

CHAPTER - II

PREPARATION OF FERRITES AND CHARACTERIZATION
BY X-RAY DIFFRACTION

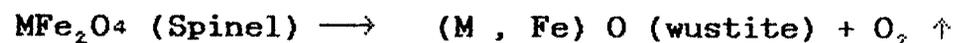
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INTRODUCTION

Ferrites are magnetic oxide materials, containing iron oxide as one of the component and the oxides of divalent metal ions such as Mg^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} etc., the members of first transition series of elements. The technological importance of ferrites is due to the fact that, they possess high resistivity with low eddy current losses [1]. To obtain high resistivity increased permeability for radio frequency applications and square loop properties, a thorough knowledge of the chemistry and technology of the ferrites is required. The preparation of ferrite phase using melting process is impossible, as all ferrites decompose, if they are melted. This is attributed to the fact that, at high temperature oxygen splits off, reducing Fe^{3+} to Fe^{2+} . In case of stoichiometric spinels, [2] oxygen splits off as,



Alternative reason is that, once the spinel phase is formed, for complete dissociation of excessive Fe_2O_3 dissolved into MFe_2O_4 , the dissociation temperature is to be considerably decreased [3]. Hence these magnetic oxides cannot be moulded into desired shape by melting as in the case of metals.

The more advanced technology for the formation of ferrite is ceramic technology. It mainly deals with the preparation of ferrites by solid state reaction. Hilpert [4] in 1909

first investigated the mechanism of solid state reaction which leads to the formation of ferrite. Hedvall [5], Tammann [6], Jandar [7] and others contributed much to the understanding of ferritic reaction. Since last thirty years, groups of scientists from Japan [8] and U.S.A. have contributed much to ferrite technology. The research for ferrite compact of definite characteristics thus depends upon methods of preparation. Hence important aspects such as mechanism of solid state reaction, sintering process, general methods of preparation of ferrite sample, actual preparation of ferrite sample and characterization by x-ray diffraction are included in this chapter.

2.1 MECHANISM OF SOLID STATE REACTION

A solid state reaction is one in which, the reaction between two solid compounds results in the formation of the third. In ferrite preparation process one compound is iron oxide and the other, divalent metal oxide. The explanation of mechanism of solid state reaction is on the basis of diffusion of metal oxides MO and ferric oxide Fe_2O_3 into one another at high temperature. During the preparation of ferrites only one phase boundary is formed between the reactants at the beginning. After the nucleation of the ferrites, the boundary is replaced by two different phase boundaries between metal oxide MO and ferrite MFe_2O_4 (fig.).

