CHAPTER - II

2.A- PREPARATION

2.B- CHARACTERISATION
2.0 Introduction

The properties of ferrites are governed by their chemical composition, and the heat treatment given during preparation. Therefore, preparation of ferrites with specific properties in a reproducible manner is rather a difficult task. The intrinsic properties of ferrites can be controlled by physicochemical composition and by using high quality starting materials. However, control of extrinsic property is rather critical, because the factors to be controlled are large in number. Thus preparation of ferrites though looks to be simple, it is rather critical. The chemical homogeneity (mixing at molecular level), maintainance of stoichiometry and development of microstructure are the important and crucial stages involved in the preparation. To achieve the goal, different methods have been adopted for preparation of ferrites. The characterisation of thus prepared ferrites, from the point of view of their crystal structure, stoichiometry and microstructure is most important, since, these are the factors that govern the properties of ferrites. Characterisation therefore, requires the instrumental analysis with high precision.

In this Chapter (Section-A) a brief survey of methods employed for the preparation of ferrites and the various factors that influence the microstructure and properties are discussed, along with the standard ceramic technique used for preparation of the materials under investigation.
Section 'B' of this chapter is devoted to characterisation of materials by X-ray diffraction technique, Infrared absorption spectroscopy, Atomic absorption spectrophotometric technique and microstructural analysis by scanning electron microscope.

2.1 Methods of Preparation of Ferrites

The preparation of homogeneous solid solution in the desired stoichiometric proportion, presintering grinding, and final sintering are the inherent steps of preparation of ferrites, irrespective of the technique employed.

2.1(a) Oxide Method

In this method high purity oxides are mixed in a desired weight proportions required in the final product. The component oxides are wet milled in rubber lined pot using stainless steel balls or by rotary ball method. After this the material is dried and pressed in to required shape, presintered ground and final sintered to obtain the final product. The drawback of this method is of contamination by mixing of steel in the final product, which is shown by Blackman’s study on preparation of manganese magnesium ferrites [1].

b) Decomposition Method

The carbonates, nitrates and oxalates of constituent metals are intermixed and presintered in air to produce oxides by thermal decomposition. The further stages are carried out in a sequence that is mentioned in oxide method. The advantage
of this method is that the oxide thus produced would readily undergo solid state reaction [2].

c) Hydroxide Precipitation

Mixing of constituent elements on molecular level can be achieved by precipitation of required metal ions in desired weight proportions. This method saves the lengthy and laborious milling operation and also solves the problem of availability of higher purity oxides. The knowledge of solubility product, measurement of pH to ascertain the completeness of reaction, are crucial stages in this method. This method was established by Economou and has been used afterwards by many workers [3-6].

d) Oxlate Precipitation

Metal oxlates have similar crystal structure, therefore the precipitation of the ferrite becomes rather simple. Washing of precipitate is not to be much worried about, because ammonium oxlates are used, then they do not leave any residue after ignition. The advantage of this method is that the mixing could be achieved on molecular scale [7].

e) Sol-Gel Method

Sol-Gel technique has been successfully utilised and optimized for the synthesis of various spinel ferrites of different chemical composition as a chief byproduct from various heavy metal ion containing waste water effluents [8]. The possible raw material sources are industrial waste water in treatment of iron
and steel industries, titanium mining etc. The raw material contains $\text{Fe}^{2+}/\text{Fe}^{3+}$ and divalent metal $M^{2+}$ $(\text{Zn}^{2+}, \text{Ni}^{2+}, \text{Mg}^{2+}, \text{Mn}^{2+}, \text{Co}^{2+})$ in an aqueous solution to which a freshly prepared alkaline solution is added till the required pH value is obtained. The careful oxidation of these gels along with their thermal transformations gives the final product. The details of this method are discussed by Banthia and Jha [9].

f) Precursor Method

In this method solid solution or precursor solution of compounds containing metal ions $M^{2+}$ and $\text{Fe}^{3+}$ in the desired ratio is taken as the starting material and decomposed the precursor to form the ferrite. This method gives excellent stoichiometry, low trace of impurity content and homogeneity approaching the theoretical density of the final product [10]. In this method the two metals are mixed on an atomic scale therefore, greater reactivity and homogeneity is achieved. The diffusion distances are smaller than those in ceramic method. The use of precursors like hydroxide, carbonate hydrazine carboxylate and oxalates have been established to form spinel ferrites [11-15]. Among these precursors, oxalates are more popular because of lower solubility and decomposition temperature. Metal oxalate hydrazines and hydrazine carboxylate are superior precursors because they give fine particle ferrites at low temperature with excellent homogeneity and purity [16,17].
g) Wet Chemical Methods

Preparation of ferrites can also be achieved from solutions of water soluble salts of component metals. Principal advantages of this method are the homogeneity achieved at molecular level, smaller grain size, low porosity and large surface area. The methods like spray reactions, freeze-drying and hydrochemical oxidation have been used for the preparation of ferrites [18-20].

h) Ceramic Technique

This method is very popular in the preparation of sintered ceramics because it is relatively simple. The simplicity lies in the fact that high purity oxides and carbonates as a starting materials are readily available. The flow chart of various stages of preparation of ferrites by this method is given in figure 2.1 [21].

In this process appropriate metal oxides (MO) or their carbonates, oxalates, nitrates which on decomposition give reactive metal oxides and Fe₂O₃ are accurately weighed and mixed in desired weight proportions. The mixing is carried out in a liquid suspension in water, alcohol, acetone or kerosene in steel ball mill or agate mortar. The slurry thus prepared is dried and heated preferably in oxygen atmosphere or in air. The next step is to grind it. A steel ball grinding gives better homogenisation of the product by bringing together unreacted particle because of decrease of diffusion distances and also reduces the particle size. The use of organic binder such as polyvinyl acetate (PVA) as a binder to increase the strength of the ferrite powder. The pressure in the range of 1
to 10 tons/sq.inch is applied for compaction of the materials in a steel die. The pellets thus formed are heated in a platinum crucible at a reaction temperature in the range of 900°C to 1500°C for several hours depending upon the chemical composition. The range of temperature can be reduced by increasing heating time.

1. **Mechanism of Solid State Reaction**

The mechanism of the solid state reaction forming spinel ferrites (MF\textsubscript{e}\textsubscript{2}O\textsubscript{4}) from the component metal oxide (MO) and ferric oxide (Fe\textsubscript{2}O\textsubscript{3}) has been discussed by several authors [23-25]. The schematic representation of this solid state diffusion reaction is as shown in Fig.2.2

Case-A: the diffusion mechanism involved in this step is called as counter diffusion [23]. The cations migrate in opposite directions whereas the oxygen anions remain stationary. The boundary between MO and Fe\textsubscript{2}O\textsubscript{3} (inert marker position) does not shift during this reaction. The amount of formation of ferrites on the sides of boundary is 1:3. Formation of magnesium ferrite is found to undergo the said mechanism [26].

Case-B: in this step oxygen enters in the diffusion process. The diffusion of either of the cations (M\textsuperscript{2+} or Fe\textsuperscript{3+}) is compensated by flux of anions. If the diffusion rate of Fe\textsuperscript{3+} is greater than that of M\textsuperscript{2+} then inert marker position shifts as shown with MF\textsubscript{e}\textsubscript{2}O\textsubscript{4}/Fe\textsubscript{2}O\textsubscript{3} boundary. This has been evidenced in the formation of zinc ferrite (ZnFe\textsubscript{2}O\textsubscript{4})[27].
Case C: The diffusion of iron through $\text{Fe}^{2+}$ reduced state in the layer of ferrite has been explained by the diffusion of oxygen through the gas phase. The oxygen is evolved at the $\text{MFe}_2\text{O}_4/\text{Fe}_2\text{O}_3$ interface and reabsorbed at the $\text{MFe}_2\text{O}_4/\text{Fe}_2\text{O}_3$ boundary. The inert marker position in this case is proportional to the amount of oxygen transported. The presence of $\text{Fe}^{2+}$ has been observed in the reaction layer [1,25,28].

**Drawbacks of Ceramic Method**

1) Possibility of chemical inhomogeneity due to evaporation of $\text{Zn,Cd,Li}$ at elevated temperatures for hours together.

ii) The efforts to obtain high density results in larger particle size.

iii) The evolution and reabsorption of oxygen increases the porosity thereby limiting the high density requirement.

iv) During excess heating the ferric oxide has a tendency to lose oxygen, thereby developing possibility of reduction of $\text{Fe}^{3+}$ to $\text{Fe}^{2+}$, thus creating chemical inhomogeneity, which adversely affects the properties.

2) Presintering, Pressing, Sintering

The presintering, pressing and sintering are the stages involved in the preparation of ferrites irrespective of the techniques employed (see flow chart figure 2.1). These stages are crucial stages in the preparation of sintered ceramics since they decide the properties of the final product. Therefore, due care should be taken while following these stages.
Flow chart 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. 2.1
3) Presintering

According to Swallow and Jorden the purpose of presintering is to decompose carbonates and higher oxides so that evolution of gas in final sintering is avoided [29]. The possible mechanism of the solid state reaction in this stage is given in figure 2.2(case A). In this process partial formation of the final product takes place. It also depends on chemical composition and temperature. Presintering also reduces the shrinkage that occurs in final sintering.

