UNIVERSITI PUTRA MALAYSIA

MAGNETIC, DIELECTRIC AND MICROSTRUCTURAL PROPERTIES OF NICKEL−ZINC FERRITE Ni0.8Zn0.2Fe2O4 PREPARED VIA CONVENTIONAL AND CO-PRECIPITATION TECHNIQUES

TANIA JAHANBIN

FS 2009 10

Abstract of the thesis presented to the Senate of Universiti Putra Malaysia
In fulfilment of the requirement for the degree of Master of Science

MAGNETIC, DIELECTRIC AND MICROSTRUCTURAL PROPERTIES OF NICKEL−ZINC FERRITE $Ni_{0.8}Zn_{0.2}Fe_2O_4$ PREPARED VIA CONVENTIONAL AND CO-PRECIPITATION TECHNIQUES

By

TANIA JAHANBIN

October 2009

Chairman: Associate Professor Mansor Hashim, Ph.D.

Faculty: Science

Nickel-zinc ferrite is a soft magnetic material having low magnetic coercivity and high resistivity values. The high electrical resistivity and excellent magnetic properties make this ferrite an automatic choice as a core material for power transformers in electronic and telecommunication applications in megahertz frequency regions .The properties of the Ni–Zn ferrite are very sensitive to the method of preparation, sintering temperature, sintering time and chemical composition . Most ferrites prepared via the conventional ceramic processing method have some drawbacks. Wet chemical methods are being pursued to overcome these drawbacks and to produce ultra-fine, homogeneous and reproducible ferrite powders using aqueous solutions of salts of constituent ions.

In this study, $Ni_{0.8}Zn_{0.2}$ Fe_2O_4 was prepared via both conventional ceramic and the co-precipitation methods. The microstructure, magnetic and dielectric properties

The permittivity in both the co-precipitation synthesis and the conventional synthesis increases with increasing sintering temperature. The dielectric constant and loss tangent of sample prepared via co- precipitation is much lower than the conventional due to the smaller grain size and higher porosity. The resistivities of samples prepared via co-precipittion were from $7.2x10^{8}$ to $3.7x10^{8}$ (Ωcm) and $4.3x10^{6}$ to $8.2x10^{5}$ (Ωcm) for samples prepared via conventional synthesis. In small grain microstructure the grain boundaries are more thus increase the resistivity. This resulted higher resistivity in co-precipitation than conventional methods.

The highest saturation magnetisation, Ms, values in samples synthesized by co-precipitation was 63 $M_s(Am^2kg^{-1})$ and 60 $M_s(Am^2kg^{-1})$ for the conventional counterpart which were sintered at 1300°C. The higher M_s in co-precipitation is probably due to better crystalline structure. The coercivity and remanence of samples prepared via co-precipitation are lower than those of the conventionally synthesized samples.

The initial permeability value lies between 4 and 17 for the co-precipitation and 14 to 24 for conventional synthesis. The widest frequency range is obtained at 700°C in co-precipitation method due to the small grin size. The relative loss factor (RLF) also studied and it was revealed that the RLF increased with sintering temperature. But

It is thus concluded that it is the better of the two methods of preparation employed in this work for Nickel-Zinc Ferrite, $Ni_{0.8}\ Zn_{0.2}\ Fe_2\ O_4$.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Sarjana Muda

MENGKAJI KEMAGNETAN, DIELEKTRIK DAN SIFAT-SIFAT MIKROSTRUKTUR BAGI $Ni_{0.8}Zn_{0.2}Fe_2O_4$ MELALUI TEKNIK PEMPROSESAN SERAMIK DAN TEKNIK MENDAKAN

Oleh

TANIA JAHANBIN

Februari 2009

Pengerusi: Prof. Madya Dr. Mansor Hashim, Ph.D.

