



**UNIVERSITI PUTRA MALAYSIA**

**EFFECTS OF NON-STOICHIOMETRY ON MAGNETIC  
PROPERTIES AND MICROSTRUCTURE OF  $\text{Ni}_{0.3}\text{Zn}_{0.7}\text{Fe}_{2\pm x}\text{O}_4$   
AND  $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_{2\pm x}\text{O}_4$**

**ROSIDAH BT. ALIAS**

**FSAS 2003 33**

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**2003**



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**By**

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**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia  
in Fulfillment of the Requirements for the Degree of Doctor of Philosophy**

**September 2003**



Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of requirements for the degree of Doctor of Philosophy

**EFFECTS OF NON-STOICHIOMETRY ON MAGNETIC PROPERTIES AND MICROSTRUCTURE OF  $\text{Ni}_{0.3}\text{Zn}_{0.7}\text{Fe}_{2-x}\text{O}_4$  AND  $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_{2-x}\text{O}_4$**

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Various non-stoichiometric compositions of Ni-Zn ferrites and Mg-Zn ferrites were investigated. The samples were prepared by the conventional sintering method while being subjected to an air atmospheric condition. The measurement of magnetic properties such as magnetic permeability, magnetic loss, Curie temperature, magnetic flux density and microstructure were performed to understand the magnetic properties of samples prepared by systematic compositional changes. X-ray diffraction results indicate that the samples are in good crystalline form. Curie temperature variation can be explained on the basis of Neel's two sub-lattices model and could be due to distribution of magnetic ions between two sub-lattices. The dependence of magnetic permeability with temperature shows that the trends exhibited by all the samples are similar. With increase in temperature, permeability increases gradually and then shows sudden drop at the Curie point because the anisotropy constant decreases more rapidly than the saturation magnetization. The dependence of permeability on iron oxide content obeys Globus model. The change of permeability in the cation-deficient region is caused



by the positive contribution of the anisotropy constant to the total anisotropy during conversion of  $\text{Fe}^{3+}$  ions to  $\text{Fe}^{2+}$  ions. However, for the anion-deficient region, the variation in permeability is mainly accounted to be due to microstructural changes.

The loss factor and the quality factor were also calculated and this study has revealed that the iron oxide concentration is a determining factor for high quality ferrites. Finally, this study shows that high permeability values of Ni-Zn and Mg-Zn ferrites occur in the cation-deficient region with  $x = 0.002-0.006$  weight percent.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**KESAN TAK STOIKIOMETRI TERHADAP SIFAT MAGNET DAN  
MIKROSTRUKTUR  $\text{Ni}_{0.3}\text{Zn}_{0.7}\text{Fe}_{2\pm x}\text{O}_4$  DAN  $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_{2\pm x}\text{O}_4$**

Oleh

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Berbagai komposisi tak-stoikiometri Ni-Zn ferit dan Mg-Zn ferit telah dikaji. Sampel-sampel disediakan dengan kaedah pensinteran lazim dan didedahkan kepada keadaan atmosfera udara. Sifat magnet yang diukur seperti ketelapan magnet, kehilangan magnet, suhu Curie, ketumpatan magnet tepu dan mikrostruktur telah dikaji untuk memahami ciri-ciri magnet bagi sampel yang disediakan melalui perubahan komposisi yang sistematik. Pembelauan sinar-X menunjukkan sampel berada dalam bentuk hablur yang baik. Perubahan suhu Curie boleh diterangkan berasaskan kepada model dua sub-kekisi Neel dan kepada taburan ion-ion bermagnet pada kedua-dua tapak. Kebergantungan ketelapan magnet terhadap suhu menunjukkan lengkung yang dipamerkan untuk semua sampel adalah sama. Dengan pertambahan suhu, ketelapan meningkat dan menunjukkan penurunan yang mendadak pada titik Curie disebabkan oleh pemalar ketak isotropan mengurang secara mendadak berbanding dengan

ketelapan magnet dengan iron mematuhi model Globus. Perubahan ketelapan pada kawasan kurang-kation adalah disebabkan oleh sumbangan pemalar ketakisotropan positif terhadap jumlah ketakisotropan semasa pertukaran ion  $\text{Fe}^{3+}$  kepada  $\text{Fe}^{2+}$ . Bagaimanapun untuk kawasan kurang-anion, perubahan ketelapan terutamanya disebabkan oleh perubahan mikrostruktur.

Faktor kehilangan dan faktor kualiti juga dikira dan kajian ini telah menunjukkan kepekatan oksida ferum adalah faktor penentu untuk kualiti ferit yang baik. Akhir sekali, kajian ini menunjukkan nilai ketelapan tinggi Ni-Zn dan Mg-Zn ferit terhasil pada kawasan kurang kation dengan  $x = 0.002-0.006$  peratus berat.

