

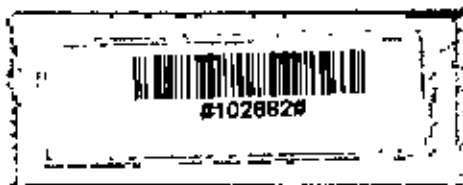
# STUDY OF MICROSTRUCTURE AND ITS EFFECTS ON THE COMPLEX PERMEABILITY OF Ni-Zn FERRITE

*A Dissertation Submitted to the Department of Physics,  
Bangladesh University of Engineering & Technology, Dhaka, in  
Partial Fulfillment of the Requirement for the Degree of  
Master of Philosophy in Physics*

SUBMITTED BY

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## CANDIDATE'S DECLARATION

*It is hereby declared that this thesis or any part of it has not been submitted elsewhere for the award of any degree or diploma.*



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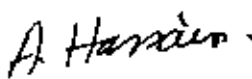
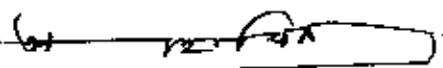
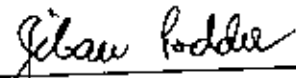
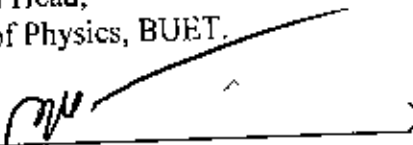



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**CERTIFICATION OF THESIS**

The thesis titled "Study of Microstructure and its Effects on the Complex Permeability of Ni-Zn Ferrite" submitted by Shaikh Tawhid Mahmud, Roll No.: 040414029F, Session: April 2004, has been accepted as satisfactory in partial fulfillment of the requirement for the degree of **Master of Philosophy** in Physics on June 20, 2006.

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The Author

Shaikh Tawhid Mahmud

## ABSTRACT

$Ni_{1-x}Zn_xFe_2O_4$  with  $x=0.2$  and  $0.4$  were prepared by a conventional solid state reaction technique. The samples were sintered at various temperatures ( $1200^\circ\text{C}$ ,  $1250^\circ\text{C}$ ,  $1300^\circ\text{C}$ ,  $1350^\circ\text{C}$  and  $1400^\circ\text{C}$ ) in air for 5 hours. Structural and surface morphology were studied by x-ray diffraction method and optical microscopy. The magnetic properties of the ferrites were characterized with high frequency (1kHz-13MHz) complex permeability and temperature dependent permeability measurements. The effects of microstructure, composition and sintering temperatures on the complex permeability of Ni-Zn ferrite are discussed. A possible correlation among sintering temperature, grain size and density is also discussed. The X-ray diffraction patterns of both compositions clearly indicate their single phase and formation of spinel structure. The lattice constant of  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  is found to be  $8.3638 \text{ \AA}$  while  $8.3705 \text{ \AA}$  for  $Ni_{0.6}Zn_{0.4}Fe_2O_4$ . The increase in lattice parameter with increasing Zn content can be explained on the basis of the ionic radii. The radius of the  $Zn^{2+}$  ( $0.82 \text{ \AA}$ ) is greater than that of the  $Ni^{2+}$  ( $0.78 \text{ \AA}$ ). The microstructural study shows that grain size increases with sintering temperature. The density of the  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  samples increases as the sintering temperature increases from  $1200^\circ\text{C}$  to  $1300^\circ\text{C}$ , and above  $1300^\circ\text{C}$  the density begins to decrease. The  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  samples show similar behaviour to that of the  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  samples except that the density is found to be maximum at  $1350^\circ\text{C}$ . During the sintering process, the thermal energy generates a force that drives the grain boundaries to grow over pores, thereby decreasing the pore volume and increasing the density of the material. At higher sintering temperatures, the density decreases because the intragranular porosity increases resulting from discontinuous grain growth. The initial permeability proportionally changes with sintering density. A sample with more uniformity and larger grain size as well as highest density is obtained at  $1350^\circ\text{C}$  sintering temperature (optimum  $T_s$ ) for  $Ni_{0.6}Zn_{0.4}Fe_2O_4$ . The real part of permeability,  $\mu'_1$ , is observed to be maximum at this optimum  $T_s$  for  $Ni_{0.6}Zn_{0.4}Fe_2O_4$ . The permeability value increases with increasing Zn content in  $Ni_{1-x}Zn_xFe_2O_4$ , because the average grain size increases with increasing Zn content. Larger grains tend to consist of a greater number of domain walls. Thus the domain wall motion is affected by the grain size and enhanced with the

increase of grain size. The  $\mu'_i$ , therefore, increases with grain size. For both the compositions,  $\mu'_i$  is found to be maximum at optimum  $T_s$  (depending on sample composition). If the sintering temperature is higher than that of the optimum  $T_s$ ,  $\mu'_i$  decreases. Higher sintering temperatures ( $>$  optimum  $T_s$ ) may increase the number of pores within the grains of the samples, which result in a decrease in permeability. The ferrite with high permeability tends to have its permeability decreases at a relatively low frequency. The  $\mu'_i$  values for all samples are found independent of frequency below the resonance frequency. The relative quality factor ( $Q$ ) for  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  is found to be  $2.1 \times 10^4$  at  $1250^\circ\text{C}$  sintering temperature. The highest  $Q$  value at  $1250^\circ\text{C}$  for  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  while  $1200^\circ\text{C}$  for  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  is probably due to the growth of lesser imperfection and defects in them than those in the samples sintered at higher sintering temperatures. The Curie temperature of  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  is found to be  $516 \pm 1^\circ\text{C}$ , while  $353 \pm 1^\circ\text{C}$  for  $Ni_{0.6}Zn_{0.4}Fe_2O_4$ .

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## LIST OF SYMBOLS AND ABBREVIATIONS

$AC$	Alternating current
$B$	Magnetic induction
CMR	Colossal magnetoresistance
$F(\theta)$	Nelson-Riley function
$f_r$	Resonance frequency
$g$	Landé splitting factor
$H_{cr}$	Critical field
$J$	Exchange integral
$K$	Total anisotropy
$K_1$	Magnetocrystalline anisotropy constant
$L_S$	Self-inductance of the sample core
$L_0$	Inductance of the winding coil without sample
$M$	Magnetization
$M_S$	Saturation magnetization
$N_A$	Avogadro's number
$P$	Porosity
$P_{intra}$	Intragranular porosity
$P_{inter}$	Intergranular porosity
$P_e$	Eddy-current loss
$Q$	Relative quality factor
$T_C$	Curie temperature
$T_N$	Néel temperature
$T_s$	Sintering temperature
$\tan \delta$	Loss factor
$Z$	Complex impedance
$\alpha$	Restoring force coefficient
$\beta$	Viscous damping factor
$\gamma$	Domain wall energy
$\omega$	Angular velocity
$\delta_w$	Domain wall thickness
$\mu_i$	Initial permeability
$\mu'$	Real part of complex permeability
$\mu''$	Imaginary part of complex permeability
$\mu_B$	Bohr magneton
$\chi_{spin}$	Intrinsic rotational susceptibility
$\chi_w$	Domain wall susceptibility



# CHAPTER 1

## GENERAL INTRODUCTION

### 1.1 Introduction

*Ni-Zn* ferrites with the spinel crystal structure are being extensively used in a number of electronic devices because of their remarkably high electrical resistivity, low magnetic coercivity, mechanical hardness, chemical stability and reasonable cost. According to their structure spinel-type ferrites are natural superlattice. It has tetrahedral *A* site and octahedral *B* site in  $AB_2O_4$  crystal structure. It shows various magnetic properties depending on the composition and cation distribution. Various cations can be placed in *A* site and *B* site to tune its magnetic properties. Depending on *A* site and *B* site cations it can exhibit ferrimagnetic, antiferromagnetic, spin (cluster) glass, and paramagnetic behavior [1-8]. Due to their remarkable behavior of magnetic and electric properties they are subjects of intense theoretical and experimental investigation for application purpose [2-16].

Most other technologically useful magnetic materials such as iron and soft magnetic alloys have low electrical resistivity. This makes them useless for applications at high frequencies, for example as inductor core in TV circuits. The problem is that their low electrical resistivity allows eddy currents to flow within the materials themselves, thereby producing heat. This wasted energy or the produced heat often causes a serious problem. Thus, non-ferrite materials become inefficient as they waste energy and the waste is more, as the frequency becomes higher. Useful temperature and time stability are important additional characteristics which have widened the use of ferrites into high frequency and wide-band transformers, adjustable inductors, quality filter circuits, delay lines, converters, particle accelerators, read/write heads for high-speed digital tape or disc readings, electromagnentic wave absorbers, rod antennas, radio frequency circuits, computer technology and telecommunication applications [7-27]. The *Ni-Zn* ferrites have been found to be on of the most versatile of the ferrite systems for general use. The antiferromagnetic *A-B* superexchange interaction is the main cause of the cooperative behaviour of magnetic dipole moments in the ferrites, known as

ferrimagnetism, which was observed in *Ni-Zn* ferrites below their Curie temperature. Recently, colossal magnetoresistance (CMR) effect has been observed in  $ZnFe_2O_4$  and *Ni* substituted  $Zn_{1-x}Ni_xFe_2O_4$  ferrites [2]. The present investigation is taken up with a view to study the effect of microstructure on the complex permeability of *Ni-Zn* ferrite prepared at varying sintering temperature.

## 1.2 Objectives of the Present Work

Ferrites are especially convenient for high frequency uses because of their high resistivity. The high frequency response of the complex permeability is therefore very useful in determining the convenient frequency range in which a particular ferrite material can be used. The mechanism of eddy current losses and damping of domain wall motion can be understood from the relative magnitudes of the real and imaginary parts of the complex permeability. The effect of composition and microstructure on the frequency response is therefore very useful. The main *objectives* of the present research are as follows:

- Preparation of various  $Ni_{1-x}Zn_xFe_2O_4$  (for  $x=0.2$  and  $0.4$ ) samples.
- Determination of structure, density and porosity of the samples.
- Study of surface morphology (grain size).
- Determination of Ferrimagnetic to Paramagnetic transition temperature ( $T_c$ ) from the measurement of temperature dependent initial permeability.
- Evaluation of initial permeability as a function of frequency (1kHz - 13 MHz) for samples having various microstructures (e.g. grain size).

From the studies of sintering temperature ( $T_s$ ) dependent grain size, an optimum  $T_s$  can be obtained for corresponding ferrite composition. A scaling of frequency dependent initial permeability with respect to grain size can also be obtained, which will be helpful for practical applications of the above-mentioned ferrites.

## 1.3 Summary of the Thesis

The format of the thesis is as follows:

Chapter 1 of this thesis deals with the importance of ferrites and objectives of the present work.



Chapter 2 gives a brief overview of the materials, theoretical background as well as crystal structure of the spinel ferrites.

Chapter 3 gives the details of the sample preparation

Chapter 4 describes the experimental side and descriptions of different measurements that have been used in this research work.

Chapter 5 is devoted to the results of various investigations of the study and a brief discussion.

The conclusions drawn from the overall experimental results and discussion are presented in Chapter 6.

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## CHAPTER 2

### LITERATURE REVIEW

*Double oxides of iron and other metals are important members of ferrimagnetic system commonly known as ferrites. The outstanding properties of ferrites are their complex magnetic structure, which can be varied to tailor their magnetic properties for various high frequency applications. In this chapter we describe a brief overview of the ferrites. The basic issue of ferrimagnetism, crystal structure of the spinel ferrites and effect of non-magnetic Zn substitution on the magnetic moments in spinel ferrites are discussed. A few theoretical aspects of complex permeability are also discussed.*

#### 2.1 Overview of the Materials

Ferrites commonly expressed by the general chemical formula  $MeO.Fe_2O_3$ , where  $Me$  represents divalent metals, first commanded the public attention when Hilpert (1909) focused on the usefulness of ferrites at high frequency [1]. A systematic investigation was launched by Snoek (1936) at Philips Research Laboratory [2]. At the same time Takai (1937) in Japan was seriously engaged in the research work on the same materials [1]. Snoek's extensive works on ferrites unveiled many mysteries regarding magnetic properties of ferrites. He was particularly looking for high permeability materials of cubic structure. This particular structure for symmetry reasons supports low crystalline anisotropy. He found suitable materials in the form of mixed spinels of the type  $MeZnFe_2O_4$ , where  $Me$  stands for metals like  $Cu$ ,  $Mg$ ,  $Ni$  or  $Mn$ , for which permeability were found to be up to 4000 [1-3]. Here after starts the story of  $Ni-Zn$  ferrites. Remarkable properties like high permeability, low loss factor, high stability of permeability with temperature and time, high wear resistance, controlled coercive force, low switching coefficient etc. have aptly placed  $Ni-Zn$  ferrites as highly demandable ferrites to both researchers and manufacturers. Every year great deals of paper are being published on various aspects of  $Ni-Zn$  ferrites. A large number of scientists and technologists are engaged in research to bring about improvements on the magnetic properties of  $Ni-Zn$  ferrites.

The sintering process is considered to be one of the most vital steps in ferrite preparation and often plays a dominant role in many magnetic properties. Tasaki *et al.* [4]

studied the effect of sintering atmosphere on permeability of sintered ferrite. They found that high density is one of the factors, which contribute to greater permeability. However, permeability decreased in an atmosphere without  $O_2$  at high sintering temperature where high density was expected. This decrease in permeability is attributed to the variation of chemical composition caused by volatilization of  $Zn$ . At low sintering temperature a high permeability is obtained in an atmosphere without  $O_2$  because densification and stoichiometry plays a principal role in increasing permeability. At high sintering temperature the highest permeability is obtained in the presence of  $O_2$  because the effect of decrease of  $Zn$  content can then be neglected.

Studying the electromagnetic properties of ferrites, Nakamura [5] suggested that both the sintering density and the average grain size increased with sintering temperature. These changes were responsible for variations in magnetization, initial permeability and electrical resistivity.

High permeability attainment is certainly affected by the microstructure of the ferrites. Roess showed that [6] the very high permeability is restricted to certain temperature ranges and the shapes of permeability versus temperature curves are strongly affected by any inhomogeneity in the ferrite structure.

Leung *et al.* [7] performed a Low-temperature Mössbauer study of a nickel-zinc ferrite:  $Zn_{1-x}Ni_xFe_2O_4$ . They found that for  $x \leq 0.5$  the resultant  $A$ - and  $B$ - site  $Fe$ -spin moments have a collinear arrangement, whereas for  $x > 0.5$  a non-collinear arrangement of  $A$ - and  $B$ -site  $Fe$ -spin moments exists. An explanation based on the relative strength of the exchange constant  $J_{AB}$  and  $J_{BB}$  is given to account for this difference.

Rezlescu *et al.* [8] reported that the sintering behaviour and microstructure of the ferrites samples largely affected by  $PbO$  addition.  $PbO$  significantly reduced the sintering temperatures, thus energy consumption is minimized and material loss by evaporation is minimized [9].

There are two mechanisms in the phenomenon of permeability; spin rotation in the magnetic domains and wall displacements. The uncertainty of contribution from each of the mechanisms makes the interpretation of the experimental results difficult. Globus [10] shows that the intrinsic rotational permeability  $\mu_r$  and  $180^\circ$  wall

permeability  $\mu_w$  may be written as:  $\mu_r = 1 + 2\pi M_s^2 / K$  and  $\mu_w = 1 + 3\pi M_s^2 D / 4\gamma$ , where  $M_s$  is the saturation magnetization,  $K$  is the total anisotropy,  $D$  is the grain diameter and  $\gamma = K\delta_v$  is the wall energy.

Rosales *et al.* [11] measured the complex permeability of  $Zn_{1-x}Ni_xFe_2O_4$  ferrites with  $0.3 \leq x \leq 0.4$ . They show that the relaxation frequency and magnetocrystalline anisotropy constant is related by the equation:  $f_r = f_{r0} + AK_1$ , where  $f_{r0}$  and  $A$  are constants.

El-Shabasy [12] studied the DC electrical resistivity of  $Zn_xNi_{1-x}Fe_2O_4$  ferrites. He shows that the ferrite samples have semiconductor behaviour where DC electrical resistivity decreases on increasing the temperature.  $\rho(T)$  for all samples follows  $\rho(T) = \rho_0 \exp(E/k_p T)$ , where  $E$  is the activation energy for electric conduction and  $\rho_0$  is the pre-exponential constant or resistivity at infinitely high temperature. The DC resistivity,  $\rho(T)$ , decreases as the  $Zn$  ion substitution increases. It is reported that  $Zn$  ions prefer the occupation of tetrahedral ( $A$ ) sites,  $Ni$  ions prefer the occupation of octahedral ( $B$ ) sites while  $Fe$  ions partially occupy the  $A$  and  $B$  sites. On increasing  $Zn$  substitution (at  $A$  sites), the  $Ni$  ion concentration (at  $B$  sites) will decrease. This lead to the migration of some  $Fe$  ions from  $A$  sites to  $B$  sites to substitute the reduction in  $Ni$  ion concentration at  $B$  sites. As a result, the number of ferrous and ferric ions at  $B$  sites (which is responsible for electric conduction in ferrites) increases. Consequently  $\rho$  decreases on  $Zn$  substitution. Another reason for the decrease in  $\rho$  on increasing  $Zn$  ion substitution is that, zinc is less resistive ( $\rho = 5.92 \mu\Omega cm$ ) than nickel ( $\rho = 6.99 \mu\Omega cm$ ). The main conductivity mechanism in ferrites is attributed to electron hopping between  $Fe^{3+}$  and  $Fe^{2+}$  in octahedral sites. Resistivity in spinels is very sensitive to stoichiometry; a small variation of  $Fe$  content in  $Zn_{0.7}Ni_{0.3}Fe_{2+x}O_{4-y}$  results in resistivity variations of  $\sim 10^7$ . Excess  $Fe$  can easily dissolve in spinel phase by a partial reduction of  $Fe$  from  $3Fe_2^{3+}O_4$  to  $2Fe^{2+}Fe_2^{3+}O_4$  (and  $1/2O_2 \uparrow$ ) [2].

## 2.2 Magnetic Ordering

The onset of magnetic order in solids has two basic requirements:

- (i) Individual atoms should have magnetic moments (spins).
- (ii) Exchange interactions should exist that couple them together.

Magnetic moments originate in solids as a consequence of overlapping of the electronic wave function with those of neighboring atoms. This condition is best fulfilled by some transition metals and rare-earths. The exchange interactions depend sensitively upon the inter-atomic distance and the nature of the chemical bonds, particularly of nearest neighbour atoms. When the positive exchange dominates, which corresponds to parallel coupling of neighbouring atomic moments (spins), the magnetic system becomes ferromagnetic below a certain temperature  $T_C$  called the Curie temperature. The common spin directions are determined by the minimum of magneto-crystalline anisotropy energy of the crystal. Therefore, ferromagnetic substances are characterized by spontaneous magnetization. But a ferromagnetic material in the demagnetized state displays no net magnetization in zero field because in the demagnetized state a ferromagnetic of macroscopic size is divided into a number of small regions called domains, spontaneously magnetized to saturation value and the directions of these spontaneous magnetization of the various domains are such that the net magnetization of the specimen is zero. The existence of domains is a consequence of energy minimization. The size and formation of these domains is in a complicated manner dependent on the shape of the specimen as well as its magnetic and thermal history. When negative exchange dominates, adjacent atomic moments (spins) align antiparallel to each other, and the substance is said to be anti-ferromagnetic below a characteristic temperature,  $T_N$ , called the Néel temperature. In the simplest case, the lattice of an anti-ferromagnet is divided into two sublattices with the magnetic moments of these in antiparallel alignment. This result is zero net magnetization. A special case of anti-ferromagnetism is ferrimagnetism. In ferrimagnetism, there are also two sublattices with magnetic moments in opposite directions, but the magnetization of the sublattices are of unequal strength resulting in a non-zero magnetization and therefore has net spontaneous magnetization. At the macroscopic level of domain structures, ferromagnetic and ferrimagnetic materials are therefore similar.

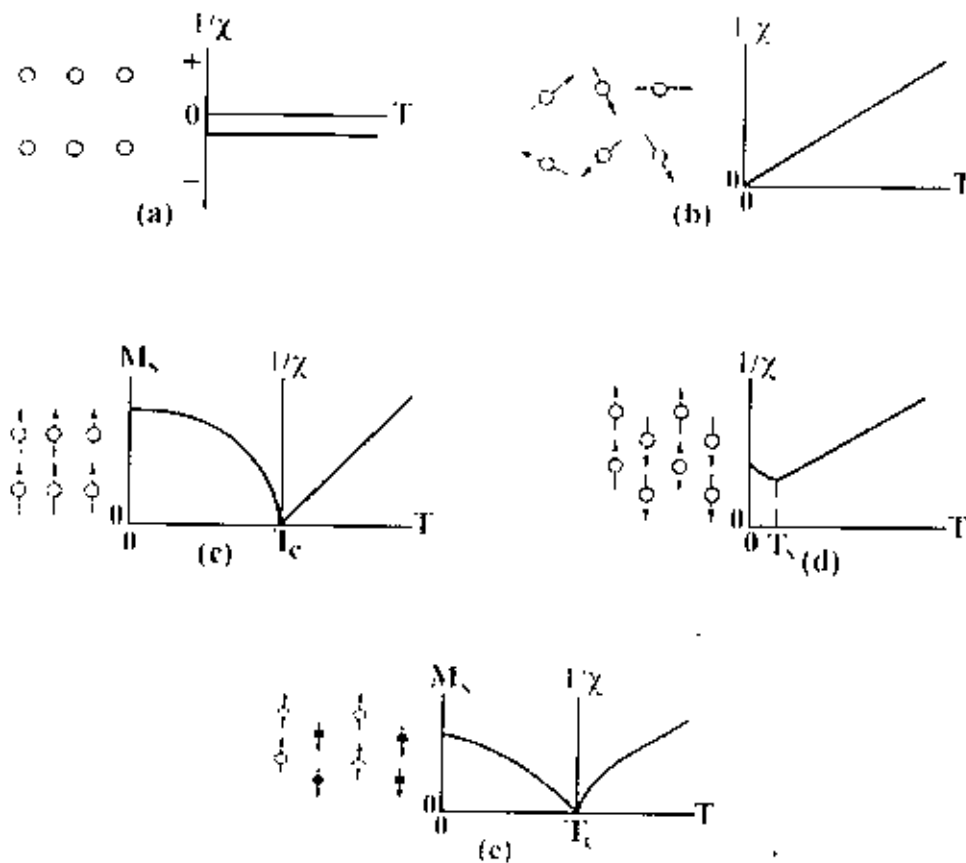


Figure 2.1. Temperature dependence of the inverse susceptibility for: (a) a diamagnetic material; (b) a paramagnetic material, showing Curie's law behaviour, (c) a ferromagnetic material, showing a spontaneous magnetization for  $T < T_c$  and Curie-Weiss behaviour for  $T > T_c$ ; (d) an antiferromagnetic material; (e) a ferrimagnetic material, showing a net spontaneous magnetization for  $T < T_c$  and non linear behaviour for  $T > T_c$ .

