Influence of Ti substitution on structural and magnetic properties of Ni-Zn ferrites

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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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The Author

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ABSTRACT

Polycrystalline $\text{Ni}_{0.5}\text{Zn}_{0.5-x}\text{Ti}_{x/2}\Box_{x/2}\text{Fe}_2\text{O}_4$ ($x=0$ to $0.27$ in the step of $0.03$) ferrites ($\Box$ represent vacancies) have been prepared by a standard solid state reaction technique. Pellet- and toroid-shaped samples have been prepared from each composition and sintered at various temperatures (1250, 1300, 1350 and 1400°C) in air for four hours. The structural and surface morphological studies were performed by X-ray diffraction technique and optical microscopy, respectively. The AC magnetic properties of these ferrites were characterized with high frequency (100 Hz-120 MHz) complex initial permeability and temperature dependent permeability measurements. The influence of microstructure, various cation substitution and sintering temperatures on the complex permeability of the samples are discussed. A possible correlation among sintering temperature, average grain size and density are also discussed.

X-ray diffraction pattern shows the formation of spinel crystal structure of the ferrites. Lattice parameters are calculated using Nelson Riley function. A compression of unit cell dimension is observed, depending on various cation substitutions in these compositions. This result is explained with the help of ionic radii of substituted cations. The microstructural study shows that both sintering temperatures and cations substitutions have great influence on the average grain size. As the sintering temperatures increases bulk density increases, therefore, porosity decreases for all ferrites. The grain size, density, and lattice parameter of $\text{Ni}_{0.5}\text{Zn}_{0.38}\text{Ti}_{0.06}\Box_{0.06}\text{Fe}_2\text{O}_4$ ferrites are found to have the highest values.

The real part of initial permeability, $\mu_i$, value decreases with increasing $T\bar{i}$ substitutions for all compositions. It is also observed that $\mu_i$ increases with sintering temperatures for all ferrites because high sintering temperature results uniform grain growth. The $\mu_i$ remains fairly constant in the frequency range up to some critical frequency which is called resonance frequency. The high resonance frequency (15.2 MHz) is found for $\text{Ni}_{0.5}\text{Zn}_{0.38}\text{Ti}_{0.06}\Box_{0.06}\text{Fe}_2\text{O}_4$. The relative quality factor is found to be maximum for $\text{Ni}_{0.50}\text{Zn}_{0.44}\text{Ti}_{0.03}\Box_{0.03}\text{Fe}_2\text{O}_4$ ferrite sintered at 1300°C. The Néel temperature increases as a result of $T\bar{i}$ substitutions. These results are helpful for practical applications.
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<table>
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<td>$B$</td>
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<tr>
<td>$CMR$</td>
<td>Colossal magnetoresistance</td>
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<td>$F(\theta)$</td>
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<td>Landé splitting factor</td>
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<tr>
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<td>Inductance of the winding coil without sample</td>
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<tr>
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<td>$\chi_{\text{spin}}$</td>
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1.1 Introduction

Ferrites have been interesting materials both from applications point of view and theoretical point of view. Ferrites are considered to be the most important useful material due to their advantages, such as applicability at higher frequency, lower price, greater heat resistance, and higher corrosion resistance. Most modern soft ferrites are showing spinel type crystal structure. It has tetrahedral A site and octahedral B site in AB$_2$O$_4$ crystal structure. It shows various magnetic properties depending on the compositions and cation distribution. Various cations be placed in A site and B site to tune its magnetic properties. Depending on A site and B site cations it can exhibit ferromagnetic, antiferromagnetic spin (cluster) glass and paramagnetic behaviour [1]. The general chemical formula of such ferrites is MeFe$_2$O$_4$, where Me represents one or several of the divalent transition metals. These types of ferrites are subjects of intense theoretical and experimental investigation due to their remarkable magnetic and electric properties [2-7].

Nickel-Zinc (Ni-Zn) ferrite is one of the most commercially popular soft ferrites due to its important magnetic and electrical properties like high permeability, low loss factor, high stability of permeability with temperature and time, high resistance, controlled coercive forces, low switching co-efficient etc. This ferrite has been extensively used as a magnetic core material for a large number of devices and electrical components, such as phase shifters, circulators, isolators, inductors, transformers, and computer memories [1, 8-15]. But for high performance, permeability and resistivity of these materials need to be increased. Microstructure, magnetic and electrical properties of Ni-Zn ferrites depend on the method of preparation, sintering conditions and the doping concentration [14]. Recently, in our laboratory, a number of studies have revealed that permeability of various divalent metal doped Ni-Zn ferrites strongly depends on grain size [15-16]. It has also been reported that preparation condition of the samples and substitutions of various divalent cations have an influence on the magnetic properties of these ferrites [1, 15-16]. In the present research, Zn$^{2+}$ will be partially
substituted by $Ti^{4+}$ in $Ni_{0.5}Zn_{0.5}Fe_2O_4$, and it is intended to investigate structural and magnetic properties of various $Ni_{0.5}Zn_{0.5-x}Ti_{x/2}\square_{x/2}Fe_2O_4$ polycrystalline ferrites (where, $\square$ represents vacancies). Here, half of substituted $Zn^{2+}$ will be replaced by $Ti^{4+}$ and half of substituted $Zn^{2+}$ will be left as vacant to neutralize the composition of the sample.

1.2 Objectives with specific aims

Ferrites are especially convenient for high frequency uses because of their high resistivity. In determining the convenient frequency range of a particular ferrite material, the high frequency response of the complex permeability is therefore very useful. The mechanism of eddy current losses and change of domain wall motion can be understood from the relative magnitudes of the real and imaginary parts of the complex permeability. The frequency response with the effect of composition and microstructure is therefore very useful.

The main objectives of the present research are as follows:

- Preparation of various $Ni_{0.5}Zn_{0.5-x}Ti_{x/2}\square_{x/2}Fe_2O_4$ ($x=0$ to 0.27 in the step of 0.03) samples.
- Characterization of crystal structure, density and porosity of the samples.
- Study the surface morphology (grain size).
- Determination of the ferrimagnetic to paramagnetic transition temperature ($T_N$) from measurement of temperature dependent initial permeability.
- Measurement of initial permeability as a function of frequency (100 Hz-120 MHz) for all samples having various microstructures (e. g. grain size).

1.3 Summary of the Thesis

The summary of the thesis is as follows:

Chapter 1 of this thesis gives an introduction 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 type ferrites.

Chapter 3 gives the details of the sample preparation and describes different measurement techniques that have been used in this research work.
Chapter 4 is devoted to the results of various investigations of the study and explanation of results in the light of existing theories.

The conclusions drawn from the overall experimental results and discussion are presented in Chapter 5.

References:


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.

2.1.1 Overview of the Materials

Ferrites are commonly expressed by the general chemical formula $\text{MeO.} \text{Fe}_2\text{O}_3$, where $\text{Me}$ 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 $\text{MeZnFe}_2\text{O}_4$, where $\text{Me}$ stands for metals like $\text{Cu}$, $\text{Mg}$, $\text{Ni}$ or $\text{Mn}$, for which permeability were found to be up to 4000 [1-3]. Here after starts the story of Ni-Zn ferrite. 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 $180^0$ 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 $\gamma = K\delta_w$ is the wall energy.