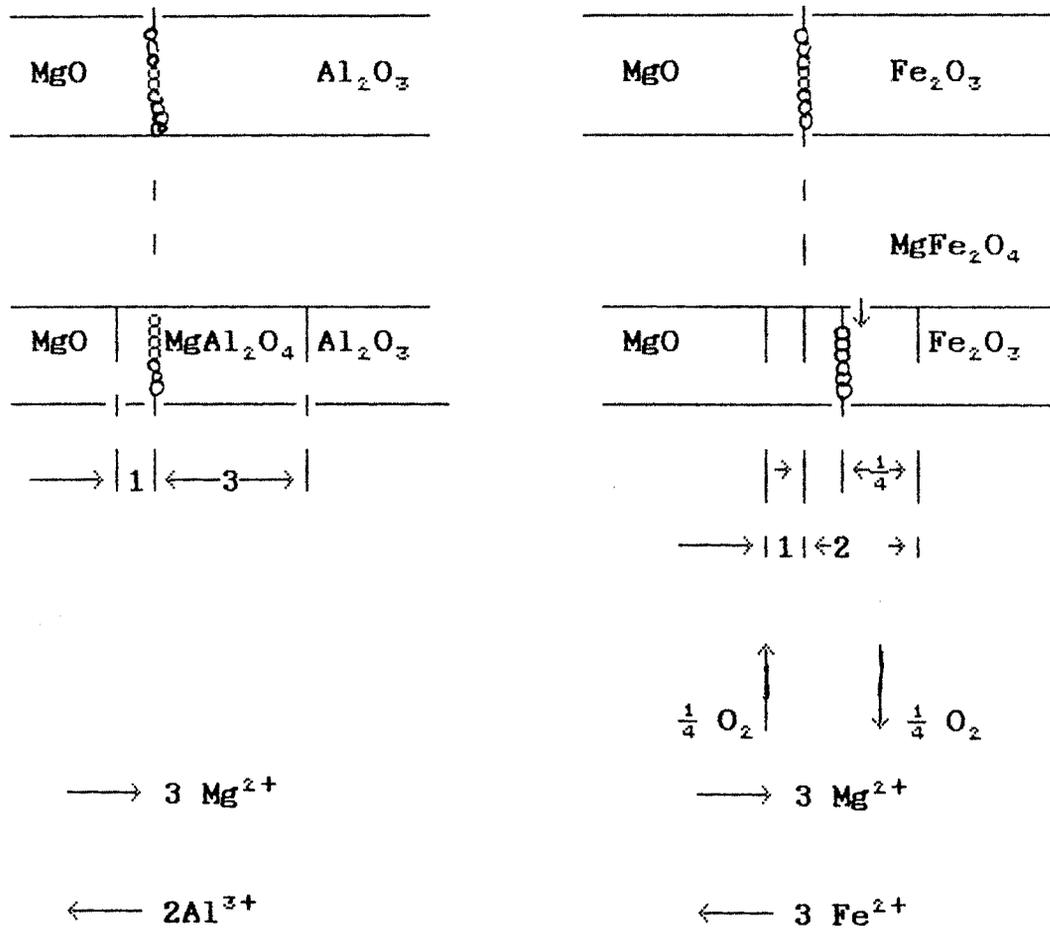


Fig. a

Fig. b

Fig. Formation of ferrite phase by counterdiffusion

- (a) Formation of $\text{Mg Al}_2\text{O}_4$: Counterdiffusion of Mg^{2+} and Al^{3+} cations, no anion diffusion (Wagner mechanism)
- (b) Formation of MgFe_2O_4 : Counterdiffusion of Mg^{2+} and Fe^{2+} cations, no anion diffuse.

In this case the reaction proceeds by transport of reactants through the ferrite phase. Transfer of MFe_2O_4 can take place by three ways [9,10].

- [1] According to Wagner [11] reaction proceeds by counterdiffusion mechanism in which only cation migration take place in opposite direction while oxygen ions are stationary.
- [2] In the second model anions diffuse. In this type of diffusion, cation diffusion is compensated by diffusion of anions.
- [3] According to third mechanism iron diffuse through ferrite layer in a reduced state Fe^{2+} . In such a case oxygen is transported through the gas phase, being given off at MFe_2O_4/Fe_2O_3 interface and taken up again at MO/MFe_2O_4 boundary.

The transport mechanism suggested by Koch and Wagner has been further used by Carter [12]. He demonstrated that $MgAl_2O_4$ is formed by counterdiffusion. The solid state reaction rate depends on several important factors such as temperature of heating, proper mixing of solids, diffusion coefficient of component oxides etc. Generally when sample is heated at about half of its temperature of melting the diffusion of ions takes place.

2.2 METHODS OF PREPARATION

A number of preparation processes are in use for ferrites and the relative merits of various methods are influenced by the volume, raw materials and end use of the final product. Fig.2.1 is a flow chart of various stages in the preparation of standard ferrite samples.

