CHAPTER 2
PREPARATION AND CHARACTERIZATION

Introduction

The intrinsic properties of the ferrites are found to be sensitive to the method of preparation and heat treatment during the preparation [1]. The properties which are technically important from the application point of view, like $M_s$, $H_c$, $T_c$, $\mu$ loss factor, resistivity etc. have to be controlled. The controlling of the properties is rather critical. And the factors like chemical homogeneity, stoichiometry, development of the microstructure etc. have to be considered. However it is not possible to prepare the ferrites with the best combination of these properties and hence the compromise has to be made to tailor the materials [2]. To achieve this goal different method of preparation of ferrites along with the most widely accepted is standard ceramic method, which was employed for the preparation of sample under investigation.

2.1 Method of preparation

Various methods have been suggested for the preparation of the ferrites. Each method is characterized by its merits and limitations. All the methods can be grouped in to two categories,

(i) Dry methods (ceramic methods).
(ii) Wet chemical methods.

Different stages have been involved in these methods, but few stages like stoichiometry in mixing of the starting materials, pre sintering, grinding, final sintering and pressing in to required shape are common in these methods are briefly discussed as follows.

2.1 (a) Ceramic methods: Depending upon the starting materials used the ceramic method can be further classified in to two methods, oxide method and decomposition method.

2.1.1 Oxide method

In this method high purity oxide are used as the starting material. The oxides are weighted in the stoichiometry weight proportion and mixed. The components are
then grinded using agate mortar. The composition are dried and subjected to the pre-sintering. To get the final product the different stages like grinding final sintering pressing etc. has to be followed. The drawback of this method is to contamination by mixing of steel or the oxidation of the ceramic crucible in the final product. This was observed by Blackman during the formation of magnesium magnise ferrites [3].

2.1.2 Decomposition method:
In this method the salts like carbonates nitrates oxalates etc. of the constituent metals are mixed and pre sintered in the air to form oxide by thermal decomposition method. Rest of the stages are same as that of the oxide method. The advantage of this method is that the oxide thus produced would readily undergo the solid stage reaction.

2.1.3 Wet chemical methods:
These methods are normally based on the principle of co-precipitation to avoid the length of reaction and tedious ball milling process involved in the dry process and to get high homogeneity and high density ferrites. These methods can be employed the different wet chemical methods discussed as briefly follows.

2.2 Hydroxide co-precipitation
In this method, the hydroxide of constituent materials is allowed to co-precipitate in the base solution. The hydroxide of the starting materials are taken in proper weight proportion are prepared as

\[ 3\text{Fe}_2\text{SO}_4 + 9\text{OH}^- \rightarrow 3\text{Fe(OH)}_3 + 3\text{SO}_4^{2-} \]

\[ \text{MgSO}_4 + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2 + \text{SO}_4^{2-} \]

Thus prepared hydroxides are simultaneously poured into the solution of NaOH. The pH of the solution must be controlled. The hydroxides get simultaneously precipitate and this contains the ferrite constituents. The precipitate then carefully washed number of times and then dried. Rest of the stages are similar to those of the oxide method. Economos had prepared the magnesium ferrite by this method [4]. Recently many workers have reported their results of investigation of the ferrites prepared by this method.
The advantages of this method are

a) The method is fast and avoids the tedious process of milling.
b) Very small particle size can be obtained.
c) The physical density and porosity can be significantly improved.

The method has certain drawbacks, and those are

a) To follow this method one has to play with the chemistry, like, solubility product of the starting material, PH of the solutions etc. For instance, precipitate of Fe (OH)$_3$ takes place in the strong basic solution of PH=10.2, where as the Mg(OH)$_2$ requires acidic PH for its precipitation.

b) The precipitation of the hydroxide quantitatively and simultaneously is difficult and if not possible then the entire effort of the method may be lost.

c) If the precipitate is gelatinous and voluminous, then its washing is rather difficult. If sodium remains in the precipitate then it forms an impurity in the ferrite system. To avoid this, instead of NAOH, the solution of NH$_4$OH can be used.

d) This method can give rise to the suspensions of minor constituents during the co-precipitation.

e) Some hydroxides decompose only at the high temperature may be equal to the crystallization temperature. This give rise to pores derived from voids between the crystallite [6].

2.3 Oxalate and co-precipitation

In this method, the oxalates of the constituents’ metals are allowed to precipitate. The precipitation is similar and washing is not a serious problem, because of the ammonium oxalate is used as a base solution and it does not leave any residue after ignition. The advantage of this method is that the mixing can be achieved at molecular scale [5]. Thus prepared hydroxides are simultaneously poured into the solution of NAOH. The PH of the solution must be controlled. The hydroxide gets simultaneously precipitated and the precipitation contains ferrite constituents. The precipitate is then carefully washed number of times and then dried. Rest of the stages are similar to the those of the of the oxide method.
2.3.1 Precursor method.

Precursor is nothing but the solution of the compounds contain metal ions M$^{2+}$ and Fe$^{3+}$ taken in the desired ratio as the starting materials and decomposed to form the ferrites. If the compounds of the two metals are isomorphic (i.e. having the identical structure), precipitation from the solution would result into the solid solution when decomposed thermally at moderate temperature yields the ferrites. The advantageous thing is that the method gives the excellent stoichiometry, homogeneity and physical density [6]. The mixing of the metals is at atomic level, therefore, by this method greater reactivity and homogeneity can be achieved. It also reduces the diffusion distance to about 1nm in comparison with the diffusion distance of 1000nm in oxide method. The use of the precursor like metal hydroxide, carbonate, hydrazine, carboxylic and oxalate have been established to form the spinel ferrites [7-10]. In the case of carbonate precursor the solution precursor, contain the required cations in the right ratio is taken and mixed with the solution of the sodium carbonate, decompose at relatively low temperature at about 300°C [60]. To avoid sodium, Krieger et al [8] have used ammonium carbonate.

2.3.2 Standard ceramic method.

Different stages for the preparation of ferrites. The flow chart [2.1] showing the various stage of this method is presented these stage s are discussed as follows.