Rosales et al. [11] measured the complex permeability of $\text{Zn}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ ferrites with $0.3 \leq x \leq 0.4$. They show that the relaxation frequency and magnetocrystalline anisotropy constant is related by the equation: $f_x = f_{x0} + AK_1$, where $f_{x0}$ and $A$ are constants.

El-Shabasy [12] studied the DC electrical resistivity of $\text{Zn}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$ 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 $\rho(T) = \rho_0 \exp(E/k_B T)$, 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 ($\rho = 5.92 \ \mu \Omega \text{cm}$) than nickel ($\rho = 6.99 \ \mu \Omega \text{cm}$). The main conductivity mechanism in ferrites is attributed to electron hopping between $\text{Fe}^{3+}$ and $\text{Fe}^{2+}$ in octahedral sites. Resistivity in spinels is very sensitive to stoichiometry; a small variation of Fe content in $\text{Zn}_{0.7}\text{Ni}_{0.3}\text{Fe}_{2+x}\text{O}_{4-y}$ results in resistivity variations of $\sim 10^3$. Excess Fe can easily dissolve in spinel phase by a partial reduction of Fe from $3\text{Fe}_2^+\text{O}_3$ to $2\text{Fe}^{2+}\text{Fe}_2^+\text{O}_4$ (and $1/2\text{O}_2\uparrow$)[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 materials 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 anti-parallel 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.
Fig. 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. (a) - (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 \( \text{MgO}.\text{Al}_2\text{O}_3 \), and are called cubic spinel. Analogous to the mineral spinel, magnetic spinel have the general formula \( \text{MeO}.\text{Fe}_2\text{O}_3 \) or \( \text{MeFe}_2\text{O}_4 \) where \( \text{Me} \) is the divalent metal ion [14]. This crystal structure was first determined by Bragg and by Nishikawa [1,13]. Formerly, spinels containing \( \text{Fe} \) 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 1.3Å) 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 0.8Å). 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 \( \text{AB}_2\text{O}_4 \), with 8 A sites, 16 B sites and 32 oxygen ions, and total of 8 x 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.

![Diagram of subcells](image)

**Fig. 2.2:** Two subcells of a unit cell of the spinel structure.

![Diagram of unit cell](image)

**Fig. 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: $Me^{2+}[Me^{3+}_2]O_4$,

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

A completely normal or inverse spinel represents the extreme cases. Zn ferrites have normal spinel structure and its formula may be written as $Zn^{2+}[Fe^{3+}Fe^{3+}]O_4^{-}$. On the other hand, $Ni$ ferrites have inverse spinel structure and its formula may be written as $Fe^{3+}[Ni^{2+}Fe^{3+}]O_4^{-}$. 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:

$$(Me^{2+}_xMe^{3+}_{1-x})(Me^{2+}_{1-x}Me^{3+}_x)O_4$$

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 $(Zn^{2+}_xFe^{3+}_{1-x})(Ni^{2+}_xFe^{3+}_{1-x})O_4^{-}$ 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 $\text{Fe}^{3+}$ (0.67Å) would go into the tetrahedral sites and the divalent ions $\text{Fe}^{2+}$ (0.83Å) go into the octahedral. Two exceptions are found in $\text{Zn}^{2+}$ and $\text{Cd}^{2+}$ which prefer tetrahedral sites because the electronic configuration is favourable for tetrahedral bonding to the oxygen ions. Thus $\text{Zn}^{2+}$ (0.82Å) prefer tetrahedral sites over the $\text{Fe}^{3+}$ (0.67Å) ions. $\text{Zn}^{2+}$ and $\text{Co}^{2+}$ have same ionic radius but $\text{Zn}$ prefers tetrahedral sites and $\text{Co}$ prefers octahedral sites because of the configuration exception. $\text{Ni}^{2+}$ (0.78Å) and $\text{Cr}^{3+}$ (0.64Å) have strong preferences for octahedral sites. Hence the factors influencing the distribution of 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° and also where the inter-ionic distances are the shortest. Fig. 2.5 shows the inter-ionic 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.

![Fig. 2.4: Nearest neighbours of (a) a tetrahedral site, (b) an octahedral site and (c) an anion site.](image)

$\phi = 125^{\circ}9'$ $154^{\circ}34'$ $90^{\circ}$ $125^{\circ}2'$ $79^{\circ}38'$

![Fig. 2.5: Interionic angles in the spinel structure for the different type of lattice site interactions.](image)
For an undistorted spinel, the \( A-O-B \) angles are about 125° and 154° [1-2, 17]. The \( B-O-B \) angles are 90° and 125° but the latter one of the \( B-B \) distances is large. In the \( A-A \) case the angle is about 80°. 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 \( \pm \frac{1}{2} \). 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.

**Fig. 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 \[14, 16, 18\],

\[
V_g = -2J_g \vec{S}_L \cdot \vec{S}_j
\]  
(2.1)

where \(J_g\) is the exchange integral given in a self explanatory notation by

\[
J_g = \int \psi_i^*(1)\psi_j^*(2) \left[ \frac{1}{r_{12}} + \frac{1}{r_{ij}} - \frac{1}{r_{j2}} \right] \psi_i(2)\psi_j(2)dv_1dv_2
\]  
(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 Neél 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 $2p$ orbits, 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 $\text{MnO}$.

**Fig. 2.7:** Illustrating superexchange in $\text{MnO}$.

**Fig. 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 form 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° [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]

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

$$\tilde{H}_B = \lambda_{AB} \tilde{M}_A + \lambda_{BB} \tilde{M}_B,$$

where $\tilde{M}_A$ and $\tilde{M}_B$ 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

\[ \hat{H}_A = -\lambda_{AA} \vec{M}_A - \lambda_{AB} \vec{M}_B, \]

\[ \hat{H}_B = -\lambda_{AB} \vec{M}_A - \lambda_{BB} \vec{M}_B. \]

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 \( \vec{H} \), the fields acting on \( A \) and \( B \) sites are

\[ \hat{H}_A = \vec{H} - \lambda_{AB} (\alpha \vec{M}_A - \vec{M}_B), \]

\[ \hat{H}_B = \vec{H} - \lambda_{AB} (\vec{M}_A - \beta \vec{M}_B). \]

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

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

\[ \vec{M}_B = \frac{C_B}{T}[\vec{H} - \lambda_{AB} (\vec{M}_A - \beta \vec{M}_B)]. \tag{24} \]

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]

\[ \frac{1}{\chi} = \frac{T}{C} - \frac{1}{\chi_0} - \frac{b}{T - \theta} \]
\[
\frac{1}{\chi} = \frac{T + (C/\chi_0)}{C} - \frac{b}{T - \theta}
\]

(2.5)

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

\[
C = C_A + C_B
\]

\[
\frac{1}{\chi_0} = -\frac{1}{C^2}[C_A^2\lambda_{AA} + C_B^2\lambda_{BB} + 2C_A C_B \lambda_{AB}]
\]

\[
b = \frac{C_A C_B}{C^3} [C_A^2(\lambda_{AA} - \lambda_{BB})^2 + C_B^2(\lambda_{BB} - \lambda_{AB})^2 - 2C_A C_B (\lambda_{AB}^2 - (\lambda_{AA} + \lambda_{BB})\lambda_{AB} + \lambda_{AA}\lambda_{BB})]
\]

\[
\theta = -\frac{C_A C_B}{C} (\lambda_{AB} + \lambda_{BB}) - 2\lambda_{AB}
\]

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.