4) Pressing or Extrusion

The dry powder is mixed with organic binders such as polyvinyl acetate, zinc stearate, ammonium alginate or gum arbo of very low concentration (1 to 5%) so as to increase the green strength. The material thus formed is dried and pressed to desired shapes by applying pressure that ranges from 1 to several tons per square inch.

5) Sintering

The presintered and pressed material is heated at a temperature of 1000 °C to 1500 °C for several hours depending on the material. The solid state reaction involved in sintering is as shown in figure 2.2. The final product formed is by interaction of constituent cations between the adjacent particles. They stick or sinter together because at this temperature ferrite has a good plasticity. The sintering process is divided into three classes such as, (a) reactive sintering (b) homogeneous
Fig. 2.2 - Schematic representation of possible reaction mechanism involved in ferrite formation [22].
Sintering and (c) hot pressing.

a) Reactive sintering

Formation of ferrites between the large and partly sintered small particles takes place at elevated temperatures [30]. The reaction results in increase of the local volume \((\Delta v > 0)\) thereby decreasing densification rates. This puts the limitations on the density of final product. If the formation of ferrites is due to Kirkendall effect porosity increases which adversely affects density.

b) Homogeneous Sintering

Truly homogeneous compounds are sintered then the solid state diffusion occurs due to volume diffusion process in which vacancies sink out at the grain boundaries. By this process, using very small particle size, ferrites greater than 95% of theoretical density have been prepared by many workers [16, 17, 20].

c) Hot Pressing

This technique was developed by Gruintjes and Oudemans to achieve simultaneously small grain and high density at lower sintering temperature, which are the extreme ends in preparation of ferrite [31]. This is achieved in this method by applying simultaneous temperature and pressure which accelerate the sintering rates [7]. Simultaneous application of pressure and temperature enhances the grain to grain contact, increases the degree of compaction thereby decreasing the porosity. The disadvantage of this method is that excess pressure may change
the degree of inversion as well as reduction of metal ions there by increasing \( \text{Fe}^{2+} \) concentration which adversely affects the properties. This technique has been used by different workers [32,33] and also have been simplified [34,35].

2.2 Factors Influencing The Sintering Process

To avoid the reduction of the sample that creates inhomogeneity and develops the desired microstructure, the factors having dominant effect on sintering should be kept in control. According to Stuijts the factors such as, particle size, particle size distribution, shape, intraparticle porosity, agglomeration, homogeneity, pore size distribution, temperature gradients, gas atmosphere and pressure have a dominant effect on sintering.

The particle size has a dominant effect on physical density of final product. Since crystal growth is activated by temperature. To obtain dense ferrite, therefore, one has to start with ultrafine powders.

a) Atmosphere

To achieve the desired stoichiometry and valence states of cations, unaffected by oxidation or reduction, requires control of correct partial pressure of oxygen in a furnace. The elements like Fe, Mn, Cu and Co are sensitive to this [37]. The effect of furnace atmosphere on formation of ferrous ferrite has been studied extensively [38,39,40]. It is found that, oxygen deficiency causes change in valency of metal cations, while excess oxygen creates cation vacancies. Formation of \( \text{Fe}^{2+} \) severely affects the resistivity since the electrical conduction is due to \( 2e^- + \text{Fe}^{2+} = \text{Fe}^{3+} \).
b) Porosity

It is the inherent part of the sintered ceramics, in which powder compaction is used. The compaction of spherical nonporous particles develops pores with more or less uniform pore structure in which the pore space is made up of interstitial voids between particles. The pore volume depends upon the particle size and average coordination number. The pore structure is modified by temperature and pressure. Heating of the materials beyond Tamann temperature causes shrinkages to occur in which particle fastening and crystal grain growth takes place. In this case voids are eliminated by diffusion of vacancies which readily occurs at grain boundaries.

Application of pressure decreases the pore volume and also the surface area. The particle size affects the porosity. Irregular particle size, lowers the coordination number therefore the voids will be more irregular and large. The porosity can be decreased by increasing sintering rates and the use of hot pressing. The porosity can be decreased by repeated sintering cycles however at the cost of increase of grain growth. Entrapped pores developed during discontinuous grain growth are less affected at ordinary sintering temperature, therefore porosity remains an inherent part exhibited in the microstructure of the sintered ceramics.

c) Grain Growth

The average grain size is a function of temperature and time, given by,

\[ D = D_0 \exp(-\frac{E}{RT}) \times k^t \]

where \( D_0 \) - original particle size, \( k \) is the temperature
dependent factor, \( t \) is time. Average grain size increases with temperature because of decrease of grain boundary energy. The grains having more than six surfaces grow at the expense of their small neighbours. The discontinuous grain growth takes place, when average grain size becomes equal to critical size. 

Zener has given an empirical relation for discontinuous grain growth as,

\[
D_{Cr} = \frac{d_i}{f_i}
\]

where \( d_i \) - diameter of inclusion

\( f_i \) - volume fraction of inclusion.

The discontinuous grain growth forms duplex structure. The discontinuous grain growth is due to impurity, chemical inhomogeneity, and variation of density. The grain size can be controlled by the use of high purity oxide, small particle size and by the use of hot pressing technique.

d) Sintering Temperature

The sintering temperature is a very important parameter since it decides the reactivity of component metal oxides to form ferrite. Strictly speaking this temperature must be equal to melt temperature of component oxides since at this temperature reactivity is high. However, in practical cases it is 2/3 of the melt temperature to avoid evaporation of component metal oxides having lower melting temperature. The requirement of high sintering temperature therefore is compensated by increasing sintering time. The increase of sintering temperature is
accompanied by grain growth, resulting in increase of permeability. It also decides grain distribution and orientation of crystallite. However, it helps in increasing density [41]. Increase of sintering temperature beyond a critical value adversely affects permeability at higher frequencies.

2.3 Preparation of Ferrites Under Present Investigation

Preparation of ferrites by different methods discussed so far is advantageous in one way or the other. Preparation of most of the commercial ferrites on a large scale is done by ceramic method, since high purity, fine particle oxides are readily available. Therefore, for the preparation of ferrites under investigation ceramic technique is preferred.

General Chemical Formula

The general chemical formula of the system is,

\[ \text{Cdx Cu}_{1-x} \text{Fe}_{2-y} \text{Gd} \text{yO}_4 \] with \( x = 0.0, 0.2, 0.4, 0.6, 0.8 \) and \( 1.0 \) for \( y = 0.0, 0.1, \) and \( 0.3. \)

Raw Materials used

1) A.R.grade \( \text{Fe}_2\text{O}_3 \), make-Riedel (Germany) purity-99.5\%, valency Fe\(^{+++}\) mol.wt. 159.69
2) G-R grade \( \text{CuO} \) - MW.79-54, valency \( \text{Cu}^{2+} \), Sarabhai chemical-purity-99%
3) A.R.grade \( \text{CdCO}_3 \)- MW. 172-41, Valency \( \text{Cd}^{2+} \), Reanal Budapest. Purity 99%.
4) A.R.Grade \( \text{Gd}_2\text{O}_3 \)-make Indian Rare Earth-Valency \( \text{Gd}^{3+} \) Purity-99.9% MW.362.52
Weighing - The required raw materials are weighed on a single pan microbalance and mixed in their molar weight proportions.

Milling - The dry mixed powders (compositions) are mechanically blended in an agate mortar using A.R. grade acetone for suspension so as to form the intimate mixture. The mixture is dried, ground, and sieved using a mesh (140 μ). The sieved material is again ground with acetone base in a repeated second cycle as before. After this the mixture is transferred to clean and dry platinum crucible.

a) Presintering

The platinum crucibles are kept in a glowbar furnace and heated in air atmosphere at 750 °C for 24 hours. The furnace temperature was controlled. The furnace was slow cooled at the rate of 80 °C/hour. The calibrated chromel alumel thermocouple was used to measure the temperature.

b) Grinding

Slowly cooled samples are ground with acetone base in an agate mortar, so that the particle size becomes nearly equal.

c) Sintering

The compositions are transferred to clean and dry platinum crucible washed with chromic acid and distilled water. The compositions are heated in air in a glow bar furnace. The sintering is carried out at 975 °C for 48 hours. The slow cooling of the compositions was carried out at the rate of 80 °C/hour.
d) Pellet formation and pressing

The sintered samples were ground with actone base to obtain uniform particles. The 5% PVA was used as binder. The pellets were formed by using a 1 cm die at the pressure of $5 \text{ tons/inch}^2$.

e) Final sintering

The pellets were kept on thin platinum foil and the furnace heating and cooling cycles were carried out in the same conditions as mentioned in sintering.

f) Polishing

The pellets thus formed are polished by using soft metal sandpaper so that they are of uniform thickness and opposite faces exactly parallel to each other.
2.4 Introduction