Fakulti: Sains

Ferit nikel-zink adalah sejenis bahan magnet lembut yang mempunyai daya paksa magnet dan nilai ke rintangan yang tinggi. keintangan elektrik yang tinggi dan sifat-sifat magnet yang bagus menjadikan ferit ini sejenis pilihan otomatik sebagai bahan teras bagi transformer kuasa dalam aplikasi elektronik dan telekomunikasi pada frekuensi megahertz. Sifat-sifat bagi ferit Ni-Zn adalah sangat sensitif lepade cara penyediaan, suhu pemanasan, masa pemanasan dan komposisi kimia. Kebanyakan ferit yang disediakan melalui teknik pemprosesan seramik yang mempunyai beberaa kelemahan. Teknik kimia basah diteruskan digunakan untuk anba membaiki kelemahan ini dan memperolehi serbuk ferit yang sangat halus, seragam dan berhasil semula dengan menggunakan larutan akuas bagi garam berion.

Dalam projek ini, $Ni_{0.8}Zn_{0.2}$ Fe_2O_4 disediakan melalui teknik pemprosesan seramik dan teknik mendakan. Mikrostruktur, kemagnetan dan sifat dielektrik dikaji untuk memahami sifat fizik, kemagnetan dan sifat dielektrik bagi bahan tersebut. Sinaran X-ray memastikan penghabluran sampel selepas pemanasan pada 700°C dan 1100

Ketelusan bagi kedua-dua teknik iaitu sintesis mendakan dan sintesis pemprosesan meningkat dengan peningkatan suhu pemanasan. Ketelusan dan tangent kehilangan dielektrik bagi sampel yang disediakan melalui teknik mendakan adalah lebih rendah berbanding dengan teknik pemprosesan seramik disebabkan saiz zarah yang kecil dan keporosan yang tinggi. Rintangan bagi sampel yang disediakan melalui teknik mendakan adalah dari $7.2x10^8$ ke $3.7x10^8$ (Ωcm) dan dari $4.3x10^6$ ke $8.2x10^5$ (Ωcm) bagi sampel disediakan melalui teknik pemprosesan seramik. Sempadan zarah yang banyak dalam mikrostrukture zarah-kecil meningkatkan ke rintangan sampel. Ini menghasilkan kerintangan yang tinggi bagi teknik mendakan berbanding dengan teknik pemprosesan seramik.

Kadar ketepuar kemagnetan, Ms, yang tertinggi bagi sampel disediakan melalui teknik mendakan adalah 63 $M_s(Am^2kg^{-1})$ dan 60 $M_s(Am^2kg^{-1})$ bagi sampel disediakan melalui teknik pemprosesan seramik yang dipanaskan pada 1300°C. M_s yang lebih tinggi bagi teknik mendakan mangkin disebabkan oleh strutur heblur yang lebih baik. Daya paksa dan remanen bagi sampel yang disediakan melalui teknik mendakan adalah lebih rendah berbanding dengan teknik pemprosesan seramik.

Ketelapan asal adalah dalam lingkungan 4 hingga 17 bagi teknik mendakan dan 14 hingga 24 bagi teknik pemprosesan seramik. Julat frekuensi yang tertinggi bagi teknik mendakan adalah pada 700°C disebabkan saiz zarah yang kecil. Faktor kehilangan relatif (RLF) juga dikaji dan RLF ditunjukkan meningkat dengan suhu pemanasan. Tetapi RLF bagi sampel yang disediakan melalui teknik mendakan adalah lebih rendah berbanding dengan teknik biasa. Oleh itu, julat operasi bagi frekuensi adalah lebih luas daripada teknik biasa. Ferit Ni-Zn yang mempunyai ketepuan kemagnetan yang lebih tinggi, kehilangan yang lebih rendah dan kerintangan yang lebih tinggi disediakan melalui teknik mendakan. Kesimpudannga, teknik ini adalah tebih baik clicatra due teknik pengediaan yang telah digaunalca dalam projek ini untuk ferit nickel-zinc , $Ni_{0.8}Zn_{0.2}Fe_2O_4$.

ACKNOWLEDGEMENTS

First and foremost, I would like to extend my deepest praise to Allah who has given me the patience, strength, determination and courage to complete this project within the allotted time frame.

It is my pleasure to acknowledge my supervisor, Assc.Prof.Dr. Mansor Hashim for giving me the platform to pursue my studies and to give me the opportunity to explore the 'insights' of ferrite science. I would also like to extend my sincere appreciation to my supervision committee member Dr.Khamirul Amin Matori who was ever willing to give his help throughout this project.