Fig. 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 $M_i$ equal to zero. This gives

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

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].

**Fig. 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 may 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 $Fe^{3+}[M^{2+}Fe^{3+}]O_4^{2-}$, 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 $\text{Zn}^{2+}[\text{Fe}^{3+}\text{Fe}^{3+}]\text{O}_4$, 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, may 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 $(Zn^{2+}Fe^{3+}_{1-x})[Ni^{2+}\text{Fe}^{3+}_{1+x}]O_4^{2-}$ [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].](image)
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 decreases in sublattice A and increase in sublattice B. If the magnetic moment of Fe and Ni are 5 and ~2.3 \(\mu_B\)/ion, respectively, then, per fopumula 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 \(M_S(0)\), then by taking the difference of A and B moments [15],

\[
M_S(0) = 2.3(1-x) + 5(1+x) - 5(1-x) \\
= x(10 - 2.3) + 2.3
\]

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.

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

\[ \text{Fig. 2.13: Porosity character: (a) intergranular, (b) intragranular.} \]

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.
Fig. 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

$$\mu_i = \frac{\Delta B}{\Delta H} \quad (\Delta H \to 0)$$

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

$$\mu' = \frac{B_0}{H_0} \cos \delta \quad (2.11)$$
and \[ \mu'' = \frac{B_0}{H_0} \sin \delta \] (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° 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

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

This \(\tan \delta\) is called loss factor.

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

\[ \text{Quality factor} = \frac{1}{\tan \delta} \] (2.14)

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

**Fig. 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. Let 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

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

From the change in the magnetization

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

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

$$(\Delta M)_{\theta} = \frac{2 M_s d}{L} \cos \theta,$$

And with $H_z = H \cos \theta$ and $d = \frac{2 M_s H_z}{K}$

we obtain

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

(2.16)

Fig. 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

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

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

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

$H_x^A$ & $H_y^A$ 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

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

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, $\chi_{r,e}$ in one crystallite becomes

$$\chi_{r,e} = \frac{M_s}{H^A} \sin^2 \theta$$

(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 $\chi_e$ of the material has to be obtained as a weighted average of $\chi_{r,e}$ 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

$$\chi = \chi_w + \chi_r = \frac{4M_s^2 \cos^2 \theta}{KL} + \frac{2M_s}{3H^A}$$  \hspace{1cm} (2.18)

If the shape and stress anisotropies cannot be neglected, $H^A$ will be larger. Any estimate of $\chi_c$ 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.

References


CHAPTER 3
SAMPLE PREPARATION, CHARACTERIZATION AND EXPERIMENTAL TECHNIQUES

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

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 1000ºC. 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 1100-1400ºC, for times of typically 1-40 h and in various atmospheres (e.g. Air, O$_2$ and N$_2$) [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

$$MeO + Fe_2O_3 \xrightarrow{\text{heat treatment}} MeFe_2O_4$$

where $Me$ is the metal 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]:

$$MeO + Fe_2O_3 \xrightarrow{\text{heat treatment}} MeFe_2O_4 \text{(Spinel)}$$

$$2Me'/2O_3 + 4Fe_2O_3 \xrightarrow{\text{heat treatment}} 4Me'/Fe_2O_4 \text{(Spinel)} + O_2$$
The $\text{NiO}$ creep into $\text{Fe}_2\text{O}_3$ as below, to form an intermediate phase $\text{NiFe}_2\text{O}_4$ at low temperature

\[
\text{Fe}_2\text{O}_3 + \text{NiO} \xrightarrow{\text{heat treatment}} \text{NiFe}_2\text{O}_4
\]

After that $\text{Zn}$ ions are introduced by

\[
(1-x)\text{NiFe}_2\text{O}_4 + x\text{ZnO} + x\text{Fe}_2\text{O}_3 \xrightarrow{\text{heat treatment}} \text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4
\]

If $x=0.50$ then the ferrite is $\text{Ni}_{0.50}\text{Zn}_{0.50}\text{Fe}_2\text{O}_4$. After divalent $\text{Zn}$ replaced by half of tetravalent $\text{Ti}$ then the compositions are $\text{Ni}_{0.50}\text{Zn}_{0.50-x}\text{Ti}_{x/2}$ $\text{Fe}_2\text{O}_4$.

Fig. 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 $10^8$ 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 all the components. 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.

![Fig. 3.2: Schematic representation of sintering stages: (a) greenbody, (b) initial stage, (c) intermediate stage, and (d) final stage.](image)

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) Néel 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

Polycrystalline $\text{Ni}_{0.50}\text{Zn}_{0.50-x}\text{Ti}_{x/2}\text{Fe}_{2}O_4$ ($0.00 \leq x \leq 0.27$) samples were synthesized using the standard solid state reaction technique which is discussed in section 3.2. High purity powders of $\text{NiO}$ (99.99%), $\text{TiO}_2$ (99.9%), $\text{ZnO}$ (99.99%), and $\text{Fe}_2\text{O}_3$ (99.99%) were mixed thoroughly in an appropriate amount. Mixing was performed in the ball mill, which consists of a lined pot with hard spheres or rods inside. Milling was carried out in a wet medium to increase the degree of mixing. The mixed powders were calcined at 950°C for 5 hours. For some time this process was continued until the mixture converted into the correct crystalline phase. The calcined powders were again crushed into fine powders. The toroid and disk shape samples (Fig. 3.3.) were prepared from these calcined powders using uniaxial or isostatic pressure and sintered at temperatures between 1250-1400°C in air for 5 hours. The temperature ramp was 5°C/minute for heating and cooling.

![Fig. 3.3: Sample (a) disk shaped and (b) Toroid shaped.](image)

3.5 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. 3.4, the Bragg diffraction condition for x-rays is given by

\[
2d \sin \theta = n\lambda
\]  

(3.1)

where \( d \) is the distance between crystal planes and \( n \) is the positive integer which represents the order of reflection. Equation (3.1) is known as Bragg law. This Bragg law suggests that the diffraction is only possible when \( \lambda \leq 2d \). 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.

Fig. 3.4: Bragg law of diffraction.

X-ray diffraction was carried out with an x-ray diffractometer for the samples in National University of Malaysia. 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

\[
a = d \sqrt{h^2 + k^2 + l^2}
\]  

(3.2)

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 [13] function \( F(\theta) \) is given as

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

(3.3)

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

\[
\rho_{x-ray} = \frac{8M_A}{N_A a_c^3} \text{g/cm}^3
\]  

(3.4)

where \( N_A \) is Avogadro's number \((6.02 \times 10^{23} \text{ mol}^{-1})\), \( M_A \) is the molecular weight. The porosity was calculated from the relation as:

\[
P(\%) = \left\{ 100 \left( \rho_{x-ray} - \rho_{\text{exp}} \right) / \rho_{x-ray} \right\} \%
\]

(3.5)

where \( \rho_{\text{exp}} \) is the bulk density measured by the formula \( \rho_{\text{exp}} = M / V \) [12].