To explore the features of the chemical composition, crystal structure, defects, phases and microstructure of the materials, characterisation is utmost important. The characterisation by different methods is helpful in predicting properties of the materials. The analytical methods of characterisation provide the on-line analysis by automated means in a rapid and reproducible manner. The use of sophisticated automatic and computerised instruments resolve the structural and compositional data with greater accuracy, which do not leave any room to personal errors. The X-ray, neutron and electron diffraction techniques, scanning electron microscopy, the Infrared absorption technique are the examples of it. However, an accuracy in the chemical compositional analysis depends to some extent on the accuracy of the analysis. Irrespective of all these, the accuracy of the results, and interpretation are also limited by the knowledge and skill of the user. This chapter includes the characterisation of the samples under investigation by X-ray diffraction, Infrared absorption (I.R.) Atomic absorption technique and scanning electron microscopy. The tools used are discussed on the lines of theoretical aspects, experimental technique used for data acquisition, calculation of related parameters and the interpretation thereof.
2.4.1 Diffraction Study

The properties of polycrystalline soft ferrites are structure sensitive. The properties therefore can not be fully understood until the structure is known. The size and shape of the unit cell determine the angular positions and 'd' spacings. The relative intensity of the reflection peaks is determined by the atomic arrangement within a crystal lattice. The diffraction analysis provides the information of structural parameters size and shape of the unit cell, the particle size, atomic positions, pore size distribution, chemical analysis, stress measurements and distribution of ion species among the available sites. The X-ray, electron and neutron diffraction techniques have been used extensively for structural studies of soft ferrites.

a) X-ray Diffraction

X-ray diffraction method was used for the first time by German physicist Max Von Laue in 1912 [42]. In 1913, Bragg solved the difficulty of determination of crystal structure from the analysis of Laue experiment [43]. The striking contribution of Bragg's experiment in the field of diffraction analysis, Bragg's diffraction condition, which is given by,

\[ 2d \sin \theta = n \lambda \]  \hspace{1cm} (3)

where \( \lambda \) - wavelength of X-rays
\( d \) - interplanar distance
\( \theta \) - angle

From the equation (3) it is clear that the diffraction experiment can be carried out by varying wavelength \( \lambda \) or angle \( \theta \). Further the permutation combination of \( \lambda \) and \( \theta \) discloses
the three possible ways in which diffraction experiment can be carried out; and accordingly they are classified as,

<table>
<thead>
<tr>
<th>Method</th>
<th>λ</th>
<th>θ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Laue method</td>
<td>variable</td>
<td>fixed</td>
</tr>
<tr>
<td>2 Rotating crystal method</td>
<td>fixed</td>
<td>variable</td>
</tr>
<tr>
<td>3 Powder method</td>
<td>fixed</td>
<td>variable</td>
</tr>
</tbody>
</table>

Among these, powder method has been used extensively for polycrystalline powder samples because of its accuracy and ability to identify the phases.

b) Neutron Diffraction

The principal advantage of this technique is that the scattering factor is independent of angles and atomic number of the scatterer. Therefore, it facilitates the accuracy in measurement when scatterers are of lower and adjacent atomic numbers.

c) Electron Diffraction

The problems encountered in diffraction with X-ray studies, when material samples are thin films or foils, due to large penetration power of X-rays are solved by electron diffraction. However, use of the X-rays and electron diffraction technique are limited because of their charge in the analysis of light element and therefore, gives weak reflection intensities. For the characterisation of the ferrite compositions under investigation X-ray diffraction technique is used.
2.4.2 Experimental Technique

In the present investigation the Philips diffractometer (Model 1710) with filtered CuK$_\alpha$ radiations ($\lambda = 1.542 \text{ Å}$) from X-ray tube operated at 30 kV and 1.5 mA current is used. The diffractograms of the polycrystalline powder samples, are obtained in the range (2θ) of 0° to 90° at U.S.I.C.(CFC) department, Shivaji University, Kolhapur. The principle of operation, preparation of the sample and the procedure adopted to calculate various structural parameters is given.

a) The Diffractometer

The schematic of the diffractometer and its essential components are as shown in figure (2.3). A powder specimen 'c' in the form of flat plate is placed on table 'H' capable of rotating about an axis '0'. The diverging beam of filtered X-rays is collimated by a slit 'A; to make incident on the specimen 'c'. The beams are diffracted by a specimen after passing through the slits B and then enters the counter G. The carriage 'E' which is free to rotate about an axis '0' holding the receiving slits moved through an angle of '2θ' of which measurements can be made on scale k. The mechanical coupling between 'E' and 'H' is such that rotation of a carriage through 'θ' rotates the specimens through '2θ'. The coupling also ensures the angles of incidence and reflection each equal and equal to half of total angle of diffraction. In order to obtain the diffractogram the counter is driven at a
Schematic X-ray Diffractometer

C - Crystal  I - Ionisation chamber
G - Current detector

Fig. 2.3
constant angular speed with increasing the value of '2\theta' until the desired range is scanned. At the same time the recorder moves through an angle '2\theta' proportional to length.

b) Preparation of Samples

A microslide (2.5 cm X 2.5 cm) with thin coating of Melrock 211 compound (Silicon) on total area (3 cm X 2.5 cm); powder sample is uniformly spread over a coated position. Sample thus prepared was kept on holder c. The spinel ferrites are having f.c.c. lattice having lattice constant 'a' in the range of 8Å to 9Å therefore, first reflection is expected for 2\theta values between 15° to 80°.

2.4.3 Indexing the Diffractograms and Calculation of Structural Parameters

(1) Indexing the diffractograms of cubic spinels.

The interplaner distance (d) in cubic lattice is (a=b=c. \(a = \beta = \gamma\)) related to Miller indices (hkl) and lattice constant 'a' by the relation

\[ d_{hkl} = \sqrt{\frac{\lambda^2}{4 (h^2 + k^2 + l^2)}} \]  

This equation gives calculated d spacings. The observed d spacing is given by,

\[ d_{obs} = \frac{\lambda}{2 \sin \theta} \]  

If d observed is equal to d(cal) then values of hkl taken are correct. The lattice constant 'a' can be calculated by the relation,

\[ a = \sqrt{\frac{\lambda^2}{4 \sin^2 \theta}} \]  

\[ (h^2 + k^2 + l^2)_{hkl} \]
The \( h^2 + k^2 + l^2 \) values of F.C.C. spinels are 3, 4, 8, 11, 12, 16 and 19 etc., and therefore allowed reflection peaks will be 111, 200, 220, 311, 222, 400, 331, 420, 422, 333, 511 and 440 etc. The most remarkable feature of F.C.C. spinel is that 311 reflection is having 100% relative intensity. Therefore from observed d space of this reflection and by assigning the Miller indices (311) to prominent peak and calculating lattice constant 'a' from this reflection and using it for all reflections, the planes can be indexed easily. However the calculation of lattice constant from prominent peak sometimes leads to incorrect values of lattice constant, because measurement of 'd' spacings at lower angles is limited due to \( \sin \theta \) values. The accurate value of \( \sin \theta \) will be therefore at an angle of '2\theta' equal to 180° and \( \theta = 90° \). Therefore accuracy in the measurement of lattice parameter lies in the use of backward reflections having 2\theta = 180° [45].

The practical method to obtain lattice constant 'a' to cover the information at higher angles is to plot the graph of lattice constant 'a' against some error function \( \cos \theta \) or \( \sin \theta \). The plot shows a straight line which can be confidently extrapolated to intersect lattice constant 'a' axis. The intercept gives the value of lattice constant at \( \theta = 90° \). The accuracy in the range of \( \pm 0.001 \AA \) can be obtained by this method [45].

2) Indexing the diffractogram of Tetragonally distorted spinel structure

The interplaner spacings 'd' in tetragonally distorted spinel structure having \( a=b=c \) and \( \alpha = \beta = \gamma \) is given by,

\[
d_{hkl} = \left( \frac{a^2}{h^2} + \frac{b^2}{k^2} + \frac{c^2}{l^2} \right)^{\frac{1}{2}}.
\]
where $a$ and $c$ are lattice parameters. The lattice constant 'a' can be calculated by using the equation,

$$a = \frac{\lambda}{2\sin \theta} \left[ (h^2 + k^2) + \frac{4}{(c/a)} \right]^{1/2}$$

(8)

The lattice constant 'a' and 'c' are calculated by following method.

i) Ignore the hkl lines and divide the remaining reflections in to two groups with indices hk0 and the other with 0kl.

ii) Calculate value of lattice constant 'a' from hko reflections (in this case $l = 0$, $c = 0$, in above equations)

iii) Calculate value of lattice constant 'c' from ool lines ($h = 0$, $k = 0$, and $a = 0$) in above equation.

iv) Two separate extrapolations are then made to find $a$ and $c$.

v) The extrapolation is made in this case against $(\cos^2 \theta / \sin \theta + \cos^2 \theta / \theta)$ since there are only few lines with hko and ool lines in backward reflections.

The allowed reflections in tetragonally distorted spinel are as, 111, 202, 220, 113, 311, 222, 004, 400, 422, 511, 404, 440.