The Curie and Néel temperatures characterize a phase transition between the magnetically ordered and disordered (paramagnetic) states. From these simple cases of magnetic ordering various types of magnetic order exists, particularly in metallic substances. Because of long-range order and oscillatory nature of the exchange interaction, mediated by the conduction electrons, structures like helical, conical and modulated patterns might occur. A useful property for characterizing the magnetic materials is the magnetic susceptibility,  $\chi$ , defined as the magnetization,  $M$ , divided by the applied magnetic field,  $H$  i.e.  $\chi = M/H$ . The temperature dependence of susceptibility or, more accurately, inverse of susceptibility is a good characterization



parameter for magnetic materials, Fig. 2.1. Fig. 2.1(e) shows that in the paramagnetic region, the variation of the inverse susceptibility with temperature of a ferrite material is decidedly non-linear. Thus the ferrite materials do not obey the Curie-Weiss law,  $\chi = C/(T - T_c)$  [2, 13].

### 2.3 Crystal Structure of Spinel Ferrites

Ferrites have the cubic structure, which is very close to that of the mineral spinel  $MgO \cdot Al_2O_3$ , and are called cubic spinel. Analogous to the mineral spinel, magnetic spinel have the general formula  $MeO \cdot Fe_2O_3$  or  $MeFe_2O_4$  where  $Me$  is the divalent metal ion [14]. This crystal structure was first determined by Bragg and by Nishikawa [1,13]. Formerly, spinels containing  $Fe$  were called ferrites but now the term has been broadened to include many other ferrimagnets including garnets and hexagonal ferrites these need not necessarily contain iron. The spinel lattice is composed of a close-packed oxygen (radius about  $1.3\text{\AA}$ ) arrangement in which 32 oxygen ions form a unit cell that is the smallest repeating unit in the crystal network. The unit cell of the ideal spinel structures is given in Fig. 2.2. Between the layers of oxygen ions, if we simply visualize them as spheres, there are interstices that may accommodate the metal ions (radii ranging from  $0.6$  to  $0.8\text{\AA}$ ). Now, the interstices are not all the same: some which we call  $A$  sites are surrounded by or coordinated with 4 nearest neighboring oxygen ions whose lines connecting their centers form a tetrahedron. Thus,  $A$  sites are called tetrahedral sites. The other type of sites ( $B$  sites) is coordinated by 6 nearest neighbor oxygen ions whose center connecting lines describe an octahedron. The  $B$  sites are called octahedral sites. In the unit cell of 32 oxygen ions there are 64 tetrahedral sites and 32 octahedral sites. If all these were filled with metal ions, of either +2 or +3 valence, the positive charge would be very much greater than the negative charge and so the structure would not be electrically neutral. It turns out that of the 64 tetrahedral sites, only 8 are occupied and out of 32 octahedral sites, only 16 are occupied. Thus the unit cell contains eight formula units  $AB_2O_4$ , with 8  $A$  sites, 16  $B$  sites and 32 oxygen ions, and total of  $8 \times 7 = 56$  ions. A spinel unit cell contains two types of subcells, Fig. 2.2.

The two types of subcells alternate in a three-dimensional array so that each fully repeating unit cell requires eight subcells, Fig. 2.3.

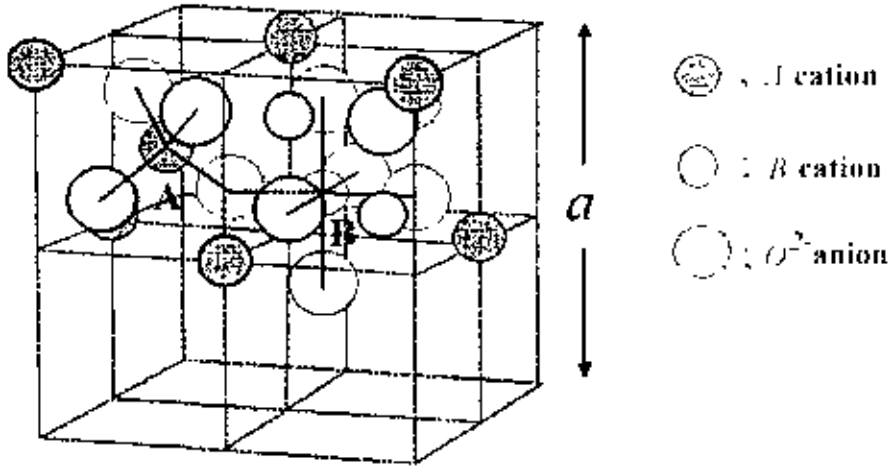


Figure 2.2. Two subcells of a unit cell of the spinel structure.

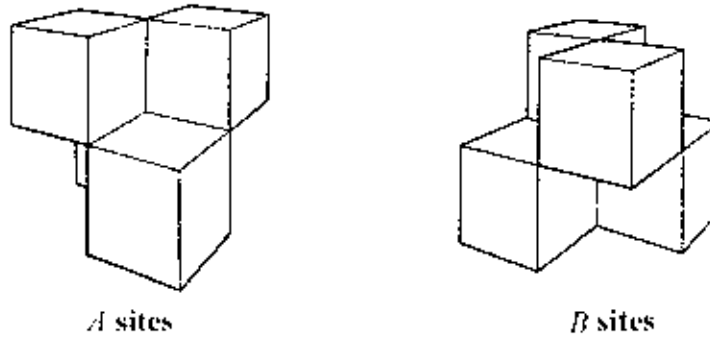


Figure 2.3. Unit cell of spinel ferrite divided into eight subcells with *A* and *B* sites.

The positions of the ions in the spinel lattice are not perfectly regular (as the packing of hard spheres) and some distortion does occur. The tetrahedral sites are often too small for the metal ions so that the oxygen ions move slightly to accommodate them. The oxygen ions connected with the octahedral sites move in such a way as to shrink the size the octahedral cell by the same amount as the tetrahedral site expands. The movement of the tetrahedral oxygen is reflected in a quantity called the oxygen parameter, which is the distance between the oxygen

ion and the face of the cube edge along the cube diagonal of the spinel subcell. This distance is theoretically equal to  $3/8a_0$  where  $a_0$  is the lattice constant [1].

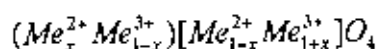
#### 2.4 Cation Distribution of Spinel Ferrites

In spinel structure the distribution of cations over the tetrahedral or *A* sites and octahedral or *B* sites can be present in a variety of ways. If all the  $Me^{2+}$  ions in  $Me^{2+}Me_2^{3+}O_4$  are in tetrahedral and all  $Me^{3+}$  ions in octahedral positions, the spinel is then called normal spinel. Another cation distribution in spinel exists, where one half of the cations  $Me^{3+}$  are in the *A* positions and the rest, together with the  $Me^{2+}$  ions are randomly distributed among the *B* positions. The spinel having the latter kind of cation distribution is known as inverse spinel. The distribution of these spinels can be summarized as [2, 15-16]:

1) Normal spinels, i.e. the divalent metal ions are on *A*-sites:  $Me^{2+}[Me_2^{3+}]O_4$ .

2) Inverse spinels, i.e. the divalent metal ions are on *B*-sites:  $Me^{3+}[Me^{2+}Me_2^{3+}]O_4$ .

A completely normal or inverse spinel represents the extreme cases. *Zn* ferrites have normal spinel structure and its formula may be written as  $Zn^{2+}[Fe^{3+}Fe^{3+}]O_4^{2-}$ . On the other hand, *Ni* ferrites have inverse spinel structure and its formula may be written as  $Fe^{3+}[Ni^{2+}Fe^{3+}]O_4^{2-}$ . There are many spinel oxides which have cation distributions intermediate between these two extreme cases and are called mixed spinels. The general cation distribution for the spinel can be indicated as:



where the first and third brackets represent the *A* and *B* sites respectively. For normal spinel  $x=1$ , for inverse spinel  $x=0$ . The quantity  $x$  is a measure of the degree of inversion. In the case of some spinel oxides  $x$  depends upon the method of preparation.

The basic magnetic properties of the ferrites are very sensitive functions of their cation distributions. Mixed ferrites having interesting and useful magnetic properties are prepared by mixing two or more different types of metal ions. The chemical formula of mixed *Ni-Zn* ferrite may be written as  $(Zn_x^{2+}Fe_{1-x}^{3+})[Ni_{1-x}^{2+}Fe_{1+x}^{3+}]O_4^{2-}$  where  $0 \leq x \leq 1$ .

Spinel oxides are ionic compounds and hence the chemical bonding occurring in them can be taken as purely ionic to a good approximation. The total energy involved, however, consists of the Coulomb energy, the Born repulsive energy, the polarization and the magnetic interaction energy. The energy terms are all dependent on lattice constant, oxygen position parameter and the ionic distribution. In principle the equilibrium cation distribution can be calculated by minimizing the total energy with respect to these variables. But the only energy that can be written with any accuracy is the Coulomb energy. The individual preference of some ions for certain sites resulting from their electronic configuration also play an important role. The divalent ions are generally larger than the trivalent (because the larger charge produces greater electrostatic attraction and so pulls the outer orbits inward). The octahedral sites are also larger than the tetrahedral. Therefore, it would be reasonable that the trivalent ions  $Fe^{3+}$  (0.67Å) would go into the tetrahedral sites and the divalent ions  $Fe^{2+}$  (0.83Å) go into the octahedral. Two exceptions are found in  $Zn^{2+}$  and  $Cd^{2+}$  which prefer tetrahedral sites because the electronic configuration is favourable for tetrahedral bonding to the oxygen ions. Thus  $Zn^{2+}$  (0.82Å) prefer tetrahedral sites over the  $Fe^{3+}$  (0.67Å) ions.  $Zn^{2+}$  and  $Co^{2+}$  have same ionic radius but  $Zn$  prefers tetrahedral sites and  $Co$  prefers octahedral sites because of the configuration exception.  $Ni^{2+}$  (0.78Å) and  $Cr^{3+}$  (0.64Å) have strong preferences for octahedral sites. Hence the factors influencing the distribution the cations among the two possible lattice sites are mainly their ionic radii of the specific ions, the size of the interstices, temperature, the matching of their electronic configuration to the surrounding anions and the electrostatic energy of the lattice, the so-called Madelung energy, which has the predominant contribution to the lattice energy under the constrain of overall energy minimization and charge neutrality.

## 2.5 Interaction Between Magnetic Moments on Lattice Sites

Spontaneous magnetization of spinels (at 0K) can be estimated on the basis of their composition, cation distribution, and the relative strength of the possible interaction. Since cation-cation distances are generally large, direct (ferromagnetic) interactions are negligible. Because of the geometry of orbital involved, the strongest superexchange interaction is expected to occur between octahedral and tetrahedral cations. The strength of interaction or exchange force between the moments of the two

metal ions on different sites depends on the distances between these ions and the oxygen ion that links them and also on the angle between the three ions. The nearest neighbours of a tetrahedral, an octahedral and an anion site are shown in Fig. 2.4. The interaction is greatest for an angle of  $180^\circ$  and also where the interionic distances are the shortest. Fig. 2.5 shows the interionic distances and the angles between the ions for the different type of interactions. In the *A-A* and *B-B* cases, the angles are too small or the distances between the metal ions and the oxygen ions are too large. The best combination of distances and angles are found in *A-B* interactions.

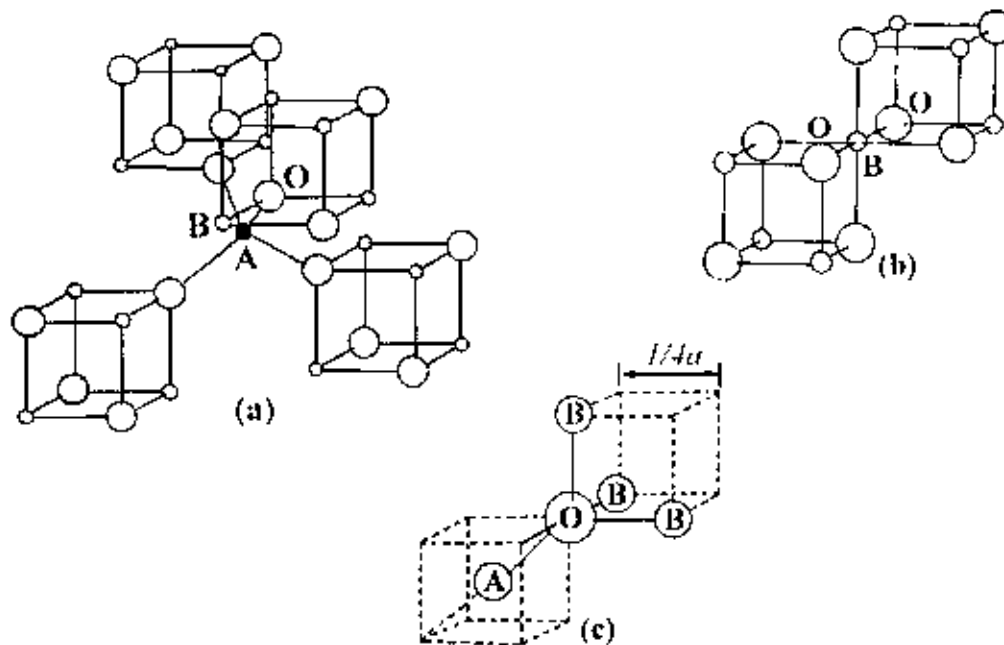


Figure 2.4. Nearest neighbours of (a) a tetrahedral site, (b) an octahedral site and (c) an anion site.

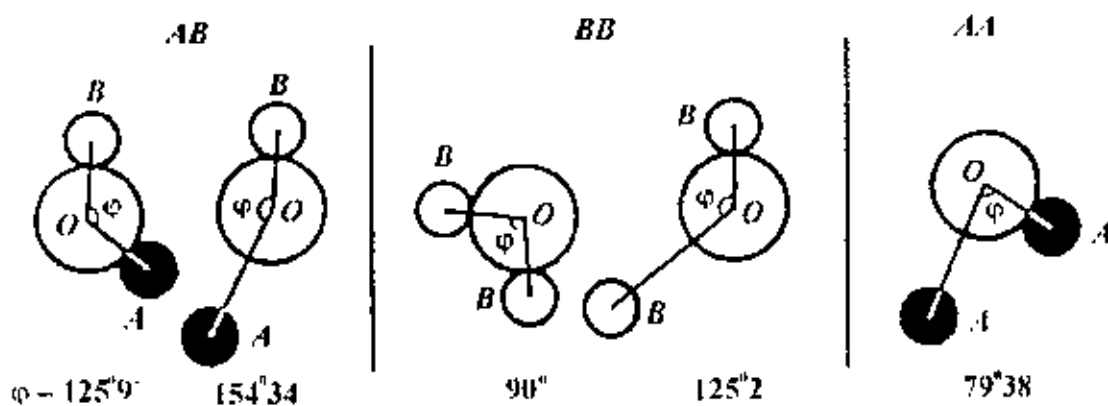


Figure 2.5. Interionic angles in the spinel structure for the different type of lattice site interactions.

For an undistorted spinel, the  $A-O-B$  angles are about  $125^\circ$  and  $154^\circ$  [1-2, 17]. The  $B-O-B$  angles are  $90^\circ$  and  $125^\circ$  but the latter, one of the  $B-B$  distances is large. In the  $A-A$  case the angle is about  $80^\circ$ . Therefore, the interaction between moments on the  $A$  and  $B$  site is strongest. The  $BB$  interaction is much weaker and the most unfavorable situation occurs in the  $AA$  interaction. By examining the interaction involving the major contributor, or the  $A-B$  interaction which orients the unpaired spins of these ions antiparallel, Néel was able to explain the ferrimagnetism of ferrites.

## 2.6 Magnetism in Spinel Ferrite

The magnetic moment of a free atom is associated with the orbital and spin motions of electrons in an incomplete sub-shell of the electronic structure of the atom. In crystals the orbital motions are quenched, that is the orbital planes may be considered to be fixed in space relative to the crystal lattice, and in such a way that in bulk the crystal has no resultant moment from this source. Moreover this orbital-lattice coupling is so strong that the application of a magnetic field has little effect upon it. The spin axes are not tightly bound to the lattice as are the orbital axes. The anions surrounding a magnetic cation subject it to a strong inhomogeneous electric field and influence the orbital angular momentum. However, the spin angular momentum remains unaffected. For the first transition group elements this crystal field effect is intense partly due to the large radius of the 3d shell and partly due to the lack of any outer electronic shell to screen the 3d shell whose unpaired electrons only contribute to the magnetic moment. We have originally defined the magnetic moment in connection with permanent magnets. The electron itself may well be called the smallest permanent magnet [1]. For an atom with a resultant spin quantum number  $S$ , the spin magnetic moment will be

$$\mu = g\sqrt{S(S+1)}\mu_B$$

where  $g$  is the Landé splitting factor and  $\mu_B$ , known as the Bohr magneton, is the fundamental unit of magnetic moment. The value of  $g$  for pure spin moment is 2 and the quantum number associated with each electron spin is  $\pm 1/2$ . The direction of the moment is comparable to the direction of the magnetization (from South to North poles) of a permanent magnet to which the electron is equivalent. Fig. 2.6 illustrates the electronic configuration of  $Fe$  atoms and  $Fe^{3+}$  ions.  $Fe$  atom has four unpaired electrons and  $Fe^{3+}$  ion has five unpaired

electrons. Each unpaired electron spin produced 1 Bohr magneton. In compounds, ions and molecules, account must be taken of the electrons used for bonding or transferred in ionization. It is the number of unpaired electrons remaining after these processes occur that gives the net magnetic moment [1]. According to the Hund's rules the moment of  $Fe$  atom and  $Fe^{3+}$  ion are  $4\mu_B$  and  $5\mu_B$  respectively. Similarly the moment of  $Fe^{2+}$  and  $Ni^{2+}$  ion are  $4\mu_B$  and  $2\mu_B$  respectively.

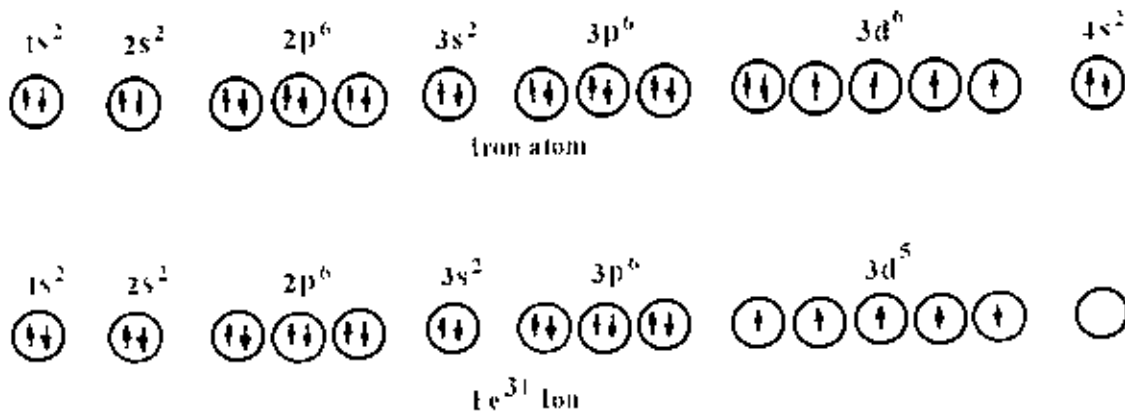


Figure 2.6. Electronic configuration of atoms and ions

### 2.6.1 Exchange Interactions in Spinel

The intense short-range electrostatic field, which is responsible for the magnetic ordering, is the exchange force that is quantum mechanical in origin and is related to the overlapping of total wave functions of the neighbouring atoms. The total wave function consists of the orbital and spin motions. Usually the net quantum number is written as  $S$ , because the magnetic moments arise mostly due to the spin motion as described above. The exchange interactions coupling the spins of a pair of electrons are proportional to the scalar product of their spin vectors [14, 16, 18],

$$V_{ij} = -2J_{ij} \vec{S}_i \cdot \vec{S}_j \quad (2.1)$$

where  $J_{ij}$  is the exchange integral given in a self explanatory notation by

$$J_{ij} = \int \psi_i^*(1) \psi_j^*(2) \left[ \frac{1}{r_{12}} + \frac{1}{r_0} - \frac{1}{r_{i1}} - \frac{1}{r_{j2}} \right] \psi_i(1) \psi_j(2) d\tau_1 d\tau_2 \quad (2.2)$$

In this expression  $r$ 's are the distances, subscripts  $i$  and  $j$  refer to the atoms, 1 and 2 refers to the two electrons. If the  $J$  in equation (2.1) is positive, we achieve ferromagnetism. A negative  $J$  may give rise to anti-ferromagnetism or ferrimagnetism.