A. Mixing

The starting material, metal oxides or their salts like carbonate, nitrates etc. which upon decomposition gives reactive oxide and Fe$_2$O$_3$ are used. The starting, materials are accurately weighted in desired stiochiometry proportion and mixed together with the acetone base. The liquid like alcohol / water can be used as the liquid for the suspension. The stating materials' should be highly pure fine particle [12]. Wet mixing of these oxides in an agate mortar in place of ball mill has significantly reduced the mixing time [2].

B. Presintering:

The composition is then presintered at moderate temperature. This pre sintering helps to control the shrinkage. The grinding after calcinations improves the reactivity of the powder. Care should be taken to get narrow particle size distribution in which
nucleation centers are scattered and avoids seed for the secondary grain growth during sintering.

C. Grinding after sintering:

The pre sintered samples are again grinded with the acetone base, to achieve the good homogeneity and this process is repeated twice or thrice.

![Flow chart of the ceramic method in the ferrite preparation](image)

**Figure: 2.1 Flow chart of the ceramic method in the ferrite preparation**

D. Sintering:

Properly grinded powder is then subjected to the process of sintering. At this stage the sintering temperature and time are important factors, which decide the entire
properties of the spinel ferrites. The sintering temperature depends on the composition of the ferrites.

**E. Pressing:**

The dry powder, if necessary mixed with the organic binder like polyvinyl acetate or polyvinyl alcohol so as to increase the grain strength, is pressed into the desired shape, by applying the pressure within the range of 1ton /sq.cm to several tons /sq cm, depending on the nature of the powder. For good compaction the powder should possess uniform flow characteristics.

**F. Final sintering:** After pressing the sample sintering is done to increase density, control grain size and pore distribution in the ferrites. The sintering temperature may vary from 900°C to 1500°C for several hours depending on the chemical composition. The range of temperature can be reduced by increasing the sintering time. The final product is formed by interaction between adjacent particles. The sintering can control the grain growth and pore distribution [13]. For good quality ferrite, the grain size should be uniform within the specified range and pores should be intergrannular. The sintering process is divided in to three classes.

**i) Reactive sintering**

Formation of the ferrites between the large and partly sintered small particles takes place at elevated temperature [14]. The reaction results into increases in the local volume leading to decreases in the densification rate. Thus this puts the limitation on the final product.

**ii) Homogeneous sintering:**

In this case the particles of the ferrites are formed with homogeneous composition are sintered. The mechanism of the solid state reaction consists volume diffusion process. During the sintering processes the vacancies sink out at the grain boundaries. This process can achieve the density up to 95% of the theoretical density [15, 16, 17].
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iii) Hot pressing:

This technique was developed by Gruintjes and Oudermans to yield ferrites at lower sintering temperature [18] and of the high density and small grain size. In this method the temperature and pressure are applied simultaneously, which enhances the grain to grain contact and hence high density and very low porosity. The disadvantage of this method is that, the excess pressure may changes the degree of inversion as well as the reduction of iron leading to increase in the Fe$^{2+}$ ion concentration. This may adversely affect the properties. This technique has employed by various researchers [19, 20].

2.3.2.1 Mechanism of the solid state reaction;

The solid state reaction, that occurring during the formation of spinel ferrites on the basis of the simple diffusion from the component metal oxide and ferrite oxide has been discussed by many authors [21, 22]. Initially there is only phase boundary between reactants. But after nucleation, this boundary is replaced by two different phase boundaries; one between MO and MFe$_2$O$_4$ and another between Fe$_2$O$_3$ and MFe$_2$O$_4$[6]. The pictorial representation of the solid state reaction is depicted in the figure 2.2.

A) The diffusion mechanism involved in this step is called counter diffusion [21]. The cation migrates in opposite direction whereas the anions remain stationary. The boundary between MO and Fe$_2$O$_3$ does not shift during the reaction. The amount of formation of ferrites on the sides of the boundary is 1:3 formation of magnesium ferrites is found to undergo solid state mechanism.[23].

B) In this step the oxygen enters into the diffusion of either of the cations (M$^{2+}$or Fe$^{3+}$) is compensated by a flux of anions. If the diffusion rate of Fe$^{3+}$ is greater than that of M$^{2+}$ then inter marker position shifts as shown together with MFe$_2$O$_4$/Fe$_2$O$_3$ boundary. This has been evidenced in the formation of the Zinc ferrite [24].

C) The diffusion of the iron through Fe$^{2+}$ reduced state in the layer of ferrite has been explained by Paulus [25]. And diffusion of the oxygen through the gas phase. The oxygen is evolved at MFe$_2$O$_4$/Fe$_2$O$_3$ interface and reabsorbed at within the specified MFe$_2$O$_4$/Fe$_2$O$_3$ boundary. The inert marker displacement in this case proportional to the amount of oxygen transported. The reaction taking place during the formation of NiFe$_2$O$_4$ is of the type [26]. The presence of Fe$^{2+}$ ions has been observed in the reaction layer.
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Case A:

\[ \text{MO} \quad \text{Fe}_2\text{O}_3 \]

\[ \text{MO} \quad \text{MFe}_2\text{O}_4 \quad \text{Fe}_2\text{O}_3 \]

\[ 3\text{M}^{2+} \quad \leftrightarrow \quad 2\text{Fe}^{3+} \]

Case B:

\[ \text{MO} \quad \text{Fe}_2\text{O}_3 \]

\[ \text{MO} \quad \text{MFe}_2\text{O}_4 \quad \text{Fe}_2\text{O}_3 \]

\[ \leftrightarrow \quad 2\text{Fe}^{3+} \]

\[ \leftrightarrow \quad 3\text{O}^{2-} \]

Case C:

\[ \text{MO} \quad \text{Fe}_2\text{O}_3 \]

\[ \downarrow \frac{1}{4}\text{O}_2 \quad \uparrow \frac{1}{4}\text{O}_2 \]

\[ \text{MO} \quad \text{Fe}_2\text{O}_3 \]

\[ \text{M} \quad \leftrightarrow \quad \text{Fe}^{2+} \]

Figure 2.2: Schematic representation of reaction mechanism
2.3.2.2 Factors influencing the sintering process:

The properties of the poly crystalline ferrites are found to be mostly sensitive to the sintering process. The sintering process affects the factors like particle size distribution, shape, inter particle porosity, agglomeration homogeneity, pore size and distribution temperature gradient etc, have a dominant also decodes the physical density of the final product.

i) Atmosphere:

During the process of sintering, there may be a possibility of oxidation-reduction reaction also change of the valence state. This causes to disturb the stoichiometry compositions. The elements like Fe, Mn, Cu and Co are found to be sensitive to the change in the valence state [27]. In order to have control on it, the furnace atmosphere should be introduced. The effects of the furnace atmosphere on formation of the ferrous ferrite have been studied extensively [27,28]. It is found that the oxygen deficiency causes change in the valence of the metal ions, while excessive oxygen create the cation vacancies. During the soaking period the atmosphere may be either air or oxygen, but during cooling cycle the partial pressure has to be changed so that ferrite is in equilibrium and no oxidation and reduction of Fe^{2+} ions takes place. This controls the concentration of Fe^{2+} ions, otherwise it affects the electrical and magnetic properties.

ii) Porosity: In case of the sintered ceramic, the porosity is the inherent property. The compaction of spherical non porous particle develops the pores with more or less uniform pore structure. The pore volume depends upon the particle size and average coordination number. The porosity is the measure of pores. Increasing the sintering temperature can modify the pore structure, but it leads to the excessive grain growth. By controlling the oxygen partial pressure the pores migration can be controlled [29]. The porosity can be reduced with the use of hot pressing and also by means repeated sintering cycles. However increased repeated sintering process increase the grain growth.

iii) Grain growth The average particle size is related to the temperature and the time as, D=DoKt^n where Do is the original particle size , K is the temperature dependence factor and t is the time. Average grain size increase with temperature
because of decrease of the grain boundary energy. Sintering temperature and hot pressing technique can control the grain growth.

iv) **Sintering temperature:** The sintering temperature is very important parameter, since it decides the reactivity of the component metal oxide to form ferrite. Actually this temperature should be about melting of the constituents, but in practice it is adjusted about 2/3 of the melt temperature, because there is the possibility of evaporation of some metals. Increasing the sintering period can compensate the requirement of high sintering temperature leads to increase the average grain size, resulting in to increase in the initial permeability, but excise temperature affects adversely at higher frequency.

2.3.2.3 **Drawback of the ceramic methods:** The standard ceramic method few draw backs

a) Possibility of the chemical homogeneity due to the evaporation of the metals like Zn Cd, Li etc, at elevated temperature.

   b) It gives higher porosity, lower density and higher particle size.

c) At relatively high temperature there may be possibility of reduction of the Fe$^{3+}$ ions to Fe$^{2+}$ ions that could affect the electrical and magnetic properties.

2.4. **The preparation of the ferrite composition under investigation.**

As discussed in the previous paragraphs, the ferrite can be prepared by number of methods. Each method is its merit and limitations. For the preparation of ferrite, the commercially accepted technique is the standard ceramic method.

The compositions of the poly crystalline ferrites with the chemical formula, Cu$_{1-x}$Zn$_x$Fe$_2$O$_4$ (X-Series) and Co$_{1-x}$Zn$_x$Fe$_2$O$_4$(x=0.0, 0.2, 0.4, 0.6, 0.8, 1.0) (Y-Series) have been prepared by this method. The details regarding the preparation are as follows

The starting materials used are AR grade oxides

Fe$_2$O$_4$, ZnO, CuO, CoO.
A) **Weighing:** The starting materials are weighted by using the single pan microbalance, in the molecular weight proportion. The materials were then mixed together in an agate mortar with pestle.

B) **Milling:** The dry mix powders are wet milled in the agate mortar using AR grade acetone as the suspension liquid. The mix is milled to active intimate mixture and dried. Then again milled. The cycle of milling is repeated twice or thrice. After this, the mixture is transferred clean and dry fused silica crucibles.

C) **Pre sintering:** The compositions were pre sintered in the furnace in air atmosphere. The pre sintering temperature was controlled at $800^\circ C$ for 4 hours. The furnace was slowly cooled down to the room temperature. The calibrated cromel allumel thermocouple was used to measure the temperature.

D) **Grinding:** The pre sintered sample materials were powdered with acetone base in agate mortar. This was done repeatedly to achieve uniform particle size distribution or homogeneity.

E) **Sintering:** The fine powdered compositions were transferred into dry and clean fused silica crucible and subjected to the process of sintering. The sintering temperature and time decides the entire properties of the polycrystalline ferrites. Therefore the sintering temperature was optimized. Firstly the composition were sintered at $1000^\circ C$ and subjected to the X-ray diffraction, to understand the formation of the spinel ferrite. But from the X-ray diffraction it was found that, there is significant reflection in between the (220) and (311) reflections. It may be due to the un sintered $\text{Fe}_2\text{O}_3$. Then by increasing the sintering temperature to the unwanted peaks is insignificantly diminished. Thus the sintering temperature was controlled at $1000^\circ C$ for 4 hours for all the compositions under investigation. The composition was slowly cooled down to the room temperature.

F) **Grinding:** The sintered samples were grind with acetone base into fine powder, to obtain uniform particle distribution.

G) **Pellet preparation:** Pressing in order to study the electric and magnetic properties, the sample should be in specific form (pellet or toroid). The pellets were formed by pressing using die 1cm, applying the pressure by means of hydraulic press. The pressure applied was 2.5 tons for 5 min. Similarly the samples in the Department of Physics Kuvempu University Shankarghatta
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toroidel shape have been formed by using the toroidel die with the inner diameter 1cm and outer diameter of 2cm.

**H) Final sintering:** The pellets and toroids were sintered. The sintering conditions were same as to that of powder sintering.

**I) Finishing:** The pellets thus formed are polished by using soft metal sand paper, so that their thickness is uniform showing opposite faces exactly parallel.

**2.5. Powder Method:** To characterize the polycrystalline materials, the powder method is used extensively used for the polycrystalline powder composition, because of its accuracy and ability to identify the existence of the phases. In this case the wavelength of the radiation is fixed but the sample is rotating. The powder sample consists of small crystal of different orientations and hence the diffractogram shows number of peaks, satisfying Bragg’s condition, at various d values. However the d values must be greater than $\lambda/2$ [32].