The increase in the number of reflections is due to distortion of the lattice. The 'd' spacings of these reflections are different than that of host lattice. To identify these reflections use of A.S.T.M. cards of the possible phases. The matching of 'd' spacings will help in identifying the crystal structure of the phases. The insignificant reflections (low relative intensity) always pose problem in identifying chemical composition of the phases.
2.4.3(a) Calculation of Structural Parameters

The lattice constant 'a' of cubic spinel is calculated by equation (6) and that of tetragonally distorted spinels by equation (8). The value of lattice constant 'c' in tetragonally distorted spinel by putting value of 'a' in equation (8) and by adopting the procedure to calculate 'a' and 'c' discussed before, the metal oxygen bond length A-O on tetrahedral 'A' site is calculated by equation

$$A - O = (u - 1/4) a \sqrt{3}$$

(9)

the bond length -B-O on octahedral 'B' site is given by,

$$B - O = (5/8 - u) a$$

(10)

where 'u'-oxygen anion parameter

The ionic radii on tetrahedral A sites and octahedral B site are calculated by using the equations:

$$r_A = (u - 1/4) a \sqrt{3} - r(O_2)$$

(11)

$$r_B = (5/8 - u) a - r(O_2)$$

(12)

The percentage porosity 'p' of a ferrite material is calculated by using the relation,

$$p(\%) = \left(\frac{\rho_x - \rho_a}{\rho_a}\right) \times 100$$

(13)

where \(\rho_a\) is the apparent density, and is calculated by taking mass and volume ratio.

The \(\rho_x\) is the X-ray density of the ferrite material which is calculated by the expression

$$\rho_x = \frac{8M}{Na}$$

(14)

where M - molecular weight of the composition and N - be the Avogadro's number. The effective lattice constant 'a*' in tetragonally distorted spinels is calculated by the relation

$$a^* = \sqrt[3]{a^2 \cdot c}$$

(15)
2.4.4 Results and Discussion

The X-ray diffractograms of polycrystalline powder samples of 
Cd$_x$Cu$_{1-x}$Fe$_{2-y}$Gd$_y$O$_4$ (where x=0, 0.2, 0.4, 0.6, 0.8 and 1.0 for 
y=0, 0.1 and 0.3) were obtained by powder diffraction 
technique. These diffractograms are presented in figures 2.4 tc 2.9. The interplaner distance (d) in cubic spinel are calculated 
by using the expression 4 and in tetragonally distorted spinel 
by 7. The diffractograms are well defined with (311) as strong 
reflection peak which is an important feature of spinel structure. 
The (hkl) values are then compared with the allowed planes 
of FCC cubic and tetragonaly distorted spinels [46].

These calculated d values are compared with observed 
d values obtained from Bragg's diffraction condition. (Miller 
indices (hkl) of reflection peaks are indexed). The (hkl) values 
and lattice parameters calculated from equations 4 and 7 suggests 
that all the compositions are FCC cubic spinels except x=0.0 
for y=0, 0.1 and 0.3 which are tetragonaly distorted spinels 
with c/a > 1. The diffractograms do not show any ambiguous 
reflections which can be immediately noticed thereby suggesting 
the formation of single phase spinels. However, some low 
intensity reflection peaks are observed in Gd$^{3+}$ substituted 
compositions of which the intensity and number increases with 
increase of Gd$^{3+}$ content. These reflections are marked by star 
on the respective diffractograms. These reflections are identified 
as due to (GdFe)$_3$O$_3$ structure of orthorhombic character.
Fig. 2-5 X-Ray diffractograms.
Fig. 2.6  X-Ray diffractograms.
Fig. 27  X-Ray diffractograms.
Fig. 2B  X-Ray diffractograms.
Fig. 2.9 X-Ray diffractograms
This type of phase formation may be due to high reactivity of iron with gadolinium at elevated temperatures. Such orthorhombic distortions in copper containing spinel ferrites have been observed and reported in literature [48,49].

The lattice constant (a) was calculated by plotting the error function (cos²θ/sin θ + cos²θ/θ) of the diffraction angle against lattice constant (a) of each reflection and extrapolated it to 90°, to cover the information at higher angles. These values of lattice constants are presented in Table 2.1/2.3 along with the structural parameters such as tetrahedral metal oxygen bondlength (A-O), Octahedral metal Oxygen bondlength (B-O). Cationic radii (r_A), (r_B) and X-ray density (ρ_x) for y=0.0, 0.1 and 0.3 series for all the values of x (Cd content). The values of lattice constant (a) and (c) calculated for Cd_xCu_{1-x}Fe_{2}O_{4} (y=0.0) system are in good agreement with those reported in literature. [50,51]. However, for the ferrite system y=0.1 and 0.3 such data are not available in literature since the system of this type is being attempted for the first time.

From the tables 2.1 to 2.3 it can be seen that no considerable change in the value of lattice constant is observed after substitution of Gd³⁺. This may be due to comparable ionic radii of Gd³⁺ (1.1 Å) and Cd²⁺ (0.99 Å). However, on substitution of Gd³⁺ the values of lattice constant (c) in tetragonally distorted spinel ferrite is found to decrease, thereby by decreasing the axial ratio (c/a). The decrease in axial ratio may be due to decrease in number of Cu²⁺ occupying octahedral B site thereby reducing the effective co-operative Jahn-Teller
Table 2.1: Structural data of Cd$_x$Cu$_{1-x}$Fe$_{2-y}$Gdy$_{4-y}$ferrite system for $y=0.0$

<table>
<thead>
<tr>
<th>Composition $x$</th>
<th>Lattice constant (Å)</th>
<th>Bond length</th>
<th>Cationic radius $r_A$ (Å)</th>
<th>Cationic radius $r_B$ (Å)</th>
<th>X-ray density $\rho_x$ (gm/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>$a=8.25$</td>
<td>A-O: 1.89</td>
<td>B-O: 2.06</td>
<td>$r_A$: 0.57</td>
<td>$r_B$: 0.74</td>
</tr>
<tr>
<td></td>
<td>$c=8.70$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>8.47</td>
<td>1.93</td>
<td>2.06</td>
<td>0.61</td>
<td>0.74</td>
</tr>
<tr>
<td>0.4</td>
<td>8.54</td>
<td>1.97</td>
<td>2.06</td>
<td>0.65</td>
<td>0.74</td>
</tr>
<tr>
<td>0.6</td>
<td>8.58</td>
<td>2.01</td>
<td>2.05</td>
<td>0.69</td>
<td>0.73</td>
</tr>
<tr>
<td>0.8</td>
<td>8.65</td>
<td>2.05</td>
<td>2.05</td>
<td>0.73</td>
<td>0.73</td>
</tr>
<tr>
<td>1.0</td>
<td>8.69</td>
<td>2.09</td>
<td>2.05</td>
<td>0.77</td>
<td>0.73</td>
</tr>
</tbody>
</table>
Table 2.2: Structural data of \( \text{Cd}_x\text{Cu}_{1-x}\text{Fe}_{2-y}\text{Gd}_y\text{O}_4 \) ferrite system for \((y=0.1)\)

<table>
<thead>
<tr>
<th>Composition ( x )</th>
<th>Lattice constant ( a = 8.26 )</th>
<th>Bond length</th>
<th>Cationic radius</th>
<th>X-ray density ((\text{gm/cm}^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x )</td>
<td>( c = 8.56 )</td>
<td>( \text{A-O} = 1.88 )</td>
<td>( \text{B-O} = 2.05 )</td>
<td>( \gamma_A = 0.56 )</td>
</tr>
<tr>
<td>0.0</td>
<td>0.2</td>
<td>8.47</td>
<td>1.93</td>
<td>2.06</td>
</tr>
<tr>
<td>0.4</td>
<td>0.6</td>
<td>8.51</td>
<td>1.97</td>
<td>2.05</td>
</tr>
<tr>
<td>0.4</td>
<td>0.8</td>
<td>8.56</td>
<td>2.01</td>
<td>2.05</td>
</tr>
<tr>
<td>0.8</td>
<td>1.0</td>
<td>8.63</td>
<td>2.05</td>
<td>2.05</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>8.69</td>
<td>2.09</td>
<td>2.05</td>
</tr>
</tbody>
</table>

Table 2.3: Structural data of \( \text{Cd}_x\text{Cu}_{1-x}\text{Fe}_{2-y}\text{Gd}_y\text{O}_4 \) ferrite system for \((y=0.03)\)

<table>
<thead>
<tr>
<th>Composition ( x )</th>
<th>Lattice constant ( a = 8.28 )</th>
<th>Bond length</th>
<th>Cationic radius</th>
<th>X-ray density ((\text{gm/cm}^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x )</td>
<td>( c = 8.60 )</td>
<td>( \text{A-O} = 1.89 )</td>
<td>( \text{B-O} = 2.05 )</td>
<td>( \gamma_A = 0.57 )</td>
</tr>
<tr>
<td>0.0</td>
<td>0.2</td>
<td>8.45</td>
<td>1.93</td>
<td>2.06</td>
</tr>
<tr>
<td>0.4</td>
<td>0.6</td>
<td>8.54</td>
<td>1.98</td>
<td>2.06</td>
</tr>
<tr>
<td>0.4</td>
<td>0.8</td>
<td>8.58</td>
<td>2.01</td>
<td>2.06</td>
</tr>
<tr>
<td>0.8</td>
<td>1.0</td>
<td>8.63</td>
<td>2.05</td>
<td>2.05</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>8.70</td>
<td>2.09</td>
<td>2.05</td>
</tr>
</tbody>
</table>
distortions [52,47]. The axial ratio c/a in y=0.3, is found to be greater than y=0.1 which is supported by the cation distribution proposed in table (5.6). The value of axial ratio (c/a) in CuFeO is found to be of the order of 1.055 suggesting that the stoichiometry is correctly maintained in the compound [53], which is also confirmed by chemical analysis done by atomic absorption technique.