Magnetic interactions in spinel ferrites as well as in some ionic compounds are different from the one considered above because the cations are mutually separated by bigger anions (oxygen ions). These anions obscure the direct overlapping of the cation charge distributions, sometimes partially and some times completely making the direct exchange interaction very weak. Cations are too far apart in most oxides for a direct cation-cation interaction. Instead, superexchange interactions appear, i.e., indirect exchange via anion  $p$ -orbitals that may be strong enough to order the magnetic moments. Apart from the electronic structure of cations this type of interactions strongly depends on the geometry of arrangement of the two interacting cations and the intervening anion. Both the distance and the angles are relevant. Usually only the interactions with in first coordination sphere (when both the cations are in contact with the anion) are important. In the Néel theory of ferrimagnetism the interactions taken as effective are inter- and intra-sublattice interactions  $A-B$ ,  $A-A$  and  $B-B$ . The type of magnetic order depends on their relative strength.

The superexchange mechanism between cations that operate via the intermediate anions was proposed by Kramer for such cases and was developed by Anderson and Van Vleck [15, 16]. A simple example of superexchange is provided by  $MnO$  which was chosen by Anderson. From the crystal structure of  $MnO$  it will be seen that the antiparallel manganese ions are collinear with their neighbouring oxygen ions. The  $O^{2-}$  ions each have six  $2p$  electrons in three antiparallel pairs. The outer electrons of the  $Mn^{2+}$  ions are in  $3d$  sub-shells which are half filled with five electrons in each. The phenomenon of superexchange is considered to be due to an overlap between the manganese  $3d$  orbits and the oxygen  $2p$  orbits with a continuous interchange of electrons between them. It appears that, for the overall energy of the system to be a minimum, the moments of the manganese ions on either side of the oxygen ion must be antiparallel. The manganese magnetic moments are thus, in effect, coupled through the intervening oxygen ion. The idea is illustrated in Fig. 2.7.

In Figs. 2.7(a) and 2.7(c) the outer electrons in a pair of  $Mn^{2+}$  ions, and in an intervening  $O^{2-}$  ion in the unexcited state, are shown by the arrows. One suggested mode of





coupling is indicated in Fig. 2.7(b). The two electrons of a pair in the oxygen ion are simultaneously transferred, one to the left and the other to the right. If their directions of spin are unchanged then, by Hund's rules, the moments of the two manganese ions must be antiparallel as shown. Another possibility is represented in Fig. 2.7(d). One electron only has been transferred to the manganese ion on the left. The oxygen ion now has a moment of  $1\mu_B$  and if there is negative interaction between the oxygen ion and the right-hand manganese ion then again the moments of the manganese ions will be antiparallel. If these ideas are accepted then the oxygen ions play an essential part in producing antiferromagnetism in the oxide. Moreover, because of the dumbbell shape of the  $2p$  orbitals, the coupling mechanism should be most effective when the metal ions and the oxygen ions lie in one straight line, that is, the angle between the bonds is  $180^\circ$ , and this is the case with  $MnO$ .

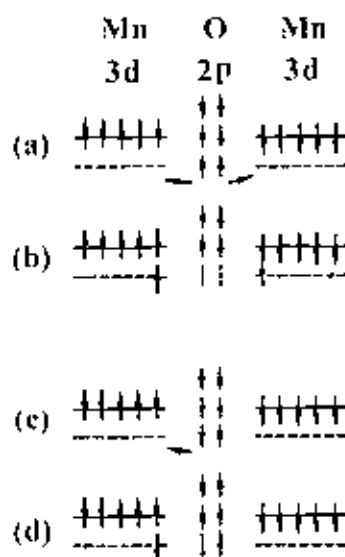


Figure 2.7. Illustrating superexchange in  $MnO$ .

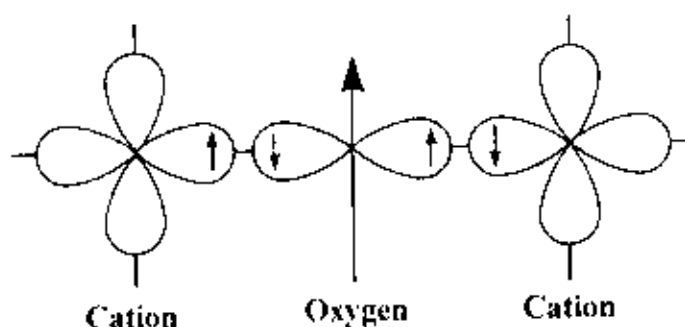


Figure 2.8. Schematic representation of the superexchange interaction in the magnetic oxides. The  $p$  orbital of an anion (center) interact with the  $d$  orbitals of the transitional metal cations.

In the case of spinel ferrites the coupling is of the indirect type which involves overlapping of oxygen wave functions with those of the neighboring cations. Consider two transition metal cations separated by an  $O$ , Fig. 2.8. The  $O^{2-}$  has no net magnetic moment since it has completely filled shells, with  $p$ -type outermost orbitals. Orbital  $p_x$  has two electrons: one with spin up, and the other with spin down, consistent with Pauli's exclusion principle. The essential point is that when an oxygen  $p$  orbital overlaps with a cation  $d$  orbital, one of the  $p$  electrons can be accepted by the cations. When one of the transition-metal cations is brought close the  $O^{2-}$ , partial electron overlap (between a  $3d$  electron from the cation and a  $2p$  electron from the  $O^{2-}$ ) can occur only for antiparallel spins, because electrons with the same spin are repelled. Empty  $3d$  states in the cation are available for partial occupation by the  $O^{2-}$  electron, with an antiparallel orientation. Electron overlap between the other cation and the  $O^{2-}$  then occurs resulting in antiparallel spins and therefore antiparallel order between the cations. Since the  $p$  orbitals are linear, the strongest interaction is expected to take place for cation- $O^{2-}$ -cation angles close to  $180^\circ$  [2].

### 2.6.2 Néel Theory of Ferrimagnetism

If we consider the simplest case of a two-sublattice system having antiparallel and non-equal magnetic moments, the inequality may be due to:

- 1) different elements in different sites,
- 2) same element in different ionic states, and
- 3) different crystalline fields leading to different effective moments for ions having the same spin.

The spins on one sublattice are under the influence of exchange forces due to the spins on the second sublattice as well as due to other spins on the same sublattice. The molecular fields acting on the two sublattices A and B can be written as [2, 13-18]

$$\vec{H}_A = \lambda_{AA}\vec{M}_A + \lambda_{AB}\vec{M}_B,$$

$$\vec{H}_B = \lambda_{BA}\vec{M}_A + \lambda_{BB}\vec{M}_B$$

where  $\vec{M}_A$  and  $\vec{M}_B$  are the magnetizations of the two sublattices and  $\lambda$ 's are the Weiss constants. Since the interaction between the sublattices is antiferromagnetic,  $\lambda_{AB}$  must

be negative, but  $\lambda_{AA}$  and  $\lambda_{BB}$  may be negative or positive depending on the crystal structure and the nature of the interacting atoms. Probably, these interactions are also negative, though they are in general quite small.

Assuming all the exchange interactions to be negative the molecular fields will be then given by

$$\bar{H}_A = -\lambda_{AA}\bar{M}_A - \lambda_{AB}\bar{M}_B,$$

$$\bar{H}_B = -\lambda_{AB}\bar{M}_A - \lambda_{BB}\bar{M}_B$$

Since in general,  $\lambda_{AA}$  and  $\lambda_{BB}$  are small compared to  $\lambda_{AB}$ , it is convenient to express the strengths of these interactions relative to the dominant  $\lambda_{AB}$  interaction.

Let  $\lambda_{AA} = \alpha\lambda_{AB}$

and  $\lambda_{BB} = \beta\lambda_{AB}$

In an external applied field  $\bar{H}$ , the fields acting on  $A$  and  $B$  sites are

$$\bar{H}_A = \bar{H} - \lambda_{AB}(\alpha\bar{M}_A - \bar{M}_B),$$

$$\bar{H}_B = \bar{H} - \lambda_{AB}(\bar{M}_A - \beta\bar{M}_B)$$

At temperatures higher than the transition temperature,  $T_N$ ,  $\bar{H}_A$ ,  $\bar{M}_A$  and  $\bar{M}_B$  are all parallel and we can write

$$\bar{M}_A = \frac{C_A}{T}[\bar{H} - \lambda_{AB}(\alpha\bar{M}_A - \bar{M}_B)], \quad (23)$$

$$\bar{M}_B = \frac{C_B}{T}[\bar{H} - \lambda_{AB}(\bar{M}_A - \beta\bar{M}_B)] \quad (24)$$

where  $C_A$  and  $C_B$  are the Curie constants for the two sublattices.

$$C_A = N_A g\mu_B^2 S_A(S_A + 1)/3K$$

and  $C_B = N_B g\mu_B^2 S_B(S_B + 1)/3K$

$N_A$  and  $N_B$  denote the number of magnetic ions on  $A$  and  $B$  sites respectively and  $S_A$  and  $S_B$  are their spin quantum numbers. Solving for the susceptibility,  $\chi$ , one gets [2, 13]

$$\frac{1}{\chi} = \frac{T}{C} - \frac{1}{\chi_0} - \frac{b}{T - \theta}$$

$$\frac{1}{\chi} = \frac{T + (C/\chi_0)}{C} - \frac{b}{T - \theta} \quad (2.5)$$

where  $C$ ,  $\chi_0$ ,  $b$  and  $\theta$  are constants for particular substance and are given by

$$\begin{aligned} C &= C_A + C_B \\ \frac{1}{\chi_0} &= -\frac{1}{C^2} [C_A^2 \lambda_{AA} + C_B^2 \lambda_{BB} + 2C_A C_B \lambda_{AB}] \\ b &= \frac{C_A C_B}{C^3} [C_A^2 (\lambda_{AA} - \lambda_{BB})^2 + C_B^2 (\lambda_{BB} - \lambda_{AA})^2 \\ &\quad - 2C_A C_B \{ \lambda_{AB}^2 - (\lambda_{AA} + \lambda_{BB}) \lambda_{AB} + \lambda_{AA} \lambda_{BB} \}] \\ \theta &= -\frac{C_A C_B}{C} (\lambda_{AA} + \lambda_{BB}) - 2\lambda_{AB} \end{aligned}$$

Equation (2.5) represents a hyperbola, and the physically meaning part of it is plotted in Fig. 2.9. This curvature of the plot of  $1/\chi$  versus  $T$  is a characteristics feature of a ferrimagnet. It cuts the temperature axis at  $T_c$ , called the Ferrimagnetic Curie point. At high temperatures the last term of equation (2.5) become negligible, and reduces to a Curie-Weiss law:

$$\chi = \frac{C}{T + (C/\chi_0)}$$

This is the equation of straight line, shown dashed in Fig. 2.9, to which the  $1/\chi$  versus  $T$  curve becomes asymptotic at high temperatures.

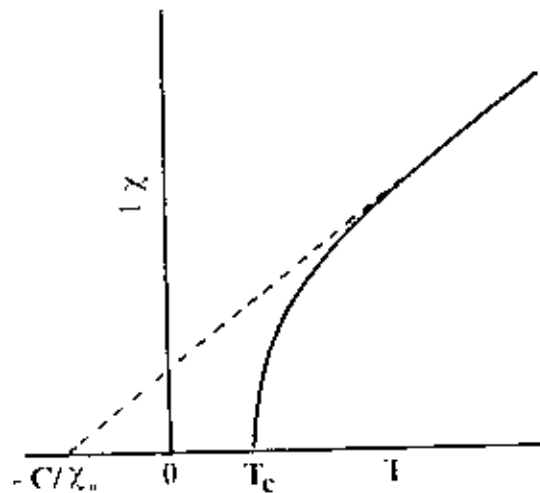


Figure 2.9. The temperature dependence of the inverse susceptibility for ferrimagnets.

The Ferrimagnetic Curie temperature  $T_c$  is obtained from equations (2.3) and (2.4) with  $H = 0$  and setting the determinant of the coefficients of  $M$ , equal to zero. This gives

$$T_c = \frac{1}{2} [C_A \lambda_{AA} + C_B \lambda_{BB} + \{(C_A \lambda_{AA} - C_B \lambda_{BB})^2 + 4C_A C_B \lambda_{AB}^2\}^{1/2}] \quad (2.6)$$

Equation (2.5) is in good agreement with the experiment, except near the Curie point. The experimental Curie temperature, the temperature at which the susceptibility becomes infinite and spontaneous magnetization appears, is lower than the theoretical Curie temperature [13]. This disagreement between theory and experiment in the region of Curie point is presumably due to the short-range spin order (spin clusters) at temperatures above experimental  $T_c$  [2, 13].

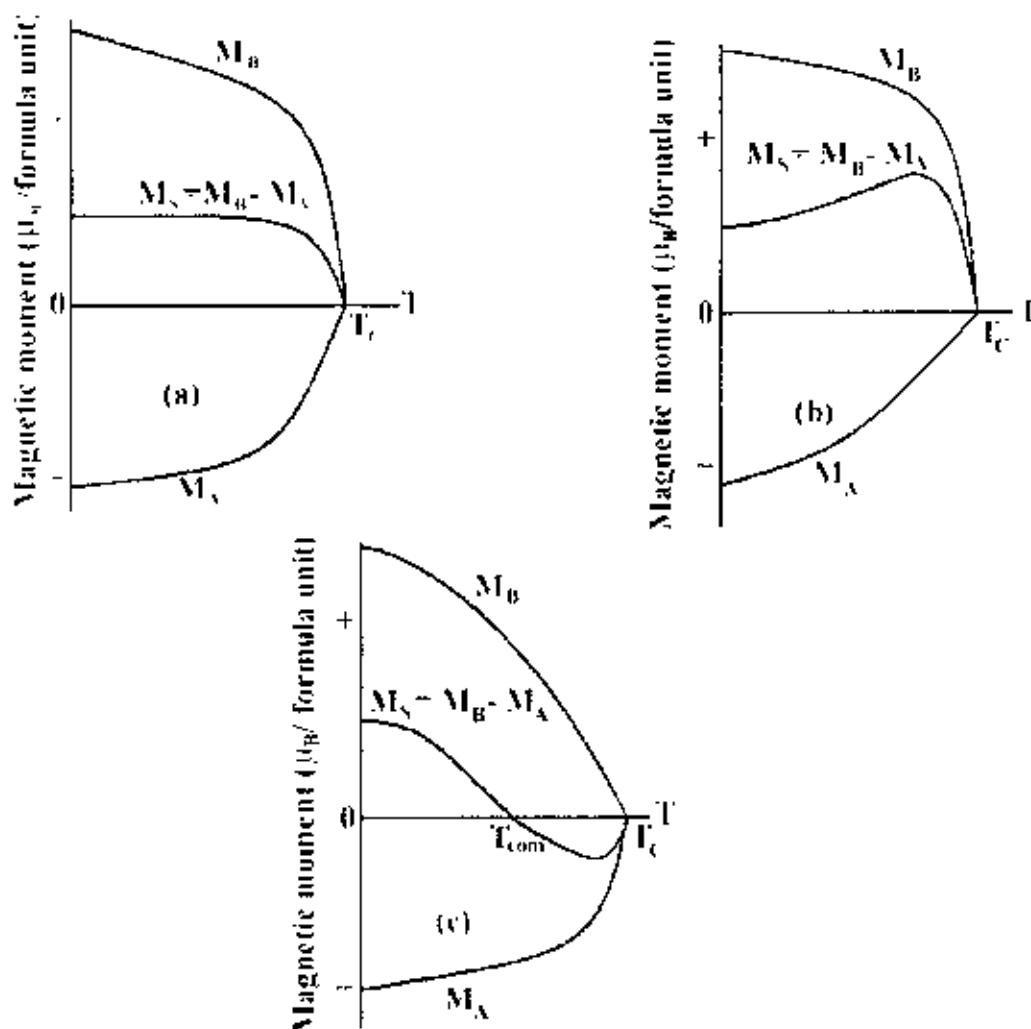


Figure 2.10. Superposition of various combinations of two opposing sublattice magnetizations producing differing resultants including one with a compensation point (schematic).

The sublattice magnetizations will in general have different temperature dependences because the effective molecular fields acting on them are different. This suggests the possibility of having anomaly in the net magnetization versus temperature curves, Fig. 2.10. For most ferrimagnets the curve is similar to that of ferromagnets, but in a few cases there be a compensation point in the curve, Fig. 2.10(c) [1, 13]. At a point below the Curie temperature point, the two sublattice magnetizations are equal and thus appear to have no moment. This temperature is called the compensation point. Below this temperature one sublattice magnetization is larger and provides the net moment. Above this temperature the other magnetization does dominates and the net magnetization reverses direction.

The essential requisite for Néel configuration is a strong negative exchange interaction between  $A$  and  $B$  sublattices which results in their being magnetized in opposite directions below the transition point. But there may be cases where intrasublattice interactions are comparable with intersublattice interaction. Neel's theory predicts paramagnetism for such substances at all temperatures. This is unreasonable since strong  $AA$  or  $BB$  interaction may lead to some kind of ordering especially at low temperature. In the cases of no  $AB$  interaction, antiferromagnetic ordering may be expected either in the  $A$  or in the  $B$  sublattice. Under certain conditions there may be non-collinear spin arrays of still lower energy.

### 2.6.3 Effect of Zinc Substitution on the Magnetic Moments in Spinel Ferrites

$Fe_3O_4$  has ferromagnetic properties because of its inverse structure which leads to the formation of domains. A unit cell of  $Fe_3O_4$  contains eight formula units each of which may be written in the form  $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4^{2-}$  [15]. Snoek and his co-workers found that oxides of inverse structure could be artificially produced in which the divalent ions of another element, for example  $Mn$ ,  $Ni$ ,  $Co$ ,  $Mg$  or  $Cu$ , could be substituted for the divalent  $Fe^{2+}$  ions in  $Fe_3O_4$ . An extensive range of ferrites could thus be made having the general formula  $Fe^{\vec{3+}}[M^{\vec{2+}}Fe^{\vec{3+}}]O_4^{2-}$ , where arrows indicate spin ordering. Since the trivalent iron ions are equally distributed on  $A$  and  $B$  sites they cancel each other out magnetically, and the magnetic moment per formula unit is then theoretically the same as the magnetic moment of the divalent ion. The  $Ni$  ferrite has a

moment of  $2.3\mu_B$  compared with a theoretical value of  $2\mu_B$  [1]. *Zn* ferrite is a normal spinel, with  $Zn^{2+}$  ( $3d^{10}$ ) ions in *A* sites have zero magnetic moment;  $Fe^{3+}$  ions in *B* sites have a magnetic moment  $5\mu_B$ . The cation distribution can be written as  $Zn^{2+}[Fe^{3+} Fe^{3+}]O_4$ , where spin ordering is indicated by arrows. The zero magnetic moment of  $Zn^{2+}$  ions leaves trivalent iron ions on *B* sites with a negative *BB* interaction between equal ions. Therefore *Zn* ferrite is not ferromagnetic. Zinc ferrite therefore be expected to be antiferromagnetic and thus to have a Néel point, though measurements show it to be paramagnetic only [1-2, 13, 15].

Magnetic properties can be modified widely by cation substitution. An illustrative case is substitution of *Ni* by *Zn* in *Ni* ferrite to form solid solutions  $Ni_{1-x}Zn_xFe_2O_4$ . The cation distribution can be written as  $(Zn_x^{2+} Fe_{1-x}^{3+})[Ni_{1-x}^{2+} Fe_{1+x}^{3+}]O_4$  [2].  $Zn^{2+}$  is diamagnetic and its main effect is to break linkages between magnetic cations. Another effect is to increase interaction distance by expanding the unit cell, since it has an ionic radius larger than the *Ni* and *Fe* radii. The most remarkable effect is that substitution of this diamagnetic cation (*Zn*) results in a significant increase in magnetic moment in a number of spinel solid solutions, Fig. 2.11.

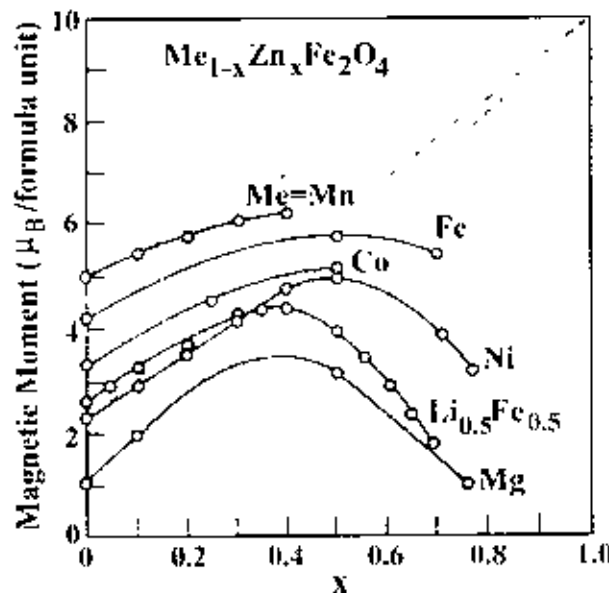


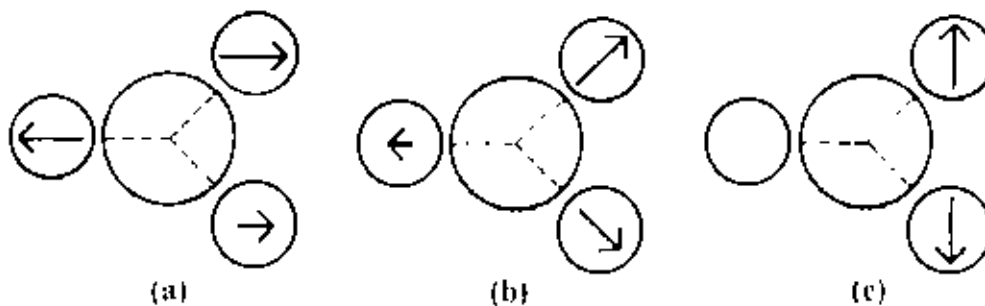
Figure 2.11. Variation of Magnetic moment (in Bohr magnetons per formula unit) with increasing zinc substitution [1, 2].