3.6 Microstructural Investigation

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 the different sintering temperatures of the samples were chosen for this purpose. The samples were visualized under a high-resolution optical microscope (Olympus DP-70) and then photographed. 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.

3.7 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 3.7.1 and 3.7.2.

3.7.1 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 behavior 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 [1] can be expressed as follows:

\[
Z = R + jX = j\omega L_0 \mu = j\omega L_0 (\mu' - j\mu'')
\]

(3.6)

where the resistive part is

\[
R = \omega L_0 \mu''
\]

(3.7)

and the reactive part is

\[
X = \omega L_0 \mu'
\]

(3.8)

The RF permeability can be derived from the complex impedance of a coil, $Z$, given by equation (3.6). The core is taken as toroidal to avoid demagnetizing effects. The quantity $L_0$ is derived geometrically as shown in section 3.7.2.

### 3.7.2 Frequency dependent permeability

The frequency characteristics of the Ni-Zn ferrite samples i.e. the initial permeability spectra were investigated using a Wayne Kerr Precision Impedance Analyzer (6500B series). The complex permeability measurements on toroid shaped specimens were carried out at room temperature on all the samples in the frequency range 100 Hz - 120 MHz. The real part ($\mu'_i$) and imaginary part ($\mu''_i$) of the complex permeability were calculated using the following relations [4]:

\[
\mu'_i = L_s / L_0
\]

and

\[
\mu''_i = \mu'_i \tan \delta,
\]

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 ($N = 4$), $S$ 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 $\frac{\mu'_i}{\tan \delta}$.
3.8 Néel Temperature Measurement

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

Néel temperature was measured from the temperature dependent initial permeability. For this measurement, the sample was kept inside a cylindrical 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. Therefore, a slow heating rate was used to eliminate this problem. Also, a slow heating ensures accuracy in the determination of Néel 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.

References:


CHAPTER 4
RESULTS AND DISCUSSION

The polycrystalline ferrites of composition \( \text{Ni}_{0.50}\text{Zn}_{0.50-x}\text{Ti}_{x/2} \quad x/2\text{Fe}_2\text{O}_4 \) \( (x=0.00 \text{ to } 0.27 \text{ in steps of } 0.03) \) were studied. All ferrite samples were sintered at temperatures of 1250, 1300, 1350 and 1400°C for four hours in air. Structural and surface morphology were studied by X-ray diffraction and optical microscopy respectively. The magnetic properties of the ferrites were characterized with high frequency (100 Hz-120 MHz) complex permeability and temperature dependent permeability measurements. The effects of microstructure, composition and sintering temperature on the complex permeability of these ferrites are discussed. The effect of varying substitution and sintering temperature on the complex permeability of these ferrites are discussed.

4.1 X-ray Diffraction Analysis

The X-ray diffraction (XRD) was performed to verify the formation of spinel structure of various \( \text{Ni}_{0.50}\text{Zn}_{0.50-x}\text{Ti}_{x/2} \quad x/2\text{Fe}_2\text{O}_4 \) ferrites, in which \( \text{Zn}^{2+} \) replaced with \( \text{Ti}^{4+} \). The x-ray radiation was from Cu-K\( \alpha \) with wavelengths of 1.5405 Å \( (\alpha_1) \). The XRD patterns of these titanium substituted \( \text{Ni}_{0.50}\text{Zn}_{0.50-x}\text{Ti}_{x/2} \quad x/2\text{Fe}_2\text{O}_4 \) (with \( x = 0.00, 0.03, 0.06, 0.09, 0.12, 0.15, 0.18, 0.21, 0.24, 0.27 \) ferrites sintered at 1300°C in air are shown in Fig. 4.1.

![X-ray diffraction patterns of Ni_{0.50}Zn_{0.50-x}Ti_{x/2} x/2Fe_2O_4 sintered at 1300°C in air.](image)

Fig. 4.1: X-ray diffraction patterns of \( \text{Ni}_{0.50}\text{Zn}_{0.50-x}\text{Ti}_{x/2} \quad x/2\text{Fe}_2\text{O}_4 \) sintered at 1300°C in air.
The XRD patterns for these compositions confirm the formation of spinel ferrite with a few peaks of impurities [1]. All peaks observed in the XRD patterns are identified with their Miller indices. The XRD peaks are well indexed to the crystal planes (220), (311), (222), (400), (422), (511) and (440) of spinel ferrite. The impurity peaks are mainly from the un-reacted ingredients of these compositions at higher x composition.

4.2 Lattice Parameters

The lattice parameter, \(a\), is calculated from the XRD patterns using Nelson-Riley function, \(F(\theta)\) [2]. Fig. 4.2(a) shows \(a\)-F(\(\theta\)) plot for \(\text{Ni}_{0.50}\text{Zn}_{0.29}\text{Ti}_{0.105}\text{Fe}_{2}\text{O}_{4}\) (\(x = 0.21\)) ferrite. From \(a\)-F(\(\theta\)) plot, precise lattice constant, \(a_0\), is calculated for each sample. The lattice constant \(a\), as a function of Ti content for various \(\text{Ni}_{0.50}\text{Zn}_{0.50-x}\text{Ti}_{x/2}\text{Fe}_{2}\text{O}_{4}\) (with \(x = 0.00, 0.03, 0.06, 0.09, 0.12, 0.15, 0.18, 0.21, 0.24, 0.27\)) is presented in Fig. 4.2(b).

![Graph](image)

Fig. 4.2: (a) Variation of lattice parameter \(a\) with \(F(\theta)\) and (b) Variation of the lattice constant \(a_0\), and the mean ionic radius of the variant ion with the composition for \(\text{Ni}_{0.50}\text{Zn}_{0.50-x}\text{Ti}_{x/2}\text{Fe}_{2}\text{O}_{4}\) ferrites sintered at 1300°C

The lattice constant of different samples are given in Table 4.1. It is noticed from Fig. 4.2(b) that the lattice constant decreases with increasing of \(\text{Ti}^{4+}\) content in the \(\text{Ni}_{0.50}\text{Zn}_{0.50-x}\text{Ti}_{x/2}\text{Fe}_{2}\text{O}_{4}\) ferrites. The decrease in lattice constant \(a_0\), with addition of \(\text{Ti}^{4+}\) can be explained in terms of ionic radii. The ionic radii of the cations used in
Ni\(_{0.50}Zn_{0.50-x}Ti_{x/2}Fe_2O_4\) are 0.74 Å (Zn\(^{2+}\)), 0.69 Å (Ni\(^{2+}\)), 0.609 Å (Ti\(^{4+}\)) and 0.645 Å (Fe\(^{3+}\)) [3]. Here Zn\(^{2+}\) is substituting by half of Ti\(^{4+}\) ion. So a small decrease in lattice constant is expected by increasing Ti content.