My particular thanks are owed to my parents , Iraj and Mitra for their loving support. Last, but not at least, to all of my friends , thank you for all your support .

I certify that a Thesis Examination Committee has met on 01/10/2009 to conduct the final examination of Tania Jahanbin on her thesis entitled "**Title of thesis**" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

Members of the Thesis Examination Committee were as follows:

ZAINAL ABIDIN TALIB, Ph.D.
Associated Professor
Faculty of Science and Environmental
Universiti Putra Malaysia
(Chairman)

JUMIAH HASSAN, Ph.D.
Associated Professor
Faculty of Science and Environmental
Universiti Putra Malaysia
(Internal Examiner)

HALIMAH MOHAMED KAMARI, Ph.D.
Doctor
Faculty of Science and Environmental
Universiti Putra Malaysia
(Internal Examiner)

SAHRIM AHMAD, Ph.D.
Professor
Faculty of Science and Environmental
Unversit Putra Malaysia
(External Examiner)

BUJANG BIN KIM HUAT, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Suppervisory Committee were as follows:

Mansor Hashim, PhD
Associate Professor
Faculty of Science and Environmental Studies
University Putra Malaysia
(Chairman)

Khamirul Amin Mantori, PhD
Doctor
Faculty of Science and Environmental Studies
University Putra Malaysia
(Member)

HASSANAH MOHD. GHAZALI, PhD
Professor and Dean
School of Graduate Studies
University Malaysia

Date: 10/12/2009

DECLARATION

I hereby declare that this thesis is based on my original work except for quotations and citation which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

TANIA JAHANBIN

Date:

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS

A	cross sectional area
H	applied field
H_c	coercive force
T_c	Curie temperature
ρ	resistivity
f	frequency
μ´	initial permeability
M	magnetization
M_s	saturation magnetization
M_r	residual magnetization
Tanδ	loss tangent
PVA	polyvinyle alcohol
RLF	relative loss factor
K_1	first anisotropy

CHAPTER I

Introduction

Ferrites are ceramic ferromagnetic materials which contain oxygen and at least two magnetic ions in order to produce spontaneous magnetization. They have been studied since the 19^{th} century due to their wide range of applications in telecommunications, power transformers, EMI suppression, memory cores and many others. Generally, ferrites are classified into three classes based on three different crystal types which are

1) The spinel type, giving spinel ferrites
2) The garnet type, giving garnet ferrites (as simply garnets)
3) The magnetoplumbite type, giving hexagonal ferrites.

Magnetically, the ferrites in categories 1) and 2) come under the class of "soft" ferrites while the ferrites in 3) belong to the class of "hard" ferrites. A Soft magnetic material becomes magnetised by a relatively low applied magnetic field. When the applied filed is removed, relatively low magnetism is retained in soft ferrites. Soft ferrites mostly contain divalent or trivalent metal ions (nickel, zinc, manganese, yttrium, etc) trivalent iron ions and divalent oxygen ions. Conversely, a high applied magnetic field is required for magnetizing hard ferrites. High remanent magnetism characterizes the properties of hard ferrites. They are prepared from iron oxide and barium oxide or strontium oxide.

Nickel zinc ferrite is the most popular composition of soft ferrites. Due to the high resistivity and low eddy current losses and coercivity, ferrites of the nickel-zinc type are used in high frequency applications as a core material for power transformers and circuit inductors in the megahertz frequency region. They are more stable than the other types of ferrites, easily manufactured, low cost and have excellent and desirable magnetic properties. The properties of NiZn ferrite are sensitive to the compositional variability and the microstructure which is governed by the preparation process (Verma et al., 2005; Verma & Chatterjee, 2006).

In nickel zinc ferrites ($Ni_{1-x}Zn_xFe_2O_4$), zinc content is known to play a decisive role in determining the properties of ferrites. Hence, the compositional variation in the ferrites has been brought about by varying the zinc content (Verma & Chatterjee, 2006). Zinc ions cause the redistribution of metal ions in tetrahedral and octahedral sites (Gul et al., 2008).