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## LIST OF SYMBOLS AND ABBREVIATIONS

A	cross sectional area
H	applied field
H <sub>c</sub>	coercive force
μ <sub>B</sub>	Bohr magneton
T <sub>c</sub>	Curie temperature
ρ	resistivity
f	frequency
μ'	real of permeability or magnetic loss
μ''	imaginary part of permeability
B	induction
B <sub>s</sub>	saturated induction
B <sub>r</sub>	remanence induction
L	inductance
D <sub>o</sub>	outer diameter
D <sub>i</sub>	inner diameter
Tan δ	loss tangent
N	number of wire turns
PVA	polyvinyl alcohol
RLF	relative loss factor
σ	internal stress
T	temperature
t	thickness
K <sub>1</sub>	first anisotropy constant.



## CHAPTER 1

### INTRODUCTION

#### General

Ferrites are ceramic ferromagnetic materials generally gray or black in color containing oxygen and at least two kinds of metal ions, one of which is usually  $\text{Fe}^{3+}$ . They are among the most widely used materials, in many low cost, high performance electronic devices since 19<sup>th</sup> century (Ishino, 1987). Commercially, ferrites are classified into three important classes due to specific crystal structures:

- 1) soft ferrites, 2) garnet structure and 3) hard ferrites with hexagonal structure (Callister, 1990; Levinson, 1988). However, this study only consider the soft ferrites with spinel structure.

Soft ferrites particularly Nickel-Zinc and Manganese-Zinc ferrites are of great interest in high frequency applications including power line filters, local area networks transformers, filter inductors and electromagnetic interference suppressors which are challenging the ferrite industry to produce high quality cores capable of meeting increasing demands. Their usage in this field has been growing unabatedly for several decades (Zhu, 2000) since the appearance of the first commercial ferrite products in about 1945 (Wolfarth, 1980). Recently, Mg-Zn ferrites have become important to industry, because of their applications in intermediate frequency

transformers and antenna cores. They are replacing Mn-Zn ferrites in these area besides offering the advantage of easy synthesis (Bhosale et al., 1997).

The main motivation for the uses of these materials are high permeability and low magnetic loss (Znidarsic, 1996, Nomura, 1995) which can only be achieved by carefully controlling the ferrite microstructure and grain boundary chemistry in addition to the chemical compositions. The preparation of high permeability ferrite is a complicated task because there are strongly dependent on several factors such as chemical composition, chemical purity, homogeneity, microstructure (grain size/pore size), stoichiometry and so on (Kang, 2000; Park, 2001; Patil, 1998). Oxygen potential in sintering atmosphere is also well known to have a great influence on magnetic and electrical properties. That is to say, it governs the non-stoichiometry of spinel phase, which can be responsible for the performance of materials (Otsuki and Yamada, 1995).

Ferrite performance is not determined by the high value of initial permeability alone; a low loss value, represented by quality factors, relative loss factors and power loss, is also important. Moreover, high saturation flux density, high-fired density and frequency characteristics are necessary in order to achieve high performance with low cost magnetic materials.

The difference in properties and performance of ferrites as compared with most other magnetic materials is due to the fact that the ferrites are oxide materials rather than metal. Ferromagnetism is derived from the unpaired electron spins in only a few metal atoms, these being iron, cobalt, nickel, manganese and rare earth elements. It is

not surprising that the highest magnetic moments and therefore the highest saturation magnetizations are to be found in metals. The oxides, on the other hand suffer from a dilution effect of the large oxygen ions in the crystal lattice. In addition the net magnetic moment resulting from ferromagnetic alignment of atomic spins is reduced because a different, less efficient type of exchange mechanism is operative. The oxygen ions do serve a useful purpose, however since they insulate the metal ions and therefore greatly increase the resistivity. These properties make the ferrites especially useful at higher frequencies.

The progress of soft ferrites was started since 1936 using Cu-Zn ferrite that was used for antenna and intermediate frequency transformer. But due to some problems its production was discontinued about 1970. They were gradually replaced by Ni-Cu-Zn ferrite. Presently Ni-Cu-Zn ferrite has many applications including noise filter, rotary transformer and multi-layer chip component. The advantages of these chip devices are the excellent magnetic shielding and capability of miniaturization (Hsu, 1995).

Presently, Mn-Zn ferrite acted as the mainstream industrial product of core materials. The main core characteristics are core losses, which contribute to the major part of the total electric loss (Znidarsic, 1996). The core loss of Mn-Zn ferrite has been remarkably decreased year by year as the result of the technical achievements made by many workers (Akashi, 1961; Stinjtjes, 1989).