The materials are also characterized by the other methods like, neutron diffraction, electron diffraction etc. In case of diffraction method, the scattering factor is the magnetic scattering factor, which takes the account of contribution due to the spin and orbital moment. It gives entire magnetic structure of the material. Neutron diffraction being the chargeless particle, the electron cloud of the atoms does not effect.

Electron diffraction technique use is limited due to the charge of the electron. Then X-ray powder diffraction technique is used to characterize the compositions under investigation.

**2.5.1 Experimental:** The compounds of Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$ and Co$_x$Zn$_{1-x}$Fe$_2$O$_4$ ($x=0.0$ to 1.0 in steps of 0.2) ferrites were characterized by using the X-ray powder diffraction. The computerized X-ray diffractometer, Philip X-pert at IISc Bangalore ($\lambda=1.5416A^0$). The X-ray tube was operated by 30KV and 1.5mA current. The counts v/s 20 scanning was done in the scan limit from 20 to 80$^0$ with the step of 5$^0$/ min, since the probable lattice constant of these composition are between 8.4358 and 8.4065A$^0$ similarly for Co$_x$Zn$_{1-x}$Fe$_2$O$_4$ series of samples it varies from 8.4177 to 8.3411A$^0$. To define the significant reflection, minimum significance was adjusted.
to 0.1. The diffractometer gives data output, which was further used for the characterization of the composition.

Various methods have been suggested for the preparation of the sample for the powder diffractometry [33] as polycrystalline monolithic specimen, bounded powder specimen, fiber supported powder specimen and encased powder specimen. A microscope slide is prepared by uniformly spreading the fine powder over a coated portion of the cello tape. The film is supported by wetted and adhesive support. Thus the prepared sample is kept on the specimen holder of the diffractometer and allowed to scan within the predicated scan limit.

2.5.2 X-ray diffractometer: X-ray diffractometer used is schematically represented in the figure 2.3. A powder specimen C is in the form of flat plate is placed on the table, capable of rotating about an axis O perpendicular to the plane of drawing. The beam filtered X-rays, collimated by the slit A is allowed to incident on the specimen C. The diffracted beam is collected at counter G after focusing it a slit F. A and B are the special slits to collimate the beam. The carriage E is supported to receiving slit and counter, which is free to rotate about an axis O. The mechanical coupling made between E and H, is such that rotation of the carriage through 2θ rotated through specimen the sample. To achieve the continuous scan within the scan limit the rotation is computer controlled. The data counts v/s angle, is stored in computer memory and processed to give out the diffractogram and related data. This data are then used to characterized the materials and investigate cation distribution from the intensity d calculations.

2.5.3 Indexing the diffractogram:

X-ray diffraction pattern of the polycrystalline material, in which crystal are oriented randomly, consists of number of reflections of different intensities and at different d spacing. The observed Bragg angle 2θ and hence the d spacing and relative intensities of reflection are required for characterization. It is not possible to deduce the unit cell dimension directly from the d spacing [34]. Therefore one has chosen some indirect method. The method used is different for different crystal system. The indexing procedure for cubic system is discussed briefly. The inter planar spacing and lattice constant and miller indices are related by the equation,
\[ d_{\text{obs}} = n \frac{\lambda}{2\sin \theta} \quad (2.5.3.1) \]

\[ d^2 = a^2 / (h^2 + k^2 + l^2) \quad (2.5.3.2) \]

For example, the \( d_{110} = a \) the lattice constant or \( d_{110} = a / \sqrt{2} \). The diffractogram consists of regular reflection with some gaps. Therefore the first reflection may not be \( (110) \). And hence indexing becomes rather difficult. The method used conventionally for the cubic system, consists of the list of \( 1/(d^2) \) values and difference in the value of successive \( 1/(d^2) \). This difference may have the common minimum factor, which is supposed to be \( 1/(a^2) \). Thus from this the lattice parameter \( a \) is decided by using this \( a \) and equation \( (2.5.3.2) \) the sum of the square \((h^2 + k^2 + l^2)\) were calculated for the corresponding observed \( d \) spacing and then from possible combinations, the values further indices \((h \ k \ l)\) were decided.

![Figure 2.3 X-ray diffractometer (Schematic)](image-url)
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In case of polycrystalline FCC spinels, the sum of square are 2, 8, 11, 12, 16, 18, 19, 20, 27 etc and hence only the corresponding reflection are allowed. The most predominant reflection is (311) having the 100% relative intensity is the characteristic of the spinel structure. Therefore in the method used for the present system the 'd' spacing of the prominent reflection (311) is taken and the value of a is calculated using the equation (2.5.3.3). This is further used to obtain the sum of the square for all other reflections and hence the miller indices of the respective planes. The value of 'a' thus obtained may not be correct, because of 'd' spacing at lower angle is limited due to sinθ values. The accurate 'd' spacing will be observed at 2θ =180 or θ =90° i.e back reflection [36]. To obtain the lattice parameter more precisely and to cover the entire information. At higher angles, the method used is the extrapolation of the error function F(θ). Various error function like cos2θ, cos2θ/θ, cos2θ/θ sinθ etc. have been suggested by Bradley and Jay [37,35] in 1932. But Nelson and Riely [38,36] have suggested the error function (θ)=1/2{(cos2θ)+((cos2θ/θ)/sinθ)} which was further supported theoretically by Taylor and Sinclair [58]. The values of the lattice constant a calculated from the equation.

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

are plotted against the values of the error function F(θ). It should be noted that the graph should have negative slope, indicating the source of error is at higher angles. The value of a is then decided by extrapolation of the F(θ) to the angle θ=90°.