In NiZn ferrites, the electrical and magnetic properties of ferrites depend on the stoichiometric composition. The nickel zinc ferrite with the well known composition of ($Ni_{0.8}Zn_{0.2}Fe_2O_4$) is chosen in this study. This composition has higher resistivity and curie temperature and lower loss than most other nickel zinc ferrites composition due to the low zinc content (Mangalaraja et al., 2003; Verma et al., 2000).

The small amount of zinc causes low zinc loss and formation of Fe^{2+} would be small. The resistivity in ferrite materials is due to the electron hopping between $Fe^{3+} \leftrightarrow Fe^{2+}$ .Thus, the resistivity is increased with decreasing zinc content.

Basis of the Work and Statement of Objective

It is well known that nickel zinc ferrites are superior to most other ferrites for use at high frequency because of the high electrical resistivity and low energy loss. However, many of the findings on their excellent properties were obtained using samples produced by the conventional ceramic processing technique.

This has been, for several decades, the most common method for preparation of ferrites. Starting powders of high purity are used to obtain good results. But this method is known to have some inherent drawbacks such as poor compositional control, chemical inhomogenity, coarser grain size and introduction of impurities during grinding. Since, wet chemical methods are widely believed to be able to overcome these drawbacks, it is envisaged that nickel-zinc ferrites with better properties can be obtained using these methods (Azadmahjiri, 2007).

Hence, the above situation provides the main drive for this research work to carry out an experimental investigation with the following main objective:

To perform a comparative study of microstructural, magnetic and electrical properties of nickel-zinc ferrite sample of a composition i.e. $Ni_{0.8}Zn_{0.2}Fe_2O_4$ prepared by two different methods of synthesis i.e. the conventional ceramic processing method and the wet-chemistry co-precipitation method.

The co-precipitation method is widely used to prepare ferrites due to its overriding advantages such as compositional flexibility, time saving, superior properties of ferrites processed at a much lower temperature and an economical way to produce ultrafine powders (Blaskov et al., 1996; Jiao et al., 2008; Mathur et al., 2008). In this work, we are concerned with the preparation of samples with low loss and high operating frequency which requires high sample resistivity.

History and Future Trend in Ferrite Technology

The development of ferrites was initiated by Hipert and Forestier (1909) independently. They studied the processing of simple ferrites, undoped zinc ferrites. They studied the magnetic properties of Zn ferrites. It was attempted to introduce this material into particular use for magnetic cores. However, these materials had a lower permeability than other alloys. In 1932, Professor Takeshi Takei and Kato were pioneered the first ferrite with promising properties. They invented high permeability ferrites which are a mixture of non magnetic zinc ferrites and ferromagnetic samples containing Cu, Mn , Ni, etc . Snoek in 1936 has studied magnetic oxide and found MnZn and NiZn had extremely high permeability and were useful for inductor cores. Snoek and his co-workers in Holland were able to continue ferrite research and produce commercial soft ferrite. They realized the most important property of a material is the loss tangent. This property resulted in the ferrites being used as a core for an inductor. In 1948, Neel published the ferrimagnetism theory that brought about a great advance in the magnetic investigation of ferrites. Albert Schonberg (1951) reported on the development of microwave ferrites as digital memory.

In the past several decades, the ferrites technology has assumed new importance. Development in ferrites is important to progress in electronic technology, high frequency power supplies and recording head, increased emphasis on electromagnetic interference suppression and efficient lighting. In addition, the application of ferrites promoted in new fields such as optics, biotechnology and medicine.

Nowadays, more efforts are being carried out to develop higher electric-magnetic properties and low-power loss materials in the MHz frequency region in accordance with the miniaturization of electronic devices (Zahi et al., 2007). Thus, the research activity is directed to prepare ferrites particle in nanosize, which have quite different properties (Upadhyay et al., 2003). The ferrites that are made up of nano particles are intensively studied due to dielectric, magnetic and electric properties and their application in various fields (Gul et al., 2008). In small grain size , the possibility of re-oxidation of Fe^{2+} to Fe^{3+} during cooling after the sintering process, as diffusion of oxygen advances more rapidly than in larger ones which improves the ferrite stoichiometry.