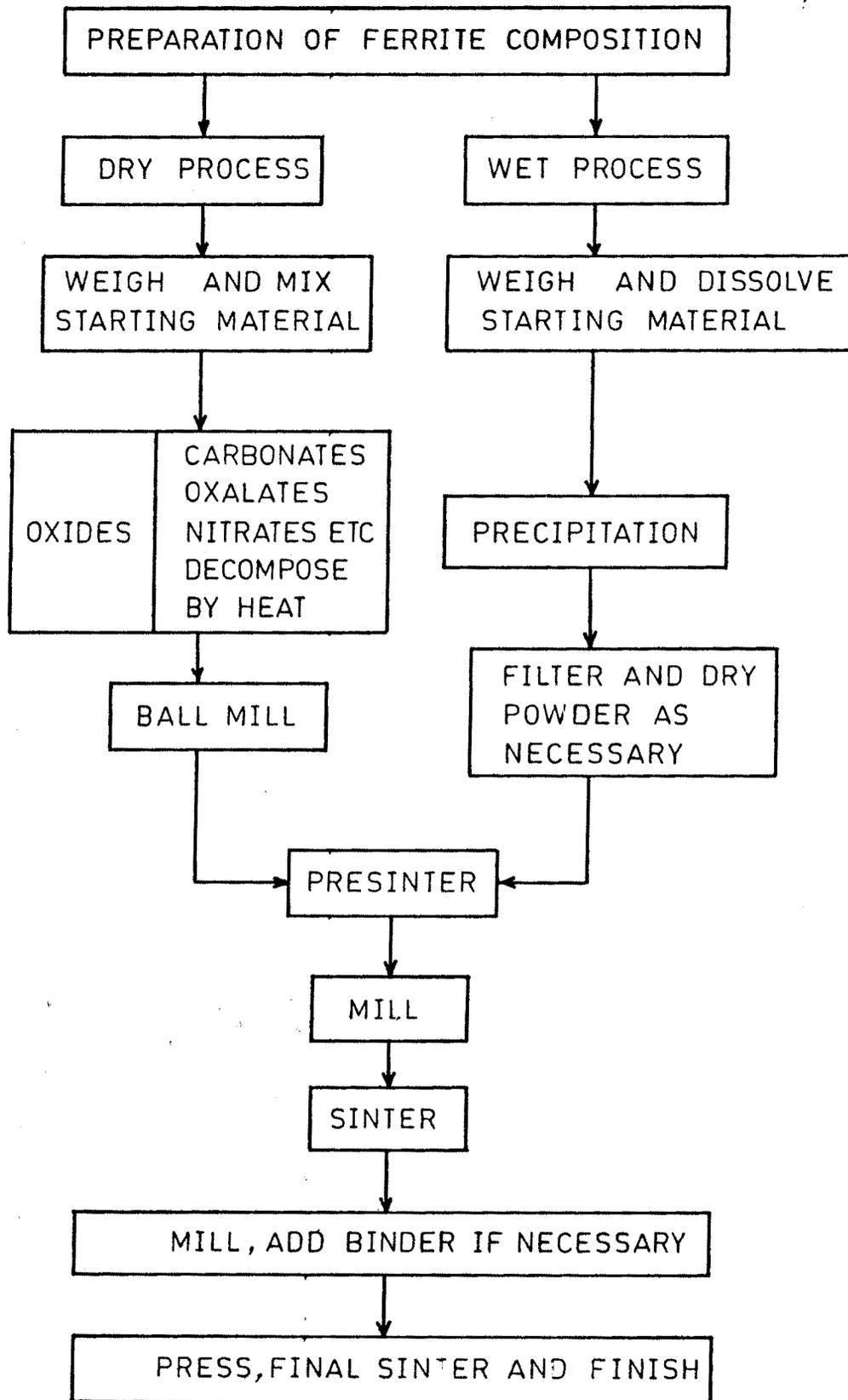


FIG.2.1 FLOW CHART OF STAGES IN THE FERRITE PREPARATION.

2.2. a) STANDARD TECHNOLOGY OF FERRITES PREPARATION

Polycrystalline ferrites are normally prepared by the following processes :

- 1) A compound which is to exhibit predetermined electrical and magnetic properties is usually prepared from oxide raw materials in a solid state reaction. For preparing very pure iron oxides or ferrite powders on a laboratory scale, by hydrothermal reaction "wet chemical" preparation methods are increasingly being employed. With these processes requirements of high purity, reactivity and fine grain size can be achieved.
- 2) Pressing the ferrite powder in moulds yields a shape very close to that of the final technical product.
- 3) Densification is attained by a sintering process.

These three processing steps, reaction, molding and densification sometimes overlap. When manufacturing of ferrites starts with moulding, upon application of pressure reaction starts in unreacted materials during a single firing process. Final reaction and sintering take place simultaneously during the last firing step. But for hot pressing technique completely reacted single phase product must be used.

2.2 b) STANDARD PROCEDURE FOR FERRITE PREPARATION

The first step is the mixing of raw materials. In most cases raw materials having a grain size of less than 1 to 5 μ m are mixed and sometimes the spectral "wet chemical" preparation condition is employed to reduce it to as small as 50 \AA . The mixing is usually carried out in water medium in steel ball mills. After the slurry is filtered and dried, the dried powder mixture is transferred to ceramic crucible for

prefiring at elevated temperature.

The next step is the actual grinding in steel ball mills. The purpose of grinding is to achieve better homogenization of the product by bringing together those particles of the initial substances which have not fully reacted, and thus reduce the diffusion distances. Grinding also reduces the grain size of product as well as grain size distribution for improvement of the sintering process.

The last stage is compacting the powder into the desired shape. Commonly two methods are used. One is compaction in a diepunch assembly and second a hydrostatic or isostatic compaction of powders or the preshaped sample immersed in liquid. For small scale production of ferrites in laboratory applications, hydrostatic pressing is preferred.

2.3. c) OTHER METHODS OF FERRITE PREPARATION ARE AS FOLLOWS

2.3.1 Decomposition Method

In this method salts such as carbonates, nitrates, and oxalates are used as starting materials instead of oxides. These salts are first mixed in the requisite proportions and then preheated in air to produce oxides by thermal decomposition. The oxides so prepared undergo, solid state reaction more readily [13]. The other details of this method are similar to the oxide method.

2.3.2 Chemical Co-precipitation Method

In this method solutions of soluble salts of divalent metals such as, $ZnCl_2$, $MgSO_4$, $Co(NO_3)_2$ and pure ferric chloride solution are mixed in a desired molar proportion. Here the cations are mixed on the molecular dimension.

a) Hydroxide Precipitation

This method is proposed to avoid lengthy milling processes in dry mixing. In this, attempts have been made, to precipitate simultaneously, the required hydroxide from a solution intimately mixed so that, the precipitate contains the required metals in requisite proportion. Economus [14] first established this method for fabrication of ferrites. This method was used by Wolf and Rodrigue [15] for the preparation of YIG. Several difficulties which arise in this method are,

- i) The qualitative understanding of the process is required to ensure the simultaneous precipitation of hydroxide. The method loses its importance in the absence of simultaneity.
- ii) Removal of impurities due to absorption of sodium ions precipitated, is quite However, Sato and his co-workers [16, 17] prepared ultrafine ferrites by this method and studied their properties.
- iii) The precipitate may form in such a way that filtration becomes difficult.

b) Oxalate Precipitation

Precipitation of metallic oxalates is preferable for two reasons. Firstly, precipitation can be carried out using ammonium oxalate which does not leave any residue after ignition. Secondly, most of the metal oxalates are very similar in crystal structure; hence the precipitation tends to produce mixed crystals containing metallic cations in the proportions in which they were present in the solution. Hence the mixing in correct ratios can be achieved on a molecular

scale. Careful calcination of the precipitate, in the case of $MgFe_2O_4$, at temperature near to $600^\circ C$ yielded a ferrite with a average particle size less than 1 micron.

c) Chelate Precipitation

Chelates are the organometallic compounds. Some of these compounds are unstable and insoluble in water. They can be co-precipitated and reduced to ferrites after calcinating. Busev and others [18] suggested a method of mixing ferrite powders by co-precipitation of compounds with B-hydroxyquinoline followed by roosting. They reported that this method gives the ferrite powders of constant composition and permits regulations of the dimensions of the precipitated particles.