2.5.4 Calculation of the other parameters: The structural parameter like, cation-oxygen bond distance on tetrahedral A site (A-O) and octahedral B site(B-O) ionic radius of respective sites, physical density, X-ray density, porosity, etc. have been calculated. The cation and oxygen bond distance on respective sites are calculated by using the relations,

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

\[
B-O = (5/8-u) a
\]

The ionic radius on A site and B sites are calculated by using the equations

\[
r_A = (u-1/4) a\sqrt{3} - r_{oxy}
\]

\[
r_B = (5/8-u) a - r_{oxy}
\]
Where \( r_{\text{oxy}} \) is the ionic radius \( (r_{\text{oxy}} = 1.40 \text{Å}) \) of the oxygen ion and \( u \) is the oxygen ion parameter.

The physical densities of the compounds were determined according to the Archimedes principle, in which the loss of weight in the liquid is considered. The liquid used to suspend the pelletized sample is xylene. The X-ray density was calculated by using the relation,

\[
\rho_x = \frac{8M}{N_0\alpha^3}
\]  
(2.5.9)

Where \( M \) is the molecular weight of the compound and \( N_0 \) is the Avogadro’s number \( = 6.0025 \times 10^{23} \). The percentage of the porosity of the compound under investigation were calculated using the relation

\[
P(\%) = \frac{\rho_p - \rho_x}{\rho_x} \times 100\%
\]  
(2.5.10)

Table 2.1 Calculation for lattice parameter of Cu-Zn ferrite:

<table>
<thead>
<tr>
<th>Concentration X Cu-Zn ferrite</th>
<th>Lattice constant ‘a’ Å</th>
<th>X-ray density gm/cm³</th>
<th>Cation oxygen bond distance in Å</th>
<th>Ionic Radii Å</th>
<th>Tetrahedral (A) site (A-O)</th>
<th>Octahedral (B) site (B-O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1=0.0</td>
<td>8.4358</td>
<td>5.2935</td>
<td>1.826</td>
<td>2.1089</td>
<td>0.3532</td>
<td>0.7089</td>
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<tr>
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<td>5.3290</td>
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</table>

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Table 2.2 Calculation for lattice parameter of Co-Zn ferrite:

<table>
<thead>
<tr>
<th>Concentration X Co-Zn ferrite</th>
<th>Lattice constant 'a' Å</th>
<th>X-ray density gm/cm³</th>
<th>Cation oxygen bond distance in Å</th>
<th>Ionic Radii Å</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Tetrahedral (A site (A-O))</td>
<td>Octahedral (B site (B-O))</td>
</tr>
<tr>
<td>Y2=0.2</td>
<td>8.4174</td>
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<td>5.518</td>
<td>1.8058</td>
<td>2.0852</td>
</tr>
</tbody>
</table>

2.4 X-ray diffraction pattern of Cu-Zn and Co-Zn ferrites at different concentrations
Some Properties of microwave ferrites

Counts

Position [°2θ]

Counts

Position [°2θ]

Counts

Position [°2θ]

Counts

Position [°2θ]
2.5 $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ferrites at different concentration ($x=0.0, 0.2, 0.4, 0.6, 0.8, 1.0$)
Some Properties of microwave ferrites

Counts

Position [2θ]

Counts

Position [2θ]

Counts

Position [2θ]

Counts

Position [2θ]
2.6 Results and discussions: From the X-ray diffraction pattern of the powder samples of Cu-Zn and Co-Zn ferrites, it shows that it has cubic phase spinel structure, because of the most prominent peak at (311) and (400). And the lattice constant decreases with increases in the Zn content in case of Co-Zn and Cu-Zn ferrites it is because of modification of the A-B interaction strength due to the change in Fe$^{3+}$ concentration between A and B sites which is confirmed by decrease in the lattice constant from 8.43 to 8.34 Å° for Cu-Zn and 8.41-8.34Å° for Co-Zn. The X-ray density exhibition increasing trend with Zn contents as mainly it depends upon the molecular weight of the samples. It increases from 5.225 to 5.518 in Co-Zn ferrites and 5.2935 to 5.4652 in case of Cu-Zn ferrites.

2.7 Far infrared absorption spectroscopy: Infrared spectroscopy is the important tool to describe the various ordering problems [39]. It is the nondestructive and rapid method of the characterization and provides the qualitative analysis regarding the structure of functional groups and their linkages. The modes of the lattice vibration are the important and specific characteristic of the crystalline material and hence they are useful for the identification of the functional groups. The vibration occurs in the frequency range from 200/cm to 800/cm and many heavy metal oxides and
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organic compounds absorb the radiation in this range of frequency. The absorption band, from which the structure information can be explored is depend on the atomic mass, cation radius, location- anion bond distance, method of preparation, chemical compositions, etc, [39,40]. Waldron was the first, who used the IR absorption spectra for the analysis of the ferrites and assigned the high frequency band to the tetrahedral group complexes and low frequency band to the octahedral group complexes [41]. Lateron Halfner [40], Tarte [62], Preudhomme and Tarte [42,43] have studied the IR for various normal and inverse ferrites. So also many researchers [44,45,46] have studied the IR absorption spectra for some mixed ferrites. The results from the IR spectra study can be used to interpret the electrical and magnetic properties [47]. From the IR spectral analysis we can extract the information regarding the spinel structure, nature of the metal oxygen bonds, cation distribution, forces constant and electronic structure etc.

Normally in case of spinel structure, the four absorption bands were seen in the wave number range of 200-800/cm, denoted by \( v_1, v_2, v_3, v_4 \). The absorption band \( v_1 \) observed around 600/cm is allotted to the intrinsic vibration of the tetrahedral A sites, whereas the second band is at 400/cm is assigned to the octahedral metal-oxygen group complexes [41, 40]. The band \( v_3 \) near about \( v_2 \) is due to the vibrations in the divalent metal ion-oxygen complexes in the octahedral sites [39]. The band \( v_4 \) is attributed to the mass of the divalent tetrahedral cation [42]. The absorption band beyond this frequency 1000/cm is due to the electronic transition, giving rise to the electronic spectra.

2.7.1 Experimental:

The FTIR spectra of the compound of the above class of the ferrites were obtained in the range from 200cm-1 to 800cm-1, using Parkin Elmer spectro photometer at IISc Bangalore. And here using KBr pellet. The spectrometer was used in the absorption mode in which high transmittance is towards top of the chart. The transparent pellet was prepared by mixing finely crushed powder of KBr in the 1:3 proportions approximately and pressed in to the die of 1mm thick. The spectrometer gives the data output in the form of spectrum of transmittance (%) against the wave number.