The samples under investigation have the chemical composition \(Ni_{0.50}Zn_{0.50-x}Ti_{x/2}Fe_2O_4\). Therefore, the mean ionic radius of the variant ions for composition \((Ni_{0.50}Zn_{0.50-x}Ti_{x/2}Fe_2O_4)\) can be written as

\[
 r(\text{variant}) = (0.50-x)r_{Zn^+}+(0.5x)r_{Ti^4+}
\]  

(4.1)

where \(r_{Ti}\) is the radius of Ti\(^{4+}\) ion ( =0.609 Å) and \(r_{Zn}\) is the ionic radius of Zn\(^{2+}\) ion (=0.74 Å). The variation of \(r(\text{variant})\) with Ti content is shown in Fig. 4.2(b), where it decreases with increasing Ti content.

### 4.3 Density and porosity

The X-ray density, bulk density and porosity of the \(Ni_{0.50}Zn_{0.50-x}Ti_{x/2}Fe_2O_4\) (with \(x = 0.00\) to 0.27 in steps of 0.03) ferrites sintered at different temperatures are given in Table 4.1. The bulk density \(\rho_b\) of each composition of \(Ni_{0.50}Zn_{0.50-x}Ti_{x/2}Fe_2O_4\) ferrites were measured by Archimede’s principle using water. X-ray density and the porosity of each sample were calculated using equation 3.4 of chapter 3.
Table 4.1: The lattice parameter, density, porosity and average grain size of the \( \text{Ni}_{0.50}\text{Zn}_{0.50-x}\text{Ti}_{x/2}\text{Fe}_{2-x/2}\text{O}_4 \) samples sintered at various temperatures with fixed dwell time 4 hrs.

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<th>( \rho_B ) (g/cm(^3))</th>
<th>( P ) (%)</th>
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Fig. 4.3 shows the variation of theoretical density, $\rho_{th}$ and bulk density, $\rho_B$ with Ti content in $Ni_{0.50}Zn_{0.50-x}Ti_{x/2}Fe_2O_4$ sintered at (a) 1250°C, (b) 1300°C, (c) 1350°C, and (d) 1400°C in air.

Fig. 4.3 shows the variation of theoretical density of the samples sintered at different temperature. As Ti contents increasingly substituted Zn contents in the $Ni_{0.50}Zn_{0.50-x}Ti_{x/2}Fe_2O_4$ ferrites, lattice constant, $a_0$ and the molecular weight of the each sample decreases and resulting theoretical density, $\rho_{x-ray}$ decreases. So the X-ray density depends on the lattice constant and the molecular weight of the samples. Both theoretical and bulk density decrease in a similar way with the increase of Ti content in $Ni_{0.50}Zn_{0.50-x}Ti_{x/2}Fe_2O_4$ ferrites for a fixed sintering temperature. As shown in fig. 4.3, it can be observed that the X-ray densities are larger in magnitude than corresponding bulk densities. This may be due to the presence of pores in the samples.
From Fig. 4.4 it is noticed that the bulk density decreases and porosity increases with increasing titanium content in the $\text{Ni}_{0.50}\text{Zn}_{0.50-x}\text{Ti}_{x/2}\text{Fe}_{2}O_{4}$ ferrites. The decrease in bulk density can be attributed to the difference in atomic weight of the ferrites components. The atomic weight of $\text{Ti}^{4+}$ (47.88 amu) is less than that of $\text{Zn}^{2+}$ (65.39 amu) [4].

Fig. 4.4: Variation of bulk density, $\rho_B$ and Porosity, P (%) with Ti content in $\text{Ni}_{0.50}\text{Zn}_{0.50-x}\text{Ti}_{x/2}\text{Fe}_{2}O_{4}$ sintered at (a) 1250°C, (b) 1300°C, (c) 1350°C, and (d) 1400°C in air

Fig. 4.5 shows the variation of bulk density and porosity with the variation of sintering temperature for $\text{Ni}_{0.50}\text{Zn}_{0.50-x}\text{Ti}_{x/2}\text{Fe}_{2}O_{4}$ ferrites. It is noticed that the density of the samples have increasing trend with increasing sintering temperature for $x=0$ to $x=0.09$ and porosity, P (%) of the samples decreased. With increasing sintering
temperature the number of pores is reduced, as a result of which individual grain comes closer to each other and the effective area of grain to grain content increases, resulting in greater densification or less porosity.

**Fig. 4.5:** Variation of bulk density, \( \rho_B \) and Porosity, \( P(\%) \) with temperature for samples (a) \( \text{Ni}_{0.50}\text{Zn}_{0.50}\text{Fe}_2\text{O}_4 \), (b) \( \text{Ni}_{0.50}\text{Zn}_{0.47}\text{Ti}_{0.015}\text{Fe}_2\text{O}_4 \), (c) \( \text{Ni}_{0.50}\text{Zn}_{0.44}\text{Ti}_{0.03}\text{Fe}_2\text{O}_4 \), (d) \( \text{Ni}_{0.50}\text{Zn}_{0.41}\text{Ti}_{0.045}\text{Fe}_2\text{O}_4 \), (e) \( \text{Ni}_{0.50}\text{Zn}_{0.38}\text{Ti}_{0.06}\text{Fe}_2\text{O}_4 \) and (f) \( \text{Ni}_{0.50}\text{Zn}_{0.35}\text{Ti}_{0.075}\text{Fe}_2\text{O}_4 \)
For the samples, \( x > 0.09 \) of \( Ni_{0.50}Zn_{0.50-x}Ti_{x/2}Fe_{2}O_{4} \) ferrites, it is found that density increases with increasing sintering temperature up to certain limit (1350°C), then decreases. Accordingly, porosity, \( P \) (%) of the samples decreases with increasing sintering temperature up to the same limit and an increasing trend observed beyond it. At higher sintering temperature density decreased because the intragranular porosity increase because of discontinuous grain growth. It is known that porosity of the ceramic samples results from two sources, intragranular porosity and intergranular porosity. 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 leads to poor magnetic and mechanical properties. Thus the total porosity could be written as $P = P_{\text{intra}} + P_{\text{inter}}$. The intergranular porosity mainly depends on the grain size [5-6].

4.4 Microstructures

The optical micrographs of various $\text{Ni}_{0.50}\text{Zn}_{0.50-x}\text{Ti}_{x/2}\text{Fe}_{2}O_{4}$ ferrites sintered at 1250, 1300, 1350 and 1400°C temperature are shown in figs. 4.6 to 4.9. It is noticed that $\text{Ti}^{4+}$ substitution has significant influence on microstructure of the samples. It is observed from the micrograph that for sintering temperature 1250°C, the average grain size increases with the increase of titanium substitution. For sintering temperature 1300°C, the average grain size decreases as the titanium content increases up to $x=0.09$ and for higher titanium content, $x \geq 0.12$ the grain size increases. For sintering temperature 1350 and 1400°C, the average grain size remain unchanged for lower titanium content and after that the grain size increases with the increase in titanium substitution.

The average grain size decreases gradually with the increase of $\text{Ti}^{4+}$ due to the fact that the melting point of Zn (692.68 K) is less than that of titanium (1941 K) and the grain size decrease is as expected. The increase in grain size for $x \geq 0.12$, perhaps related to complicated chemistry of titanium with other materials. It is also found that the sintering temperatures have influence on grain size for a particular composition.