Magnetic moment as a function of  $Zn$  content shows an increase for small substitutions, goes through a maximum for intermediate values, decreases and finally vanishes for high  $Zn$  contents

A simple analysis shows that this increase can be expected for an antiparallel alignment. As the  $Zn$  content increases, magnetic moments decrease in sublattice  $A$  and increase in sublattice  $B$ . If the magnetic moment of  $Fe$  and  $Ni$  are 5 and  $\sim 2.3 \mu_B$ /ion, respectively, then, per formula unit, the total moment in Bohr magnetons on  $B$  sublattice is  $2.3(1-x) + 5(1+x)$  and on  $A$  sublattice the total antiparallel moment is  $5(1-x)$ . If the resultant moment per formula unit is  $M_x(0)$ , then by taking the difference of  $A$  and  $B$  moments [15],

$$\begin{aligned} M_x(0) &= 2.3(1-x) + 5(1+x) - 5(1-x) \\ &= x(10 - 2.3) + 2.3 \end{aligned}$$

A linear relationship is obtained with a slope of 7.7, predicting a moment value of  $10\mu_B$  per formula unit for  $Zn$  substitution  $x=1$ , as shown by the broken lines in Fig. 2.11. This relationship is not followed over the entire composition range. However, as the  $Zn$  content increases,  $A-O-B$  interactions become too weak and  $B-O-B$  interactions begin to dominate. That is, the average distance between the interacting spins gets larger. As a consequence, the system becomes frustrated causing a perturbation to the magnetically ordered spins as large number of  $B$  sites spins gets non-magnetic impurity atoms as their nearest neighbors.



**Figure 2.12.** Schematic representation of spin arrangements in  $Ni_{1-x}Zn_xFe_2O_4$ : (a) ferrimagnetic (for  $x \leq 0.5$ ); (b) triangular or Yafet-Kittel (for  $x > 0.5$ ); and (c) antiferromagnetic for  $x \approx 1$ .



The  $B$  spins are no longer held in place due to this weak anti-ferromagnetic  $A$ - $B$  interaction leading to non-collinearity or canting among the  $B$  sublattice. Thus for  $x > 0.5$  Zn content, instead of a collinear antiparallel alignment, canted structure appears, where spins in  $B$  sites are no longer parallel [2, 19], Fig. 2.12. Evidence of this triangular structure has been observed by neutron diffraction [20]; a theoretical analysis showed that departure from collinear order depends on the ratio of the  $A-O-B$  to  $B-O-B$  molecular field coefficients,  $\lambda_{AB} / \lambda_{BB}$  [21]. For high Zn concentration,  $B-O-B$  interactions dominant and the ferrite become antiferromagnetic for  $x = 1$  [2].

## 2.7 Microstructure

A polycrystal is much more than many tiny crystals bonded together. The interfaces between the crystals, or the *grain boundaries* which separate and bond the grains, are complex and interactive interfaces. The whole set of a given material's properties (mechanical, chemical and especially electrical and magnetic) depend strongly on the nature of the microstructure.

In the simplest case, the grain boundary is the region, which accommodates the difference in crystallographic orientation between the neighbouring grains. For certain simple arrangements, the grain boundary is made of an array of dislocations whose number and spacing depends on the angular deviation between the grains. The ionic nature of ferrites leads to dislocation patterns considerably more complex than in metals, since electrostatic energy accounts for a significant fraction of the total boundary energy [2].

For low-loss ferrite, Ghate [1] states that the grain boundaries influence properties by

- 1) creating a high resistivity intergranular layer,
- 2) acting as a sink for impurities which may act as a sintering aid and grain growth modifiers,
- 3) providing a path for oxygen diffusion, which may modify the oxidation state of cations near the boundaries.

In addition to grain boundaries, ceramic imperfections can impede domain wall motion and thus reduce the magnetic property. Among these are pores, cracks, inclusions, second phases, as well as residual strains. Imperfections also act as energy wells that pin the domain walls and require higher activation energy to detach. Stresses are microstructural imperfections that can result from impurities or processing problems such as too rapid a cool. They affect the domain dynamics and are responsible for a much greater share of the degradation of properties than would expect [1].

Grain growth kinetics depends strongly on the impurity content. A minor dopant can drastically change the nature and concentration of defects in the matrix, affecting grain boundary motion, pore mobility and pore removal [2, 22]. The effect of a given dopant depends on its valence and solubility with respect to host material. If it is not soluble at the sintering temperature, the dopant becomes a second phase which usually segregates to the grain boundary.

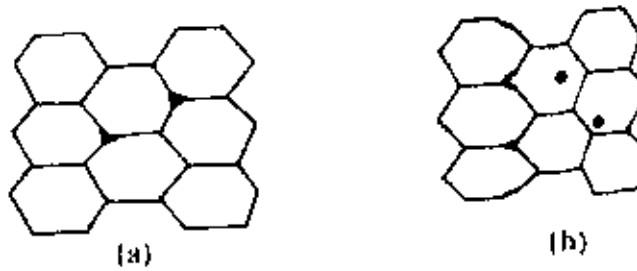


Figure 2.13. Porosity character: (a) intergranular, (b) intragranular.

The porosity of ceramic samples results from two sources, intragranular porosity and intergranular porosity, Fig. 2.13. An undesirable effect in ceramic samples is the formation of exaggerated or discontinuous grain growth which is characterized by the excessive growth of some grains at the expense of small, neighbouring ones, Fig. 2.14. When this occurs, the large grain has a high defect concentration. Discontinuous growth is believed to result from one or several of the following: powder mixtures with impurities; a very large distribution of initial particle size; sintering at excessively high temperatures; in ferrites containing *Zn* and/or *Mn*, a low  $O_2$  partial pressure in the sintering atmosphere. When a very large grain is surrounded by smaller ones, it is called 'duplex' microstructure.

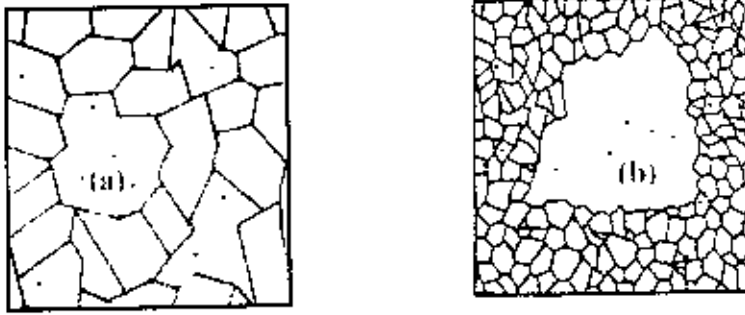


Figure 2.14. Grain growth (a) discontinuous, (b) duplex (schematic).

## 2.8 Theories of Permeability

Permeability is defined as the proportionality constant between the magnetic field induction  $B$  and applied field intensity  $H$  [2, 17, 23]:

$$B = \mu H \quad (2.7)$$

If the applied field is very low, approaching zero, the ratio will be called the initial permeability, Fig. 2.15 and is given by

$$\mu_i = \frac{\Delta B}{\Delta H}_{(\Delta H \rightarrow 0)}$$

This simple definition needs further sophistications. A magnetic material subjected to an ac magnetic field can be written as

$$H = H_0 e^{i\omega t} \quad (2.8)$$

It is observed that the magnetic flux density  $B$  lag behind  $H$ . This is caused due to the presence of various losses and is thus expressed as

$$B = B_0 e^{i(\omega t - \delta)} \quad (2.9)$$

Here  $\delta$  is the phase angle that marks the delay of  $B$  with respect to  $H$ . The permeability is then given by

$$\mu = \frac{B}{H} = \frac{B_0 e^{i(\omega t - \delta)}}{H_0 e^{i\omega t}} = \frac{B_0 e^{-i\delta}}{H_0} = \frac{B_0}{H_0} \cos \delta - i \frac{B_0}{H_0} \sin \delta = \mu' - i\mu'' \quad (2.10)$$

where 
$$\mu' = \frac{B_0}{H_0} \cos \delta \quad (2.11)$$

$$\text{and } \mu'' = \frac{B_0}{H_0} \sin \delta \quad (2.12)$$

The real part ( $\mu'$ ) of complex permeability ( $\mu$ ), as expressed in equation (2.10) represents the component of  $B$  which is in phase with  $H$ , so it corresponds to the normal permeability. If there are no losses, we should have  $\mu = \mu'$ . The imaginary part  $\mu''$  corresponds to that of  $B$ , which is delayed by phase angle  $90^\circ$  from  $H$  [13, 17]. The presence of such a component requires a supply of energy to maintain the alternating magnetization, regardless of the origin of delay. The ratio of  $\mu''$  to  $\mu'$ , as is evident from equation (2.12) and (2.11) gives

$$\frac{\mu''}{\mu'} = \frac{\frac{B_0}{H_0} \sin \delta}{\frac{B_0}{H_0} \cos \delta} = \tan \delta \quad (2.13)$$

This  $\tan \delta$  is called loss factor.

The quality factor is defined as the reciprocal of this loss factor, i.e.

$$\text{Quality factor} = \frac{1}{\tan \delta} \quad (2.14)$$

And the relative quality factor,  $Q = \frac{\mu'}{\tan \delta}$  (2.15)

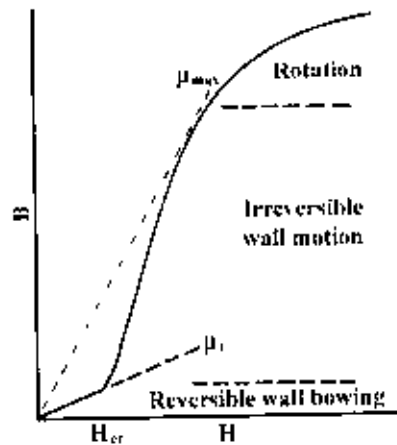


Figure 2.15. Schematic magnetization curve showing the important parameter: initial permeability,  $\mu_i$  (the slope of the curve at low fields) and the main magnetization mechanism in each magnetization range.

The curves that show the variation of both  $\mu'$  and  $\mu''$  with frequency are called the magnetic spectrum or permeability spectrum of the material [13]. The variation of permeability with frequency is referred to as dispersion. The measurement of complex permeability gives us valuable information about the nature of domain wall and their movements. In dynamic measurements the eddy current loss is very important. This occurs due to the irreversible domain wall movements. The permeability of a ferrimagnetic substance is the combined effect of the wall permeability and rotational permeability mechanisms.

### 2.8.1 Mechanisms of Permeability

The mechanisms can be explained as follows: A demagnetized magnetic material is divided into number of Weiss domains separated by Bloch walls. In each domain all the magnetic moments are oriented in parallel and the magnetization has its saturation value  $M_s$ . In the walls the magnetization direction changes gradually from the direction of magnetization in one domain to that in the next. The equilibrium positions of the walls result from the interactions with the magnetization in neighboring domains and from the influence of pores; crystal boundaries and chemical inhomogeneities which tend to favour certain wall positions.

#### 2.8.1.1 Wall Permeability

The mechanism of wall permeability arises from the displacement of the domain walls in small fields. Lets us consider a piece of material in the demagnetized state, divided into Weiss domains with equal thickness  $L$  by means of  $180^\circ$  Bloch walls (as in the Fig. 2.16). The walls are parallel to the  $YZ$  plane. The magnetization  $M_s$  in the domains is oriented alternately in the  $+Z$  or  $-Z$  direction. When a field  $H$  with a component in the  $+Z$  direction is applied, the magnetization in this direction will be favoured. A displacement  $dx$  of the walls in the direction shown by the dotted lines will decrease the energy density by an amount [24, 25]:

$$\frac{2M_s H_z dx}{L}$$

This can be described as a pressure  $M_s H_z$ , exerted on each wall. The pressure will be counteracted by restoring forces which for small deviations may assume to be  $kdx$  per unit wall surface. The new equilibrium position is then given by

$$d = \frac{M_s H_z dx}{L}$$

From the change in the magnetization

$$\Delta M = \frac{2M_s d}{L},$$

the wall susceptibility  $\chi_w$  may be calculated. Let  $H$  makes the angle  $\theta$  with  $Z$  direction. The magnetization in the  $\theta$  direction becomes

$$(\Delta M)_\theta = \frac{2M_s d}{L} \cos \theta, \text{ And with } H_z = H \cos \theta \text{ and } d = \frac{2M_s H_z}{K}$$

we obtain

$$\chi_w = \frac{(\Delta M)_\theta}{H} = \frac{4M_s^2 \cos^2 \theta}{KL} \quad (2.16)$$

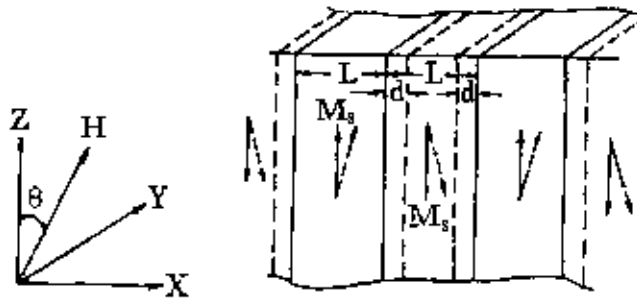


Figure 2.16. Magnetization by wall motion and spin rotation.

### 2.8.1.2 Rotational Permeability

The rotational permeability mechanism arises from rotation of the magnetization in each domain. The direction of  $M$  can be found by minimizing the magnetic energy  $E$  as a function of the orientation. Major contribution to  $E$  comes from the crystal anisotropy energy. Other contributions may be due to the stress and shape anisotropy. The stress may influence the magnetic energy via the magnetostriction.

The shape anisotropy is caused by the boundaries of the sample as well as by pores, nonmagnetic inclusions and inhomogeneities. For small angular deviations,  $\alpha_x$  and  $\alpha_y$  may be written as

$$\alpha_x = \frac{M_x}{M_s} \text{ and } \alpha_y = \frac{M_y}{M_s}.$$

For equilibrium  $Z$ -direction,  $E$  may be expressed as [24, 25]

$$E = E_0 + \frac{1}{2}\alpha_x^2 E_{xx} + \frac{1}{2}\alpha_y^2 E_{yy}$$

where it is assumed that  $x$  and  $y$  are the principal axes of the energy minimum. Instead of  $E_{xx}$  &  $E_{yy}$ , the anisotropy field  $H_x^A$  and  $H_y^A$  are often introduced. Their magnitude is given by

$$H_x^A = \frac{E_{xx}}{2M_s} \text{ and } H_y^A = \frac{E_{yy}}{2M_s},$$

$H_x^A$  &  $H_y^A$  represent the stiffness with which the magnetization is bound to the equilibrium direction for deviations in the  $x$  and  $y$  direction, respectively. The rotational susceptibilities  $\chi_{r,x}$  and  $\chi_{r,y}$  for fields applied along  $x$  and  $y$  directions, respectively are

$$\chi_{r,x} = \frac{M_s}{H_x^A} \text{ and } \chi_{r,y} = \frac{M_s}{H_y^A}.$$

For cubic materials it is often found that  $H_x^A$  and  $H_y^A$  are equal. For  $H_x^A = H_y^A = H^A$  and a field  $H$  which makes an angle  $\theta$  with the  $Z$  direction (as shown in Fig. 2.16) the rotational susceptibility,  $\chi_{r,c}$  in one crystallite becomes

$$\chi_{r,c} = \frac{M_s}{H^A} \sin^2 \theta \quad (2.17)$$

A polycrystalline material consisting of a large number of randomly oriented grains of different shapes, with each grain divided into domains in a certain way. The rotational susceptibility  $\chi_r$  of the material has to be obtained as a weighted average of  $\chi_{r,c}$  of each crystallite, where the mutual influence of neighbouring crystallites has to

be taken into account. If the crystal anisotropy dominates other anisotropies, then  $H^A$  will be constant throughout the material, so only the factor  $\sin^2 \theta$  (equation 2.17) has to be averaged. Snoek [26] assuming a linear averaging of  $\chi_{r,c}$  and found

$$\chi_r = \frac{2M_s}{3H^A}$$

The total internal susceptibility

$$\chi = \chi_w + \chi_r = \frac{4M_s^2 \cos^2 \theta}{KL} + \frac{2M_s}{3H^A} \quad (2.18)$$

If the shape and stress anisotropies cannot be neglected,  $H^A$  will be larger. Any estimate of  $\chi_r$  will then be rather uncertain as long as the domain structure, and the pore distribution in the material are not known. A similar estimate of  $\chi_w$  would require knowledge of the stiffness parameter  $k$  and the domain width  $L$ . These parameters are influenced by such factors as imperfection, porosity and crystallite shape and distribution which are essentially unknown.



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# CHAPTER 3

## SAMPLE PREPARATION AND STRUCTURAL CHARACTERIZATION

### 3.1 Introduction

A goal common to all the ferrites is the common formation of the spinel structure. Today, the large majority of ferrite powders are made by the conventional Ceramic process or Solid State Reaction method. Most non-conventional process involves producing the powder by a wet method. Among these methods, some are [1]:

- 1) Co-precipitation
- 2) Organic precursors
- 3) Sol-gel synthesis
- 4) Spray-drying
- 5) Freeze-drying
- 6) Combustion synthesis
- 7) Glass crystallization

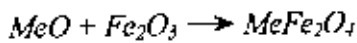
In this chapter, we describe the solid state reaction method that is used in this research work.

### 3.2 Conventional Solid State Reaction Method

In the solid state reaction method, the required composition is usually prepared from the appropriate amount of raw mineral oxides or carbonates by crushing, grinding and milling. The most common type of mill is the ball mill, which consists of a lined pot with hard spheres or rod inside. Milling can be carried out in a wet medium to increase the degree of mixing. This method depends on the solid state inter-diffusion between the raw materials. Solids do not usually react at room temperature over normal time scales. Thus it is necessary to heat them at higher temperatures for the diffusion length  $(2Dt)^{1/2}$  to exceed the particle size, where  $D$  is the diffusion constant for the fast-diffusing species, and  $t$  is the firing time. The ground powders are then calcined in air

or oxygen at a temperature above 1000°C. For some time, this process is continued until the mixture is converted into the correct crystalline phase. The calcined powders are again crushed into fine powders. The pellets or toroid shaped samples are prepared from these calcined powders using die-punch assembly or hydrostatic or isostatic pressure. Sintering is carried out in the solid state, at temperature ranging 1100-1400°C, for times of typically 1-40 h and in various atmospheres (e.g. Air, O<sub>2</sub> and N<sub>2</sub>) [3-6]. Fig. 3.1 shows, diagrammatically, the stages followed in ferrite preparation.

The general solid state reaction leading to a ferrite  $MeFe_2O_4$  may be represented as

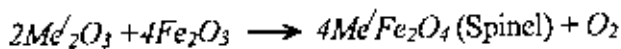
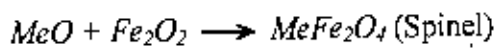


where  $Me$  is the divalent ions. There are basically four steps in the preparation of ferrite:

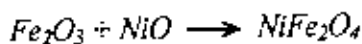
- 1) Preparation of materials to form an intimate mixture with the metal ions in the ratio which they will have in the final product,
- 2) Heating of this mixture to form the ferrite (often called calcining),
- 3) Grinding the calcined powders and pressing the fine powders into the required shape, and
- 4) Sintering to produce a highly densified product.

### 3.3 Details of Calcining, Pressing and Sintering

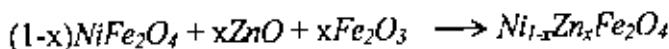
*Calcining* is defined as the process of obtaining a homogeneous and phase pure composition of mixed powders by heating them for a certain time at a high temperature and then allowing it to cool slowly. During the calcining stage, the reaction of  $Fe_2O_3$  with metal oxide (say,  $MeO$  or  $Me_2O_3$ ) takes place in the solid state to form spinel according to the reactions [7]:

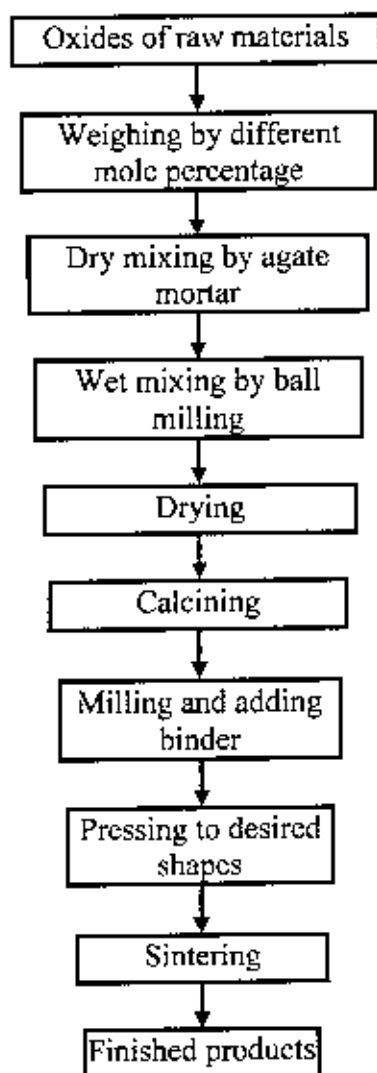


The  $NiO$  creep into  $Fe_2O_3$  as below, to form an intermediate phase  $NiFe_2O_4$  at low temperature



After that  $Zn$  ions are introduced by





**Figure 3.1.** Flow chart of the stages in preparation of spinel ferrite.

The calcining process can be repeated several times to obtain a high degree of homogeneity. The calcined powders are crushed into fine powders. The ideal characteristics of fine powders are [2]:

- 1) small particle size (sub micron)
- 2) narrow distribution in particle size
- 3) dispersed particles
- 4) equiaxed shape of particles
- 5) high purity
- 6) homogeneous composition.

A small particle size of the reactant powders provides a high contact surface area for initiation of the solid state reaction; diffusion paths are shortened, leading to more efficient completion of the reaction. Porosity is easily eliminated if the initial pores are very small. A narrow size distribution of spherical particles as well as a dispersed state is important for compaction of the powder during green-body formation. Grain growth during sintering can be better controlled if the initial size is small and uniform.

