

CHAPTER I

Methods of Preparation and
Crystal Structure of Ferrites.



1.1 INTRODUCTION

During the beginning of the second half of the twentieth century the ferrimagnetic oxides, known as 'ferrites' have aroused considerable interest among the researchers. On the one hand there was academic interest owing to their crystal structure, scope for employing a large number of different ingredients, a vast variation in their properties depending upon method of preparation, dependence of their properties on physical parameters like grain size, porosity, homogeneity etc. and on the other owing to their important electrical and magnetic properties the aim was to develop certain ferrites which will have immediate industrial applications. Presently, the ferrites have proved to be very useful materials in electrical and electronic industries.

Basically, ferrites are semiconductors having their resistivity values in the range 10^{-3} to 10^{+11} ohm-cm. They were developed with the main objective of reducing eddy current losses in inductors and transformers, particularly at high frequencies. This work was initiated by Hilpert¹ in the year 1909. However, the ferrites produced by him exhibited large losses, low permeability and were less reliable in reproduction. Now a days an extensive number of such materials have been developed with precise properties having definite applications.

Presently a very large number of oxides, selenides, sulphides, fluorides having general chemical formula AB_2X_4 have been developed and they are said to possess the "spinel" structure. In the compounds with general formula AB_2O_4 , the spinel structure consists of 32 oxygen atoms in a unit cell in a cubic close packing. The electrical neutrality of the structure AB_2O_4 can be satisfied in the following manner.

- 1) A^{2+}, B^{3+} (2) A^{4+}, B^{2+} (3) A^{6+}, B^{1+} .

These types are therefore, known as 2-3 spinels, 4-2 spinels or 6-1 spinels. All the types of 2-3 spinels are further classified as alluminates, $M^{2+}Al^{3+}_2O_4$; ferrites, $M^{2+}Fe^{3+}_2O_4$; chromates, $M^{2+}Cr^{3+}_2O_4$ etc.

Eventhough the ferrites have been developed to have immense applications in electrical and electronic industry, the emphasis is always being given on their manufacture and improvement of properties, with greater reliability of reproduction i.e. the "Tailor making" of these materials because of their increasing demand in the manufacture of microwave components and switching and memory devices in computer industry.

1.2 ELECTRICAL NEUTRALITY AND TYPES OF COMPOUNDS

In a stable structure of spinel, it is expected, according to the formula AB_2O_4 that the ratio of charges from anions to cations should be 1:1. The compound satisfying the electrical neutrality of the structure (i.e. charge ratio 1:1) are called the stoichiometric compounds, while the compounds those do not satisfy the electrical neutrality of the structure are called as the non-stoichiometric compounds² e.g. $Cu_x Fe_{3-x}O_4$. The ratio of charges in this case are $1:1+(1-x)/8$ where $x \ll 1$.

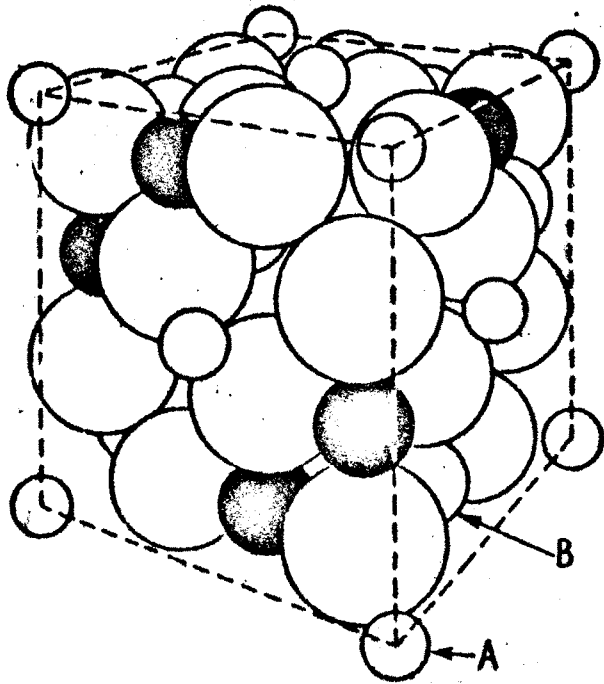
The modern concept of perfectly stoichiometric crystal is that it does not represent a condition of perfect order but it is a system in which these are exactly balanced, extremely low concentration of intrinsic point defects. However, there are some systems which exist over a chemically significant range of composition and are thermodynamically bivariant. Their unit cell size as determined by x-ray diffraction apparently varies smoothly with composition. Such systems are said to be non-stoichiometric. It should be clearly appreciated that non-stoichiometry is a high temperature phenomenon. In these systems it has been investigated that the significant point defect concentrations interaction is found to occur with formation of a new ordered structure element. To study the high temperature structure of the samples they may be frozen in by quenching from different temperatures and can be detected with the help of x-ray diffraction method.

