UNIVERSITI PUTRA MALAYSIA

PARALLEL EVOLVING MORPHOLOGY, MAGNETIC PROPERTIES AND THEIR RELATIONSHIPS IN $Ni_{0.5}Zn_{0.5}Fe_2O_4$

ISMAYADI ISMAIL

ITMA 2012 18

PARALLEL EVOLVING MORPHOLOGY, MAGNETIC PROPERTIES AND THEIR RELATIONSHIPS IN $Ni_{0.5}Zn_{0.5}Fe_2O_4$

By

ISMAYADI ISMAIL

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

January 2012

In appreciation of their love and sacrifices, this thesis is dedicated to Parents Haji ISMAIL AWANG and Hajah MEK ESAH AWANG, to my beloved wife SAKINAH SHAMSUDIN and my three children, ZAFRAN HAKIM, ARIF AMSYAR and HIJRIN BALQISH.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

PARALLEL EVOLVING MORPHOLOGY, MAGNETIC PROPERTIES AND THEIR RELATIONSHIPS IN $Ni_{0.5}Zn_{0.5}Fe_2O_4$

By

ISMAYADI ISMAIL

January 2012

Chairman: Associate Professor Mansor Hashim, PhD

Institute: Institute of Advanced Technology

For more than seven past decades, the ferrite research literature has only very superficially dealt with the question of how the evolving microstructure of a ferrite material relates to its accompanying, resultant magnetic properties. The literature has only covered in great detail the answers for the case of ferrite materials obtained from final sintering. Thus, this work was a fresh attempt to critically track the evolution of magnetic properties parallel to the microstructural changes in bulk $Ni_{0.5}Zn_{0.5}Fe_2O_4$ samples and to relate the properties to the changes wherever possible. The study was divided into five parts. The first part involved two variables (milling time and ball to powder weight ratio (BPR)) of a mechanical alloying process where they were varied in order to study their effect on the magnetic properties of the material. The alloyed powders were used as starting powders for the rest of the research work. In the second

part, parallel sintering of a number of samples was carried out with sintering temperatures of 500 to 1400^{o}C, subjecting one sample to only one particular sintering temperature. This was a multi-sample sintering process with 100^{o}C increments. The third part dealt with higher-precision multi-sample sintering of several samples with sintering temperatures of 800 to 1000^{o}C with much smaller increments of 25^{o}C. The fourth part involved studies of the effect of soaking time on microstructural evolution and its influence on the magnetic properties. The last part carried out was similar to the second part (multi-sample), but it was run more carefully and critically with only one sample (single-sample) being subjected to various ascending sintering temperatures from 500 to 1400^{o}C.

The results from first-part on the mechanical alloying parameters variation showed that there were no significant trends to relate the milling time and BPR with the permeability and losses of the material studied. After the samples were sintered at 1150^{o}C, all the effects of the alloying process seemed to diminish. The results from the multi-sample sintering with the nanosized starting powders subjected to various sintering temperatures showed a clear development trend of the phase, morphology and magnetic properties of the samples. It is very interesting that the results revealed a critical region of sintering temperature for the development of magnetic properties which was observed at 800^{o}C and 900^{o}C with the sigmoid B-H curve shape taken to indicate a strong magnetic order. For the first time, this work has reported the evolution of the B-H hysteresis loops associated with the changes of magnetic states from paramagnetism to moderate ferromagnetism to strong ferromagnetism with microstructural changes. The results of the higher precision third part on the relationship between ordered magnetism and the microstructure of the samples revealed a very startlingly systematic trend: a highly refined evolution trend covering a critical region of ordered magnetism which emerged and developed in step with morphological changes. Further work on the soaking time parameter was to study another possible way for the microstructure to influence the magnetic properties. The results showed a slow grain growth rate indicating a slow diffusion of atoms during the sintering process: it is believed that there was an increase in number of grain growth spots and these were the regions of mixed superparamagnetic and paramagnetic mass with ferromagnetic mass starting to dominate the samples. The last part of this work, carried out using single-sample sintering, also produced very gratifying results from the research point of view: the fascinating results from the single-sample sintering showed very systematically the evolution of microstructure-magnetic property relationships with a clarity superior to that shown by the multi-sample sintering.