From the IR spectra, the center frequency of the absorption band \( v_1 \) and \( v_2 \) were obtained. From these values of \( v_1 \) and \( v_2 \) and cation distribution, the force constant
Kt and K0 for respective sites have been calculated by using the relation suggested by Waldron [41].

\[
K_t = (0.04416) (\nu_1^3) (M_2) \left[ \frac{V}{(V+3)} \right] \\
K_o = (0.94218) \times M_1 \times \nu_2^2 \\
V = \frac{(64 - 2xM_1xu)}{M_2} \\
U = \frac{2K_o}{(\nu_1^2 M_1 - 2K_o)}
\]

Where M1 and M2 are the molecular weights of the A and B sites respectively.

2.7.6. Results and discussions:

FTIR spectra for the compounds under investigation are obtained from IR spectrometer are presented in the figures. These spectra show two strong absorption bands at the frequency 400 cm\(^{-1}\) and 564 cm\(^{-1}\) for the given compounds, shown in the table 2.3 and 2.4. The absorption bands observed within these specific frequency limits reveals the formation of single phase spinel structure [41]. Many researchers have reported such nature of IR spectra [48, 49, 53, 46]. The absorption band \(\nu_1\) observed about 600 cm\(^{-1}\) is attributed to the vibration of ions in the crystal lattice according to Waldron and Hafner the ferrites can be considered as continuously bounded crystals. In ferrites the metal ions are situated in two different sub lattice, tetrahedral A site and octahedral B site according to the geometrical configuration of the oxygen nearest neighbors. Waldron and Hafner, attributed the \(\nu_1\) band to the intrinsic vibrations of the tetrahedral groups, the \(\nu_2\) band to the octahedral groups and \(\nu_3\) band associated with the metal ions in the isotropic force fields of their octahedral or tetrahedral environments. The positions of these bands are presented in the table 2.3 and 2.4. From these tables, it is observed that the position of the bands is compositional dependence. The band \(\nu_1\) due to tetrahedral group of complexes is observed within the range of 550 cm\(^{-1}\) to 600 cm\(^{-1}\) and it is found to decreasing with increasing the zinc content similarly \(\nu_2\) due to the octahedral group complexes is observed within the range of 425 to 440 cm\(^{-1}\) and found to be increasing with increasing zinc concentration. This variation in the band position is due to variation in the respective cation –oxygen bond distance. These frequencies shows the close agreement with previous results [39, 41, 34].
The room temperature FTIR spectra of the above-mentioned compounds were recorded. The spectra recorded in the range 300 cm\(^{-1}\) up to 4000 cm\(^{-1}\). No absorption bands were observed above 1000 cm\(^{-1}\). The spectra show two main absorption bands below 1000 cm\(^{-1}\) is a common feature of all the ferrites. The bands around 387 cm\(^{-1}\) and at 543 cm\(^{-1}\) are assigned as \(v_2\) and \(v_1\), for Co-Zn ferrites and 532 and 441 cm\(^{-1}\) for Cu-Zn ferrites respectively. Also, it can be seen that frequency \(v_1\) is shifted to lower frequencies with increasing Zn ion concentration. Waldron and Hafner, attributed the \(v_1\) band to the intrinsic vibrations of the tetrahedral groups, the \(v_2\) band to the octahedral groups. According to Prakash and Baijal [8] Zn\(^{2+}\) ions have preference for the tetrahedral sites replacing Fe\(^{3+}\) ions in Cu-Zn and also in Co-Zn ferrites. The replacement of Fe\(^{3+}\) ions with Zn\(^{2+}\) ions having larger ionic radius and higher atomic weight at tetrahedral site in the ferrite lattice affects the Fe\(^{3+}\)-O\(^{2-}\) stretching vibration. This may be a reason for the observed change in \(v_1\) band positions.
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\[ S_3 = 0.4 \]

\[ S_4 \]

\[ S_5 = 0.8 \]

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Figure 2.6 FTIR graph of Cu-Zn ferrites at different concentration (X=0.0 to 1.0)
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![Graph Y3](image)

![Graph Y4](image)
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Figure 2.7 FTIR graph of Co-Zn ferrites at different concentration

(X=0.0 to 1.0)

Table 2.3: Value of Saturation Magnetization, and lattice constant
Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ Samples

<table>
<thead>
<tr>
<th>sample</th>
<th>Zn concentration</th>
<th>$\nu_1$ (cm$^{-1}$)</th>
<th>$\nu_2$ (cm$^{-1}$)</th>
<th>a in Å$^2$</th>
<th>Saturation magnetization</th>
<th>Average size of the particle in µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y1</td>
<td>0.0</td>
<td>543.27</td>
<td>441.66</td>
<td>8.4358</td>
<td>8.9</td>
<td>0.40</td>
</tr>
<tr>
<td>Y2</td>
<td>0.2</td>
<td>556.79</td>
<td>398.09</td>
<td>8.4174</td>
<td>0.54</td>
<td>0.39</td>
</tr>
<tr>
<td>Y3</td>
<td>0.4</td>
<td>565.14</td>
<td>393.52</td>
<td>8.4121</td>
<td>0.56</td>
<td>0.32</td>
</tr>
<tr>
<td>Y4</td>
<td>0.6</td>
<td>577</td>
<td>388</td>
<td>8.3977</td>
<td>0.82</td>
<td>0.477</td>
</tr>
<tr>
<td>Y6</td>
<td>1.0</td>
<td>580.03</td>
<td>387.28</td>
<td>8.3411</td>
<td>0.88</td>
<td>0.266</td>
</tr>
</tbody>
</table>
Table 2.4: Value of Saturation Magnetization, and lattice constant Cu1-xZnxFe2O4 samples