1.3 CRYSTAL STRUCTURE OF FERRITES

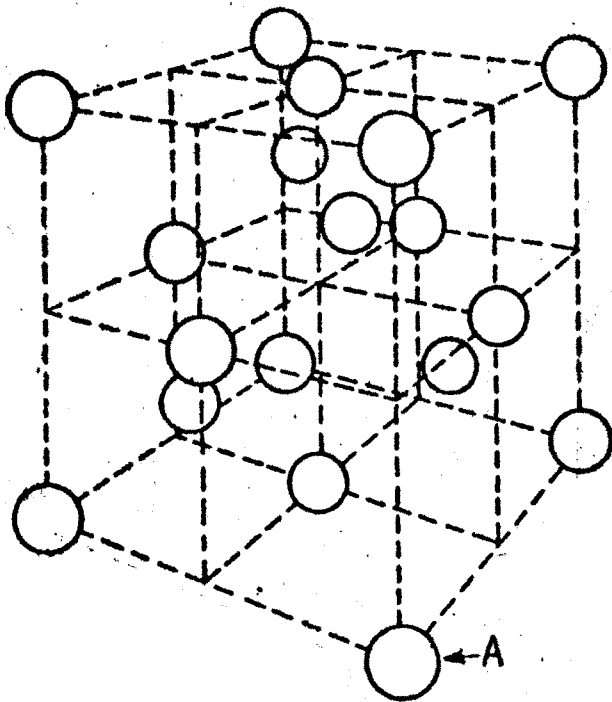
The mineral MgAl_2O_4 is said to have spinel structure. There exists an extensive group of ferrimagnetic oxides with the same structure which are now a days commonly referred to as the spinel ferrites. The naturally occurring magnetite, Fe_3O_4 , has also a spinel structure.

In general ferrites may be described as compounds derived from magnetite (FeOFe_2O_3) by substituting other metal atoms in place of the divalent iron. Suitably the atoms of metals such as Mn, Mg, Ni, Cu, Co, Zn and Cd replace the divalent iron atoms. If the divalent iron in magnetite is replaced by single divalent metal atoms; the ferrite formed is called a single ferrite or a simple ferrite e.g. CuFe_2O_4 , NiFe_2O_4 , MgFe_2O_4 . However, if the divalent iron is partially replaced by one and partially by other metal atoms, the ferrite formed is termed as a binary ferrite or a mixed ferrite e.g. $\text{Mg}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$.

The ferrites are ionic crystals of chemical composition MFe_2O_4 , where M stands for any divalent metal ion. The oxygen ions form a close-packed face-centred cubic structure as shown in fig. (1.1a), leaving the interstices of two kinds between them. The metal ions occupy suitably these interstices. The position of the metal ion in a void surrounded by six equidistant oxygen ions as nearest neighbours is called an octahedral (O) or B site and the position of a metal ion in a void packed by four oxygen ions is called a tetrahedral (T) or A site.



← Fig. 1.1 a



← Fig. 1.1 b

Fig 1.1: Crystal structure of completely inverse ferrite.

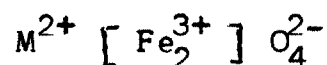


In a unit cube of spinels, there are 32 possible octahedral, B sites and 64 possible tetrahedral, A sites. Out of these, the metal ions occupy only 24 sites³.

The unit cell contains 32 oxygen ions, 16 Fe³⁺ ions, and 8 divalent metal ions. Out of 24 metal ions, 8 metal ions get distributed on A sites, while remaining 16 metal ions get distributed on B sites.

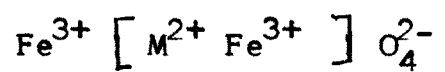
The properties of the ferrite are dependent on the kinds of metal atoms, their proportions and geometric arrangement among the voids of a cube. If Fe²⁺ is replaced by Zn or Cd alone, a non-magnetic material is obtained at room temperature, while the replacement by other atoms such as Mg, Ni results in a magnetic material. The distribution of the divalent metal ions in a ferrite can take place in the following manner⁴⁻⁵.

i) In the normal spinel structure of a ferrite, the 8 divalent metal ions are distributed on A sites; the 16 Fe³⁺ ions are distributed on B sites. This can be shown by a notation



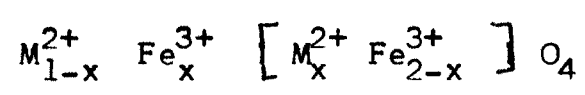
the bracketted ions indicate the atoms on B site. The standard examples of this type are Zn Fe₂O₄ and CdFe₂O₄. The non-magnetic ferrites are having the normal spinel structure.

ii) In the inverse spinel structure of a ferrite, the 8 divalent 8 M²⁺ ions lie on B sites; the Fe³⁺ ions lie in equal numbers on A and B sites. The arrangement may be represented by



the bracketed atoms once again represent the B site. The particular examples of inverse spinel structure are CuFe_2O_4 , NiFe_2O_4 etc. The magnetic ferrites possess the inverse spinel structure.

iii) There is a possibility of intermediate case of spinel structure of a ferrite whose arrangement would be



where $x = 0.1$ to 1.0

1.3a The Inverse Spinel Structure of Ferrite

The magnetic ferrites are said to have an inverse spinel structure. The completely inverse spinel structure of a ferrite is shown in fig. (1.1).