A binder is usually added prior to compaction, at a concentration lower than 5wt % [2]. Binders are polymers or waxes; the most commonly used binder in ferrite is polyvinyl alcohol. The binder facilitates the particles flow during compacting and increases the bonding between the particles, presumably by forming bonds of the type *particle-binder-particle*. During sintering, binders decompose and are eliminated from the ferrite. Pressures are used for compacting very widely but are commonly several tons per square inch (i. e., up to  $10^8 \text{ N m}^{-2}$ ).

*Sintering* is defined as the process of obtaining a dense, tough body by heating a compacted powder for a certain time at a temperature high enough to significantly promote diffusion, but clearly lower than the melting point of the main component. The driving force for sintering is the reduction in surface free energy of the powder. Part of this energy is transferred into interfacial energy (grain boundaries) in the resulting polycrystalline body [2, 8]. The sintering time, temperature and the furnace atmosphere play very important role on the magnetic property of ferrite materials. The purposes of sintering process are:

- 1) to bind the particles together so as to impart sufficient strength to the product,
- 2) to densify the material by eliminating the pores and

- 3) to homogenize the materials by completing the reactions left unfinished in the calcining step.

Sintering of crystalline solids is dealt by Coble and Burke [9] who found the following empirical relationship regarding rate of grain growth:

$$\bar{d} = kt^n$$

where  $\bar{d}$  is the mean grain diameter,  $n$  is about  $1/3$ ,  $t$  is sintering time and  $k$  is a temperature dependent parameter. Sintering is divided into three stages, Fig. 3.2 [2, 10].

- Stage 1. Contact area between particles increases,
- Stage 2. Porosity changes from open to closed porosity,
- Stage 3. Pore volume decreases; grains grow.

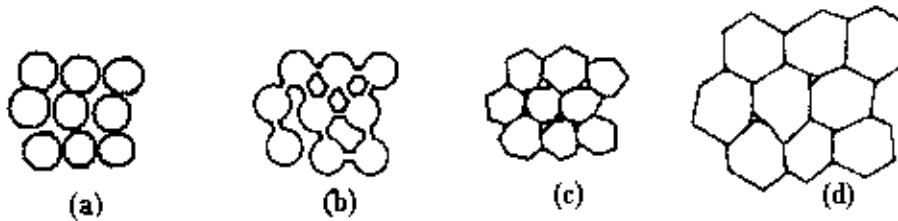


Figure 3.2 Schematic representation of sintering stages: (a) greenbody, (b) initial stage, (c) intermediate stage, and (d) final stage.

In the initial stage, neighbouring particles form a neck by surface diffusion and presumably also at high temperatures by an evaporation-condensation mechanism. Grain growth begins during the intermediate stage of sintering. Since grain boundaries are the sinks for vacancies, grain growth tends to decrease the pore elimination rate due to the increase in distance between pores and grain boundaries, and by decreasing the total grain boundary surface area. In the final stage, the grain growth is considerably enhanced and the remaining pores may become isolated.

In *Ni-Zn* ferrites, the presence of *Zn* complicates the sintering process because high temperature coupled with low oxygen firing will cause *Zn* loss. High density is important for high permeability, but so is *Zn* conservation. Tasaki [1] described two alternative firings to achieve high density:

- 1) Low sintering temperature excluding  $O_2$  (Vacuum, argon, nitrogen),
- 2) High temperature in pure oxygen to reduce *Zn* loss.

Accordingly, other properties correlated along with density:

- 1) Lattice constant is greater for  $O_2$ , smaller for vacuum
- 2) Curie temperature is greater for vacuum, smaller for  $O_2$
- 3) Resistivity is greater for  $O_2$ , smaller for vacuum.

### 3.4 Preparation of the Present Samples

The  $Ni_{1-x}Zn_xFe_2O_4$  (for  $x = 0.2, 0.4$ ) samples were synthesized using the standard solid state reaction technique which is discussed in section 3.2. Powder of  $NiO$  (99.9%),  $ZnO$  (99.999%) and  $Fe_2O_3$  (99.99%) were used as raw materials. Stoichiometric amounts of required powders were mixed thoroughly and then calcined at  $1100^\circ\text{C}$  for 24 hours. The calcined powders were then pressed into disk shaped and toroid shaped samples, Fig. 3.3. The samples were sintered at various temperatures ( $1200^\circ\text{C}$ ,  $1250^\circ\text{C}$ ,  $1300^\circ\text{C}$ ,  $1350^\circ\text{C}$  and  $1400^\circ\text{C}$ ) in air for 5 hours. The temperature ramp was  $10^\circ\text{C}/\text{minute}$  for both cooling and heating.



Figure 3.3. Sample (a) disk shaped, (b) Toroid shaped.

X-ray diffraction study was carried out to determine the sample's structure using an X-ray diffractometer with  $Cu-K\alpha$  radiation. The formation of the single-phase spinel structure was thus confirmed from the diffraction patterns. Results of X-ray diffraction are discussed in Chapter 5.



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# CHAPTER 4

## EXPERIMENTAL TECHNIQUES

*In this chapter we describe basic experimental techniques to measure the lattice parameters, average grain sizes and frequency dependent AC permeability of ferrite samples. We describe also the experimental technique for the measurement of temperature dependent initial permeability. The Curie temperatures of the samples were determined from this temperature dependent initial permeability*

### 4.1 X-ray Diffraction

Bragg reflection is a coherent elastic scattering in which the energy of the X-ray is not changed on reflection. If a beam of monochromatic radiation of wavelength  $\lambda$  is incident on a periodic crystal plane at an angle  $\theta$  and is diffracted at the same angle as shown in Fig. 4.1, the Bragg diffraction condition for X-rays is given by

$$2d \sin\theta = n\lambda \quad (4.1)$$

where  $d$  is the distance between crystal planes and  $n$  is the positive integer which represents the order of reflection. Equation (4.1) is known as Bragg law. This Bragg law suggests that the diffraction is only possible when  $\lambda \leq 2d$  [1]. For this reason we cannot use the visible light to determine the crystal structure of a material. The X-ray diffraction (XRD) provides substantial information on the crystal structure.

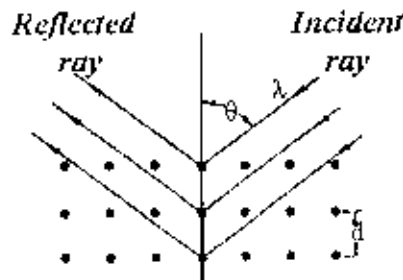


Figure 4.1. Bragg law of diffraction.

X-ray diffraction was carried out with an X-ray diffractometer for the samples  $Ni_{1-x}Zn_xFe_2O_4$  (where  $x = 0.20, 0.40$ ). For this purpose monochromatic  $Cu-K_\alpha$  radiation

was used. The lattice parameter for each peak of each sample was calculated by using the formula

$$a = d\sqrt{h^2 + k^2 + l^2} \quad (4.2)$$

where  $h$ ,  $k$  and  $l$  are the indices of the crystal planes. To determine the exact lattice parameter for each sample, Nelson-Riley method was used. The Nelson-Riley function  $F(\theta)$  is given as

$$F(\theta) = \frac{1}{2} \left[ (\cos^2 \theta / \sin \theta) + (\cos^2 \theta / \theta) \right] \quad (4.3)$$

The values of lattice constant 'a' of all the peaks for a sample are plotted against  $F(\theta)$ . Then using a least square fit method exact lattice parameter 'a<sub>0</sub>' is determined. The point where the least square fit straight line cut the y-axis (i.e. at  $F(0) = 0$ ) is the actual lattice parameter of the sample. The theoretical density  $\rho_{th}$  was calculated using following expression:

$$\rho_{th} = \frac{8M}{N_A a_0^3} \text{ g/cm}^3 \quad (4.4)$$

where  $N_A$  is Avogadro's number ( $6.02 \times 10^{23} \text{ mol}^{-1}$ ),  $M$  is the molecular weight. The porosity was calculated from the relation  $\{100(\rho_{th} - \rho_b) / \rho_{th}\}\%$ , where  $\rho_b$  is the bulk density measured by the formula  $\rho_b = M / V$  [2].

## 4.2 Microstructure Study

The microstructural study of the *Ni-Zn* ferrite samples was performed in order to have an insight of the grain structures. The samples of different compositions and sintered at different temperatures were chosen for this purpose. The samples were visualized under a high-resolution optical microscope and then photographed. The pictures were taken at 400× magnification. Average grain sizes (grain diameter) of the samples were determined from optical micrographs by linear intercept technique [3]. To do this, several random horizontal and vertical lines were drawn on the micrographs. Therefore, we counted the number of grains intersected and measured the length of the grains along the line traversed. Finally the average grain size was calculated.

### 4.3 Complex Permeability Measurement

For high frequency application, the desirable property of a ferrite is high permeability with low loss. One of the most important goals of ferrite research is to fulfill this requirement. The techniques of permeability measurement and frequency characteristics of the present samples are described in sections 4.3.1 and 4.3.2.

#### 4.3.1 Techniques for the Permeability Measurement

Measurements of permeability normally involve the measurements of the change in self-inductance of a coil in presence of the magnetic core. The behaviour of a self-inductance can now be described as follows. We assume an ideal loss less air coil of inductance  $L_0$ . On insertion of a magnetic core with permeability  $\mu$ , the inductance will be  $\mu L_0$ . The complex impedance  $Z$  of this coil [4] can be expressed as follows:

$$Z = R + jX = j\omega L_0 \mu = j\omega L_0 (\mu' - j\mu'') \quad (4.5)$$

$$\text{where the resistive part is} \quad R = \omega L_0 \mu'' \quad (4.6)$$

$$\text{and the reactive part is} \quad X = \omega L_0 \mu' \quad (4.7)$$

The r. f. permeability can be derived from the complex impedance of a coil,  $Z$ , given by equation (4.5). The core is taken as toroidal to avoid demagnetizing effects. The quantity  $L_0$  is derived geometrically as shown in section 4.3.2.

#### 4.3.2 Frequency Characteristics of the Present Samples

The frequency characteristics of the *Ni-Zn* ferrite samples i.e. the initial permeability spectra were investigated using an Agilent Impedance Analyzer (model no. 4192A). The complex permeability measurements on toroid shaped specimens were carried out at room temperature on all the samples in the frequency range 1 kHz - 13 MHz. The real part ( $\mu'$ ) and imaginary part ( $\mu''$ ) of the complex permeability were calculated using the following relations [4]:  $\mu' = L_s / L_0$  and  $\mu'' = \mu' \tan \delta$ , where  $L_s$  is the self-inductance of the sample core and  $L_0 = \mu_0 N^2 S / \pi d$  is derived geometrically. Here  $L_0$  is the inductance of the winding coil without the sample core,  $N$  is the number

of turns of the coil ( $N = 5$ ),  $S$  is the area of cross section of the toroidal sample as given below:

$$S = d \times h,$$

where  $d = \frac{d_2 - d_1}{2},$

$d_1 =$  inner diameter,

$d_2 =$  outer diameter,

$h =$  height

and  $\bar{d}$  is the mean diameter of the toroidal sample as given below:

$$\bar{d} = \frac{d_1 + d_2}{2}$$

The relative quality factor is determined from the ratio  $\frac{\mu_1'}{\tan \delta}.$

#### 4.4 Curie Temperature Measurement

Curie temperature measurement is one of the most important measurements for magnetic materials. Curie temperature provides substantial information on magnetic status of a substance in respect of the strength of exchange interaction. So, the determination of Curie temperature is of great importance.

Curie temperature was measured from the temperature dependent initial permeability. For this measurement, the sample was kept inside a little oven with a thermocouple placed at the middle of the sample. The thermocouple measures the temperature inside the oven and also of the sample. The sample was kept just in the middle part of the cylindrical oven in order to minimize the temperature gradient. The temperature of the oven was then raised slowly. If the heating rate is very fast then temperature of the sample may not follow the temperature inside the oven, and there can be misleading information on the temperature of sample. The thermocouple showing the temperature in that case will be erroneous. Due to the closed winding of wires, the sample may not receive the heat at once. Therefore, a slow heating rate was used to eliminate this problem. Also, a slow heating ensures accuracy in the

determination of Curie temperature. The oven was kept thermally insulated from the surroundings. The temperature dependent permeability was measured at a constant frequency (100 kHz) of a sinusoidal wave.

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# CHAPTER 5

## RESULTS AND DISCUSSION

The polycrystalline  $Ni_{1-x}Zn_xFe_2O_4$  ( $x=0.2$  and  $0.4$ ) ferrites were studied. Various Ni-Zn ferrite samples were sintered at various temperatures (1200°C to 1400°C) for five hours. Structural and surface morphology were studied by x-ray diffraction method and optical microscopy. The magnetic properties of the ferrites were characterized with high frequency (1kHz-13MHz) complex permeability, and temperature dependent permeability measurements. The effects of microstructure, composition and the sintering temperature on the complex permeability of Ni-Zn ferrites are discussed. A possible correlation among sintering temperature, grain size and density is also discussed.

### 5.1 Lattice Parameters, Density and Porosity of the Samples

The X-ray diffraction (XRD) patterns for the samples  $Ni_{1-x}Zn_xFe_2O_4$  with  $x = 0.2, 0.4$  are shown in Fig. 5.1. Analyzing the XRD patterns, we notice that the positions of the peaks comply with the reported values [1]. The XRD patterns of both compositions clearly indicate their single phase and formation of spinel structure. The positions of the peaks and their corresponding miller indices for the samples investigated are given in Table-5.1. The values of lattice parameter 'a' of all the peaks for both compositions are plotted against Nelson-Riley function,  $F(\theta)$ , Fig. 5.2. The measured lattice parameter, density and porosity for different samples sintered at different temperatures are given in Table-5.2. It is observed that the lattice parameter increases with increasing Zn substitution for both the compositions. The increase in lattice parameter with increasing Zn content can be explained on the basis of the ionic radii. The radius of the  $Zn^{2+}$  (0.82 Å) is greater than that of the  $Ni^{2+}$  (0.78 Å) [1].

Table-5.1. X-ray peak positions for  $Ni_{1-x}Zn_xFe_2O_4$  samples.

Sample composition	X-ray peak position with Miller indices					
	$2\theta$ (degree)					
	(220)	(311)	(400)	(422)	(511)	(440)
$Ni_{0.8}Zn_{0.2}Fe_2O_4$	30.40	35.77	43.43	53.82	57.37	62.97
$Ni_{0.6}Zn_{0.4}Fe_2O_4$	30.21	35.62	43.29	53.72	57.25	62.89



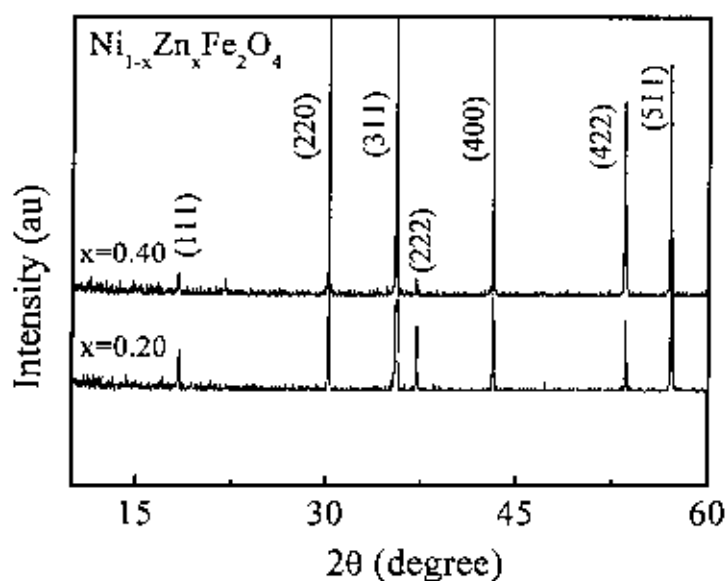


Figure 5.1. The X-ray diffraction patterns for the samples  $Ni_{1-x}Zn_xFe_2O_4$  with  $x = 0.2, 0.4$ .

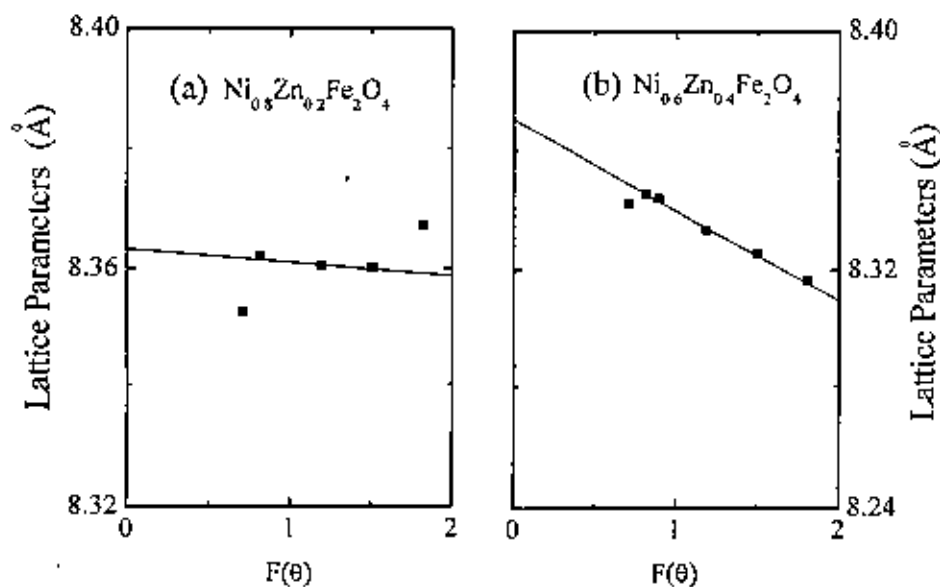


Figure 5.2. The variation of ' $a$ ' with  $F(\theta)$  for (a)  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  and (b)  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  samples.

Table-5.2. The lattice parameter, density, porosity, average grain size and resonance frequency of the  $Ni_{1-x}Zn_xFe_2O_4$  samples sintered at various temperatures with fixed dwell time 5 hours.

Sample composition	Sintering temperature (°C)	$a_0$ (Å)	$\rho_{th}$ (g/cm <sup>3</sup> )	$\rho_B$ (g/cm <sup>3</sup> )	P (%)	<grain size> ( $\mu$ m)	$f_r$ (MHz)
$Ni_{0.8}Zn_{0.2}Fe_2O_4$	1400	8.3638	5.35	4.9693	7.1	13.1	5
	1350			4.9775	6.9	10.7	6
	1300			4.9896	6.7	8.8	7
	1250			4.9306	7.8	7.2	12
	1200			4.5749	14.5	6.9	-
$Ni_{0.6}Zn_{0.4}Fe_2O_4$	1400	8.3705	5.37	4.8632	9.4	24.7	3
	1350			4.9661	7.5	22.3	3
	1300			4.9072	8.6	17.4	3
	1250			4.9010	8.72	11.7	4
	1200			4.8163	10.3	8.9	9

Fig. 5.3 shows the density and porosity as a function of sintering temperature for both compositions. The density of the  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  samples increases as the sintering temperature increases from 1200°C to 1300°C and above 1300°C the density decreases slightly. On the other hand, porosity ( $P$ ) of the sample decreases as increasing sintering temperature up to 1300°C, and above 1300°C the porosity increases slightly. The  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  samples show similar behaviour of changes to that of  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  samples except that density is found to be maximum at 1350°C. It is known that the porosity of ceramic samples results from two sources, intragranular porosity and intergranular porosity [2]. Thus the total porosity could be written as  $P = P_{intra} + P_{inter}$ . The intergranular porosity mainly depends on the grain size [2]. At higher sintering temperatures the density decreases because the intragranular porosity increases resulting from discontinuous grain growth. Such a conclusion is in agreement with that previously reported in case of  $MgCuZn$  ferrites [3].

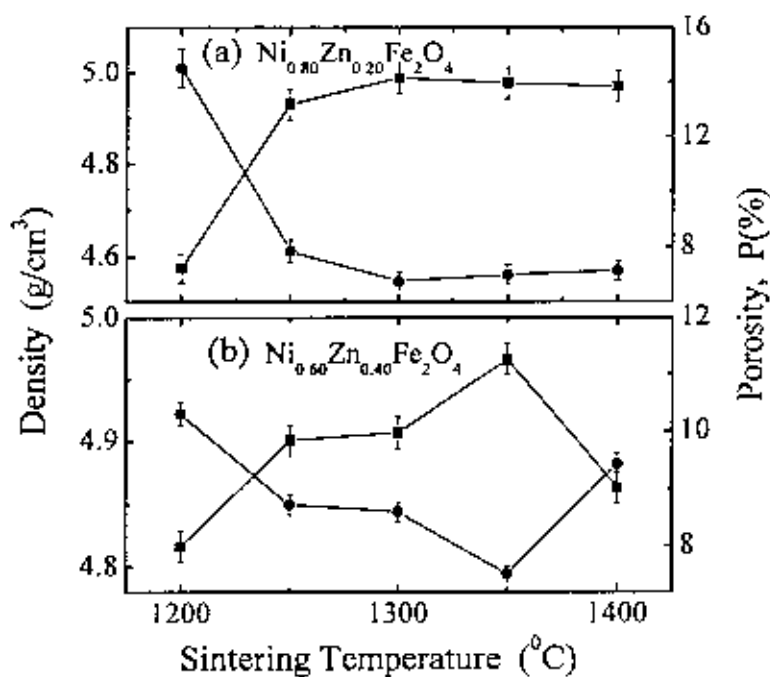


Figure 5.3. The variation of density (■) and porosity (●) with sintering temperature for (a)  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  and (b)  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  samples.