Therefore, all efforts are considered to develop a technique to produce better stoichiometry and reproducible ferrites which involves heat treatment at lower temperatures and shorter duration (Verma et al., 1999).

CHAPTER II

LITERATURE REVIEW

Introduction

Synthesis of magnetic material has been an interesting area of study for a long time. Studies shown that the physical properties of ferrites depend on the processing of preparation. Ferrites are mostly prepared via conventional ceramic processing involves commercially both long and high temperature treatments for the oxides used in their preparation. The studies on magnetic and dielectric properties in Ni-Zn ferrites synthesized by conventional technique have been reported by so many workers. The conventional method is the most common method for preparing ferrites for so decades.

Mohan et al., (1999) studied the dielectric properties of nickel zinc ferrites $Ni_x\ Zn_{1-x}\ Fe_2\ O_4$, where *x* changed from 0.2 to 1.0 and synthesized by standard ceramic technique. They investigated the frequency, temperature and composition dependence of NiZn ferrites. They found the dielectric constant and loss tangent decrease with increasing of zinc content up to x=0.4. Beyond x=0.4, they observed these parameters increased progressively. They suggested the variation of dielectric constant depends linearly on the variation of available ferrous ions on octahedral sites. Dielectric constant declined with increasing frequency. The maximum dielectric dispersion was seen for x=0.8 which be explained on the basis of available ferrous ions on octahedral sites. The variation of the dispersion with composition for mixed nickel–zinc ferrites was explained by the fact the electron exchange between Fe^{2+} and Fe^{3+} in an n-type semiconducting ferrite and hole exchange between Ni^{3+} and Ni^{2+} in a p-type semiconducting. They measured resistivity and concluded dielectric constant was inversely proportional to the square root of resistivity. Additionally, the dielectric loss reflected in resistivity that the lower loss exhibited higher resistivity and vice versa. In their research the dielectric constant increased gradually with increasing temperature up to the particular temperature, which is designated as the dielectric transition temperature T_s. However, beyond this temperature the values of the dielectric constant for all the samples were found to decrease continuously. In a later paper, Ranga and Revinder (1999) discussed the conductivity of $Ni_{1-x}Zn_xFe_2O_4$ as a function of composition and temperature. They observed conductivity increase with zinc content and temperature. They calculated the charge carrier concentration and observed the higher charge carrier in higher temperature up to magnetic transition temperature. Beyond this temperature the concentration of charge carrier decreased.

Further research was also done by El-Sayed (2003) on the electrical conductivity of $Ni_{1-x}Zn_xFe_2O_4$ (x = 0.1, 0.3, 0.5, 0.7 and 0.9) which were prepared by the ceramic processing technique .They found the lowest conductivity and higher activation energy for x=0.3 in nickel zinc ferrite. Ajmal and Maqsood (2007) investigated the substitution of Zn in the $Ni_{1-x}Zn_xFe_2O_4$ system and checked the effect on the physical properties. They studied the variation of zinc content on DC resistivity, dielectric constant and loss factor. It was observed that dielectric constant increased with the increase in Zn concentration. The resistivity values was in the range of 1.629×10^6 to 3.0×10^3 Ωcm. Loss factor remained in the range of 9.057–0.456 with the variation in frequency from 80 Hz to 1 MHz, respectively.

In conventional methods, there are some inherent drawbacks such as poor compositional control, chemical inhomogenity, coarser particle and introduction of some impurities during ball milling. Thus, the coarser and nonuinform particles cause the formation of some voids and low-density areas in the green compact (Kumar et al., 1996).

However, recently wet chemical methods have been used to prepare ultrafine, homogenous and reproducible powder (Mangalaraja et al., 2002). In the recent past, the wet methods have been found to have distinct advantages over the conventional dry processing. The variety wet methods such as ball milling, hydrothermal, sol-gel, micro emulsions, and co-precipitation have been used to synthesize ferrite materials. Each method has unique advantages. But trying to improve the physical properties of ferrites by new designing in synthesize is still a matter of primary interest. The final goal is to fabricate the ferrites with better physical and magnetic properties that are useful in a variety of industrial applications.