If the M ion and iron ion have considerably different scattering power for x-rays used, the x-ray diffraction intensity measurements distinguishes the normal and inversed cation distribution in a spinel. By this method Barth and Posnjack (1932) showed that MgFe_2O_4 has the inverse structure. Verwey and Heilmann (1947) similarly found the inverse spinel structure in CuFe_2O_4 .

The octant within the cube shown by the broken lines in fig.(1.1b) corresponds to eight formula units of $\text{M Fe}_2\text{O}_4$ in Fig.(1.1a). If the centres of the ions lie outside the cube, those have been omitted. The larger spheres represent the

oxygen ions on face centred cubic structure. 8 Fe^{3+} ions are situated on A sites, ions on A sites are abstracted and shown in fig.(1.1b). The ions on A sites have four near neighbour oxygen ions in tetrahedral position, while the remaining 3 Fe^{3+} ions have six neighbouring oxygen ions in octahedral positions, as shown in fig.(1.2).

Certain characteristic features of the structure can be shown by representing the spinel lattice in another way as in fig. (1.3). The fig.(1.3) is due to W.L.Bragg. The figure shows a section through a plane containing oxygen ions and cations in octahedral interstices, parallel to the front face of the cube in fig. (1.1a) and lying a short distance behind it. The black circles represent oxygen ions, and the open crossed circles denote cations in tetrahedral and octahedral voids, respectively. For clear understanding, several oxygen ions lying in planes above (P) and below (Q) the plane of the section, and the cations in tetrahedral voids slightly above (p) and slightly below (q) this plane, have been shown in fig.(1.3). From this figure it is clear that cations in octahedral voids form continuous chains running right through the structure, with a relatively small distance between adjacent ions.

The chains of octahedral voids in the inverse spinel structure contain equal number of M^{2+} and Fe^{3+} cations, which in a statistical distribution must occur alternately. This fact may have effect on ionic interactions related to ferromagnetic behaviour in magnetite the octahedral cation chains form alternately by Fe^{2+} and Fe^{3+} ions, that helps easy electron

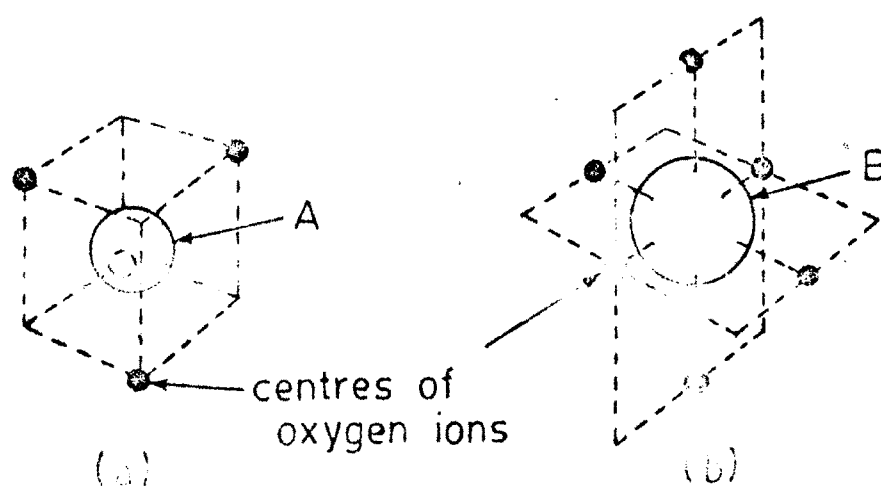


Fig. 1.2 a : A is an Fe ion in an A-site with four near-neighbour oxygen ions . . .
b : B is an Fe ion or M(metal) ion in a B-site with six near-neighbour oxygen ions .

exchange to occur; this explains the electronic conductivity of magnetite. The magnetite lattice is of immense interest because its supposedly inverse cation arrangement could be converted into the normal arrangement merely by shifting eight electrons per unit cell from octahedral to tetrahedral cations.

1.4 CERAMIC TECHNIQUE

The ceramic technique, can be used to prepare ferrites, which involves the sintering of the component oxides at temperatures in a range 1000°C to 1450°C depending upon the reaction temperature which varies from constituent to constituent. The main stages in the preparation are as follows :

- | | | |
|------------------------------------------------|---|-----------------------------------------|
| 1) Raw Materials |) | Mixing and Preparation
of materials. |
| 2) Decomposition to oxide |) | |
| 3) Milling |) | |
| 4) Pre-sintering (partial reaction) | | |
| 5) Remilling | | |
| 6) Pressing and Extruding to shape | | |
| 7) Final sintering at the reaction temperature | | |
| 8) Cooling (slow cooling or quenching) | | |
| 9) Grinding | | |
| 10) Pressing to shape. | | |

1.4a Methods of Preparation 6-8

1) Oxide Method :

High purity oxide materials are chosen and mixed together in proper proportions as would be expected by the final product. By wet milling this mixing is performed for a long period using stainless steel balls. The attritor and the vibratory ball mill saves more time. The milled mixture is dried and then pressed into a suitable shape before presintering. The pinking-up of steel from the balls during milling is insufficient to affect the final product.