## 5.2 Microstructures of $Ni_{1-x}Zn_xFe_2O_4$

The optical micrographs of  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  and  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  samples sintered at 1400°C, 1350°C and 1300°C are shown in Figs. 5.4 and 5.5, respectively. The results show that an increase in sintering temperature increases the grain size and decreases the porosity; the black areas are voids. It is observed that the samples sintered at 1200°C (not shown) with fairly small grains and open porosity devoid of intragranular pores. It indicates that the 1200°C sintering temperature and the 5-hour sintering time were insufficient for the complete formation of the microstructure. On the other hand, it can be noted that the sintering temperature of 1350°C suffices to produce a homogeneous microstructure with large grain size and a uniform size distribution, Fig. 5.5(b). The average grain sizes for all samples are presented in Table 5.2. The sintering temperature has a great influence on the microstructure. We observed that there was no noticeable variation of lattice parameter with grain size for a composition.

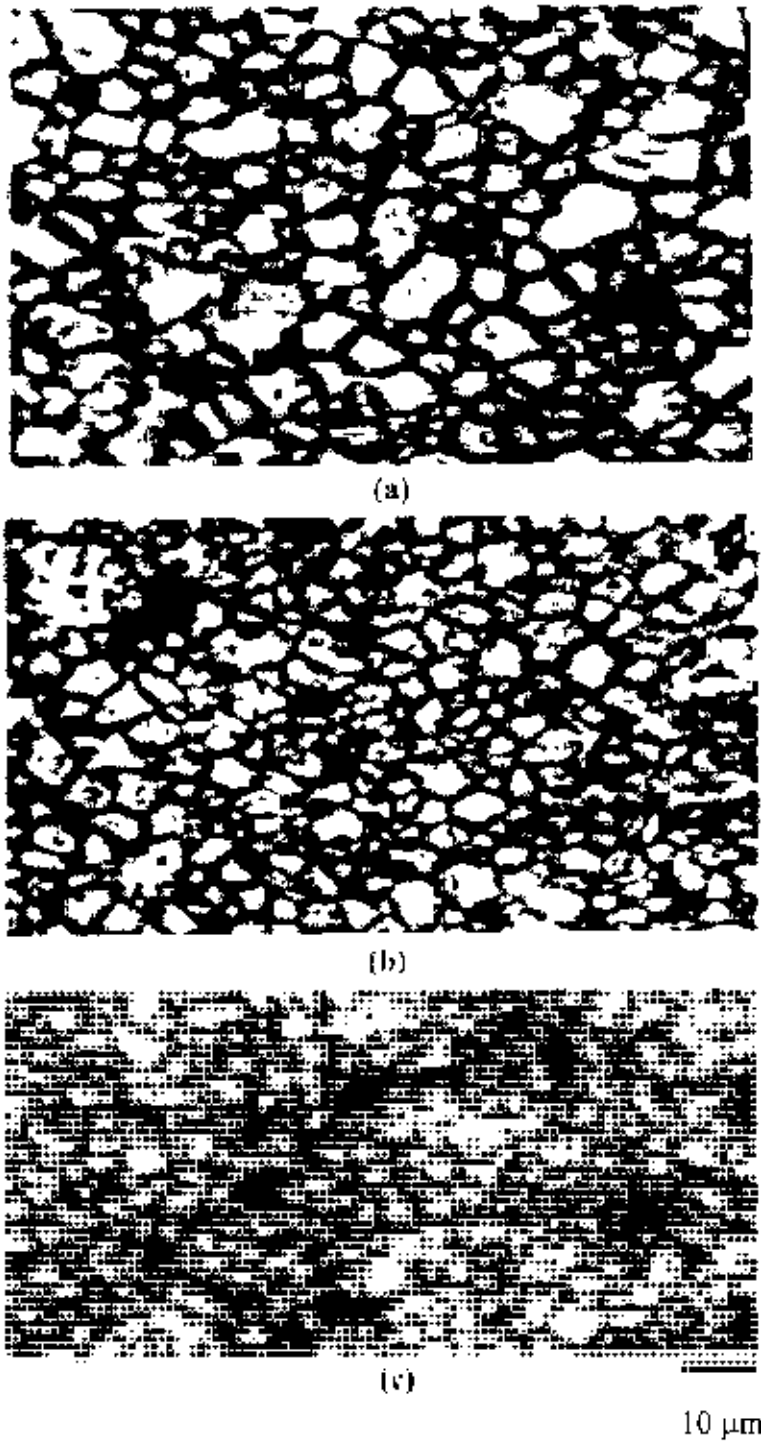


Figure 5.4. The optical micrographs of  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  samples sintered at temperatures (a) 1400°C, (b) 1350°C and (c) 1300°C in air (magnification 400 $\times$ ).

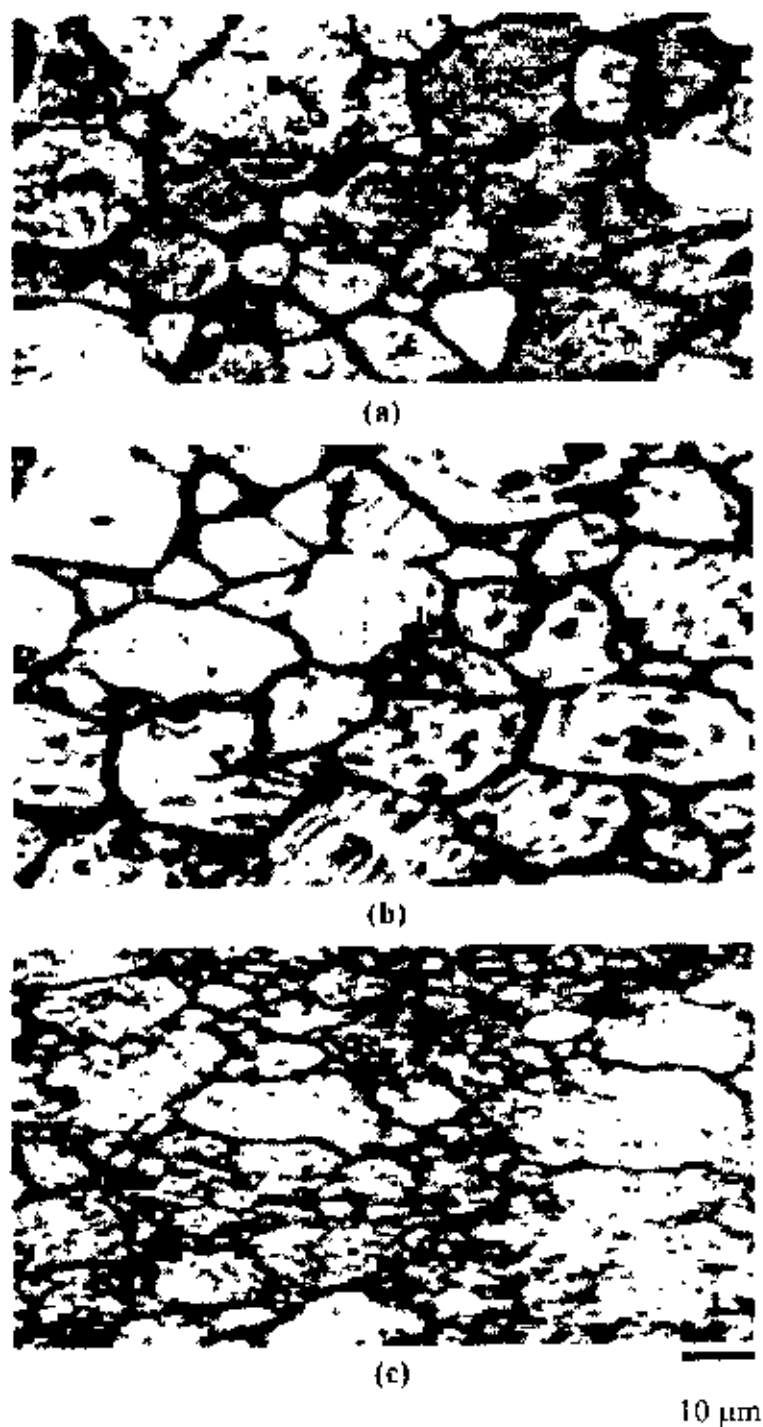


Figure 5.5. The optical micrographs of  $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$  samples sintered at temperatures (a)  $1400^\circ\text{C}$ , (b)  $1350^\circ\text{C}$  and (c)  $1300^\circ\text{C}$  in air (magnification  $400\times$ ).

It is observed that the average grain size of the sample increases with increasing sintering temperature. It is also observed that the sample composition has an influence on the enhancement of grain size. The average grain sizes for the samples  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  are greater than that of  $Ni_{0.8}Zn_{0.2}Fe_2O_4$ .

The grain size reflects the presence of more or less grain boundary area. Even porosity may be strongly related to boundaries since they can remove porosity. The uniformity in the grain size and the average grain diameter can control properties such as the magnetic permeability. When the grain growth rate is very high, pores may be left behind by rapidly moving grain boundaries, resulting in pores that are trapped inside the grains. This intragranular porosity is practically impossible to eliminate, leading to poor magnetic and mechanical properties.

The behaviour of grain growth reflects the competition between the driving force for grain boundary movement and the retarding force exerted by pores [4]. During the sintering process, the thermal energy generates a force that drives the grain boundaries to grow over pores, thereby decreasing the pore volume and densifying the material. When the driving force of the grain boundary in each grain is homogeneous, the sintered body attains a uniform grain size distribution; in contrast, discontinuous grain growth occurs if this driving force is inhomogeneous. The discontinuous growth of grain rises with temperature, hindering the migration of the pore to the grain boundary and hence, contributing toward the reduction of the sintered density.

### 5.3 Complex Permeability

Figs. 5.6 and 5.7 show the real and imaginary permeability spectra for  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  and  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  samples, respectively. The permeability value increases with increasing Zn content in  $Ni_{1-x}Zn_xFe_2O_4$ . With the increase of sintering temperature,  $T_s$ , the real part of the initial permeability is found to increase at first and then decreases. In case of  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  samples,  $\mu'_i$  increases as the  $T_s$  increases up to  $1300^\circ\text{C}$  and above  $1300^\circ\text{C}$ ,  $\mu'_i$  decreases. The  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  samples show similar change of permeability to that of  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  samples except that  $\mu'_i$  is found to be maximum at  $1350^\circ\text{C}$ .

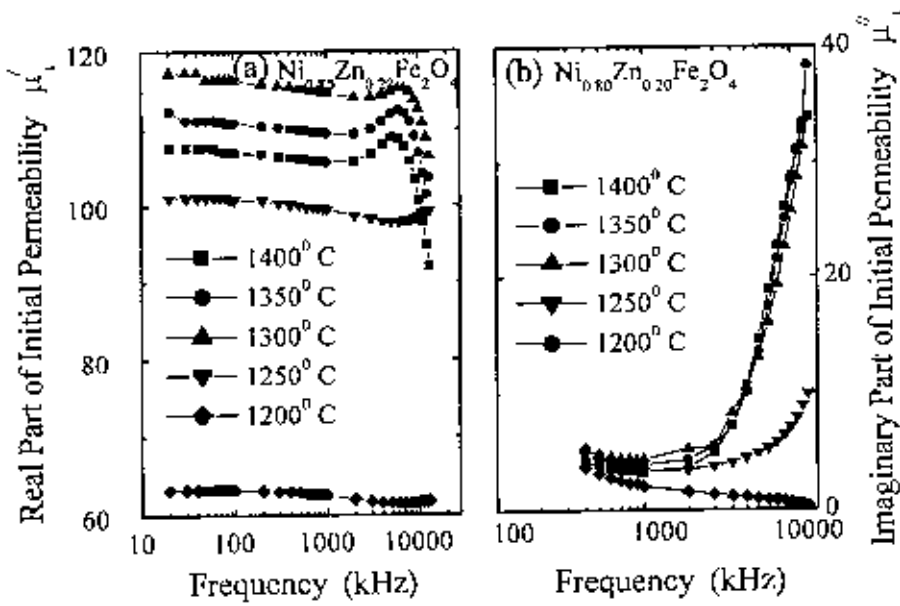


Figure 5.6. (a) The real and (b) imaginary permeability spectra for  $Ni_{0.80}Zn_{0.20}Fe_2O_4$  samples sintered at temperatures  $1200^{\circ}C$ ,  $1250^{\circ}C$ ,  $1300^{\circ}C$ ,  $1350^{\circ}C$  and  $1400^{\circ}C$  in air.

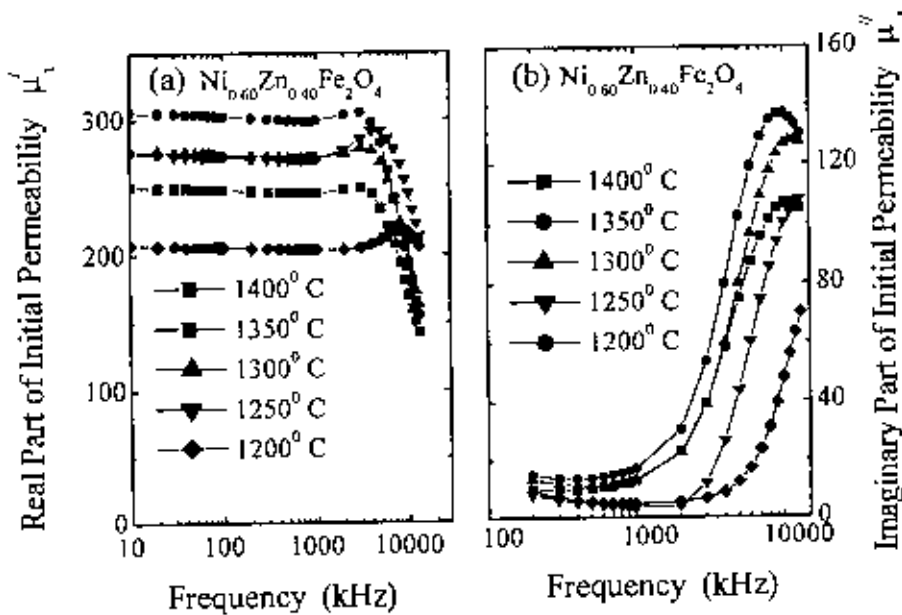


Figure 5.7. (a) The real and (b) imaginary permeability spectra for  $Ni_{0.60}Zn_{0.40}Fe_2O_4$  samples sintered at temperatures  $1200^{\circ}C$ ,  $1250^{\circ}C$ ,  $1300^{\circ}C$ ,  $1350^{\circ}C$  and  $1400^{\circ}C$  in air.

As the sintering temperature increases, the resonance frequency for the  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  samples shifted from 12MHz to 5MHz and from 9MHz to 3MHz for  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  samples. The  $\mu'_i$  values for all samples are found independent of frequency below the resonance frequency. There is a sharp decrease of  $\mu'_i$  and an increase of  $\mu''_i$  above the resonance frequency. These curves are coupled in that the increase losses due to the increase in frequency result in a lowering of the permeability. The resonance frequencies for all samples are presented in Table 5.2. The ferrite with high permeability tends to have its permeability decreases at a relatively low frequency.

It is well known that the permeability of polycrystalline ferrite is related to two different magnetizing mechanisms: spin rotation and domain wall motion [5, 6], which can be described as follows:

$$\mu_i = 1 + \chi_w + \chi_{spin}$$

where  $\chi_w$  is the domain wall susceptibility;  $\chi_{spin}$  is intrinsic rotational susceptibility.  $\chi_w$  and  $\chi_{spin}$  may be written as :  $\chi_w = 3\pi M_s^2 D / 4\gamma$  and  $\chi_{spin} = 2\pi M_s^2 / K$  with  $M_s$  saturation magnetization,  $K$  the total anisotropy,  $D$  the average grain diameter, and  $\gamma$  the domain wall energy. Thus the domain wall motion is affected by the grain size and enhanced with the increase of grain size. The initial permeability is therefore a function of grain size. In our microstructural study we have seen that Zn promotes sintering, bringing about an increase in grain sizes. Larger grains tend to consist of a greater number of domain walls. The magnetization caused by domain wall movement requires less energy than that required by domain rotation. As the number of walls increases with the grain sizes, the contribution of wall movement to magnetization increases. Therefore, permeability increases with the increase of Zn content.

The study of microstructures reveals that the average grain sizes increases with increasing  $T_s$ . Thus for a large grain, permeability should increase as it varies proportionally with grain diameter. Thus one can expect higher  $\mu'_i$  for the sample sintered at higher  $T_s$ . However, we have observed that for both the compositions  $\mu'_i$  is found to be maximum at optimum  $T_s$  (depending on sample composition) as shown in Fig. 5.8. If the sintering temperature is higher than that of the optimum  $T_s$ ,  $\mu'_i$  decreases. It is possible that the samples sintered at higher sintering temperatures ( $>$  optimum  $T_s$ )



may increase the number of pores within the grains which results in a decrease in permeability. Similar behaviour was observed by Guillaud [7] in *Mn-Zn* ferrites. He demonstrated that the permeability decreased with increasing percentage of grains possessing pores despite increasing grain size. The evidence is clear that, if pores can be suppressed or located at the grain boundaries, the permeability will increase with grain size. The relationship between grain size and permeability would generally be linear only if the grain growth is normal, that is, if all the grains grow pretty much at the same time and same rate. Porosity at the grain boundaries is less damaging to the permeability, because it causes less hindrance to domain wall motion than porosity within grains. Both types are evident in Figs. 5.4 and 5.5. If, indeed, some grains grow very rapidly, they would trap pores, which as we have seen, can limit permeability by pinning domain walls. For the composition of  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  sintered at temperature  $1350^\circ\text{C}$  the increase of  $\mu_i'$  is pronounced. This is because the microstructure is homogeneous with large grain size and a uniform size distribution, and the sintered density is highest for this temperature.

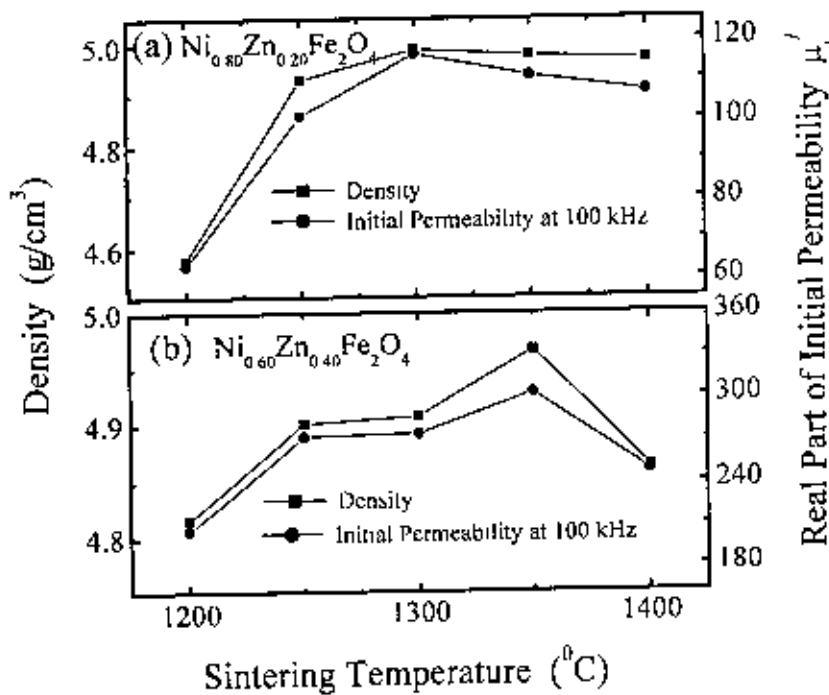


Figure 5.8. The variation of  $\mu_i'$  and  $\rho$  with  $T_s$  for (a)  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  and (b)  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  samples.

The two ferrites obviously show relaxation resonance, with the real part  $\mu'_i$  decreases drastically at high frequency above 3MHz (depending on compositions and  $T_s$ ). If  $H$  is a weak alternating field of high frequency, the domain wall will oscillate back and forth through small distances about their mean position. The differential equation for oscillating boundaries can be written as  $m d^2 x / dt^2 + \beta dx / dt + \alpha x = 2M_s H(t)$ , where  $m$  is the effective wall mass,  $\beta$  the viscous damping factor,  $\alpha$  the restoring constant,  $x$  the wall displacement and  $H(t)$  the driving force [8, 9]. The first term on the left hand side represents the wall inertia as a product of mass times acceleration; the second term is the damping opposing the propagation velocity, and the third term is associated with wall pinning to defects, expressed as a restoring force. It is also observed that the higher the permeability of the material, the lower the frequency of the onset of ferrimagnetic resonance. This really confirms with Snoek's limit  $f_r \mu'_i = \text{Constant}$  [10], where  $f_r$  is the resonance frequency for domain wall motion above which  $\mu'_i$  decreases. This means that there is an effective limit to the product of resonance frequency and permeability so that high frequency and high permeability are mutually incompatible.

For polycrystalline material it has been shown [11, 12] that the resonance frequency can be related to the anisotropy constant by  $f_r = \text{constant} \times K_1$ ; i.e., the resonance frequency decreases with the decrease of anisotropy constant. The  $f_r$  variation can be attributed to variation of  $K_1$  which mainly depends on the microstructure and composition. In our permeability spectrum we have seen that the resonance frequency decrease with the increase of Zn content. The reason is that Zn not only increases the magnetic moment but also lowers anisotropy [13]. On the other hand, the permeability increases with a decrease of  $K_1$ , as we know from the relation  $\mu_i \approx M_s^2 / K_1^{1/2}$  [8, 12]. The high permeability values at low frequencies show the dominant role played by wall motion.