Of all the methods stated above ceramic method is simple and straightforward. It gives good results. Decomposition method of preparation relies upon mechanical process, to produce uniform dispersion of the constituents, hence it is disadvantageous. In chemical co-precipitation techniques, for using hydroxide precipitation, knowledge of the solubility products of the substances is essential in order to determine the pH values for complete precipitation. Hence it is quite complex. In case of oxalate precipitation technique, mixed crystals do not form uniformly if precipitation occurs at widely different rates. Hence ceramic method is an important, ferrite fabrication method.

2.4 SINTERING

Sintering is the most common technological process in the manufacturing of crystalline materials. Sintering in crystalline solids has been explained by Coble and Burke [19].

In solids, sintering occurs in three stages so as to increase the density of solid to make it technically attractive.

ASPECTS OF SINTERING

1) Initial Stage

In this stage of sintering, neck area formed between pairs of ionic spheres initially grow on account of atomic diffusion. Grain growth is totally inhibited.

2) Intermediate Stage

Due to neck growth, when the density reaches to 60% of its theoretical value, grain growth sets in. The structure still contains continuous pore phase. The density increases with the logarithm of time. The densification rate decreases somewhat due to an increase in grain size. When density reaches 95% of its theoretical value, the pore phase becomes discontinuous, termination of intermediate stage occurs.

3) Final Stage

This stage is influenced by the fact that, if discontinuous grain growth occurs, a large number of closed pores, trapped inside the grains and isolated from the grain boundaries cannot shrink any more. Since grain boundaries have a surface tension, sintering is practically stopped. In this stage of sintering the last few percent of porosity remaining in the sample can be eliminated by discharging vacancies at grain boundaries. Thus dense, compact samples can be prepared having actual density comparable to X-ray density.

2.5 HOT PRESSING

Hot pressing technique consist of formation of dense solid by simultaneous application of external temperature and pressure [20]. For good high power properties of microwave

ferrites the grain size has to be small and uniform. Hot pressing is the only means of achieving a dense ferrite material at sufficiently low temperatures without grain growth. In this process applied pressure provides normal driving force for densification. Factors affecting the hot pressing process are time, temperature, pressure, environment and particle characteristic. Considering hot pressing as a function of particle size of starting material by keeping all factors constant, it is observed that material with finer particle size densifies more rapidly than that with coarser particles. With rise in hot pressing pressure the concentration of Fe^{2+} ions, density, Curie point and degree of inversion increases.

Bratton et al [21] studied the densification phenomena in the hot pressing of natural spinel $MgAl_2O_4$. They have demonstrated that hot pressing does not occur by single mechanism. It depends upon variables such as time, temperature, stress and microstructure. It is occurring in three stages. The initial stage of hot pressing is often characterized by particle rearrangement, whereas intermediate stage is characterized by plastic flow, viscous flow and Nabarro-Herring diffusional creep. All these mechanisms of intermediate stage are applicable to final stage. Increased driving force from surface tension of small pores or grain growth causing pore entrapment, are also included in final hot pressing stage.

The densification of solids by hot pressing is the most important method of all ceramic processing techniques.

2.6 PREPARATION OF FERRITE SAMPLES

For the preparation of ferrite samples, oxide method (ceramic method) is used. Ferric oxide (Fe_2O_3), Magnesium oxide (MgO) and cobalt oxide (CoO) were taken as raw materials and weighed accurately to the required molar composition using semi-microbalance.

The compositional weights of powders were mixed physically and blended in agate mortar in acetone medium. All the three samples listed in table (2.4) were first presintered at 800°C for 20 hours keeping them in platinum crucibles. The presintered powders were subjected to hard milling process in acetone medium for six hours. The dried powders were sieved to eliminate the large size particles.

To prepare pellets, approximately 1 gm of powder was taken and ground in acetone by adding few drops of the binder (Poly-Vinyl acetate). The powder was subjected to a pressure of about 5 tonnes per square inch for three minutes by keeping it in a die of 1 cm diameter. The pellets were subjected to final sintering, at 900°C . Sintering time for the pellets was 20 hrs and 30 hrs respectively.

CHARACTERIZATION BY X RAY DIFFRACTION

The phenomenon of X-ray diffraction by crystal was first discovered in 1912 by Von Laue [22]. It has revolutionized the entire field of physics, as it provides information about the internal structure of crystals. X-ray diffraction also plays an important role in ferrite research. It is used to confirm the spinel structure of ferrites and the completion of solid state reaction during their preparation.