2) Decomposition Method :

Instead of using oxides one may start with salts such as carbonates, nitrates and oxalates. These salts are milled in the proper proportions and heated in air to produce the oxides by thermal decomposition. The other details of the method are similar to the oxide process. The preparation of oxides in situ at a temperature about which solid state reaction commence more readily.

c) Hydroxide Precipitation :

The required hydroxides are precipitated from a solution so that the precipitate contains the required metals in the correct proportions being already intimately mixed. Economos (1955) prepared magnesium ferrite by this method. Wolf and Rodrigue (1958) successfully prepared the yttrium and rare-earth garnets. In using this method, there are possible

troubles i) The quantitative understanding of the chemical process is essential. ii) The precipitation may make filtration difficult. iii) Sometimes sodium ions are absorbed on the precipitate forms impurities.

4) Oxalate Precipitation

The precipitation of the metallic oxalates using ammonium oxalate, does not leave any residue after ignition. Most of the metal oxalates being similar in crystal structure, can be used for precipitation to produce mixed crystals containing the metallic cations in the proportions. Thus the mixing in the correct ratios can be obtained on a molecular scale.

Mixed crystals do not form uniformly if precipitation occurs with widely differing rates. Careful calcinating of the precipitate is required at a particular temperature to yield a ferrite.

1.4b Pre-sintering

The mixture of raw materials is fired at a temperature some 200°C below its final firing temperature, the process is called pre-sintering. Swallow and Jordan⁹ (1964) note the following purposes of the process :

i) It decomposes carbonates and higher oxides, that reduces the evolution of gas in the final sintering process.

ii) It helps in homogenizing the material.

iii) It controls the shrinkage of the material during the final firing.



Partial reaction takes place to form the final product during pre-sintering. The amount of reaction depends upon the reactivity of the components and the pre-sintering temperature. The solid-state reaction is a diffusion process whose rate depends upon the temperature. The pre-sintering temperature can be maintained upto 1000°C for several hours depending upon the constituents of the material. The correct partial pressure of oxygen in the furnace must be maintained throughout the firing cycle in order to ~~deserve~~^{retain} the stoichiometry and valence states achieved; otherwise those will be destroyed during the cooling period.

1.4c Moulding and Extrusion

The presintered powder is then remilled, usually with an organic medium such as alcohol. The alcohol is then removed. A binding agent mixed with the oxides is pressed in a die to a pressure as high as 10 tons per sq. inch to form a desired shape. The sample is gently heated to remove the binder otherwise violent volatilisation could cause the sample to crack. The rod specimens may be formed by extrusion. For satisfactory extrusion a higher percentage of binder is required than for moulding. A solution of wax in petroleum is preferred as a binder for extrusion. A very dense samples may be produced by a careful choice of extrusion orifice. Extrusion technique is mainly used for the manufacture of long thin rods, a shape often required in microwave applications.

1.4d Final Sintering and Cooling

The properties of the final product depend upon the sintering process. The sintering time, temperature and atmosphere is required to maintain at closest value. Generally the sintering temperature is maintained between 1000°C and 1450°C for 4 hours to 24 hours depending upon the ferrite. Ferrites containing lithium and cadmium are usually sintered at lower temperatures due to the volatility of LiO and CdO_2 while those containing nickel, cobalt and magnesium are sintered at the highest temperatures. The near absence of pores with a uniform product is required for microwave ferrites which can be achieved by sintering the sample for a long time at high temperatures. The oxygen equilibrium pressure increases with temperature that limits the maximum sintering temperature.

The cooling conditions also affect the properties of the final product. Since the ferrites have a very low thermal conductivity, it is essential that they be cooled slowly after sintering. To achieve the stoichiometry and desired valence states, the partial pressure of oxygen in the furnace must be maintained throughout the whole firing cycle. The partial pressure of oxygen changes due to oxidation during sintering period and reduction during the cooling period, so the rate of heating and cooling must be almost the same. The distribution of metal ions can be quenched by means of quick cooling from the sintering temperature. If the treatment temperature is lower than the sintering temperature, the distribution is not

at equilibrium. The quenching of the sample can be made by quick cooling of it either in air or water.

1.4e Grinding to Shape

The final dimensions to the sample can be given by grinding. Cutting can be carried out by use of a thin diamond slitting wheel or by use of an ultrasonic machine with a knife edge cutting head. The final finish can be made by surface grinding with a carborundum wheel.

1.5 Conditions of Preparation and Properties of Material :

1.5a) Calcination Treatment -

A powder calcined at higher temperature produces better crystallinity and expected less sinterable than a powder calcined at lower temperature¹⁰⁻¹³.