Finally, after analysing the results and the observations of the work mentioned above, it is strongly believed that there are three factors found to sensitively influence the samples content of ordered magnetism –their ferrite-phase crystallinity degree, the number of grains above the critical grain size and large enough grains for domain wall accomodation. This research work has shed new light on the microstructure-magnetic properties evolution in ferrites.

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

PERKEMBANGAN SEIRING EVOLUSI SIFAT-SIFAT MORFOLOGI, MAGNETIK DAN HUBUNGANNYA DALAM $Ni_{0.5}Zn_{0.5}Fe_2O_4$

Oleh

ISMAYADI ISMAIL

Januari 2012

Pengerusi: **Profesor Madya Mansor Hashim, PhD**

Institut: **Institut Teknologi Maju**

Bagi lebih daripada tujuh dekad yang lampau, literatur penyelidikan ferit hanya telah menangani secara amat cetek persoalan bagaimana sesuatu mikrostruktur ferit yang sedang mengalami evolusi berkait dengan sifat magnet yang terhasil seiring dengannya. Maka kerja ini adalah cubaan terbaru untuk mencerap secara kritikal evolusi ciri-ciri magnet seiring dengan perubahan mikrostruktur bagi sampel $Ni_{0.5}Zn_{0.5}Fe_2O_4$. Kajian ini telah dibahagikan kepada lima bahagian. Bahagian pertama melibatkan dua pemboleh ubah (masa mengisar dan nisbah berat bola terhadap berat serbuk (BPR)) bagi proses pengaloian mekanik dimana pemboleh ubah tadi dipelbagaikan untuk mengkaji kesannya terhadap sifat magnet bahan. Dalam bahagian kedua, pensinteran selari bagi sampel-berbagai telah dilakukan dengan suhu pensinteran dari 500 sehingga 1400^{o}C dengan setiap sampel hanya dikenakan satu suhu pensinteran. Ini adalah proses pensinteran pelbagai sampel dengan kenaikan 100^{o}C. Bahagian ketiga berurusan dengan pensinteran selari pelbagai sampel yang lebih persis dengan suhu pensinteran dari 800

sehingga 1000^{o}C dengan kenaikan yang jauh lebih kecil, 25^{o}C. Bahagian keempat melibatkan kajian pada kesan masa rendaman pembakaran terhadap evolusi mikrostruktur dan pengaruhnya ke atas sifat magnet. Bahagian terakhir telah dibuat sama seperti bahagian kedua (pelbagai-sampel), tetapi dilakukan secara kritikal dengan hanya satu sampel (sampel-tunggal) dan dikenakan pelbagai suhu pensinteran secara menaik dari 500^{o}C sehingga 1400^{o}C.

Keputusan daripada bahagian pertama mengenai variasi parameter pengaloian mekanik menunjukkan bahawa tiada hala perubahan yang bermakna untuk mengaitkan masa mengisar dan BPR dengan keboleh-telapan dan ‘kehilangan’ bahan yang dikaji. Selepas sampel dibakar pada 1150^{o}C, semua kesan-kesan proses pengaloian didapati hilang. Keputusan daripada pensinteran pelbagai-sampel dengan serbuk permulaan bersaiz nano dikenakan pelbagai suhu pensinteran menunjukkan perkembangan jelas fasa, morfologi dan sifat magnet bagi bahan. Adalah sangat menarik melihat keputusan-keputusan yang menyingkap suatu kawasan kritikal suhu pensinteran bagi pembinaan sifat magnet yang diperhatikan pada 800^{o}C dan 900^{o}C dengan bentuk sigmoid B-H diambil sebagai petunjuk tertib magnet yang kuat. Buat pertama kalinya kerja ini telah melaporkan evolusi gelung histeresis BH dikaitkan dengan perubahan keadaan dari keparamagnetan kepada keferomagnetan sederhana seterusnya kepada keferomagnetan kuat. Keputusan bahagian ketiga mengenai hubungan kemagnetan bertertib dengan mikrostruktur sampel menyingkap suatu hala perubahan sistematik yang amat menakjubkan: suatu hala evolusi yang amat halus yang meliputi suatu kawasan kritikal kemagnetan bertertib yang muncul dan berkembang seiring dengan perubahan-