Energy loss is an extremely important subject in soft ferrimagnetic materials, since the amount of energy wasted on process other than magnetization can prevent the AC applications of a given material. The ratio of  $\mu'_i$  and  $\mu''_i$  representing the losses in the material are a measure of the inefficiency of the magnetic system. Obviously this

parameter should be as low as possible. The magnetic losses, which cause the phase shift, can be split up into three components: hysteresis losses, eddy current losses and residual losses. This gives the formula  $\tan \delta_m = \tan \delta_h + \tan \delta_e + \tan \delta_r$ .  $\mu_i$  is the initial permeability which created at low field. Hysteresis losses vanish at very low field strengths. Thus at low field the remaining magnetic losses are eddy current losses and residual losses. Residual losses are independent of frequency. Eddy current losses increase with frequency and are negligible at very low frequency. Eddy current loss can be expressed as  $P_e \approx f^2 / \rho$ , where  $P_e$  is the energy loss per unit volume and  $\rho$  is the resistivity [8]. To keep the eddy current losses constant as frequency is increased; the resistivity of the material chosen must increase as the square of frequency. Eddy currents are not problem in the *Ni-Zn* ferrites until higher frequencies are encountered because they have very high resistivity about  $10^5 \Omega\text{cm}$  [14]. The ferrite microstructure is assumed to consist of grains of low resistivity separated by grain boundaries of high resistivity. Thicker grain boundaries are preferred to increase the resistance. Fig. 5.9 shows the variations of loss factors with frequency of the two compositions of the samples sintered at different sintering temperature  $T_s$ . At frequencies with which we observe loss factor as shown in Fig. 5.9, there is another type of loss that becomes important and may predominate at certain frequencies. This loss is ascribed to a magnetic phenomenon called ferrimagnetic resonance.

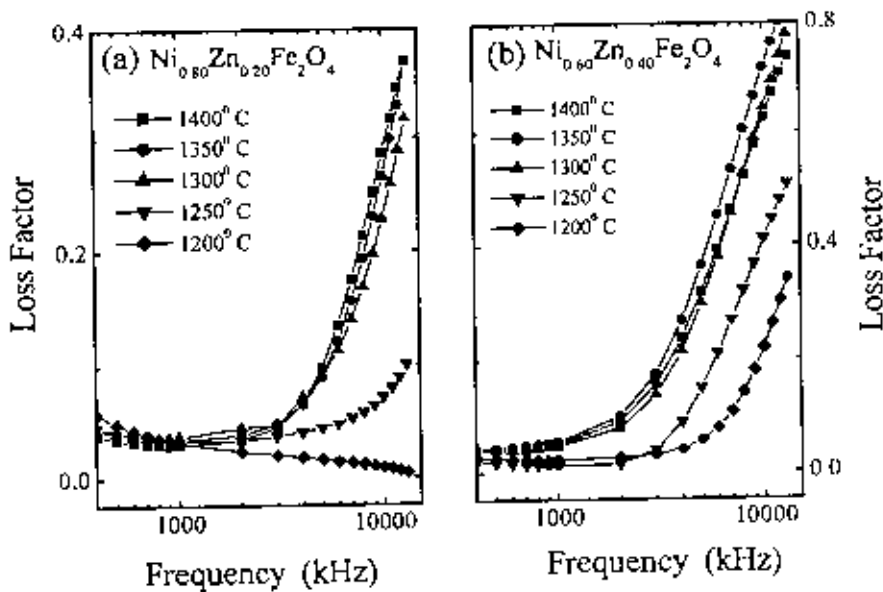


Figure 5.9. The variation of Loss factor with frequency for (a)  $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$  and (b)  $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$  samples.

Loss factors are minimum for frequencies up to 1MHz (depending on compositions and  $T_s$ ). The rise in the value of loss factor after that can be associated with resonance phenomenon occurring in the domains. The addition of Zn lowers the anisotropy constant and reduces the resonance frequency at low frequency. It is further known that most of the electromagnetic characteristics of a ferrite material depend strongly on the microstructure of the sintered body besides composition. The loss factor decreases with decreasing grain size. At high frequencies, losses are found to be lower if domain wall motion is inhibited, and the magnetization is forced to change by rotation [14]. For this reason some grades of Ni-Zn ferrites are deliberately sintered at low temperature. Evidently, the grain boundary can be modified by sintering and this has profound effects on the intergranular strength and magnetic properties. The initial permeability is therefore affected by the grain size, sintered density and the anisotropy constant.

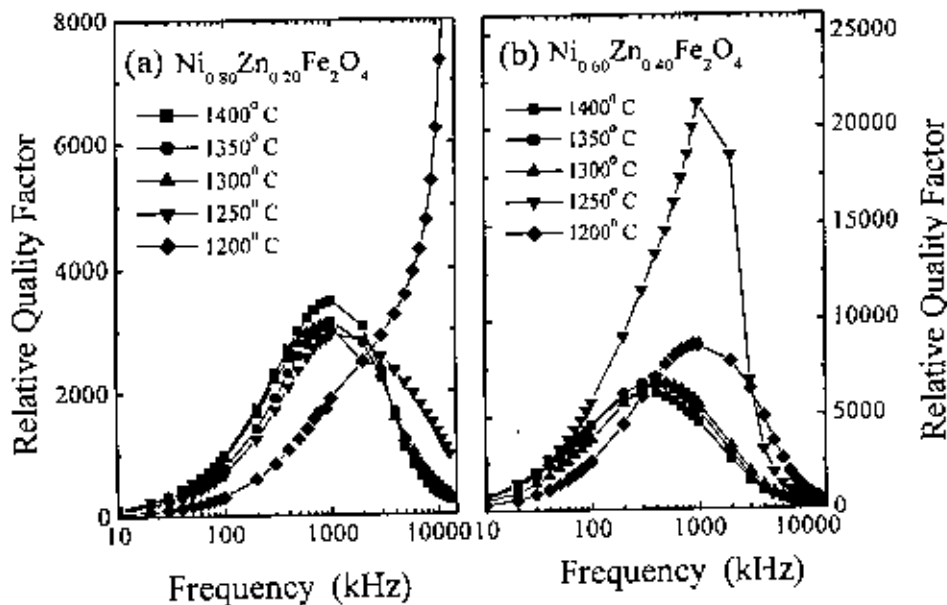


Figure 5.10. The variation of  $Q$  factor with frequency for (a)  $Ni_{0.80}Zn_{0.20}Fe_2O_4$  and (b)  $Ni_{0.60}Zn_{0.40}Fe_2O_4$  samples.

From the loss factor we have calculated the relative quality factor (or  $Q$  factor) for both composition sintered at various temperatures. The  $Q$  factors are shown in Fig. 5.10. For inductors used in filter applications, the quality factor is often used as a

measure of performance. It is observed from the Fig. 5.10 that the sample sintered at 1200°C is of highest  $Q$  value for  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  while 1250°C for  $Ni_{0.6}Zn_{0.4}Fe_2O_4$ . The highest  $Q$  value at 1250°C for  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  while 1200°C for  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  is probably due to the growth of less imperfection and defects in them than the samples sintered at higher  $T_s$ . Smaller grain size is competent for larger  $Q$  values. The highest  $Q$  value for  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  is found to be  $2.1 \times 10^4$  at 1250°C sintering temperature.

#### 5.4 Temperature Dependent Permeability and Curie Temperature

The initial permeability as a function of temperature for both compositions of  $Ni_{1-x}Zn_xFe_2O_4$  is shown in Figs. 5.11 and 5.12. For applications, the temperature dependence of  $\mu'_i$  is very important. The initial permeability of the substances as a function of temperature is measured at a constant frequency (100 kHz) of a sinusoidal wave. It is observed that the permeability falls sharply when the magnetic state of the ferrite samples changes from ferrimagnetic to paramagnetic. The vertical drop of the permeability at the Curie point indicates the degree of homogeneity in the sample composition [15, 16]. Our samples have showed an excellent degree of homogeneity. Measurement of the initial permeability as a function of temperature can therefore be used as a material characterization method. The  $T_c$  for different samples is given in Table-5.3.

It is noted that the samples of two compositions contain different Zn contents. It is observed from the Figs. 5.11 and 5.12 that the  $T_c$  is lower when Zn content is higher. This is expected because of the inclusion of higher concentration of non-magnetic Zn in the materials. This is in harmony with the theoretical and experimental findings. It is also observed that the  $T_c$  slightly increases with increasing sintering temperature for both compositions.

Table-5.3. The Curie temperature,  $T_c$ , for  $Ni_{1-x}Zn_xFe_2O_4$  samples.

Sample composition	Sintering temperature (°C)	Curie temperature (°C)
$Ni_{0.8}Zn_{0.2}Fe_2O_4$	1400	516
	1250	506
$Ni_{0.6}Zn_{0.4}Fe_2O_4$	1400	353
	1250	350

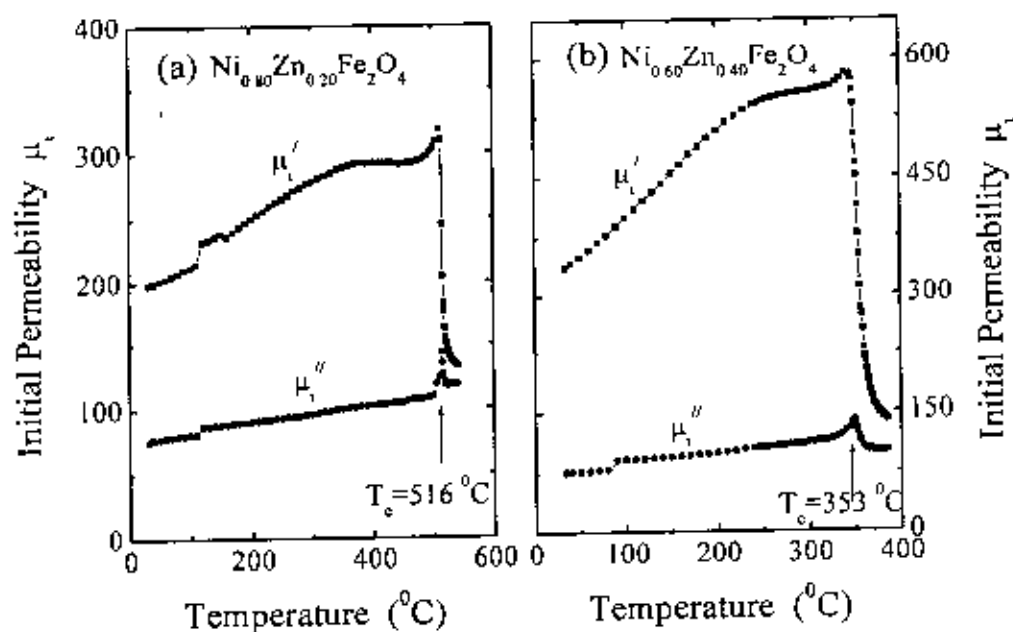


Figure 5.11. The temperature dependence of the initial permeability for (a)  $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$  and (b)  $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$  samples sintered at  $1400^\circ\text{C}$  in air.

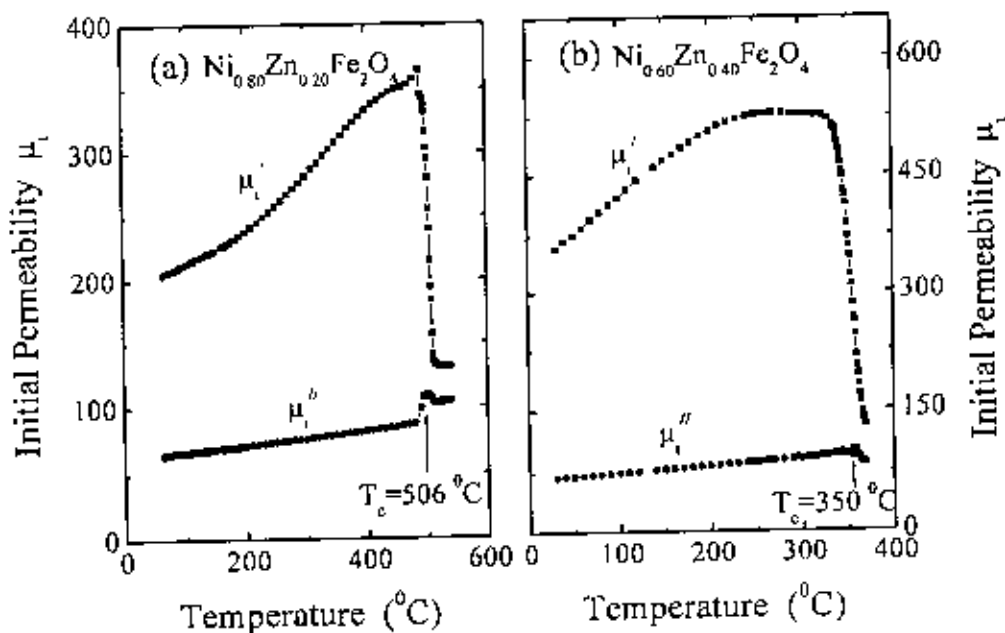


Figure 5.12. The temperature dependence of the initial permeability for (a)  $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$  and (b)  $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$  samples sintered at  $1250^\circ\text{C}$  in air.

*Ni-Zn* ferrite is a mixed normal-inverse spinel type with a general formula  $Fe_{1-x}Zn_x[Ni_{1-x}Fe_{1+x}]O_4$ , where the term within the square brackets indicates the octahedral (*B*) sites and the first term is tetrahedral (*A*) sites. The decrease of  $T_c$  with an increasing *Zn* content may be explained by a modification of the *A-B* exchange interaction strength due to the change of the  $Fe^{3+}$  distribution between *A* and *B* sites. The decrease of the Curie temperature is due to the weakening of the *A-B* interaction. This could be attributed to the increase in distance between the moments of *A* and *B* sites, which is confirmed by the increase in the lattice parameter with increasing *Zn* content. The larger distances between moments in samples  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  leads to decrease the *A-B* interaction relative to that of  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  samples and consequently the  $T_c$  decreases.

Anisotropy constants vary considerably with temperature. In most cases, anisotropy decreases steeply from a high value at low temperature and then slowly decreases down to zero at  $T_c$  [8]. There is then no preferred crystallographic direction for the magnetization of a domain. It is observed that the initial permeability,  $\mu_i$ , increases with temperature to a maximum value just below the  $T_c$ . This occurs, because the crystal anisotropy normally decreases with increasing temperature [14]. The initial permeability varies as  $\mu_i \approx M_s^2 / K_1^{1/2}$  [8, 12]. Since anisotropy decreases faster than magnetization on heating, the initial permeability expectantly increases with temperature, tends to infinity just below the  $T_c$  and then drops for the paramagnetic phase. The peak near  $T_c$  is known as the 'Hopkinson' peak [8].

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## CHAPTER 6

### CONCLUSIONS

#### 6.1 Conclusions

Soft ferrite applications are based on their ability to transform AC signals of small amplitude into substantially large variations of magnetic flux. The response of any magnetic material in an applied magnetic field can be understood on the basis of magnetic domains and domain walls. The value of the (relative) initial permeability gives a good indication of how easily a given material can be magnetized, since  $\mu_r = 1$  represents the free space. Large permeability, i.e., substantially large magnetization produced by small field, can only occur because of domain walls.

The XRD patterns of both compositions clearly indicate their single phase and formation of spinel structure. The lattice constant of  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  is found to be 8.3638 Å while 8.3705 Å for  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  samples. The increase in lattice parameter with increasing Zn content in these samples can be explained on the basis of the ionic radii. The radius of the  $Zn^{2+}$  (0.82 Å) is greater than that of the  $Ni^{2+}$  (0.78 Å). The study of microstructure shows that grain size increases with sintering temperature. The density of the  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  samples increases as the sintering temperature increases from 1200°C to 1300°C and above 1300°C the density decreases slightly. The  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  samples show similar behaviour of changes to that of  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  samples except that the density is found to be maximum at 1350°C. During the sintering process, the thermal energy generates a force that drives the grain boundaries to grow over pores, thereby decreasing the pore volume and increasing the density of the materials. At higher sintering temperatures the density decreases, because the intragranular porosity increases as a result of discontinuous grain growth. The discontinuous growth of grain rises with temperature, hindering the migration of the pore to the grain boundary and hence, contributing toward the reduction of the sintered density. There is an enlargement of grain size obtained for increasing Zn content. This is because of the fact that Zn promotes sintering, bringing about an increase in grain size.

The permeability value increases with increasing Zn content in  $Ni_{1-x}Zn_xFe_2O_4$ , because the average grain size increases with increasing Zn content. Larger grains tend to consist of a greater number of domain walls. Thus the domain wall motion is affected by the grain size and enhanced with the increase of grain size. The initial permeability, therefore, increases with grain size. The  $\mu'_i$  also increases with the increase of sintering temperature, because the average grain size increases with increasing sintering temperature. But for both compositions,  $\mu'_i$  is found to be maximum at optimum  $T_s$  (depending on sample composition). If the sintering temperature is higher than that of the optimum  $T_s$ ,  $\mu'_i$  decreases. Higher sintering temperatures ( $>$  optimum  $T_s$ ) may increase the number of pores within the grains of the samples, which results in a decrease in permeability. A sample with more uniform and bigger grain size as well as highest density is obtained at 1350°C sintering temperature for  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  composition. The maximum  $\mu'_i$  is observed at this optimum  $T_s$  for  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  composition. When the grain is large, the grain contains multidomain, and the permeability is mainly affected by domain wall displacement or by wall bowing. The initial permeability proportionally changes with sintering density. Porosity and other defects do not affect the initial permeability if they are confined to the grain boundaries (intergranular defects); otherwise, the initial permeability severely decreases since porosity within grains acts as pinning sites, reducing the volume swept by wall bowing or by wall displacement. The permeability drops off and the magnetic losses increase because of the occurrence of a ferrimagnetic resonance. This factor limits the frequency at which a magnetic material can be used. The  $\mu'_i$  values for all samples are found to be independent of frequency below the resonance frequency. The ferrite with high permeability tends to have its permeability decreases at a relatively low frequency. This is because of the fact that the addition of Zn content increases the permeability but lowers the resonance frequency by lowering the anisotropy. The variation of  $K_1$  mainly depends on the microstructure and composition. The requirements of high permeability and high working frequency lead to a compromise, since for a given composition, an increase in grain size leads simultaneously to an increase in permeability and decrease in resonance frequency. The choice of the basic composition also represents a compromise, since both resonance frequency and permeability are related to crystalline anisotropy

(Resonance frequency increases with the increase of  $K_1$ , and permeability decreases with the increase of  $K_1$ ).

The highest  $Q$  value for  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  is found to be  $2.1 \times 10^4$  at  $1250^\circ\text{C}$  sintering temperature. The highest  $Q$  value obtained for  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  sample at  $1250^\circ\text{C}$  and for  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  sample at  $1200^\circ\text{C}$  is probably due to the growth of lesser imperfection and defects in them than those in the samples sintered at higher  $T_s$ . Smaller grain size is competent for larger  $Q$  values. For this reason, some grades of Ni-Zn ferrites are deliberately sintered at low temperature.

The Curie temperature of  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  is found to be  $516 \pm 1^\circ\text{C}$  while  $353 \pm 1^\circ\text{C}$  for  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  samples sintered at  $1400^\circ\text{C}$ . The decrease of the Curie temperature is due to the weakening of the  $A$ - $B$  interaction. This could be attributed to the increase in distance between the moments of  $A$  and  $B$  sites, which is confirmed by the increase in the lattice parameter with increasing Zn content. The larger distances between moments in samples  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  leads to decrease the  $A$ - $B$  interaction relative to that of  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  samples and consequently the  $T_c$  decreases. From this investigation, we may finally conclude that the highest permeability can be obtained by choosing the proper composition and sintering temperature (optimum  $T_s$ ).

## LIST OF PUBLICATIONS

1. S. T. Mahmud, A. K. M. Akther Hossain, A. K. M. Abdul Hakim, M. Seki, T. Kawai and H. Tabata, "Influence of microstructure on the complex permeability of spinel type Ni-Zn ferrite," *Journal of Magnetism and Magnetic Materials*, **305**, 269 (2006).
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## Influence of microstructure on the complex permeability of spinel type Ni–Zn ferrite

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### Abstract

$\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$  with  $x = 0.2$  and  $0.4$  are prepared by a conventional solid-state reaction technique. Samples were sintered at various temperatures. Structural and surface morphology are studied by X-ray diffraction and optical microscopy. The magnetic properties of the ferrites were characterized with high-frequency (1 kHz–13 MHz) measurements. The Curie temperature of  $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$  is  $516 \pm 1^\circ\text{C}$ , while  $353 \pm 1^\circ\text{C}$  for  $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ . The relative quality factor for  $\text{Ni}_{0.4}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$  sample sintered at  $1250^\circ\text{C}$  is found maximum ( $2.1 \times 10^4$ ). The effects of microstructure, composition and the sintering temperatures on the complex permeability of Ni–Zn ferrites are discussed.

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Keywords: Complex initial permeability; Quality factor; Grain size; Cure temperature

### 1. Introduction

According to their structure spinel-type ferrites are natural superlattices. It has tetrahedral A site and octahedral B site in  $\text{AB}_2\text{O}_4$  crystal structure. It shows various magnetic properties depending on the composition and cation distribution. Various cations can be placed in A site and B site to tune its magnetic properties. Depending on A site and B site cations it can exhibit ferrimagnetic, antiferromagnetic, spin (cluster) glass, and paramagnetic behavior [1]. Due to their remarkable behavior of magnetic and electric properties they are subjects of intense theoretical and experimental investigation for application purpose [1–5]. Most other technologically useful magnetic materials such as iron and soft magnetic alloys have low electrical resistivity. This makes them useless for applica-

tions at high frequencies, for example, as inductor core in TV circuits. The problem is that their low electrical resistivity allows eddy currents to flow within the materials themselves, thereby producing heat and waste energy. The produced heat is often causing a serious problem [6–11]. Thus, non-ferrite materials become inefficient as they waste energy and the wastage is higher as the frequency becomes higher. Recently, colossal magnetoresistance (CMR) effect has been observed in  $\text{ZnFe}_2\text{O}_4$  and Ni-substituted  $\text{Zn}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$  ferrites [1]. This paper focuses on the effect of microstructure and the sintering temperature on the complex permeability of Ni–Zn ferrites. A possible correlation between sintering temperature, grain size and density is also discussed.

### 2. Experimental

The  $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$  (for  $x = 0.2, 0.4$ ) samples were synthesized using the standard solid-state reaction technique.