2.7 BRAGG FORMULATION OF X-RAY DIFFRACTION BY A CRYSTAL

In 1913, W.H and W.L Bragg [23] found that substances whose macroscopic forms were crystalline gave remarkably characteristic patterns of reflected X - radiation. In crystalline materials, for certain sharply defined wavelengths and incident directions, intense peaks of scattering radiations (known as Bragg peaks) were observed.

W.L.Bragg accounted for this by regarding a crystal as made out of parallel planes of ions, spaced a distance 'd' apart. The conditions for a sharp peak in intensity of the scattered radiation were,

- 1) That the X-rays should be specularly reflected by the ions in any one plane and,
- 2) The rays reflected from the adjoining plane should interfere constructively.

The diffraction maxima are found to occur only when the waves coming from two scattering centres are in phase and this condition is fulfilled provided the Bragg's law [24] is obeyed Bragg's law can be put into mathematical equation as,

$$n\lambda = 2 d \sin \theta \quad 2.1$$

The integer 'n' is known as the order of the diffraction.

d = Interplaner distance

λ = Wavelength of monochromatic radiation.

For producing the Bragg peaks several techniques are available [25].

1) The Laue Method

The Laue method is probably best suited for determining the orientation of single crystal specimen, whose structure is known. In this case when the incident radiation lies along a

symmetry axis of the crystal, the pattern of spots produced by the Bragg reflected rays is obtained.

2) The Rotating Crystal Method

This method uses monochromatic x-rays but allows the angle of incidence to vary. In practice the direction of the x-ray beam is kept fixed and the orientation of the crystal is varied. In the rotating crystal method the crystal is rotated about the fixed axis and all Bragg peaks that occur during the rotation are recorded on a film.

3) The powder Method

This method of x-ray diffraction was first developed by Debye and Scherrer [26] in 1916 and later on by Hull [27] in 1917. By using this method the structural information about the sample under investigation can be obtained. In this method the sample holder rotates about the axis of camera in a beam of x-rays where as the film is placed on the inside cylindrical surface of Debye Scherrer camera.

This is equivalent to a rotating crystal method, in addition that the axis of rotation is varied over all possible orientations. In practice this isotropic averaging of incident direction is achieved by using a polycrystalline sample or powder, grains of which are capable of diffracting x-rays. Because the crystal axes of the individual grains are randomly oriented, the diffraction pattern produced by such a powder is a combination of diffractions patterns of all possible orientations of a single crystal. Experimental details of this method are as follows.

In this method small amount of smoothy ground powder can be coated on the surface of fine glass fibre with a glue or

petroleum jelly. The specimen is then mounted in its holder. Since the fine grains of the powder are randomly oriented the reciprocal lattice vectors of all the crystallites points in all the directions. The incident monochromatic radiation finds same crystal planes which may satisfy the Bragg condition to produce maxima. The diffracted radiation is received by a counter in diffractometer. The counter directly gives the graphical record, proportional to the intensity of diffracted X-rays.

2.8 EXPERIMENTAL

The X-ray diffraction patterns were obtained from Regional Sophisticated Instrumentation Centre, University of Nagpur, Nagpur. Fe K α - radiations of wavelength 1.93604 A $^{\circ}$ was used. The diffractograms were taken within the range of 2 θ between 10 $^{\circ}$ to 85 $^{\circ}$.

2.9 INDEXING AND CALCULATION OF THE LATTICE PARAMETERS

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

$$d = \frac{a}{\sqrt{h^2 + k^2 + \ell^2}} \quad n \quad (2.2)$$

where,

a = lattice parameter.

h, k, ℓ = Miller Indices

n = order of diffraction.

From equation (2.1) and (2.2) the lattice parameters is given by,

$$a = \frac{\lambda}{2 \sin \theta} \left[\sqrt{h^2 + K^2 + \ell^2} \right] \quad (2.3)$$

Rearranging equation 2.3,

$$(h^2 + K^2 + \ell^2) = \frac{4a^2}{\lambda^2} \sin^2 \theta \quad (2.4)$$

for $n = 1$

Equation (2.3) is used to calculate the lattice parameter in the cubic system. For indexing the peaks in the diffraction patterns equation (2.4) is used.

The peak of maximum height corresponds to the plane (311) in spinel structure so the lattice parameter 'a' in this case is calculated by using the relation (2.3). For other planes the (h,K,ℓ) values were determined by the usual process [27] and the peak indexed.

2.10 RESULTS AND DISCUSSION

The X-ray diffraction patterns of magnesium, ferrite magnesium-cobalt ferrite and cobalt ferrites are as shown in figures 2.2, 2.3 and 2.4. Tables 2.1, 2.2 and 2.3 contain the data on observed and calculated 'd' values and the miller indices of diffracting planes. The indexing of the diffraction maxima is done by method mentioned above. The miller indices tally very well with those for spinel