1.5b) Repeated Calcinations with Interspaced Grinding -

With every additional calcination step followed by grinding results in a larger bulk density in the sintered product which gives improved electrical properties by reducing the permeability and increasing Q values¹⁴. The frequency at which the losses become predominant get improved.

1.5c) Sintering Treatment -

The surface energy of the particles gives the driving force for the sintering process so that a powder compact grow together and the pores in the compact are filled up with material which leads to shrinkage of the material¹⁵. The interface between

crystallites, the grain boundaries, represents an amount of energy that is reduced by grain growth. During grain growth some grains grow due to absorption of their neighbours.

Sintering, densification and grain growth occur at the same time. The sinter reactivity must be sufficiently high for the process to continue which requires necessarily the small particle size of the powder. In spinels and garnets, the volume diffusion is the main transport mechanism leading to densification. Surface diffusion also plays a part in the beginning of the process during the formation of a contact area between the particles. The Nabarro-Herring theory¹⁶⁻¹⁷ for diffusional microcreep describes the principal mechanism for densification. The surface of the pore acts as a source of vacancies. The vacancies diffuse through the bulk of the particle to the grain boundaries, where they can be discharged. The resulting effect is material transport by the migration of individual ions from the grain boundaries to the pores, producing shrinkage.

The grain boundaries play a major role in the elimination of porosity. The grain boundary energy which is roughly isotropic, gives the driving force for grain growth on heating. The grain boundary energy decreases during the grain growth as a result the boundaries move to their centre of curvature. The rate of grain growth is reported to be depending on temperature and the time¹⁸⁻¹⁹. The presence of impurities lowers the rate of grain growth. The microstructure with intragranular porosity may be useful for the processing of ferrites. To

avoid the reaction with the gas atmosphere during cooling from the sintering temperature the closed porosity structure is more advantageous.

Ram Prasad and V.K.Murthy¹⁴ have reported that the bulk density of the samples increases with an increase in either the sintering temperature or time. After a critical temperature further increase in enhancement of density does not result. The permeability values obtained by raising the sintering temperature highly deteriorate the high frequency behaviour. Thus, during the sintering process the changes in grain size, crystallinity and redistribution and the nature of the porosity affect the electrical properties.

1.5d) Control of Grain size -

Subtle changes in the impurity content, the packing density and processing parameters have a large effect on the final product. A better control is possible with pure materials, otherwise the grain growth does occur during sintering which is highly unwanted. According to Zener¹⁰, for the constant diameter of the inclusion, the inverse relation between the pore volume and the critical grain size is exhibited. Thus possibly the discontinuous grain growth may occur during sintering by decreasing the pore volume. In most ferrites this is not indicated at all. The sufficiently high sintering rate controls the discontinuous grain growth in a ferrite. Thus it should be concluded that grain size cannot be well controlled in the normal sintering unless very pure raw materials are used, or the grain growth inhibitors are used.

1.5e) Control of Porosity -
aims of

One of the ceramic technique is to achieve the lowest possible porosity in the product. This is possibly made by promoting the sintering rate by using powders with large surface area. For this purpose wet chemical preparation methods such as co-precipitation are more preferred. The theoretical and experimental studies on sintering process in oxide materials done by Reijnen²¹, showed that the microstructure with large pores is related to compounds having intrinsically a low sintering rate. In an optimum concentration, the lowest diffusing species oxygen vacancies in spinel have to be present to give a high sintering rate. This condition is fulfilled in Fe_2O_3 deficient spinels. The spinels with excess Fe_2O_3 , on the other hand, have a very low concentration of oxygen vacancies which reduces strongly the sintering rate and the pore growth becomes predominant. In these materials very long sintering times are needed to achieve densification. If no pore growth occurs, discontinuous grain growth is found.

Thus the combination of a low porosity and small grain size is extremely difficult to obtain by the normal ceramic process. For this achievement an external force, by pressing the sample, during the sintering is necessary. This may promote the sintering process but not grain growth. Hence hot pressing and continuous hot pressing methods are highly appreciated.

1.6 CONDUCTIVITY IN SPINEL FERRITES

The transport of electrons through the lattice in ferrites is of great interest because it is related to anisotropy relaxation and also since the presence of an ordered spin system influences the conduction process. The value of the resistivity of ferrites lies in a wide range 10^{-3} to 10^9 ohm-meter at room temperature.

The resistivity of magnetite $\text{Fe}^{2+} \text{Fe}_2^{3+} \text{O}_4^{2-}$ is approximately 5×10^{-5} ohm-meter at room temperature. Its high conductivity is associated with the simultaneous presence of Fe^{2+} and Fe^{3+} ions upon identical (octahedral) lattice sites in the spinel structure. The electrons move from ferrous (Fe^{2+}) to ferric (Fe^{3+}) ions through the continuous chain of the octahedral positions. The transitions of electrons do not cause any change in the energy state of the Fe^{2+} crystal.