The c/a ratio in tetragonally distorted spinel ferrite is sensitive to preparation conditions and is found to vary from 1.03 to 1.06 [54-56]. Further it is also found that c/a ratio decreases with increasing quenching temperature because at elevated temperature crystal structure gets arrested in quenching. The tendency of formation of square bonds of Cu$^{2+}$ ion on B site of ferrites decreases with increasing quenching temperature thereby decreasing tetragonality ratio [51].

The critical fraction (fc) of Cu$^{2+}$ ions on B site which gives tetragonal distortions in cubic spinel ferrite is 80% [53]. As Cu$^{2+}$ is replaced by paramagnetic divalent cations like Zn$^{2+}$ and Cd$^{2+}$ in the proportions y0.2 M$_{x}$Cu$_{1-x}$Fe$_{2}O$_4 (m=Cd or Zn) in the system, becomes cubic [50,51]. This is due to strong preference of Zn$^{2+}$ and Cd$^{2+}$ to occupy tetrahedral (A) site in spinel structure which replaces equal number of Fe$^{3+}$ from A site to B site. This can be immediately seen from the cation distribution proposed from magnetisation study (Chapter III) and presented in Table 5.4. In the present case the change over of tetragonal to cubic crystal
Structure occurs at $x > 0.2 (Cd)$ concentration which is in good conformity with that of reported in literature [50,51].

The compositional dependence of lattice constant (a) and (c) is presented in figure 2.10 for $x=0.0$ and 0.1, and in figure 2.11 for $y=0.3$. From the plots it can be seen that the lattice constant (a) increases linearly with increase of cadmium content in all the compositions. This can be attributed to large ionic radius of $Cd^{2+}$ (0.99 Å) replacing the $Cu^{2+}$ (0.70 Å) of comparatively lower ionic radius. The linear dependence of lattice constant thus found to obey Vegard's law, there by confirming the formation of homogeneous solid solution.

From the tables 2.1 and 2.3 it can be easily seen that the tetrahedral metal oxygen bondlength ($A-O$) and tetrahedral catonic radius ($r_A$) increase with increase of cadmium content which also suggests the occupancy of $Cd^{2+}$ ions at $A$ site. However, no considerable change in the values of octahedral metal oxygen bondlength ($B-O$) and octahedral catonic radius ($r_B$) are observed. This could be due to the fact that increase in $Cd^{2+}$ occupancy at $A$ site replaces $Fe^{3+}$ to $B$ site having comparable ionic value to that of $Cu^{2+}$ (0.70 Å) and $Fe^{3+}$ (0.67 Å) already sitting on $B$ site. The bondlength $B-O$ in all the compositions is found to be greater than bondlength $A-O$ except $CdFe_2O_4$. This is rather a normal behaviour of spinel ferrite [58]. The substitution of Gd has not affected $A-O, B-O, r_A$ and $r_B$.
Fig. 2-10 Dependence of lattice constant on Cd content of Cd\textsubscript{x}Cu\textsubscript{1-y}Fe\textsubscript{2-y}Gd\textsubscript{y}O\textsubscript{4} ferrite system (for y = 0.0, 0.1).
Fig. 2.11 - Dependence of lattice constant on Cd constant (x) of Cd$_x$Cu$_{1-x}$Fe$_{2-y}$Gd$_y$O$_4$. 

- $y = 0.3$
which is obvious because no considerable change in the values of lattice constant (\(a\)) was observed on Gd\(^{3+}\) substitution.

For the calculations of the above said structural parameters the value of oxygen (\(U\)) parameter for CuFe\(_2\)O\(_4\) is 0.381 [59] and that of CdFe\(_2\)O\(_4\) as 0.389 [60] are used, while for intermediate compositions the value of (\(U\)) parameter is obtained as,

\[
U = UCd_x + UCu_{1-x}
\] (16)

The occupancy of Gd\(^{3+}\) on B site is further supported from our d c conductivity study [47]. However it is often supposed that \(U\) parameter will be less affected by substitution, since it is determined by larger ion in the lattice, i.e. Cd\(^{2+}\) in this case, which is having comparable ionic volume with Gd\(^{3+}\). This may also be one of the reasons for almost constant values of above parameters.

The X-ray densities are calculated by using the relation (14) and are presented in the tables 2.1,2.2 and 2.3, show increasing trend with increase in Cd\(^{2+}\) and Gd\(^{3+}\) concentration. This behaviour is quite obvious because of higher atomic weights of Cd\(^{2+}\) and Gd\(^{3+}\) with no considerable change in volume. The width of the reflection peak (311) in all the samples is approximately the same, therefore, it can be concluded that substituted cations Cd\(^{2+}\) and Gd\(^{3+}\) have occupied the available lattice sites of cations in spinel structure only [61].
2.5 Introduction

It is non-destructive and rapid method of characterisation applicable to all phases. The method provides qualitative analysis of complex structure from the point of view of atomic groups, their linkages 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 therefore, are useful fingerprints for identification. The heavy metal oxides and many inorganic compounds absorb radiations in the above mentioned frequency range. These lattice vibrational frequencies can be correlated with crystal structure. These frequencies are also found to depend on atomic mass and radius of cation or anion. IR absorption spectrum has been used for the first time by Waldron (1955) for the analysis of ferrite [60\(^+\)]. He has observed vibrational modes and I.R. active modes of metal oxygen polyhedra in oxides. The analysis of I.R spectra of ferrite and applicability in determining the structural correlation to electrical and magnetic behaviour has been given by Waldron.

The I.R spectra provide following information:

1) Completeness of solid state reaction.

2) Distribution of cations among non-equivalent sites and their valency.
iii) Nature of metal oxygen bonds.
iv) Calculation of force constant
v) Nature of electronic transitions and calculation of activation energy \( \Delta E' \).

2.5 Analysis of I.R. Spectra

Group theoretical considerations suggest four fundamental I.R. active modes in spinel structure. An absorption band \( \nu_1 \) around \( 550 \text{ cm}^{-1} \) is caused by stretching of tetrahedral metal oxygen bonds. The second absorption band \( \nu_2 \) \( (400 \text{ cm}^{-1}) \) is due to oxygen vibrations in a direction perpendicular to tetrahedral cation oxygen axis. The remaining two bands \( \nu_3 \) and \( \nu_4 \) are associated with the vibrations of metal oxygen ions in the isotropic force fields of the octahedral and tetrahedral environments. These bands are located in the 'far I.R.' region.

Waldron (1955) and Hafner (1961) assigned \( \nu_1 \) band around \( 600 \text{ cm}^{-1} \) to intrinsic vibrations of tetrahedral complexes and the band around \( 400 \text{ cm}^{-1} \) to octahedral complexes \([62,63]\). The absorption beyond the frequency \( 1000 \text{ cm}^{-1} \) is due to electronic transitions, therefore these are called electronic spectra. The electronic band spectra give direct indication of structure at high frequency. From the measurement of threshold frequency one can calculate activation energy \( \Delta E' \). The I.R. absorption nowadays is being extensively used by many workers \([62-75]\). The structural distortions in cubic and tetragonal manganese ferrites has been studied by Braberg et al. \([64]\) and have concluded that
tetragonal distortion in cubic spinel is due to Jahn-Teller effect. The presence of third I.R. active mode at 335 cm\(^{-1}\) has been observed by Klerk in vibrational spectra of manganese ferrite. The absorption bands below 300 cm\(^{-1}\) also have been observed by Preudhomne et al and have attributed it to mass of bivalent tetrahedral cations [68]. The absorption band in the range of 400\(^{-1}\) cm to 450 cm\(^{-1}\) was reported by Blass and has assigned it to the vibrations of the bivalent metal ion oxygen complexes [69]. The I.R. spectra of Co, Ni, Cu ferrites and magnetite have been reported in literature [67, 69, 70, 71, 72].

2.5.1 Experimental Techniques

The IR absorption spectra of series of samples of Cd\(_x\) Cu\(_{1-x}\) Fe\(_{2-y}\) Gd\(_y\) O\(_4\) with (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) for y = 0.0, 0.1 and 0.3 are obtained in the range of 200 cm\(^{-1}\) to 800 cm\(^{-1}\) on Perkin-Elmer (Model 783) spectrophotometer by using KBr pellet technique. The spectrometer was used in absorption mode in which high absorbance is towards the top of the chart. The transparent pellets of (0.01 to 0.02 cm thick) KBr and a finely crushed ferrite powder mixed in the 3:1 ratio, and pressed in a die of 1 cm and a pressure of 200-300 mesh were used.