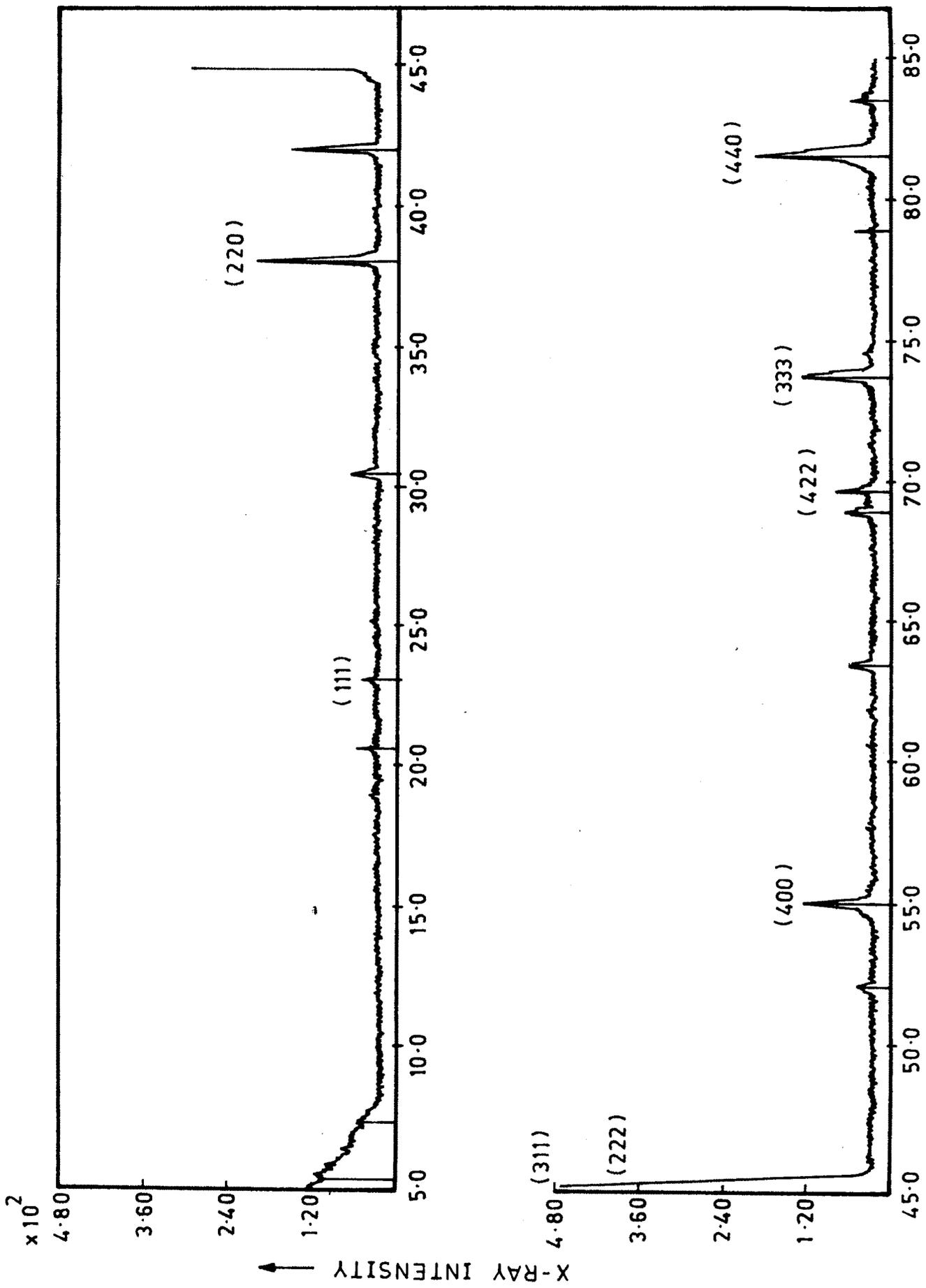


FIG. 2.2 - DIFFRACTION PATTERN OF $MgFe_2O_4$ SAMPLE.