Verwey, Haayman, Romeijn and Oosterhout²² have shown that the conduction can be increased by mixing a very small amount of foreign oxides in high resistivity oxides. In general, if a cation of a high resistivity material is replaced by a cation which tends to stay in a lower valence state leads to a p-type conduction, while the substitution by a cation that tends to stay in a higher valence state leads to a n-type conduction. Additions from the one category can be employed to suppress the affects of the other.

1.6a) Dependence of Resistivity on Excess Iron

Fig.(1.4) shows the effect on resistivity due to the presence of excess iron above and below the stoichiometric ratio $1(\text{Ni}+\text{Zn}):2\text{Fe}$. The excess iron leads to the formation of ferrous (Fe^{2+}) ions and therefore the high conductivity in the solid solution is expected. The presence of ferrous (Fe^{2+}) ions reduces magnetostriction but it is highly undesirable in microwave ferrite applications²³. Snoek²⁴ points out that the presence of ferrous (Fe^{2+}) ions can be reduced strongly by taking iron less than the stoichiometric ratio in the composition. Van Uitert (1959) showed that an excess of iron above stoichiometry and high firing temperature both cause remarkable reduction in the resistivity see fig.(1.5).

1.6b) Dependence of Resistivity on the System Composition

For iron deficient Ni-Zn ferrites, the relation between resistivity and composition is shown in fig (1.5). The broken line indicates the values of resistivity that were obtained before the grinding of the surfaces of the sample and the solid line indicates the values after doing so. It is observed by chemical check up that the zinc loses from the surface of the sample. The loss of zinc leads to the presence of ferrous(Fe^{2+}) ions, which forms a low resistivity surface layer. It is clear that the resistivity of the sample can be increased by mixing the p-type and n-type conductor ferrites e.g. NiFe_2O_4 and ZnFe_2O_4 . The electrons get compensated with holes in a mixed system that increases the resistivity of the sample. The

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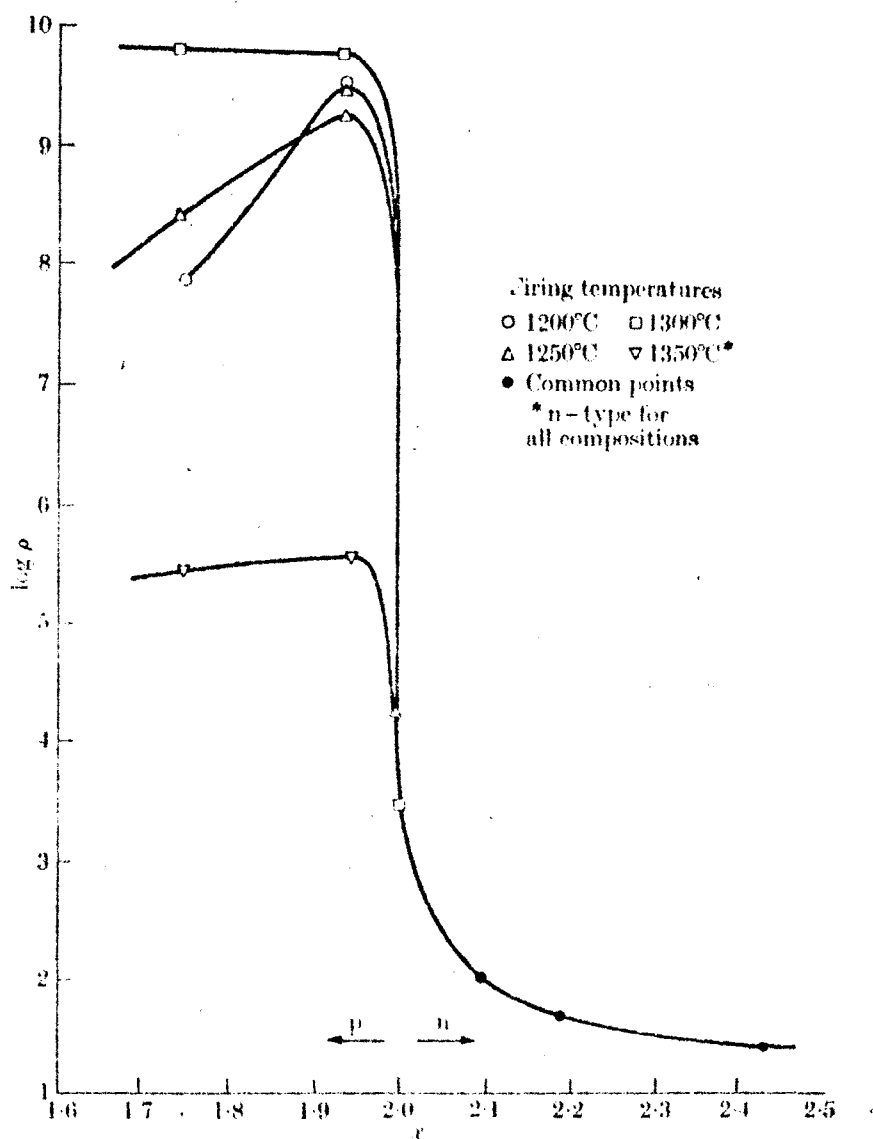


Fig. 1.4 The variation of resistivity with firing temperature and iron stoichiometry for the series $\text{Ni}_{0.3}\text{Zn}_{0.7}\text{Fe}_r\text{O}_4$ (after Van Uitert 1955).