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Powder of NiO (99.9%), ZnO (99.999%) and Fe<sub>2</sub>O<sub>3</sub> (99.99%) were used as raw materials. Stoichiometric amounts of required powders were mixed thoroughly and then calcined at 1100 °C for 24 h. The calcined powders were then pressed into disk-shaped and toroid-shaped samples. The samples were sintered at various temperatures 1200, 1250, 1300, 1350 and 1400 °C in air for 5 h. The temperature ramp was 10 °C/min for both cooling and heating. Microstructural properties were investigated with a high-resolution optical microscope. X-ray diffraction was carried out with an X-ray diffractometer with Cu-K<sub>α</sub> radiation. The theoretical density,  $\rho_{th}$ , was calculated using the expression,  $\rho_{th} = 8M/N_A a^3$ , where  $N_A$  is the Avogadro's number,  $M$  is the molecular weight and  $a$  is the lattice constant. The porosity was calculated from the relation  $100(\rho_{th} - \rho_B)/\rho_{th}$ %, where  $\rho_B$  is the bulk density measured by the formula  $\rho_B = M/V$ . Average grain sizes (grain diameter) of the samples were determined from optical micrographs by linear-intercept technique [12]. The frequency characteristics of the Ni–Zn ferrite samples i.e. the initial permeability spectra were investigated using an Agilent Impedance Analyzer (model no. 4192A). The complex permeability measurements on toroid-shaped specimens have been carried out at room temperature on all the samples in the frequency range 1 kHz–13 MHz. The values of the measured parameters obtain as a function of frequency and the real ( $\mu'$ ) and imaginary part ( $\mu''$ ) of the complex permeability have been calculated using the following relations:  $\mu' = L_1/L_0$  and  $\mu'' = \mu' \tan \delta$ , where  $L_1$  is the self-inductance of the sample core and  $L_0 = \mu_0 N^2 S/\bar{d}$  is derived geometrically. Here  $L_0$  is the inductance of the winding coil without the sample core,  $N$  is the number of turns of the coil ( $N = 5$ ),  $S$  is the area of cross section, and  $\bar{d}$  is the mean diameter of the sample. The temperature-dependent permeability was measured at a constant frequency (100 kHz) of a sinusoidal wave. The Curie temperature of the samples was determined from the temperature-dependent permeability measurements.

### 3. Results and discussions

#### 3.1. Lattice parameters, density and porosity of the samples

The X-ray diffraction patterns for the samples Ni<sub>1-x</sub>Zn<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> with  $x = 0.2, 0.4$  are shown in Fig. 1. The X-ray diffraction patterns for both compositions clearly indicate their single phase and formation of spinel crystal structure. Analyzing the XRD patterns we notice that the positions of the peaks comply with the reported value [1]. The measured lattice parameter, density, porosity and average grain size for different samples sintered at different temperatures are given in Table 1. It was observed that the lattice parameter increases with increasing Zn substitution for the sample Ni<sub>1-x</sub>Zn<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub>. The increase in lattice parameter with increasing Zn content can be explained on the basis of the ionic radii. The radius of the Zn<sup>2+</sup> (0.82 Å) is greater than that of the Ni<sup>2+</sup> (0.78 Å) [1]. We observed that there is no noticeable variation of lattice parameter with grain size.

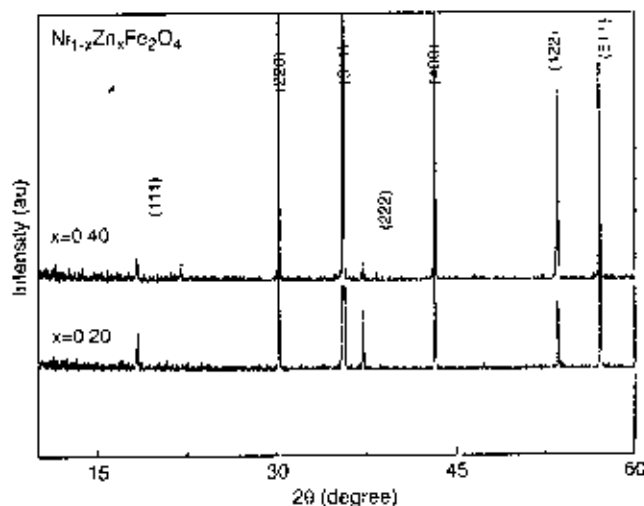


Fig. 1. The X-ray diffraction patterns for the samples Ni<sub>1-x</sub>Zn<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> with  $x = 0.2, 0.4$ .

Table 1

The lattice parameter, density, porosity, average grain size and natural resonance frequency of the Ni<sub>1-x</sub>Zn<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> samples sintered at various temperatures with fixed dwell time 5 h

Sample composition	Sintering temperature (°C)	$a$ (Å)	$\rho_{th}$ (g/cm <sup>3</sup> )	$\rho_B$ (g/cm <sup>3</sup> )	$P$ (%)	grain size ( $\mu$ m)	$f_r$ (MHz)
Ni <sub>0.8</sub> Zn <sub>0.2</sub> Fe <sub>2</sub> O <sub>4</sub>	1400	8.3638	5.35	4.9693	7.1	13.1	5
	1350			4.9775	6.9	10.7	6
	1300			4.9896	6.7	8.8	7
	1250			4.9306	7.8	7.2	12
	1200			4.5749	14.5	6.9	13
Ni <sub>0.6</sub> Zn <sub>0.4</sub> Fe <sub>2</sub> O <sub>4</sub>	1400	8.3705	5.37	4.8632	9.4	24.7	3
	1350			4.9661	7.5	22.3	3
	1300			4.9072	8.60	17.4	3
	1250			4.9010	8.72	11.7	4
	1200			4.8163	10.3	8.9	9

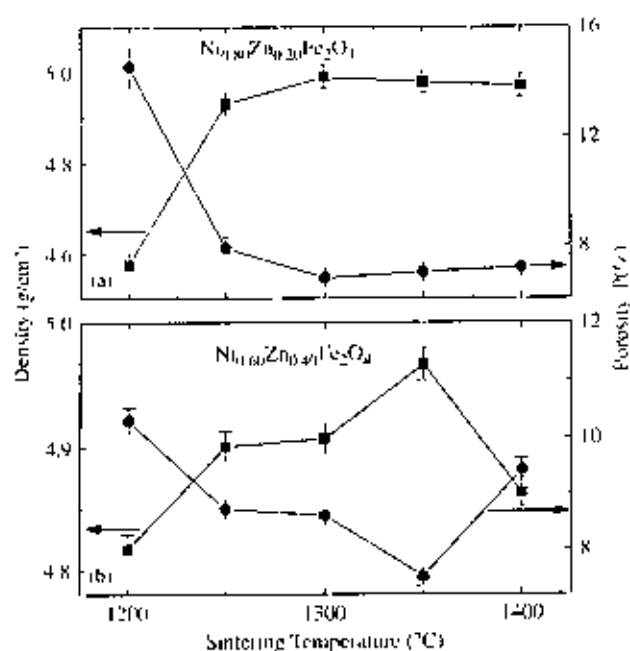


Fig. 2. The variation of density and porosity with sintering temperature for (a)  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  and (b)  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  samples.

Fig. 2 shows the density and porosity as a function of sintering temperatures for both compositions. The density of the  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  samples increases as the sintering temperature increases from 1200 to 1300 °C and above 1300 °C the density begins to decrease as shown in Fig. 2. On the other hand, porosity ( $P$ ) of the sample decreases as increasing sintering temperature up to 1300 °C, and above 1300 °C the porosity increases. The  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  samples also show similar behavior except that density is reached to maximum at 1350 °C. It is known that the porosity of ceramic samples results from two sources, intragranular porosity and intergranular porosity [2]. Thus, the total porosity could be written as  $P = P_{intra} + P_{inter}$ . The intergranular porosity mainly depends on the grain size [2]. At higher sintering temperatures the density is decreased because the intragranular porosity is increased resulting from discontinuous grain growth. This result agrees with the result for MgCuZn ferrites [13].

### 3.2. Microstructure of $Ni_{1-x}Zn_xFe_2O_4$ ferrites

The optical micrographs of various  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  and  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  samples sintered at 1400, 1350 and 1300 °C are shown in Figs 3(a–c) and 4(a–c), respectively. Their average grain sizes for all samples are presented in Table 1. The sintering temperature has great influence on the microstructure. It was observed that the average grain size of the sample increased with increasing sintering temperature. It was also observed that the sample composition has an influence on the enhancement of grain size. The average grain size for the sample  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  is greater than that of  $Ni_{0.8}Zn_{0.2}Fe_2O_4$ . There is an

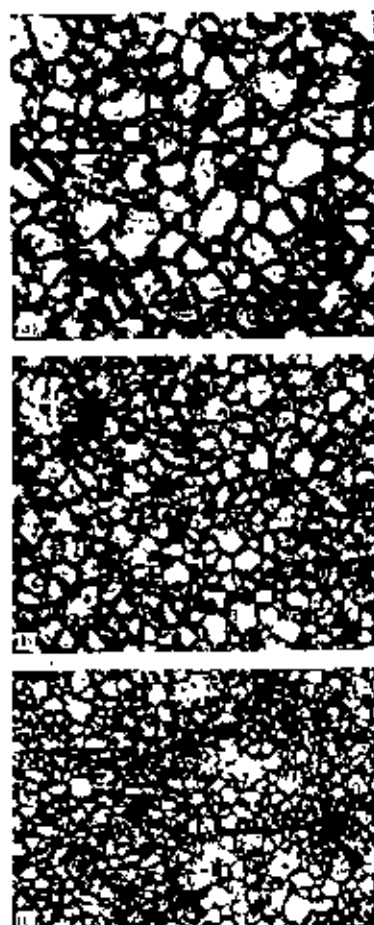


Fig. 3. The optical micrographs of  $Ni_{0.4}Zn_{0.2}Fe_2O_4$  samples sintered at temperatures (a) 1400 °C, (b) 1350 °C, and (c) 1300 °C in air (magnified 400 ×).

enlargement of grain size is obtained for increasing Zn content.

### 3.3. Complex permeability

Figs. 5(a,b) and 6(a,b) show the real and imaginary permeability spectra for  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  and  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  samples, respectively. The permeability value increases with increasing Zn content in  $Ni_{1-x}Zn_xFe_2O_4$  ferrite. With increase of sintering temperatures,  $T_s$ , the real part of the initial permeability,  $\mu'_i$ , is found to increase at first and then decrease. In case of  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  samples  $\mu'_i$  increases as  $T_s$  increases up to 1300 °C and above 1300 °C,  $\mu'_i$  decreases. The  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  samples also show similar behavior except that  $\mu'_i$  is found to maximum at 1350 °C. As sintering temperature increases, the natural resonance frequency for the  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  samples shifted from 13 to 5 MHz and from 9 to 3 MHz for  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  samples. The  $\mu'_i$  values for all samples are found independent of frequency below the resonance frequency. There is a sharp decrease of  $\mu'_i$  and increase of



Fig. 4 The optical micrographs of  $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$  samples sintered at temperatures (a) 1400 °C, (b) 1350 °C, and (c) 1300 °C in air (magnified 400 ×).

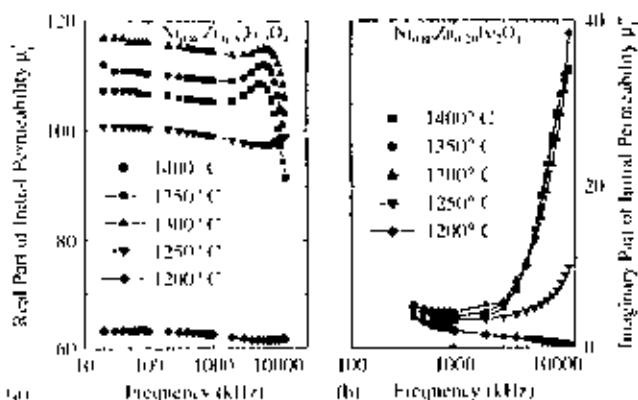


Fig. 5 (a) The real and (b) imaginary permeability spectra for  $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$  samples sintered at temperatures 1200, 1250, 1300, 1350 and 1400 °C in air.

the imaginary part,  $\mu''$ , of the initial permeability above the resonance frequency. The resonance frequencies for all samples are presented in Table 1.

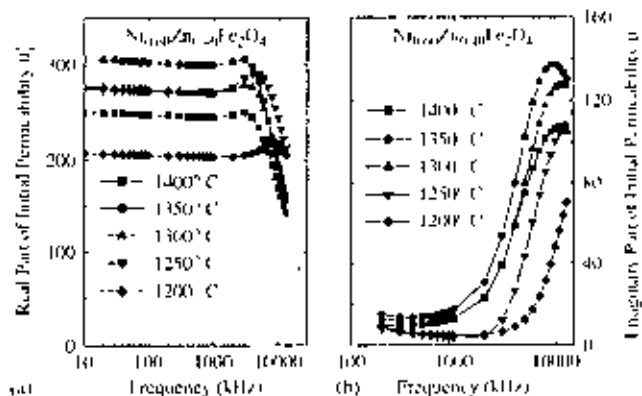


Fig. 6 (a) The real and (b) imaginary permeability spectra for  $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$  samples sintered at temperatures 1200, 1250, 1300, 1350 and 1400 °C in air.

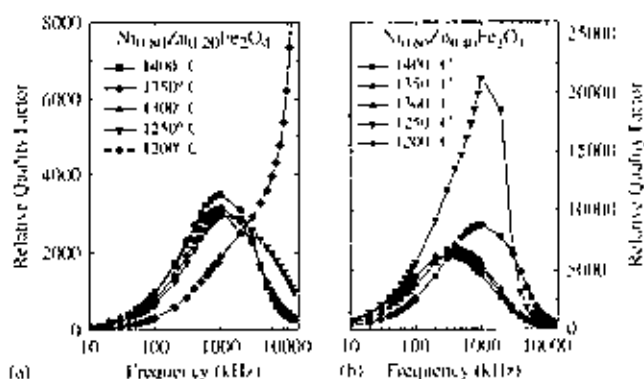


Fig. 7 The variation of  $Q$  factor with frequency for various (a)  $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$  and (b)  $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$  samples.

From the loss factor, we have calculated the relative quality factor (or  $Q$  factor) for both composition sintered at various temperatures. The  $Q$  factors are shown in Fig. 7(a) and (b) for  $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$  and  $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ , respectively. For inductors used in filter applications, the quality factor is often used as a measure of performance. It is observed from Fig. 7(a,b) that the sample sintered at 1200 °C is of highest  $Q$  value for  $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$  while 1250 °C for  $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ .

The study microstructure revealed that as  $T_s$  increases, the grain size also increases. Thus, for a large grain the permeability should increase as it varies proportionally with grain diameter. Thus, one can expect higher  $\mu'_i$  for the sample sintered at higher  $T_s$ . However, we observed that this increase of  $\mu'_i$  was found to be observed for some optimum  $T_s$ , depending on the sample composition as shown in Fig. 8(a,b). Above the optimum  $T_s$ ,  $\mu'_i$  decreases. We believe that the reason behind this phenomenon is that the sample heat treated at higher temperatures (above optimum  $T_s$ ) contains increasing number of pores within the grains which results in decrease in permeability. Similar behavior was observed by Guillaud [14]. The author



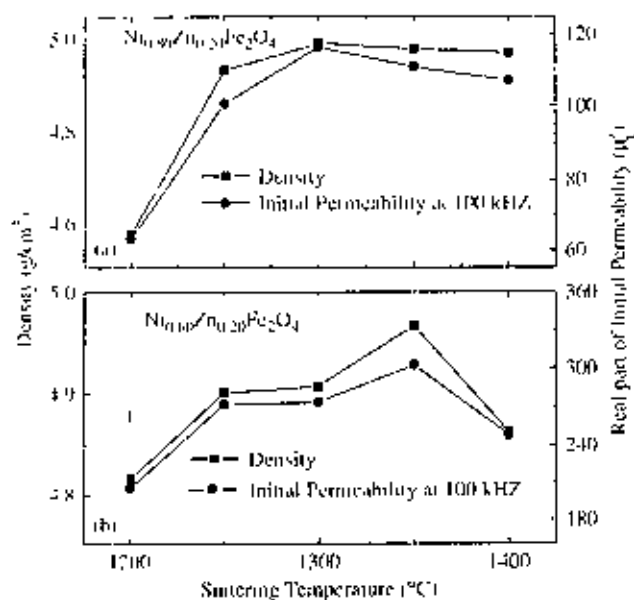


Fig. 8. The variation of  $\mu'_i$  and  $\rho$  with  $T_s$  for various (a)  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  and (b)  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  samples.

demonstrated that the permeability decreased with increasing percentage of grains possessing pores despite increasing grain size. For the composition of  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  sintered at temperature 1350  $^{\circ}C$ , the increase of  $\mu'_i$  is pronounced. This is because the sintered density is highest and the porosity is lowest for this temperature.

It is well known that the permeability of polycrystalline ferrite is related to two different magnetizing mechanisms: spin rotation and domain wall motion [9,15], which can be described as,  $\mu_i = 1 + \chi_w + \chi_{spin}$ , where  $\chi_w$  is the domain wall susceptibility,  $\chi_{spin}$  is intrinsic rotational susceptibility.  $\chi_w$  and  $\chi_{spin}$  may be written as:  $\chi_w = 3\pi M_s^2 D / 4\gamma$  and  $\chi_{spin} = 2\pi M_s^2 / K_u$  with  $M_s$  saturation magnetization,  $K_u$  the total anisotropy,  $D$  the grain diameter, and  $\gamma$  the domain wall energy. Thus, the domain wall motion is affected by the grain size and enhanced with the increase of grain size. The two ferrites obviously showed relaxation resonance, with the real part  $\mu'_i$  decreasing drastically at high frequency of more than 3 MHz (depending on compositions and  $T_s$ ), because the spin rotation plays a relatively more important role when the domain wall motion reduces. This result agrees with the result for  $Mn_{0.2}Ni_{0.3}Zn_{0.5}Fe_2O_4$  [17]. It is observed that as the permeability started to decrease, the natural resonance frequency,  $f_r$  (i.e. the frequency at which  $\mu'_i$  shows peak) gets higher. This really confirms with Snoek's relation  $\mu_i f_r = \text{constant}$  [16].

The highest  $Q$  value at 1250  $^{\circ}C$  for  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  while 1200  $^{\circ}C$  for  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  is probably due to the growth of less imperfection and defects in them than the samples sintered at higher  $T_s$ . Smaller grain size is competent for larger  $Q$  values. The  $Q$  value increases with an increase of Zn substitution because it is believed to be due to the high resistivity of the material.

### 3.4. Temperature-dependent permeability and Curie temperature

The initial permeability as a function of temperature for both compositions of  $Ni_{1-x}Zn_xFe_2O_4$  is shown in Fig. 9(a,b). For applications, the temperature dependence of  $\mu'_i$  is very important. The initial permeability of the substances as a function of temperature was measured at a constant frequency (100 kHz) of a sinusoidal wave. It was observed that the permeability falls sharply when the magnetic state of the ferrite samples changes from ferrimagnetic to paramagnetic. The Curie temperature,  $T_c$ , is determined by drawing a tangent for the curve at the rapid decrease of  $\mu'_i$ . The intersection of the tangent with the temperature axis determines  $T_c$ .

It is observed from the Fig. 9(a,b) that when  $Zn^{2+}$  content is higher, the  $T_c$  is lower. This is expected because of the inclusion of higher concentration of non-magnetic Zn in the materials. This is in harmony with the theoretical and experimental findings. It is also observed (not shown) that the  $T_c$  is slightly increased with increasing sintering temperature for both compositions.

Ni–Zn ferrite is a mixed normal-inverse spinel type with a general formula  $Fe_{1-x}Zn_x[Ni_{1-x}Fe_{1+x}]O_4$ , where the term within the square brackets indicates the octahedral (B) sites and the first term is tetrahedral (A) sites. The decrease of  $T_c$  with an increasing  $Zn^{2+}$  content may be explained by a modification of the A–B exchange interaction strength due to the change of the  $Fe^{3+}$  distribution between A and B sites. The decrease of the Curie temperature is due to the weakening of the A–B interaction. This could be attributed to the increase in the distance between the moments of A and B sites which is confirmed by the increase in the lattice parameter with increasing Zn content. The longest in distances between moments leads the A–B interaction to decrease for samples  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  relative to  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  samples and consequently the  $T_c$  is decreased.

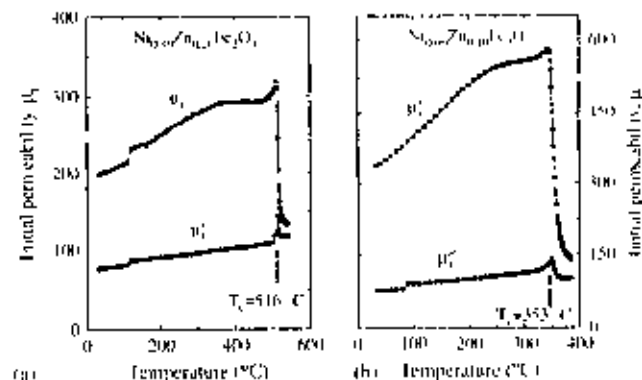


Fig. 9. The temperature dependence of the initial permeability for (a)  $Ni_{0.8}Zn_{0.2}Fe_2O_4$  and (b)  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  samples.

#### 4. Conclusions

The microstructure study shows that grain size increases with sintering temperature. A sample with more uniform and larger grain size as well as highest density is obtained at 1350 °C sintering temperature for  $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$  composition. The maximum  $\mu'_i$  is also observed at this optimum  $T_s$  for  $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$  composition. The initial permeability is proportionally increased with sintering density. The highest  $Q$  value ( $2.1 \times 10^4$ ) for  $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$  is obtained for the sample sintered at 1250 °C. The  $T_c$  of  $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$  is  $516 \pm 1$  °C while  $353 \pm 1$  °C for  $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ . From the investigation carried out in this work we may say that the highest permeability can be obtained by choosing the proper composition and sintering temperature (optimum  $T_s$ ). These results are helpful for practical applications of Ni–Zn ferrites.

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