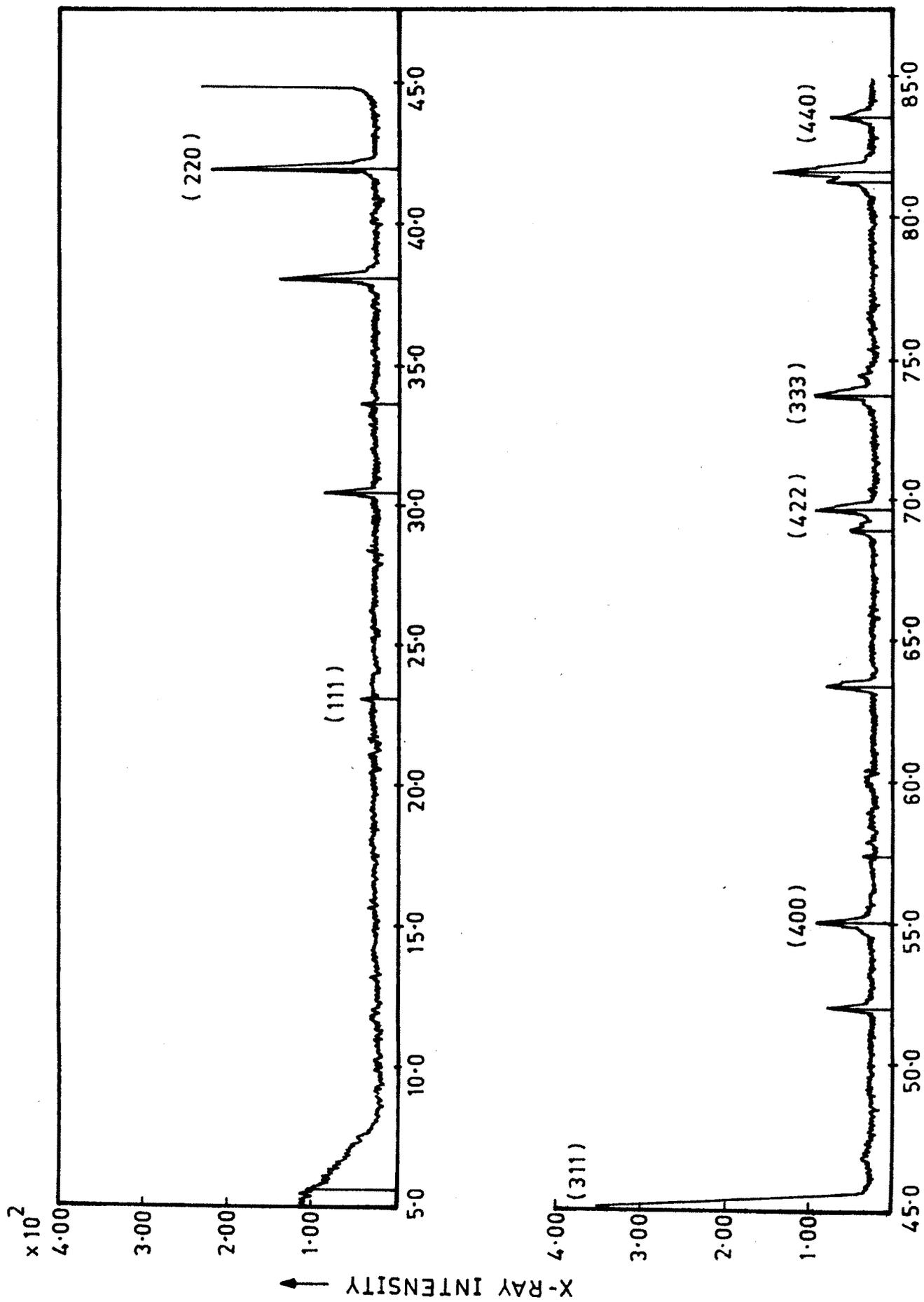


FIG. 2.3 — DIFFRACTION PATTERN OF $Mg_{0.6}Ce_{0.4}Fe_2O_4$ SAMPLE.