The Ni-Zn ferrites cores exhibit volume resistivity, moderate temperature stability and high Q factors for the 500 kHz to 100 MHz frequency range. They are well suited for low power, high inductance resonant circuits. Their low loss on frequency

higher than 1 MHz made these ferrites suitable for low flux density applications. The Mn-Mg ferrites with rectangular hysteresis loop properties and usually used for memory and switching cores in digital computers and one of the fastest growing and practically applicable ferrites.

Since 1950s, ferrite materials have been used for many microwave devices such as magneto-static resonator, switches, turnable electro optics modulator, shifters etc. Presently, bulk ferrites and thick film ferrites yttrium iron garnet and Ni-Zn ferrites and Mn-Mg-Zn are most often used as microwave ferrites (Horvath, 2000).

In the preparation of microwave ferrite materials particular attention should be given to the purity of the raw materials, stoichiometry of the composition and the porosity as well as grain characteristics of the final product. A ferrite wave absorber (Ishino, 1987) has received much worldwide attention in response to an increasing demand of EMC. The material used for wave absorbers should have high permeability materials from frequency attenuation from 100 kHz to 1 MHz (Bruce, 1990).

Automotive electronic uses will also expand, for example in electrochemical valve opening and closing and direct fuel injection. From the standpoint of advanced Ceramics, magnetic materials should be developed with new manufacturing technologies such as synthesis by the super-lattice process and plasma jet spraying. Improvement in the conventional sintering process is also urgently required, such as casting ferrite, homogenous ferrite film, single crystal fiber and no pores ferrites (Sugimoto, 1999). However, the new challenge of ferrite technology should consider the cost as the most important factor to an increase in performance.

## Non-Stoichiometry Overview

Soft magnetic materials (ferrites) are non-stoichiometric compound (Tanaka, 1978) where the term of the non-stoichiometry of spinel ferrites  $(\text{Me, Fe})_{3-8}\text{O}_4$  (Me = Mg, Mn, MgMn and so forth) is due to a direct measure of average oxidation states of transition metal ions and point defect concentration therein (Kang et al., 1999). Consequently, it plays an important role in the magnetic, electrical and mechanical properties of ferrite materials such as permeability, magnetic loss, disaccommodation and microstructure (Gundlach, 1998). So, it is necessary to study the magnetic properties as a function of non-stoichiometry not only to the oxygen partial pressure but also to the  $\text{Fe}^{2+}$  content in the bulk and the grain boundary (Inaba, 1997).

Non-stoichiometry effects on the ceramic properties especially for the ferrite material usually exist with two valence (or ionic) states for one of the ion types. For example, the iron oxide which can be present in both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  states; the number of each of these ion types depends on the temperature and the ambient oxygen pressure. The formation of an  $\text{Fe}^{3+}$  ion disrupt the electro-neutrality of the crystal by introducing an excess +1 charge, which must be offset by some type of defect. This may be accomplished by the formation of one  $\text{Fe}^{2+}$  vacancy (or removal of two positive charges) for every two  $\text{Fe}^{3+}$  ions that are formed. The crystal is no longer stoichiometric because there is one more O ion than Fe ion; however the crystal remains electrically neutral. This phenomenon is fairly iron-oxide, and in fact, its chemical formula is often written as  $\text{Fe}_{1-x}$  (where x is some small and variable fraction substantially less than unity) to indicate a condition of non-stoichiometry with a deficiency of Fe (Callister, 1990).

## Ni-Zn ferrites

Ni-Zn ferrites were developed for a wide range of applications where high permeability and low loss were the main requirement. Ni-Zn ferrite is still one of the most important ferrites for such application and constitutes a substantial portion of present-day soft ferrite production. Ni-Zn ferrite has been extensively used as core materials for large number of devices and electrical components and its application is summarized in Table 1 (Hemeda 2001; Anil Kumar 1997; Wolfarth 1980; Seo,1999).

Table 1.1: Summary of Ni-Zn ferrite applications.

Device	Device Function	Frequencies
Inductor	Frequency selection network	1-100 MHz
Magnetic shielding } Suppression bead }	Block unwanted signal (Cellular phone)	Up to 250 MHz
Antenna rod	EM receiver	Up to 15 MHz
Recording head	Information recording	Up to 10 MHz

## Mg-Zn ferrites

Besides Ni-Zn ferrites, Mg-Zn ferrites also play a useful role in technological and magnetic application because of the favorable performance (Ahmed 2001, Rezlescu, 1998). In commercial practice, Mg-Zn ferrites used in lower requirement television yokes and fly back transformers because of the lower cost of Mg and because of the