The average grain size of all samples increases with the sintering temperatures which are shown in Table 4.1. The interaction of grain boundary and porosity along with sintering temperature is important in determining the limiting grain size [7]. During the early stage of sintering temperature, the volume fraction of pores is large and the grain growth is inhibited. Once the porosity decreased as the sintering temperature increases many of small pores disappear. The grains that grow consume their neighbor and become larger. The behavior of grain growth reflects the competition between the driving force for grain boundary movement and the retarding force exerted by pores [8]. 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 to the reduction of the sintered density.
Fig. 4.6: The optical micrographs of $Ni_{0.50}Zn_{0.50-x}Ti_{x/2}Fe_{x/2}O_4$ samples sintered at temperatures 1250 °C.
Fig. 4.7: The optical micrographs of $Ni_{0.90}Zn_{0.50-x}Ti_{x/2}Fe_{3}O_{4}$ samples sintered at temperatures $1300$ °C.
Fig. 4.8: The optical micrographs of Ni$_{0.50}$Zn$_{0.50}$Ti$_{x/2}$Fe$_{2-x/2}$O$_4$ samples sintered at temperatures 1350 °C.
Fig. 4.9: The optical micrographs of $Ni_{0.50}Zn_{0.50-x}Ti_{x/2}Fe_{x/2}O_4$ samples sintered at temperatures 1400 °C.
4.5 Complex initial permeability

The initial permeability ($\mu_i$) of various $Ni_{0.50}Zn_{0.50-x}Ti_{x/2}Fe_2O_4$ ferrites has been measured in the frequency range of 100 Hz-120 MHz. Fig. 4.10 shows the complex initial permeability spectra for various $Ni_{0.50}Zn_{0.50-x}Ti_{x/2}Fe_2O_4$ ferrites sintered at 1250, 1300, 1350 and 1400°C.

The general characteristic of the spectra shown in Figs. 4.10 is that real part of the initial permeability, $\mu_i$, remains fairly constant in the frequency range up to some critical frequency characterized by the onset of resonance. At these frequencies, after a small rise, the curves drop rapidly. This trend of the curve is clearly visible for lower Ti content, i.e. $x \leq 0.15$. It is also observed that with increasing Ti substitution in $Ni_{0.50}Zn_{0.50-x}Ti_{x/2}Fe_2O_4$ ferrites, the permeability decreases but the resonance frequency increases.

The $\mu_i$ increases with increasing sintering temperature, $T_s$ up to 1350°C as shown in Table-4.1 and it decreases at 1400°C. The resonance frequency decreases with increasing $T_s$ for lower Ti substitution, i.e. $x \leq 0.15$. Similar behavior was observed by Wang et al in barium ferrites [9]. The resonance frequency increases with increasing $T_s$ for higher Ti substitution.

The resonance frequency, $f_r$ and $\mu_i$ values measured at room temperature and at 100 Hz are listed in Table 4.1. The highest value of $\mu_i$ (=348.02) is observed for $Ni_{0.50}Zn_{0.50}Fe_2O_4$ ferrite sintered at 1350°C where the sample is without Ti substitution. After Ti substitution, highest $\mu_i$ (319.69) was found for $Ni_{0.50}Zn_{0.44}Ti_{0.03}Fe_2O_4$ ferrite sintered at 1300°C. On the other hand, maximum resonance frequency, $f_r$ (15.20 MHz) is observed for $Ni_{0.50}Zn_{0.38}Ti_{0.06}Fe_2O_4$ ferrite sintered at 1250°C with the corresponding value of $\mu_i$ =50.76.
Fig. 4.10: The variation of $\mu_i^{\prime}$ and $\mu_i^{\prime\prime}$ spectra for $Ni_{0.50}Zn_{0.50-x}Ti_xFe_2O_4$ sintered at (a) 1020°C, (b) 1300°C, (c) 1350°C and (d) 1400°C in air.
Fig 4.11 shows the variation of $\mu_i$ (at 1.00 MHz) and $f_r$ with Ti content for $Ni_{0.50}Zn_{0.50-x}Ti_x/2Fe_{2}O_4$ ferrites sintered at 1250, 1300, 1350 and 1400°C in air. It is found that with the increase of sintering temperature, $\mu_i$ decreases and $f_r$ increases. Approximately an inversely proportional relation between $\mu_i$ and $f_r$ confirms the Snoek’s limit [10]. Similar trend is observed for all other sintering temperatures.

The permeability phenomena can be explained in the following way. The permeability of polycrystalline ferrite is related to two different magnetizing mechanisms: spin rotation and domain wall motion [11-12, 19], which can be described as follows:

$$\mu_i = 1 + \chi_w + \chi_{spin}$$  \hspace{1cm} (4.2)
where $\chi_{w}$ is the domain wall susceptibility and $\chi_{\text{spin}}$ is intrinsic rotational susceptibility. $\chi_{w}$ and $\chi_{\text{spin}}$ may be written as: $\chi_{w} = 3\pi M_{s}^{2}D/4\gamma$ and $\chi_{\text{spin}} = 2\pi M_{s}^{2}/K$ with $M_{s}$ saturation magnetization, $K$ the total anisotropy, $D$ the average grain size, and $\gamma$ the domain wall energy. $M_{s}$ decreases linearly with increasing titanium concentration [13], hence with the increasing $Ti$ substitution the decrease of permeability, $\mu_{i}'$ of $Ni_{0.50}Zn_{0.50-x}Ti_{x/2}Fe_{2}O_{4}$ ferrites is expected.

Moreover, the magnetic properties of soft ferrite are strongly influenced by it’s composition, additives and microstructures. In microstructure studies of $Ni_{0.50}Zn_{0.50-x}Ti_{x/2}Fe_{2}O_{4}$ ferrites, it is observed that average grain size increases with the function of $Ti$ content for sintering temperature 1250 and 1400˚C, whereas the grain size decreases for lower Ti content of sintering temperature 1300 and 1350˚C. But for all the cases, permeability of the ferrites decreases. Therefore in present case, variation of the initial permeability is independent of grain size.

The increasing value of $\mu_{i}'$ with the increase of $T_{s}$ up to 1350˚C is due to lower porosity for samples sintered at higher sintering temperature. The porosity causes hindrance to the domain wall motion. As sintering temperature increases pores and voids are reduced. The value of $\mu_{i}'$ decreases above 1350˚C, because the sample heated at higher sintering temperatures (above optimum $T_{s}$) contains increasing number of
pores within the grains which results a decrease in permeability. Similar trend was observed by Guillaud [14].

The variation of initial permeability $\mu_i$, with frequency can be explained on the basis of Globus model [15]. According to this model, the relaxation character is

$$(\mu_i - 1)^2 f_r = \text{constant.} \quad (4.3)$$

Initial permeability in ferrites is due to domain wall displacement and remains constant with frequency as long as there is no phase lag between the applied field and domain wall displacement. In ferrites, two resonance peaks are normally observed: one at lower frequency (1-100 MHz) which is due to the domain wall oscillations [16-17] and the other at higher frequencies (~1 GHz) due to Larmour precession of electron spins [18]. In the present case, the resonance frequency of domain wall oscillations is found in the range of 1.5 MHz~25 MHz.