2.5.2 Results and Discussion

The infrared absorption spectra of the Cd\(_x\) Cu\(_{1-x}\) Fe\(_{2-y}\) Gd\(_y\) O\(_4\) ferrite system (for x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0 for y = 0.0, 0.1 and 0.3) are obtained and presented in figures 2.12 to 2.17. The absorption spectra show two strong bands in the frequency range of 300 cm\(^{-1}\) to 700 cm\(^{-1}\). Waldron (1955) has observed the
Fig. 2:12  IR absorption spectra of $\text{Cd}_x \text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ ferrite system.
Fig. 2.13. IR absorption spectra of Cd$_x$Cu$_{1-x}$Fe$_2$O$_4$ ferrite system.
Fig. 14 - IR absorption spectra of $\text{Cd}_x \text{Cu}_{1-x} \text{Fe}_{1.9} \text{Gd}_{0.1} \text{O}_4$ ferrite system.
Fig. 2. IR absorption spectra of \( \text{Cdx Cu}_{1-x} \text{Fe}_{1.9} \text{Gd}_{0.1} \text{O}_4 \) ferrite system.
Fig. 2.16 IR absorption spectra of $Cd_xCu_{1-x}Fe_{1.7}Gd_{0.3}O_4$ ferrite system
Fig. 2-17 - IR absorption spectra of \( \text{Cd}_x \text{Cu}_{1-x} \text{Fe}_{1.7} \text{Gd}_{0.3} \text{O}_4 \) ferrite system.
two strong bands in the same frequency range [62]. Later on
many others have observed the similar nature [62-75], and have
attributed the band around $v_1$ (600 cm$^{-1}$) to tetrahedral
complexes and $v_2$ around (400 cm$^{-1}$) to octahedral complexes.
The band positions are given in table 2.4 to 2.6 for $y=0.0,0.1$
and 0.3 respectively.

From I.R. absorption spectra the centre frequency of
the bands are measured, the force constant $K_t$ (tetrahedral)
and $K_o$ (octahedral) are calculated by the method of Waldron
(1955) [62]. The calculations of bond lengths $R_A$ (tetrahedral
metal—oxygen) and $R_B$ (octahedral metal—oxygen) are calculated
by the procedure followed in section 2.8.1. The plots of force
constants $K_t$ and $K_o$ against the bond length $R_A$ and $R_B$ are
presented in figures 2.18 and 2.19.

The force constant $K_t$ is found to be greater than $K_o$
[73] which is rather expected because bond lengths $R_B$ are greater
than $R_A$ except for $x < 1.0$ for $y = 0.0, 0.1$ and 0.3 [58].
However, increase in $R_A$ with content of Cd$^{2+}$ upto $x = 0.4$ shows
increasing trend of force constant $K_t$ however, we expect the
decrease of force constant with increase of bond lengths. This
behaviour is similar to oxides of metals with $26 < z < 29$ [74].
This behaviour may be attributed to formation of strong bonds
by oxygen in favourable conditions. The variation in the values
of force constant $K_t$ is small with $R_B$ because, it is almost
constant in all the samples. The substitutions of Cd$^{2+}$ in CuFe$_2$O$_4$
Table 2.4: Band Positions and force constants of Cd$_x$Cu$_{1-x}$Fe$_2$O$_4$ ferrite system

<table>
<thead>
<tr>
<th>Content $x$ (Cd)</th>
<th>Wave numbers</th>
<th>Force constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\omega_A$</td>
<td>$\omega_B$</td>
</tr>
<tr>
<td></td>
<td>(cm$^{-1}$)</td>
<td>(cm$^{-1}$)</td>
</tr>
<tr>
<td>0.0</td>
<td>605</td>
<td>425</td>
</tr>
<tr>
<td>0.2</td>
<td>590</td>
<td>405</td>
</tr>
<tr>
<td>0.4</td>
<td>585</td>
<td>480</td>
</tr>
<tr>
<td>0.6</td>
<td>575</td>
<td>470</td>
</tr>
<tr>
<td>0.8</td>
<td>565</td>
<td>460</td>
</tr>
<tr>
<td>1.0</td>
<td>560</td>
<td>410</td>
</tr>
</tbody>
</table>

Table 2.5: Band positions and force constants of Cd$_x$Cu$_{1-x}$Fe$_2$-yGdy$_y$O$_4$ ferrite system (y=0.1)

<table>
<thead>
<tr>
<th>Content $x$ (Cd)</th>
<th>Wave numbers</th>
<th>Force constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\omega_A$</td>
<td>$\omega_B$</td>
</tr>
<tr>
<td></td>
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<td>(cm$^{-1}$)</td>
</tr>
<tr>
<td>0.0</td>
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<tr>
<td>0.4</td>
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<td>0.6</td>
<td>602</td>
<td>470</td>
</tr>
<tr>
<td>0.8</td>
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<td>480</td>
</tr>
<tr>
<td>1.0</td>
<td>565</td>
<td>450</td>
</tr>
</tbody>
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Table 2.6: Band positions and force constants of Cd$_x$Cu$_{1-x}$Fe$_2$-yGdy$_y$O$_4$ ferrite system (y=0.3)

<table>
<thead>
<tr>
<th>Content $x$ (Cd)</th>
<th>Wave numbers</th>
<th>Force constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\omega_A$</td>
<td>$\omega_B$</td>
</tr>
<tr>
<td></td>
<td>(cm$^{-1}$)</td>
<td>(cm$^{-1}$)</td>
</tr>
<tr>
<td>0.0</td>
<td>600</td>
<td>430</td>
</tr>
<tr>
<td>0.2</td>
<td>605</td>
<td>470</td>
</tr>
<tr>
<td>0.4</td>
<td>600</td>
<td>430</td>
</tr>
<tr>
<td>0.6</td>
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</tr>
<tr>
<td>0.8</td>
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<td>430</td>
</tr>
<tr>
<td>1.0</td>
<td>570</td>
<td>410</td>
</tr>
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</table>
Fig. 2.18 Variation of force constants $K_t$ and $K_o$ with $A - O$ (RA), $B - O$ (RB) for $Cd_{x}Cu_{1-x}Fe_{2-y}GdyO_{4}$ ferrite system ($Y = 0^\circ, 0.1^\circ$)
Fig. 2. Variation of force constants $K_t$ and $K_o$ with $A-O$ ($R_A$), $B-O$ ($R_B$) for $\text{Cd}_x\text{Cu}_{1-x}\text{Fe}_{2-y}\text{Gd}_y\text{O}_4$ ferrite system ($Y = 0.5$).
occupies tetrahedral sites therefore bond length $R_B$ remains almost unaffected. The bond lengths $R_A$ and $R_B$ in copper rich ferrites are lower than cadmium rich ferrites, may be because of the fact that $\text{CuFe}_2\text{O}_4$ is strong in covalent character. The decrease in bond lengths corresponds to increase of covalent character [75].

The plots of bond lengths and force constants are not exactly straight lines as expected, it may be because of uneven distribution of $\text{Cu}^{2+}$ Jahn-Teller ion on A and B sites of the spinel structure, which can be immediately seen from the cation distribution proposed. The cation distribution used for calculation of force constant is presented in the same table, and is obtained from magnetisation studies (Chapter 5A.)

On substitution of $\text{Gd}^{3+}$ the bond lengths are almost unaffected therefore, variation in lattice constant 'a', $R_A$ and $R_B$ is small. However, the values of force constants $K_t$ and $K_0$ are found to be increased. This may be due to change of cation distribution on substitution of $\text{Gd}^{3+}$. The cation distribution presented in the tables 5.4, 5.5, 5.6 supports this. So also, the ratio of ionic radius of ($\text{Gd}^{3+}$) to the ionic radius of oxygen ($\text{O}_2^-$) is greater than 0.73 therefore, $\text{Gd}^{3+}$ requires eight fold co-ordination. The eight fold co-ordination is not available in spinel structure, therefore, to minimise the energy configuration tetrahedral and octahedral oxygen symmetry is perturbed. This may reflect in the values of force constants and centre frequencies of bands.
The I.R. absorption spectrum within the experimental range of frequencies and conditions does not show any band splitting thereby ruling out the possibility of presence of multivalence states of cations present in the system. However, some band broadening takes place on substitution of Gd$^{3+}$ which may be attributed to occupancy of cations with different character and valency, occupying the same site. The cation distribution proposed indicates the presence of Gd$^{3+}$, Fe$^{3+}$ and Cu$^{2+}$ at octahedral B site and Cd$^{2+}$, Fe$^{3+}$ and Cu$^{2+}$ at A site. The d.c conductivity study shows increasing trend in resistivity on Gd$^{3+}$ substitution thereby ruling out the possibility of band splitting due to different valence states of either of the cations [76].

The intensity of octahedral band around 400 cm$^{-1}$ decreases with increase of broadening of the band on Gd$^{3+}$ substitution. This suggests the occupancy of Gd$^{3+}$ at B site. The bands on substitution of Cd and Gd show fine structure splitting of tetrahedral and octahedral bands. The fine structure of the bands has been observed by Braber, who attributed it to cation ordering which may result in lowering of overall symmetry which in turn increases the number of I.R. active modes [77]. Therefore, I.R. absorption spectra of ordered spinel show fine structure. In the present case the possibility of band splitting and presence of multivalence states of cations is ruled out because of insignificant nature of fine structure splitting. The observed fine structure may be due to formation of strong metal oxygen bonds at each site and the vibration levels are very close [78].
Atomic absorption spectroscopy is a useful tool for quantitative chemical analysis of metallic elements in the concentration range of 0.01 to 0.1 ppm. This technique was first used by Alan Walsh for chemical analysis of metallic element [79]. Later on Alkemade and Miltaz used this tool [80]. The importance of Walsh's contribution as a discoverer of this technique is to bring out the suitability of atomic absorption over atomic emission flame spectroscopy [79]. Nowadays, this technique is an important part of research in astrophysics in determining qualitative and quantitative compositions of stellar bodies. This technique permits the estimation of 60 to 70 elements in organic and mixed organic aqueous solutions in traces or microquantities.