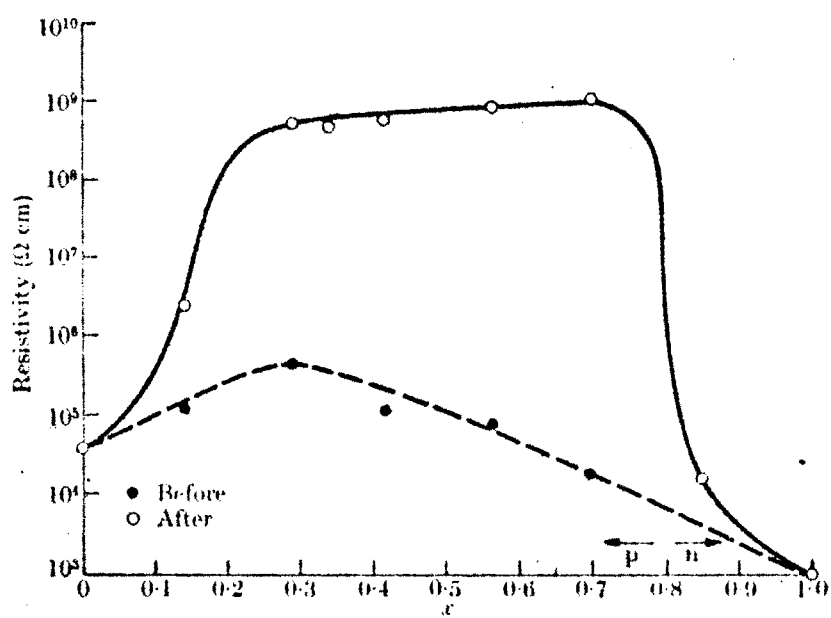


Fig. 1.5 The resistivities of samples of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_{1.5}\text{O}_4$ fired at 1250°C , before and after surface grinding (after Van Uitert 1956b).

dilution of the conduction mechanism in both sets of lattice sites is another reason of high resistivity in a mixed system.

1.6c) Effect of Impurity on Resistivity

The conductivity can be suppressed by the use of impurities when the corresponding partially filled levels are situated about half-way over the bandgap⁵. The E_g value for Mn is smaller than for Ni and Co. This is in agreement with the decrease in conductivity that was obtained by Van Uitert²⁵ by substitution of a few mole percent Mn for the divalent ions in Ni and Co ferrite.

1.6d) Effect of Temperature on Resistivity

In many cases the temperature dependence of conductivity σ can be described by

$$\sigma = \sigma_0 \exp \left(- E_a / kT \right)$$

where k is the Boltzmann constant and E_a is the activation energy, T is the absolute temperature. The slopes of the resulting straight line segments from the graph of $\log \sigma$ against $1/T$ represent E_a/k values for different conduction mechanisms.

Komar and Kliushin²⁶ observed breaks in the vicinity of the ferromagnetic Curie-temperatures of several ferrites. But at low temperature, discontinuity (e.g. in magnetic at 120°K) has been explained by Verwey and Haayman²⁷ as being due to the ordering of ferrous and ferric ions in the octahedral lattice sites.

This ordering is expected by a small change in crystal structure. Breaks in the curves can also occur where the dominant mechanism of conduction changes.²⁸ A final category of thermal breaks is that embodying hysteresis effects. The thermal hysteresis effects can be related to phase transitions.

1.6e) Effect of Physical Parameters

The pores, probably air filled; the grain size contribute to the resistivity, so also does the chemical inhomogeneity.

1.7 SOME IDEAS ON CONDUCTIVITY IN FERRITES

1.7a) The conductivity σ can be written as

$$\sigma = e (n_e \mu_e + n_h \mu_h) \quad | \quad 1$$

where e is the electronic charge, $n_e(n_h)$ is the concentration of mobile electrons (holes), $\mu_e(\mu_h)$ is the mobility of the electrons (holes).

1.7b) The temperature dependence of σ can be described by

$$\sigma = \sigma_0 \exp (- E_a / kT) \quad | \quad 2$$

where E_a is the activation energy and k is the Boltzmann constant.

1.7c) To determine the value of μ , which is much smaller and frequently temperature dependent, in transition metal oxides, the model of the hopping electron has been proposed.²⁹ In this model electrons take part in a diffusion process by jumps from

one lattice site to another. The expression for mobility μ can be written as

$$\mu = l_j^2 e f_0 (kT)^{-1} \exp(-q/kT) \quad 13$$

where μ is μ_e or μ_h

l_j jump length

f_0 frequency of the lattice vibrations

q activation energy for the hopping process.