Fig. 4.13: The variations of Loss factor with frequency for $Ni_{0.5}Zn_{0.5-x}Ti_{x/2}Fe_2O_4$ ferrites sintered at (a)1250°C, (b)1300°C, (c) 1350°C and (d) 1400°C in air.
The variation of loss factor, $\tan \delta = \mu''/\mu'$ with frequency for all samples has been studied. Fig. 4.13 shows the variations of loss factors with frequency for $Ni_{0.50}Zn_{0.50-x}Ti_{x/2}Fe_2O_4$ ferrites sintered at 1250, 1300, 1350 and 1400°C.

At lower frequencies, a rapid decrease in loss factor is observed and at higher frequencies, it remains constant with frequency. The loss factor observed to decrease with the sintering temperature up to 1350°C. The loss factors of $Ni_{0.50}Zn_{0.41}Ti_{0.045}Fe_2O_4$ ferrite at different sintering temperatures are shown in Fig. 4.14.

![Graph showing loss factor vs. frequency for Ni-Zn-Ti-Fe ferrites sintered at different temperatures.](image)

**Fig. 4.14:** The variations of Loss factor with frequency for $Ni_{0.50}Zn_{0.41}Ti_{0.045}Fe_2O_4$ ferrite sintered at 1250, 1300, 1350 and 1400°C in air.

From the loss factor, the relative quality factor (or $Q$-factor) is calculated. The $Q$-factor versus frequency plots of all the samples sintered at 1250, 1300, 1350 and 1400°C are shown in Fig. 4.15.
Calculated $Q$-factors for various $Ni_{0.50}Zn_{0.41}Ti_{0.045}Fe_{2}O_{4}$ ferrites sintered at various temperatures are listed in Table 4.1. It can be seen that the value of $Q$-factor increases with an increase of frequency and shows a peak around 0.6–1.5 MHz. It is observed from fig 4.15 (a) that the maximum value of $Q$-factor, $Q_{\text{max}}$, decreases with increasing Ti contents linearly for sintering temperature 1250°C, but the change of $Q_{\text{max}}$ is different for other sintering temperature. It shows a similar trend of $\mu'_i$ of the present system as it is proportional to the $Q$-factor from the relation: $Q = \mu'_i / \tan\delta$, as loss factor also shows an increasing trend with the increase of Ti contents. Among all the studied samples, highest value of $Q$-factor (=10024) is observed for $Ni_{0.50}Zn_{0.44}Ti_{0.03}Fe_{2}O_{4}$ ferrite sintered at 1300°C, similar to $\mu'_i$. The maximum value of $Q$-factor, $Q_{\text{max}}$ shows comparatively higher values for $Ni_{0.50}Zn_{0.50-x}Ti_{x/2}Fe_{2}O_{4}$ ferrites sintered 1300 and 1350°C.
Fig. 4.16: (a) The variations of $Q_{\text{max}}$ with Ti content for $\text{Ni}_{0.50}\text{Zn}_{0.50-x}\text{Ti}_{x/2}\text{Fe}_2\text{O}_4$ ferrites sintered at 1300°C and (b) the variations of $Q_{\text{max}}$ for $\text{Ni}_{0.50}\text{Zn}_{0.44}\text{Ti}_{0.03}\text{Fe}_2\text{O}_4$ ferrite sintered at 1250, 1300, 1350 and 1400°C.

Fig 4.16 (a) shows the variation of $Q$ values with Ti contents sintered at 1300°C. The maximum $Q$ value obtained for $\text{Ni}_{0.50}\text{Zn}_{0.50-x}\text{Ti}_{x/2}\text{Fe}_2\text{O}_4$ ferrite sintered at 1300°C. Fig 4.16 (b) shows the variation of $Q$ value for $\text{Ni}_{0.50}\text{Zn}_{0.44}\text{Ti}_{0.045}\text{Fe}_2\text{O}_4$ ferrite for different sintering temperature. Above 1350°C, $Q$-factor is found to decrease because at higher sintering temperature, abnormal grain growth occurs which creates trapped pores inside the grain. This increasing amount of pores influences the loss factor and turns into higher value which results a lower value of $Q$-factor.

4.6 Temperature Dependent Initial Permeability and Néel Temperature

Temperature dependence of $\mu_i$ is an important factor for designing any magnetic component. The $\mu_i$ as a function of temperature for $\text{Ni}_{0.50}\text{Zn}_{0.50-x}\text{Ti}_{x/2}\text{Fe}_2\text{O}_4$ ferrites ($x = 0.00, 0.03, 0.06, 0.09, 0.12, 0.15, 0.21, 0.27$) sintered at 1350 °C shown in Fig. 4.17. The $\mu_i$ measured at a constant frequency (100 kHz) of a sinusoidal wave. It was found that initial permeability increases with increasing temperature and it falls abruptly close to the Néel temperature where the ferrite samples change state. The sharp falling of $\mu_i$ with temperature suggests the formation of the ferrite of the samples, which have been confirmed with the result of XRD diffraction. The Néel temperature, $T_N$, 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 $T_N$. From these curves the $T_N$’s of these samples are determined.
Fig 4.18 represents the variation of Néel temperature as a function of Ti content of Ni$_{0.50}$Zn$_{0.50-x}$Ti$_{x/2}$Fe$_2$O$_4$ ferrites. The $T_N$ is the transition temperature above which the ferrite material losses its magnetic properties. The Néel temperature gives an idea of the amount of energy takes to break up the long-range ordering (magnetic) in the materials. It is observed that $T_N$ increases with increasing Ti content [25].

The increase of $T_N$ with increasing Ti content may be explained as a modification of the A-B exchange interaction strength due to the change of the Fe$^{3+}$...
distribution between A and B sites. This could be attributed to the decrease in distance (Hopping length, $L$) between the magnetic ions of tetrahedral A-site ($L_A$) and the octahedral B-sites ($L_B$). This is also confirmed with decrease lattice parameter in $\text{Ni}_{0.50}\text{Zn}_{0.50-x}\text{Ti}_{x/2}\text{x/2Fe}_2\text{O}_4$ ferrites with increasing Ti content. The shorter distance between moments in $\text{Ni}_{0.50}\text{Zn}_{0.50-x}\text{Ti}_{x/2}\text{x/2Fe}_2\text{O}_4$ ferrites lead to increase the A-B interaction and consequently $T_N$ increases.

Anisotropy constants of magnetic materials 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 $T_N$ [20]. 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 $T_N$. This occurs, because the crystal anisotropy normally decreases with increasing temperature [22]. The initial permeability varies as $\mu_i \approx M_S^2 / K_1^{1/2}$ [20, 21], where $M_S$ is the saturation magnetization and $K_1$ is the anisotropy constant. Since anisotropy decreases faster than magnetization on heating, the increase of initial permeability with temperature expected, and then drops for the paramagnetic phase for the sample. The peak near $T_N$ is known as the ‘Hopkinson’ peak [20].