2.6.1 Principle

When a dispersion of the atoms of a sample is produced in a flame, some of those atoms get thermally excited and emits characteristic radiations as they return to ground state. The dispersed atoms absorb incident light passing through flame. Similarly, the light passing through solution will be absorbed by the dispersed molecules of a solute. The absorption of the band is proportional to the concentrations of the atoms in a flame and the wavelength of the band is the characteristic of elements concerned. The absorption lines
In atomic absorption are very sharp (0.02 Å width). Therefore measurement of wavelength should be precise.

2.6.2 Experimental Technique

The technical details of the atomic absorption flame technique, block diagram and operation of each block have been discussed elsewhere [81].

Preparation of sample

The sample is normally a liquid solution or fine suspension. The chemical analysis of the samples under investigation was carried out by using the computerised atomic absorption spectrophotometer, Perkin Elmer Model 301 at U.S.I.C. Department, Shivaji University, Kolhapur. The chemical analysis of the constituent elements in 100 milligram of each of the compositions of CdCu1–xFenFe2–yGdyO4 (with x=0.0, 0.2, 0.4, 0.6, 0.8 and 1.0 for y=0.0, 0.1 and 0.3) has been carried out.

Preparation of solution-

For the preparation of solutions, the procedure for dissolving higher oxides was used [82]. 100 milligram of the sample was accurately weighed on a single pan microbalance (LC=10^{-5} gm) and was dissolved in 6M HCl & HNO3 (A.R.grade). The dissolved quantity was then diluted in double distilled water to 100 cc. This is used as stock solution, from which successive dilutions were carried out as per requirement so that reading in ppm is obtained. By back calculations the quantity in 100 milligram is estimated. The chemical analysis of Cd, Cu, and Fe
were carried out by this technique in all the compositions. However, the chemical analysis of gadolinium was not possible since non availability of source for this element. The analysis of oxygen is not possible by this technique because this technique can not be used for gas phase. The limits of detection of these elements by absorption technique in ppm are as follows [83].

1) Cd-1.01 ppm
2) Cu-0.01
3) Gd-4.0
4) Iron-0.01

The estimated quantity in 100 mg of \( \text{Cd}_x\text{Cu}_{1-x}\text{Fe}_{2-y}\text{Gd}_y\text{O}_4 \) ferrite samples for \( x=0.0,0.2,0.4,0.6,0.8 \) and 1.0 for \( y=0.0,0.1, \) and 0.3 are presented in Table 2.7 along with that of expected in hundred milligram compositions of the system under investigation. From the data presented in Table 2.7, it can be seen that the elements cadmium, copper and iron are present in their stoichiometric weight proportions.
<table>
<thead>
<tr>
<th>Cd Content $x$</th>
<th>Gd Content $y$</th>
<th>Copper (in 100 mg)</th>
<th>Cadmium (in 100 mg)</th>
<th>Iron (in 100 mg)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>23.56</td>
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</tr>
<tr>
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<td>13.17</td>
<td>38.4</td>
</tr>
<tr>
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<td>0.1</td>
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<td>8.13</td>
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</tr>
<tr>
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<td>-</td>
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<td>18.19</td>
<td>32.9</td>
</tr>
<tr>
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<tr>
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<td>0.3</td>
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2.7 Introduction

Characterisation of materials by studying their microstructure plays a crucial role in the systematic study of structure-sensitive polycrystalline materials. Most of the ceramics, however, have structures so complex that they defy adequate description. Now-a-days the wide use of ceramics in electronics applications has a great relevance of microstructure to electronic ceramics and in quality control of metallic components. Ceramics are usually prepared by solid state diffusion therefore, fine grains and high density are at opposite end of the processing technique. These extremities can be bridged only with the proper understanding of microstructure and efforts to tailor-make a desired microstructure. The scanning electron microscope (SEM) is the most versatile tool for the microstructural characterisation. The principal advantages of this tool are large focusing depth, higher resolution, high magnification and easy sample preparation.

The scanning electron microscope was first designed and constructed by Ardenne based on the possibilities predicted by Knoll. The striking contribution due to Ardenne is that to use secondary electron current to examine opaque samples. An improved version of SEM on the basis of ideas of Ardenne, was constructed by Zworykine et al. Later on, many workers have contributed in achieving the sophistication and high resolution of SEM. Now-a-days SEM has become a regular tool for
characterisation in the science of sintering and the micrographs are abundantly seen in literature of this topic.

2.7.1 Scanning Technique

The old seaming technique requires a large number of observations for the accurate determination of microstructural aspects. The optical accessories like cell counting plates and ocular grids along with automatic scanning techniques, increase the speed and accuracy of quantitative analysis. The scanning techniques used for size measurement, counting and measurement of areal fractions are discussed by Fischmeister [84]. The measurement of grain size [85,86], determinations of inclusions [87] and analysis of porosity [88] was done previously by direct visual observation called as feature to feature technique. This technique was important in measuring the particle size of the powder samples [89,90]. The use of photoelectric area determinator has been employed for size measurement [91]. The scanning in step helps in the determination of areal volume fractions by point count method. Now-a-days fully automatic step motion facility is available with all SEM [92].

The grain size distribution, analysis of degree of mixing in a two phase and measurement of grain continuity line scanning technique is used. The quantitative microscopy has now become sophisticated by the aid of automatic scanning depending on photocell to register the microstructural contrast [93]. The use of digital computer in the analysis of metallurgical purposes has been practised [94]. However, resolution, poor quality
image and background noise are the problems associated with automatic scanning techniques which puts limits on the degree of resolution and accuracy in quantitative analysis. The operational principles and structural description of SEM is discussed by Hend et al. [95].

2.7.2 Microstructure of Ferrites

Ferrites are often single phase therefore, porosity and grain boundaries are inherent part of the ceramic structure. The presence of porosity decreases the physical density. An attempt to increase physical density is always accompanied with grain growth. The increased grain growth changes the pore structure and influences the properties such as permeability and coercive force. The grain boundaries are related to grain growth. Finer the grain size more are grain to grain contact boundaries and larger will be the hindrances to the motion of Bloch wave, that and increases electrical resistance coercive force. Increase of grain growth decreases grain to grain contact boundaries, less hindrance to Bloch wave motion therefore, decreases resistivity and coercive force.

The porosity is affected by temperature and pressure as discussed in introductory chapters. The inclusion of foreign particles, and formation of phases also affect the electrical behaviour. Along with these, grain distribution, orientation of crystallites texture also are the important part of microstructural aspects. These aspects are discussed in short as follows.
a) Porosity

Porosity is an inherent phase of sintered ceramics. If nonporous spherical particles are compacted and are sintered, generate pore structure in which the interstitial voids will 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) Effect of Temperature

The microstructure develops during sintering process. As temperature increases, sintering i.e. coalescence of particles commences. The work on metal powders gives three stages of sintering.

i) Smoothing- Elimination of internal porosity of the discrete particles [96]. The external topographical changes of particles are not considered in this stage.

ii) Adhesion- As temperature increases the discrete particle develops points of contact with sufficient strength. The temperature at which this stage occurs is \( \frac{2}{3} \) of the melting temperature of the material called as "Tamman Temperature". The solid mass in this stage constitutes mesopores and macropores.

iii) Shrinkage - Heating of the material beyond Tamann temperature causes shrinkage in which particle fastening takes place. At this stage grain growth takes place and entire porous body shrinks. The isolated voids are eliminated by diffusion of vacancies which occurs at grain boundaries. The sintering theories and development of
microstructure are primarily developed for metals and have been adopted to explain the microstructure of ceramics \[97\]. Since, the metal and ceramics are basically different in the sense that structure as electronic and later ionic therefore, these theories need to be improved.

Rijnen showed that microstructure with large pores is developed at lower sintering rates \[97\]. Therefore, to obtain low porosity we have to increase the sintering rate. However, sintering rate in ferrites is limited by diffusion rate of the oxygen ions. The cation vacancies keep oxygen vacancies low therefore sintering rate must be low.

The optimum sintering rate is given by,

\[
D_c C_c = D_o C_o
\]

where \(D_c\) - Diffusion constant of cation vacancies.
\(C_c\) - bulk concentration of cation vacancies
\(D_o\) - diffusion constant of oxygen vacancies
\(C_o\) - bulk concentration of oxygen vacancies.

