export (A and B in Table 2.1) for the last 50 years, a low grade (< 50(%) Fe) iron ores are piling up as rejects - a national waste. In Goa, there is an estimate of > 900 mt of low grade iron ore rejects and tailing that are being dumped around mining areas which create environmental problems. And tapping of such low grade iron ore rejects to make useful in preparing iron oxide through chemical method is our objective. If we economically exploit the iron ore rejects and synthesize iron oxide useful in ferrites synthesis, we may look forward to be a leader in ferrites market, in future. Any, this may be the reason why in his keynote address, Dr. B. B. Ghat (Bell Lab, USA) during the 5th International Conference on Ferrites (ICF - 5, Bombay, India, 1989) made it clear [48] that “there was ample opportunity for entrepreneurs, scientists and technologists trained in ferrites and related disciplines to contribute to the economic growth in India and to the world ferrite market”. Prof. P. S. Deodhar (chairman, ICF - 5) in his inaugural address also made similar emphasis.

Any possible use of waste enhances the economic development. Our endear our is therefore, lies in making use of iron ore reject in preparing active iron oxide for synthesizing ferrites.

Having done elaborate work in our laboratories to easily synthesize γ-Fe₂O₃ from iron rejects, it was felt that some more systematic investigations are needed to chemically beneficiate iron ores to finally obtain γ-Fe₂O₃ economically useful in ferrite synthesis.
Objectives / Methodology

After aiming at the synthesis of ferrites from γ-Fe₂O₃ and considering the scope of the present work, it is natural to have objectives in our mind before actually planning our research and adopting a methodology to successfully fulfill our aim.

The objectives are as under,

- Sampling of the ore rejects and choosing of a representative sample.
- Determination of the main impurity constituents of iron ore rejects and the chemically beneficiated ore sample.
- Synthesizing α-Fe₂O₃ and γ-Fe₂O₃ from the ore.
- Using α-Fe₂O₃ and γ-Fe₂O₃ in the synthesis of ferrites, Mg ferrite and MnZn ferrite and comparing their characteristics with the ferrites that obtained from commercial α-Fe₂O₃ (hematite) and a standard γ-Fe₂O₃ (maghemite).
- Studying the ferrite synthesis thoroughly, especially, MnZn ferrite whose preparation procedure requires knowledge of exact atmospheric and thermal control.
- Investigating structural aspects of γ-Fe₂O₃ and look for their role in ferrite formation.

Organisation of the thesis

Chapter 1 General Introduction

An exhaustive literature survey made is used to introduce the subject matter of the thesis. Here it has been highlighted that India is insignificant in the world ferrite market, although it has one of the best iron sources in the world. Since the technological demand for ferrites (both soft and hard) is going to be increased considerably, India can play an important role in tapping its natural iron resources. Among various iron oxide sources like spray roasted iron oxide from acid pickle solution of steel industry, it is going
to be upgraded hematite ore which would meet major iron oxide requirement for ever increasing ferrite industry. And, hence India can look forward for such sources.

Importance of magnetic oxides, Fe$_3$O$_4$ (magnetite) and γ-Fe$_2$O$_3$ (maghemite) in ferrite synthesis in preference to usual starting material, hematite, α-Fe$_2$O$_3$ has been sketched in this chapter. Therefore, upgradation of hematite ore, no doubt eases the iron oxide demand for ferrites industry but if γ-Fe$_2$O$_3$ could be prepared directly from ore, after chemical beneficiation, then one can effectively use this oxide for high tech ferrite preparation of better quality. To realise this importance of γ-Fe$_2$O$_3$ in the synthesis of ferrites, two known ferrites systems, magnesium ferrite MgFe$_2$O$_4$ and manganese zinc ferrite, Mn$_{1/2}$Zn$_{1/2}$Fe$_2$O$_4$ have been introduced.

Chapter 2 Chemical beneficiation of iron ore rejects

Although physically upgraded hematite ore is useful in ferrite synthesis, the ferrites may have impurities that are inherent in the ore. A chemical beneficiation consists to acid treatment and hence pure iron oxide can be obtained by adopting suitable precipitation and heat treatment techniques. This is an energy consuming process. Hence, ferrite industry goes for spray roasted iron oxide from easily available acid pickle solution of steel industry. The iron oxide, α-Fe$_2$O$_3$, may contain impurities depending on steel variety. Since γ-Fe$_2$O$_3$ is found to be superior to α-Fe$_2$O$_3$ in ferrite synthesis, one can find out an easy method to directly prepare γ-Fe$_2$O$_3$ from acid pickle solution or acid leached ore. And when iron ore (of any grade now) can thus be used for the preparation of γ-Fe$_2$O$_3$ the energy burden in leaching can be profitably lessened if γ-Fe$_2$O$_3$ gives better ferrites than α-Fe$_2$O$_3$ and that too at lower temperature.

Chapter 3 Preparation and characterization of iron oxides from iron hydroxides, iron formates and their hydrazinated complexes

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The iron hydroxides and formates obtained from iron ore rejects as described in chapter 2 are utilised to synthesize iron oxides. Both iron hydroxides and iron formates are then hydrazinized. These precursors and their thermal end products are characterized.

Chapter 4 Studies on the magnesium ferrite and manganese zinc ferrites

The iron oxides, $\alpha$-Fe$_2$O$_3$ and $\gamma$-Fe$_2$O$_3$ synthesized from iron ore rejects are made use as starting materials to synthesize magnesium ferrite and manganese zinc ferrites. The important properties of the ferrites are then compared with the characteristics of the ferrites that prepared from commercial hematite, $\alpha$-Fe$_2$O$_3$ and standard gamma ferric oxide, $\gamma$-Fe$_2$O$_3$. The chapter is divided into three parts:

Part I: Microstructure and property correlation of MgFe$_2$O$_4$ (ore rejects [46])

Part II: Synthesis and characterization of MgFe$_2$O$_4$ (study sample I)

Part III: Synthesis and characterization of Mn$_{\frac{1}{2}}$Zn$_{\frac{1}{2}}$Fe$_2$O$_4$ (study sample II)

Chapter 5 Structural aspects of $\gamma$-Fe$_2$O$_3$: Hydrogen iron oxide or hydrogen ferrite

Ferrites prepared from $\gamma$-Fe$_2$O$_3$ seem to show superior characteristics to those synthesized from $\alpha$-Fe$_2$O$_3$. Hence, it may be attributed to the structural aspect as $\alpha$-Fe$_2$O$_3$ is different from that of $\gamma$-Fe$_2$O$_3$. The hexagonal close packed arrangement of oxide ions accommodate Fe$^{3+}$ in their octahedral sites in the corundum structure of $\alpha$-Fe$_2$O$_3$ which then reacts with MgO/MnO + ZnO which are cubic in nature giving cubic spinel. On the other hand, cubic spinel $\gamma$-Fe$_2$O$_3$ (vacancy ordered) reacts with MgO/MnO + ZnO giving cubic ferrite spinel. The cubic spinel $\gamma$-Fe$_2$O$_3$ and the other reactants which are also cubic find no difficulty in nucleating cubic ferrite phase, whereas corundum structured $\alpha$-Fe$_2$O$_3$ may require an extra energy to break and form bonds.

The cubic spinel $\gamma$-Fe$_2$O$_3$ is not only similar in structure to that of nucleating...
ferrites but it has vacancies in its unit cell, mainly on octahedral sites and these vacancies may help easy diffusion of cations which is indeed needed in solid state reaction to occur. Hence, a detailed structural aspects of $\gamma$-Fe$_2$O$_3$ is being studied and their results are compiled in the chapter.

Chapter 6 Conclusion