Reference:


[16] Kang, S. H. and Yoo, H. I.; “The effect of nonstoichiometry (δ) on the magnetic properties of (Mg0.22Mn0.78Fe0.71)3-δO4 ferrite”, J. Appl. Phys., Vol. 88, pp 4754-4757, 2000.


CHAPTER 5
CONCLUSIONS

5.1 Conclusions
Form the study of \( \text{Ni}_{0.50}\text{Zn}_{0.50-x}\text{Ti}_{x/2} \text{Fe}_{x/2} \text{O}_4 \) ferrites, the following conclusions are drawn:

- XRD analysis of \( \text{Ni}_{0.50}\text{Zn}_{0.50-x}\text{Ti}_{x/2} \text{Fe}_{x/2} \text{O}_4 \) ferrites with different Ti content substitution confirms formation of spinel structure. Few impurity peaks were found in XRD pattern for higher Ti contents \((x \geq 0.09)\).

- The lattice constant slightly decreases with increasing of Ti content in \( \text{Ni}_{0.50}\text{Zn}_{0.50-x}\text{Ti}_{x/2} \text{Fe}_{x/2} \text{O}_4 \) ferrites. This phenomenon is explained on the basis of ionic radii. In the present case variant contents are Ti and Zn, while Zn is substituted by Ti. The variation of the lattice constant \( a_o \), and the mean ionic radius of the variant ions show similar decreasing trend for \( \text{Ni}_{0.50}\text{Zn}_{0.50-x}\text{Ti}_{x/2} \text{Fe}_{x/2} \text{O}_4 \) ferrites.

- The density variations are observed in \( \text{Ni}_{0.50}\text{Zn}_{0.50-x}\text{Ti}_{x/2} \text{Fe}_{x/2} \text{O}_4 \) ferrites with different Ti content substitution. It is observed that the density of \( \text{Ni}_{0.50}\text{Zn}_{0.50-x}\text{Ti}_{x/2} \text{Fe}_{x/2} \text{O}_4 \) ferrites decreases with increasing Ti contents to substitute Zn contents in the samples. The decrease in density is due to the difference in atomic weight of the ferrites components, Ti\(^{4+}\) \((47.88 \text{ amu})\) and Zn\(^{2+}\) \((65.39 \text{ amu})\) ions.

- Sintering temperature has an effect on the density and porosity of the samples. It is observed that the density of \( \text{Ni}_{0.50}\text{Zn}_{0.50}\text{Fe}_{2} \text{O}_4 \), \( \text{Ni}_{0.50}\text{Zn}_{0.47}\text{Ti}_{0.015} \text{Fe}_{0.015} \text{O}_4 \), \( \text{Ni}_{0.50}\text{Zn}_{0.44}\text{Ti}_{0.03} \text{Fe}_{0.03} \text{O}_4 \) and \( \text{Ni}_{0.50}\text{Zn}_{0.41}\text{Ti}_{0.045} \text{Fe}_{0.045} \text{O}_4 \) ferrites increased with increasing sintering temperature up to 1350°C and the density remain unchanged for sintering temperature above 1350°C. On the other hand, porosity \((P)\) of the sample decreased with increasing sintering temperature up to 1350°C and remained unchanged beyond it. 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. It is observed that the density of \( \text{Ni}_{0.50}\text{Zn}_{0.38}\text{Ti}_{0.06} \text{Fe}_{0.06} \text{O}_4 \),
Ni$_{0.50}$Zn$_{0.35}$Ti$_{0.075}$Fe$_2$O$_4$, Ni$_{0.50}$Zn$_{0.32}$Ti$_{0.09}$Fe$_2$O$_4$ and Ni$_{0.50}$Zn$_{0.29}$Ti$_{0.105}$Fe$_2$O$_4$ ferrites increases with increasing sintering temperature up to 1350°C, then decreases. On the other hand, porosity ($P$) of the samples decreases with increasing sintering temperature up to 1350°C and an increasing trend is shown beyond it. At higher sintering temperatures density decreases, because the intragranular porosity increases as a result of discontinuous grain growth that leads to decrease the sintered density.

As sintering temperature goes higher, enlargement of grain occurs in Ni$_{0.50}$Zn$_{0.50-x}$Ti$_{x/2}$Fe$_2$O$_4$ ferrites. The thermal energy generates a force that drives the grain boundaries to grow over pores and reinforces to increase the grain size.

Optical micrographs of Ni$_{0.50}$Zn$_{0.50-x}$Ti$_{x/2}$Fe$_2$O$_4$ ferrites show that sintering temperature has significant effect on average grain size. The average grain size of all samples increases with the sintering temperatures. It is also noticed that Ti$^{4+}$ substitutions have significant influence on microstructures of the sample.

The $\mu'_i$ and $\mu''_i$ decrease with Ti$^{4+}$ substitution in Ni$_{0.50}$Zn$_{0.50-x}$Ti$_{x/2}$Fe$_2$O$_4$ ferrite. In contrast resonance frequency is found to increase with Ti substitution. The $\mu'_i$ increases with the increase of sintering temperature up to 1350°C and above 1350°C it decreases. The increasing value of $\mu'_i$ with the increase of sintering temperature up to the 1350°C is due to the lower porosity for samples sintered at higher sintering temperature. The porosity causes hindrance to the domain wall motion. As sintering temperature increases pores and voids are reduced with increasing sintering temperature. The value of $\mu'_i$ decreases above 1350°C, because the sample heated at higher sintering temperatures (above optimum $T_s$) contains increasing number of pores within the grains which results a decrease in permeability.

It is found that resonance frequency is shifted to higher value as sintering temperature increases for all samples. An inversely proportional relation of $\mu'_i$ and $f_r$ confirms the Snoek’s limit.
The tanδ is observed to decrease with the increase of sintering temperature. From the loss factor we have calculated the relative quality factor (or $Q$ factor) for all compositions sintered at various temperatures. It is observed that $Q$ factor increases with increasing sintering temperature up to $1350^\circ C$ and beyond it shows a decreasing trend. It is also observed that $Q$ factor decreases with increasing Ti content at sintering temperature $1250^\circ C$. For sintering temperature $1300$, $1350$ and $1400^\circ C$, $Q$ factor increases for lower Ti substitution and decreases for higher Ti substitution. The highest $Q$ value obtained is probably due to the growth of lesser imperfection.

The $T_N$ increases with increasing Ti contents. The increase of $T_N$ with increasing Ti 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. This could be attributed to the decrease in distance between the moments of $A$ and $B$ sites, which is confirmed by the decrease in the lattice parameter with increasing Ti content. The shorter distances between moments in samples $Ni_{0.50}Zn_{0.50-x}Ti_{x/2}Fe_{2}O_{4}$ lead to increase the $A$-$B$ interaction and consequently the $T_N$ increases.

### 5.2 Suggestions for future work

It was found that the permeability, $\mu_i$ of $Ni_{0.50}Zn_{0.50-x}Ti_{x/2}Fe_{2}O_{4}$ ferrites decreases with Ti substitution. To confirm the magnetic properties and cation distribution of the sample, the magnetization measurement as a function of applied magnetic field would be helpful.