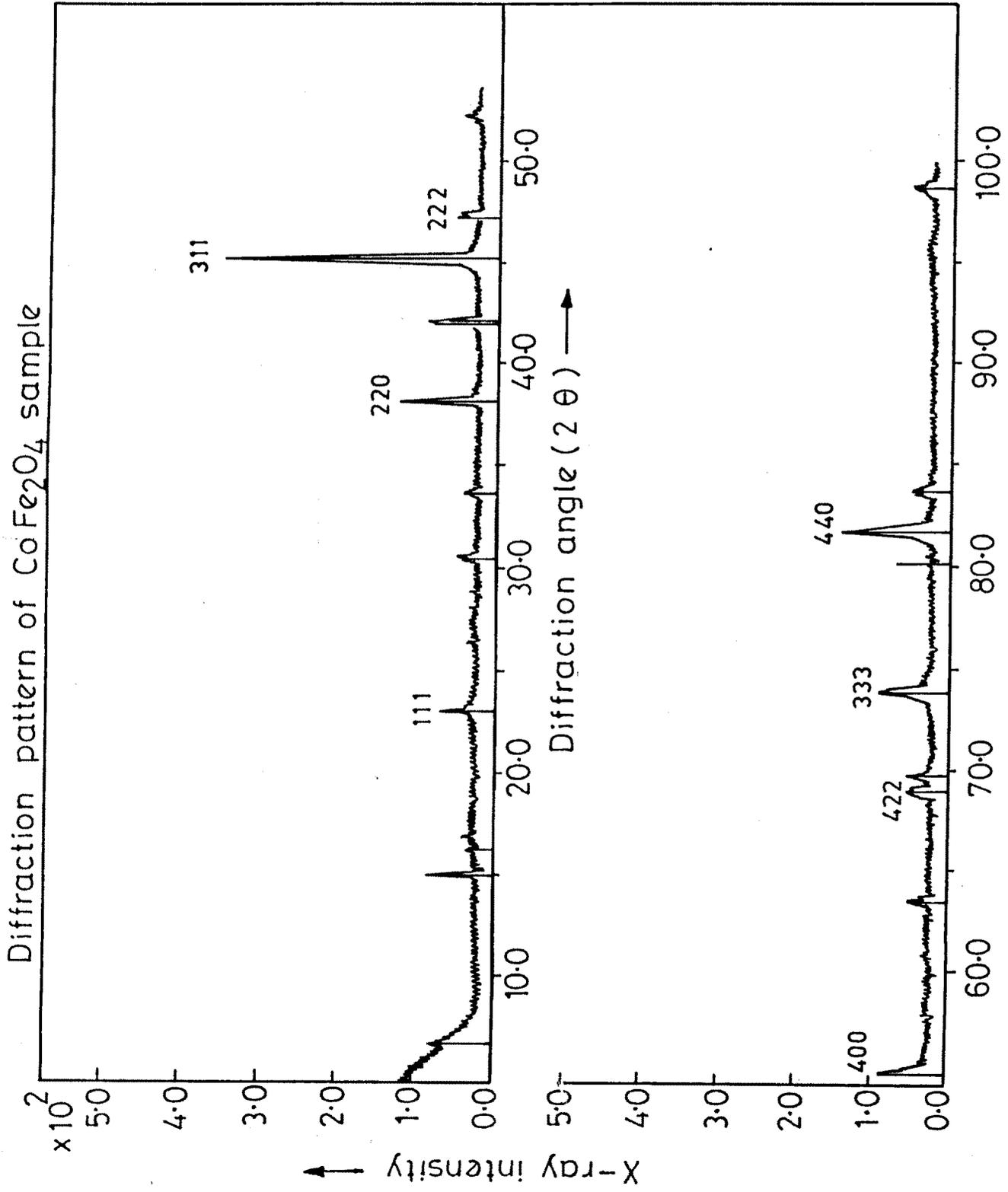


Fig. 2.4

T A B L E - 2.1

Sample-MgFe₂O₄

a = 8.380 A°

structure - Cubic

λ = 1.93604 A°

2θ°	θ°	Sin θ	hkl	Observed d, A°	Calculated d, A°
23.07	11.53	0.2000	111	4.8398	4.8401
38.13	19.06	0.3267	220	2.9630	2.9628
45.05	22.52	0.3831	311	2.5264	2.5267
45.14	22.57	0.3838	222	2.5219	2.4865
55.07	27.53	0.4622	400	2.0939	2.0950
69.68	34.84	0.5712	422	1.6944	1.6947
73.75	36.87	0.6000	333	1.6131	1.6131
81.55	40.77	0.6531	440	1.4821	1.4821

T A B L E - 2.2

Sample-Mg₆Co₄Fe₂O₄
structure - Cubic

a = 8.3096 Å°

λ = 1.93604 Å°

2θ°	θ°	Sin θ	hkl	Observed d, Å°	Calculated d, Å°
23.09	11.54	0.2001	111	4.8364	4.8790
38.14	19.07	0.3267	220	2.9628	2.9888
45.07	22.53	0.3832	311	2.5255	2.5479
55.06	27.53	0.4622	400	2.0942	2.1126
69.69	34.84	0.5716	422	1.6942	1.7091
73.77	36.88	0.6002	333	1.6127	1.5948
83.31	41.65	0.6646	440	1.4563	1.4692

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T A B L E - 2.3

Sample-CoFe₂O₄

a = 8.354 Å°

structure - Cubic

λ = 1.93604 Å°

2θ°	θ°	Sin θ	hkl	Observed d, Å°	Calculated d, Å°
23.11	11.555	0.2003	111	4.8326	4.8326
38.22	19.11	0.3274	220	2.9592	2.9585
45.00	22.50	0.3827	311	2.5290	2.5189
47.20	23.60	0.4003	222	2.4187	2.4182
55.10	27.55	0.4625	400	2.0965	2.1510
69.05	34.525	0.5666	422	1.7088	1.7085
73.86	36.93	0.6009	333	1.6110	1.6063
81.70	40.85	0.6541	440	1.4800	1.4799

T A B L E - 2.4

Sample	Crystal structure	Molecular weight gm.	Lattice constant, A°
MgFe ₂ O ₄	Cubic		8.3801
Mg _{0.6} Co _{0.4} Fe ₂ O ₄	Cubic	13.869	8.3096
CoFe ₂ O ₄	Cubic	34.671	8.3548

structures [28]. The 'd' values are in good agreement with each other. Hence the formation of spinel structure is confirmed. The reflecting planes observed in all ferrite samples are

(111), (220), (311), (400), (422), (333) and (440).

Non appearance of any other unwanted peak shows the purity of the compound formed.

Table 2.4 gives the lattice constant of magnesium ferrite, Magnesium-cobalt ferrite and cobalt ferrite. From the table it is clear that lattice constants are approximately the same. This is attributed to the fact that the ionic radius of Co^{2+} ions and Mg^{2+} ions are nearly the same. Thus when cobalt is mixed with magnesium ferrite it gets directly substituted in B-site replacing Fe^{3+} ions. Hence the lattice site remains the same, without expansion. Recently Rao and Keer [29] calculated lattice parameters of Mg-Co ferrites of chemical formula $\text{Mg}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ (with $x = 0.01$) and reported that the composition $\text{Mg}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ to be monophasic cubic spinel. Further, they showed that the unit cell parameter did not change appreciably with the variation of cobalt concentration from those of parent compounds.

In the case of cubic structure the cyclic sum of the miller indices $(h + k)$, $(k + l)$ and $(l + h)$ is even integer. This is observed in case of (i) Mg - ferrite (ii) Mg-Co ferrite (iii) Co - ferrites indicating that all the three compositions have cubic structures.

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