At lower sintering rates pore growth is less, but it may promote discontinuous grain growth. Therefore, control of pore structure and porosity during calcination is a difficult task. The external variables such as temperature, time, heating rate and the ambient atmosphere influence porosity so also the internal factors such as number of nucleation sites available for decomposition in the parent materials is difficult to control.
c) Effect of Pressure

The low porosity, small grains and high density therefore, are difficult to obtain with normal ceramic sintering. Application of pressure is found to promote the sintering by inhibiting the grain growth. The pressure reduces pore volume and also diminishes surface area. The hot pressing technique combines both the feature of sintering and pressing simultaneously therefore, by inhibiting grain growth one can achieve lower porosity and higher density [21].

2.7.3 Solid State Sintering And Grain Growth

Sintering and grain growth are the words used simultaneously in connection with the microstructure of ceramics. Therefore, it looks that both are acting simultaneously in the sense that sintering causes grain growth. However, they are basically different. The sintering involves coalescence of particles on the basis of volume fraction, shape, size and distribution of porosity while grain growth is a change in size of grains and morphology with time. The grain growth takes place on heating because the grain boundaries offer some driving force (interfacial energy). Usually larger grains are having more sides than small grains therefore, at the cost of small grains, grain growth takes place. the grain growth is given by the relation [99,100] equation 1. It is found that grain growth as straining effect due to presence of inclusion or the impurities [101]; since they hinder the movement of grain boundaries. The grain growth causes the decrease in surface energy because of decrease in
number of grains and grain boundary area.

Normal grain growth

According to Zener the grain growth occurs until the critical grain size is reached [102]. The critical grain size is given by equation 2. When the grain size reaches the critical value the normal grain is inhibited.

a) Exaggerated Grain Growth

The exaggerated grain growth starts when the heating takes place beyond the critical grain size limits. In this case grains grow rapidly at the expense of their near neighbours. The disadvantage of this growth is the possibility of entrapping the pores, which can not be eliminated even by sintering at higher temperatures. The chemical inhomogeneity, variation of density, and presence of inclusions favour exaggerated grain growth [103]. The technical ferrite materials require fine grains and continuous grain growth. Therefore to control grain size, one can start with fine particles of large surface area and to avoid discontinuous grain growth mixing at molecular level or starting materials can be achieved.

b) Texture

The texture is preferential grain growth in any particular direction or axis of the unit cell. The nonspherical powder particles in case of hexagonal materials show preferential crystal growth in basal plane and very less in the direction of c axis. The texture of starting material is even improved by sintering it at a low temperature where normal grain growth occurs. To obtain a texture alignment of crystallites a material powder is packed in a sealed steel tube and rolling the tube at high
2.7.4 Microstructure and Properties of Ferrites

a) Effect of Microstructure on Electrical Properties

The electrical behaviour of ferrite is influenced by grain boundaries, since they act as source of resistance. Guillaud et al., observed dominance of grain boundary resistivity in the observed resistivity of Mn-Zn ferrites[105]. Effect of structural distortions and grain boundary on the resistivity of ferrite have been reported by Long Kla et al [106].

The electrical behaviour is influenced by grain growth. The technical requirement of uniform grain growth to reduce eddy current is based on the studies of Heister et al [107]. The grain size affects the dielectric constant. The relation between grain size and dielectric constant was established by Kramer et al [108]. The effect of grain size on dielectric behaviour of Ni-Zn ferrites have been discussed by Largenteau et al [109].

b) Magnetic Properties

The dependence of coercive force (Hc) on grain size and porosity is well understood. The permeability in polycrystalline ferrites is found to increase with increase in grain size. The saturation magnetisation decreases as porosity increases. The porosity at grain boundary is found to be severely affecting the initial permeability and saturation magnetisation [110]. The permeability is found to increase linearly with grain diameter [111]. The relaxation frequency and maximum losses are lowered with increase of grain size [112]. The relation between hysteresis losses and boundary structure have been discussed by Berger.
et al [113]. The technological requirement of critical grain size for memory material is well known.

2.7.5 Experimental Technique

For the investigation of microstructural aspects in the present study scanning electron microscope STEREO SCAN 250 mK 3 (Cambridge Instrument at R.S.I.C. Nagpur) is used. The micrographs of Cd$_x$Cu$_{1-x}$Fe$_{2-y}$Gd$_y$O$_4$ with (x=0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) for y = 0.0, 0.1 and 0.3 were obtained in reflection mode on scanning electron microscope, at Regional Instrumentation Centre, Nagpur. Measurement of the average grain size is carried out by counting the number of grain boundaries intersected by a known measured length from the magnification used. By drawing random such lines and repeating same procedure average grain size is calculated [114]. The percentage porosity is calculated by X-ray method. The SEM microphotograph are presented in Figures 2.29, 2.21, 2.22. The microstructure data of the system under investigation is given in Tables 2.8, 2.9, 2.10.
2.7.6 Results and Discussion

The scanning electron micrographs of fractured surfaces of polycrystalline Cd\textsubscript{x}Cu\textsubscript{1-x}Fe\textsubscript{2-y}Gd\textsubscript{y}O\textsubscript{4} (\(x=0.0, 0.2, 0.4, 0.6, 0.8\) and \(y=0.0, 0.1, 0.3\)) ferrites are presented in figures 2.20, 2.21, 2.22. From these micrographs the average grain size is measured and is presented in tables 2.8, 2.9, 2.10 along with the X-ray density, physical density, and percentage porosity in the pellets. From the data of average grain size, it is found that in unsubstituted Cu-Cd ferrites (y=0.0) the grain growth does not follow any regular trend with cadmium content. The grain size is found to increase up to \(x \leq 0.6\) except \(x = 0.4\) and beyond that it is decreased. The composition \(x = 0.8\) shows minimum grain growth in all the compositions for \(y=0.0\). However, no exaggerated grain growth is observed in any of these compositions.

From the a.c. susceptibility study (Chapter 5B) it is observed that the copper ferrites (CuFe\textsubscript{2}O\textsubscript{4}) exhibits the S-D particles. However, on substitution of Cd\textsubscript{2+} \(0.2\) it changes from S-D to M-D particles. Therefore, it was excepted that grain growth may be affected by the above said change over, and the results are in good agreement. The hinderances to grain growth in Mg-Co ferrites due to S-D behaviour of cobalt ferrites has been reported in literature [115]. However in the present system the grain growth shows generally an increasing trend with cadmium content up to \(x \leq 0.6\) except for \(x = 0.4\), which is rather expected because of M-D behaviour of these compositions.
Fig. 2.20 — Scanning electron micrographs of fractured surfaces of \( \text{Cd}_x\text{Cu}_{1-x}\text{Fe}_{1.9}\text{Gd}_{0.1} \) ferrite system.
Fig. 2.21 - Scanning electron micrographs of fractured surfaces of Cd$_x$Cu$_{1-x}$Fe$_{1.5}$Cu$_{1.0}$ ferrite system.
Fig. 2.22 — Scanning electron micrographs of fractured surfaces of Cd$_x$Cu$_{1-x}$Fe$_{1.7}$Gd$_3$O$_4$ ferrite system.
Table 2.8: Microstructure data of $\text{Co}_{x}\text{Cu}_{1-x}\text{Fe}_{2}\text{O}_{4}$ ferrites system

<table>
<thead>
<tr>
<th>Composition $x$</th>
<th>X-ray density (gm/cm$^3$)</th>
<th>Physical density (gm/cm$^3$)</th>
<th>Porosity (%)</th>
<th>Grain size (μm)</th>
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Table-2.9: Microstructure data of Cd Cu Fe Gd O Ferrite System

<table>
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<th>Composition</th>
<th>X-ray density (gm/cm³)</th>
<th>Physical density (gm/cm³)</th>
<th>Porosity (%)</th>
<th>Grain size (μm)</th>
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Table-2.10: Microstructure data of Cd Cu₁₋ₓ Feₓ Gd O Ferrite System

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<tr>
<th>Composition</th>
<th>X-ray density (gm/cm³)</th>
<th>Physical density (gm/cm³)</th>
<th>Porosity (%)</th>
<th>Grain size (μm)</th>
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<td>27.92</td>
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</table>
The X-ray and physical densities of the ferrites show increasing trend with cadmium content. This behaviour can be attributed to larger atomic weight of cadmium. The physical densities in all samples have been obtained above 4 gm/cc up to 5.23 gm/cc which are about 80 to 90% of the physical or X-ray densities. By hot pressing, these densities can be further improved. By the cold pressing technique, these values of density are reasonable. Porosity up to 20% has been reported in literature [116]. The percentage porosity shows decreasing trend on increase of cadmium content, which is therefore obvious.

In Gd$^{3+}$ substituted compositions ($y=0.1, 0.3$) it is found that average grain size is found to be reduced than that of unsubstituted versions ($y=0.0$). The behaviour can be attributed to anisotropy effects of rare earth element Gd$^{3+}$. The increase of coercive field in $x=0.0$ for $y=0.1$ and $0.3$ on substitution reveals the increasing trend of anisotropy effects as content of Gd$^{3+}$ is increased. So also the S-D behaviour of CuFe$_2$O$_4$ has been enhanced on Gd$^{3+}$ substitution which can be immediately seen from ac susceptibility plots (Chapter 5B), therefore, retardation of the grain growth because of the anisotropy effects is rather expected.

The percentage porosity is found to be increasing with increase of Gd$^{3+}$ content. This behaviour can be seen from the proportionate decrease in physical density.
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