<table>
<thead>
<tr>
<th>sample</th>
<th>Zn doping in %</th>
<th>u_1 (cm⁻¹)</th>
<th>u_2(cm⁻¹)</th>
<th>a in Å</th>
<th>Saturation magnetization</th>
<th>Average size of the particle in nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.0</td>
<td>543.27</td>
<td>441.66</td>
<td>8.4358</td>
<td>0.005</td>
<td>162.6</td>
</tr>
<tr>
<td>S2</td>
<td>0.2</td>
<td>552.92</td>
<td>409</td>
<td>8.4349</td>
<td>11</td>
<td>201.5</td>
</tr>
<tr>
<td>S3</td>
<td>0.4</td>
<td>541.84</td>
<td>418.7</td>
<td>8.4255</td>
<td>12.5</td>
<td>159.98</td>
</tr>
<tr>
<td>S4</td>
<td>0.6</td>
<td>532.93</td>
<td>446.33</td>
<td>8.4126</td>
<td>17.5</td>
<td>159.6</td>
</tr>
<tr>
<td>S5</td>
<td>0.8</td>
<td>55.93</td>
<td>452.93</td>
<td>8.4065</td>
<td>11.5</td>
<td>205.5</td>
</tr>
<tr>
<td>S6</td>
<td>1.0</td>
<td>532.43</td>
<td>452.99</td>
<td>8.3680</td>
<td>0.0054</td>
<td>266.6</td>
</tr>
</tbody>
</table>

2.8 Thermal analysis: The application of thermal analysis in different fields of science and engineering is an extensive topic which has been the subject of significant interest particularly since the beginning of the modern era of thermal analysis in the early 1960s. With the continuous development of new techniques and the rapid improvements in data acquisition, manipulation and presentation using modern computers, more and more applications are constantly being explored and reported. In the last several years, applications in the fields of cement chemistry [1], clays and minerals [2], polymeric materials [3,4], pharmaceuticals [5] and other general applications [6,7], have been discussed in detail. Thermal analysis techniques have also been used extensively in the field of metallurgy and a large number of publications (several thousands in the last four decades) on this subject have been identified in the literature. These cover topics such as corrosion, solidification/microstructure, extractive metallurgy, sintering, roasting, catalysis, powder metallurgy, thin films, composite materials and others, in which thermal analyses were used as primary techniques, were chosen to address metallurgical topics that have received most attention in the recent past. From the many thermal analysis techniques that have been used in a wide variety of applications, thermogravimetry (TG), differential thermal analysis (DTA) and differential
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scanning calorimetric (DSC) were found to be the most commonly used in metallurgy and for the poly crystalline materials. The principles, operation and commercial availability of these and other techniques are discussed in detail in Volume 1 of the Hand book (M.E.Brown, Kluwer, Dordrecht). Though the analysis of thermal behavior in oxygen of finally grained ferrite and magnetic spinels, it is possible to obtain the information on the valence of the state of cations [43]. This information can be utilized to determine the distribution of oxidable cat ions between the tetrahedral (A) and octahedral (B) sites of the spinel structure. Recently considerable attention has focused on thermal behavior of nano sized MgCoFe\(_3\)O\(_4\), these materials allow investigation of the relative stabilities of the metal ions in A and B sites and a better understanding of the correlations between structure and some properties such as coercivety [44], electrical conductivity [45] and application in catalysis [46]. For example, it has been shown that the vacancies generated during the oxidation enhances or hinder the movement of cat ions between equivalent cations sites and cause the directional order phenomenon that has the property of greatly increasing the coercive field for each oxidized cation [47].

The weight % versus temperature curves are presented for the prepared Cu–Zn and Co–Zn ferrite samples, during heating in air up to 1000\(^\circ\)C. At temperatures between 200 and 1000\(^\circ\)C, subsequent reduction–oxidation Zn present in the powder occurs, resulting in weight gain or weight loss, observed in the TGA plots. In the temperature range between 200 and 400\(^\circ\)C a weight gain is observed due to the oxidation of Zn\(^{2+}\), to Zn\(^{3+}\) or Zn\(^{4+}\). At temperatures above 400\(^\circ\)C and up to 650\(^\circ\)C, a weight loss is observed, due to subsequent reduction of Zn\(^{4+}\) to Zn\(^{3+}\), while in the range 650–750\(^\circ\)C, further weight gain is observed because of Zn\(^{2+}\) to Zn\(^{3+}\) oxidation that is not completed at lower temperatures. At temperatures above 750\(^\circ\)C, a continuous weight loss occurs that corresponds to the sintering of the ferrite powders and the formation of the final spinel structure. Although the shape of the TGA between 200 and 1000\(^\circ\)C curves is similar for all samples, the observed weight gain and weight losses are different for each sample and as expected, are analogous to the Zn\(^{2+}\) content of the powder. Thus the larger variations are observed for the sample with the higher Zn content.
2.9. Scanning electron microscopy: The electrical and magnetic properties of the spinel ferrites are found to be sensitive to their microstructures. The microstructure in turn depends upon the method of preparation and preparation conditions. Therefore it is important to know the microstructure of the newly prepared materials. The microstructure, which includes grain size, grain distribution, grain boundaries, and their migration, pores, inclusions, and voids, etc., can be studied by means of scanning electron microscopy. The scanning electron microscopy is the most suitable tool for this purpose, because it has very high magnification and resolving power and great depth of focus. It permits the observation and characterization of the heterogeneous organic and inorganic bulk materials in the nanometer scales. It provides the important information about the topography, morphology, grain boundary, grain size, and its distribution, pores, and homogeneity of the materials. During the process of sintering, the microstructure develops. The finer grain gives more grain-to-grain contact and grain growth reduces the grain-grain contact. Porosity, the inherent property of the ceramic materials, depends upon the grain structure and average coordination number. Since the microstructures develop in the sintering stage, the sintering temperature and time play a crucial role in it. These effects are discussed in brief as follows.

a) Effect of sintering temperature and pressure: Temperature: The process of sintering may be divided into three stages: smoothing (elimination of internal porosity) [48], adhesion; shrinkage (grain growth starts).