1.7d) When the number of charge carriers, n is known, the mobility can be obtained from σ . The value of μ obtained in this way is called the drift mobility. One method of determining n is to measure the Seebeck effect, Θ given by

$$\Theta = (k/e) \ln(N/n) + a_k \quad 14$$

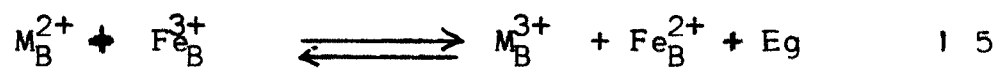
where Θ is the voltage per degree difference

N is the concentration of lattice sites available to the electrons (or holes)

n is the concentration of the charge carriers.

$a_k^{2\Theta}$ is a constant depending on kinetic energy.

1.7e) In spinels the charge carriers can be introduced by forming mixed systems of a ferrite and Fe_3O_4 . In perfect stoichiometric compounds ferrous (Fe^{2+}) ions can be produced by thermal activation of the reaction



where the index B denotes the octahedral sites.

M is a divalent metal ions such as Mn, Co, Ni



E_g is the band gap, the energy required to transfer an electron from M^{2+} to Fe^{3+} .

1.7f) Measurements of the Hall effect have confirmed the n-type conductivity.³¹ In ferromagnetic materials, the Hall voltage depends upon the applied field H_z and the magnetization. The two Hall constants R_0 and R_s are introduced by the relation

$$E_x = J_y (R_0 H_z + R_s \cdot 4 \pi M_s) \quad 16$$

where E_x is the transverse voltage per centimeter.

J is the current density. The increase of M_s with field raises some complication, even in large fields. This is particularly noticed near the Curie-point. In equation (6) $R_0 = \frac{1}{ne}$ is the ordinary Hall constant and R_s is the ferromagnetic Hall coefficient. The ratio of R_s/R_0 has been found to depend on the magnetization as M_s^2 .

1.8 ELECTRICAL SWITCHING

Many oxides and semiconductors exhibit the switching and memory effects at high fields and in all these cases the space charge traps the flow; the recombination effect plays also the major role in the phenomenon. However, the transport properties at high fields are still unknown. Therefore the detailed study is being concentrated on the structural changes, variation of conductivity with fields, the self-heating effect, field distribution in structure, incubation time, photo response and electro luminance effects.

Switching and memory phenomena are already reported in amorphous semiconductors,³²⁻³³ oxides. The same phenomenon was firstly reported in stoichiometric quenched copper ferrites by T. Yamashiro³⁴. He ascribed the electric switching to the Jahn-Teller distortion transformation by a unknown way, Hisatake et al³⁵ studied and reported switching behaviour in lithium ferrite, free from Jahn-Teller ions. He attributed the property owing to 'Jahn-Teller-Thomson self heating' and reported the phenomena as the general character of ferrites. Patil, S.A. et al³⁶ have also reported switching as well as memory phenomena in stoichiometric copper ferrite. They attribute the electric switching to Jahn-Teller transformation of Cu^{2+} ions at B site of the spinel structure. These studies and concerned reports are inadequate and require their further study together with that of the non-stoichiometric ferrites; quenched and slow cooled samples.

1.9 ORIENTATION OF THE DISSERTATION PROBLEM

Switching phenomenon in the solid state bulk material is an interesting and important property; which leads its application to electrical and electronic industry. Ferrites, which are magnetic oxides, have immense industrial application owing to their high resistivity and minimum eddy currents. Copper ferrite in particular has been reported to exhibit the switching behaviour in both the bulk and thin film form; during the last decade. However, no much work is found in literature in this direction. The switching behaviour in ferrimagnetic oxides is also reported

to be sensitive to the nonstoichiometry of the compound. Therefore, it is proposed to prepare the stoichiometric and non-stoichiometric copper ferrites with a general formula $\text{Cu}_x \text{Fe}_{3-x} \text{O}_4$ ($x = 0.2, 0.4, 0.6, 0.8, 1.0$) and subject them to the study of switching behaviour. The non-stoichiometric copper ferrite is expected to show some improved and different properties, they being more sensitive. The switching is expected also to be sensitive to the structural properties of the materials which in turn depend upon the heat treatment. Therefore, copper ferrite with different compositions in the pellet form will be given different heat treatment and it will be observed if there is any striking change in the exhibition of the phenomenon.

Moreover, the properties of the ferrites depend upon the physical properties like grain size, porosity, etc. and therefore it is always difficult to control the properties of the final product. The attempts are always therefore in the direction of 'Tailor-making' of the material with desired properties.

The copper ferrite has very high resistivity and falls in the range of insulators; and therefore are expected to exhibit the space charge limited currents. A similar work is already reported. It is therefore decided to attempt to calculate some SCL currents for the samples where the necessary supporting data will be available. The copper ferrite has ^{been} reported exhibiting the spinel structure. It is expected that the copper ferrite with different percentage of copper may exhibit different structural planes. So the diffractometric study of some selected samples is proposed to identify the single phase spinel structure.

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