b) The sintering temperature and the rate of the sintering temperature are the decisive parameters to control microstructure. This temperature should be sufficiently high to complete the solid state reaction. However, its range is limited by the grain growth and evaporation of certain constituents like Zn, Li, Cd, etc. Raijnen showed that the microstructure with large pores is developed at a lower sintering rate [61]. To reduce the porosity, the sintering rate can be increased, but it is constrained by the rate of diffusion of oxygen ions. Increase of temperature and time results in grain growth. This relation obeys up to certain critical grain size and limited due to the presence of pores. The grain growth due to the surface tension offered by the grain diameter with time is linear up to a certain limit [49]. This relation holds as long as the inclusions or voids do not hinder the migration of grain boundaries.

c) Pressure: The low porosity, small grains, and high physical density are therefore difficult to achieve by means of normal process. Application of the pressure is found
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to promote the sintering inhabiting the grain growth and reducing pore volume. For this hot pressing is the best method.

d) Grain growth:
The grain growth is the change in size and morphology of grain with time. The grain growth takes place on heating because of the surface tension that causes the boundaries to migrate towards their center of curvature; there are two types of exaggerated grain growth and duplex grain growth. The normal grain growth means to get narrow range of grain size.

e) Exaggerated grain growth: if grain grows very rapidly they trap the pores. Is called exaggerated grain growth. Kumara et.al prepared the sample of the magnesium ferrites with the exaggerated grain growth and found decrease in the surface area of the grain boundary [50]. Drofricket et.al (1985) have reported the presence of exaggerated grain growth for zinc ferrites and growth of giant grains was attributed to the zinc loss [51].

f) Microstructure and properties of ferrites:
The intrinsic properties, magnetic and electrical properties are found to be dependent on the microstructure of ferrites. Grain size, grain distribution and porosity play the dominant role in governing these properties. Therefore the effects of the microstructure on these properties are discussed in brief as follows.

g) The effect of microstructure on electrical properties: The electrical resistance of the poly crystalline ferrites i.e. due to the presence of grain boundary [52]. Therefore the grain size and porosity would affect the electrical properties. The increase of porosity results into increases in resistivity, causing decrease in the physical density. The effect of the structural distortion on the resistivity of the ferrites as been reported by Longet.al [53]. The technological important ferrites composition should have low eddy current losses, foe which small grains and large grain to grain contact is essential. The dielectric behavior of predominately sensitive to the microstructure. The dispersion in the dielectric constant with frequency was explained by Koops with help of double layer model wherein one is poorly conducting grain and another is a fairly well conducting grain [54]. The low dielectric los and high resistivity are the essential properties for microwave applications.
h) Effect of microstructure on magnetic properties: The magnetic properties, saturation magnetization, permeability, ac susceptibility, coercivity etc. are sensitive to the grain size and porosity of the compositions. The saturation magnetization decrease with increase in the porosity due to the decrease in the physical density. Smith and Wien showed the variation of Hc with porosity in Ni-Zn ferrites [55]. The increase in the Hc with the porosity is linear up to low porosity and deviates from linearity for higher values of Hc. This effect may be due to the fact that higher porosity samples have smaller particles (probably single domain) which have higher coercive force. Economos (1959) showed decrease in the Hc of Mg ferrites with decreases in the porosity [25]. Magnetization is independent of the grain size but relates with the porosity as (1-P) 4πMs. And coercivity is inversely proportional to the grain radius. The shape of the B-H loop of Ni-Zn ferrites changes due to the porosity [56]. Permeability is found to be greatly influenced by the microstructure [57]. To have high permeability the grain size should be large. This increase in the permeability with the grain size is up to certain limit and then drops down. This may be due to porosity. Increase in the grain size results in to increase in the permeability but it creates the serious problem of the high frequency losses, which are due to the grain boundaries, acting as an impediment to the domain wall motion. The temperature dependent behavior of the permeability and ac susceptibility depends upon the grain size suggesting the existence of SD, MD and Sp particles [58,59,60]. The pore and other imperfection would cause to pin the domain walls. Economos (1959) noted the increase in the permeability with increase in the density of MgFe₂O₄ [25].

2.9.1 Experimental: To understand the microstructure, grain size, shape, grain growth, grain boundary, segregation, migration, cracks, voids, Pores, etc. the compositions of the ferrites were studied by the scanning electron microscopy model at IISc Bangalore. The samples were fractured to expose the inside portion and mounted on the standard specimen mounting stub by using conducting silver paste. The samples were coated with the thin layer of the gold in the polaron coating unit to prevent the charging of the specimen. For comparative study, the electron beam parameters were kept constant while analyzing all the samples.
h) Effect of microstructure on magnetic properties: The magnetic properties, saturation magnetization, permeability, ac susceptibility, coercivity etc. are sensitive to the grain size and porosity of the compositions. The saturation magnetization decrease with increase in the porosity due to the decrease in the physical density.

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2.10. **Result and discussion:** The scanning electron microscopy of the composition Cu-Zn and Co-Zn ferrites was done and the micrographs of all the composition are presented as shown in the figure. From these micrographs, it can be seen that no exaggerated grain growth has taken place in the sample during the sintering. The average grain size is obtained by measuring number of grains intersected on the straight line of the specific length in micrometer/nanometer. This process of counting the number of grains i.e. repeated for different positions of the micrograph and data are averaged to get the average grain size. Thus obtained grain diameter for all the samples are presented in the table 2.3. from the table it is found that the average grain diameter is within the range of 0.40μm and 0.266μm for Co-Zn composition and in case Cu-Zn it varies from 159.6 to 266.6nm.However the grains size less for substituted composition than for the un substituted compositions as shown in the table2.4.
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Figure 2.8 SEM micrographs of Cu-Zn Fe$_2$O$_4$ at different concentration (S1, X=0.0, S2, X=0.2, S3, X=0.4, S4, X=0.6, S5, X=0.8, S6, X=1.0)

Figure 2.9 SEM photograph of Co-Zn ferrites at different concentration (Y1, X=0.0, Y2, X=0.2, Y3, X=0.4, Y4, X=0.6, Y6, X=0.8)
References:


Some Properties of microwave ferrites


[31] W.H Bragg and W.L Bragg the reflection of x-ray by crystal Proceed. A 88 (1913) 423


Some Properties of microwave ferrites


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[54] C.G.Koops, Phys, Rev., 83 (1951) 123.