perubahan morfologi. Kajian lanjut dibuat terhadap parameter masa rendaman pensinteran bagi mengkaji suatu lagi cara yang mungkin bagi mikrostruktur mempengaruhi sifat magnet. Keputusan-keputusan kajian ini menunjukkan kadar pembesaran butiran yang perlahan, menandakan resapan atom-atom semasa proses pensinteran: dipercayai terdapat peningkatan jumlah tompok-tompok pembesaran butiran dan ini adalah kawasan percampuran jisim superparamagnet dan paramagnet dengan jisim feromagnet yang mula mendominasi sampel. Bahagian terakhir kerja ini yang telah dijalankan dengan menggunakan pensinteran sampel-tunggal juga telah menghasilkan keputusan-keputusan yang amat memuaskan hati dari sudut penyelidikan: keputusan-keputusan menarik dari pembakaran sampel-tunggal menunjukkan secara amat sistematik evolusi hubungan mikrostruktur-sifat magnet dengan kejelasan yang lebih baik berbanding kes pensinteran pelbagai sampel.

Akhir sekali, selepas menganalisis keputusan dan pemerhatian kerja tadi, ianya amatlah diyakini bahawa terdapat tiga faktor yang secara sensitif mempengaruhi kandungan kemagnetan bertertib sampel iaitu darjah fasa kehabluran, jumlah butiran melepasi saiz kritikal butiran dan butiran yang cukup besar untuk penempatan dinding domain. Kerja penyelidikan ini telah menyumbangkan pengetahuan baharu tentang terhadap evolusi mikrostruktur-sifat magnet dalam bahan ferit.

ACKNOWLEDGEMENTS

It is neither my strength nor my wisdom, but Allah's mercies that made this work a success, thus, I glorify Him. May all praises and salutations of the Lord be upon the Messenger of Allah and upon his Family and Companions, and those who are guided by the light of his 'sunnah' till the Day of Judgment.

Countless of people contribute to this thesis; mentors and /or supervisors, family, friends and even some strangers have set off trains of thought and spark ideas or understandings. This means that, by mentioning names, I would be omitting someone. Never the less, my unreserved appreciation goes to my able supervisor Associate Professor Dr. Mansor Hashim for his guidance and suggestions, without which, this work would not have been a success. This thesis is, but a fraction of evidence reflecting his vast insight into magnetism and magnetic materials. I am highly indebted and eternally grateful. To my co-supervisors, Dr. Khamirul Amin Matori, Dr. Rosidah Alias and Assoc. Prof. Dr. Jumiah Hassan, I thank them for keeping me right on track. Their contributions would forever remain indelible in my memories.

To my colleagues in the magnetic materials research group (Idzariati, Rodziah, Norailiana, Hapishah, Shamsul, Fadzidah, Masni, Ghazaleh, Mehran and last but not least Samaila), I appreciate the memorable interactions that we had from where I drew my strength, thank you very much for lighting my path; 'please lets keep the ball rolling, and bit faster, if possible'. To my numerous friends including but not limited to Sarinawani, Rosnah, Kadri, Noor Lina, Kak Ani, I say thanks for everything.

In measuring the characteristics of my samples, the efforts of Mr. Rafiuszaman from Institute of BioScience UPM (TEM), Mr Mohd Zin and Mrs. Kamsiah from Physics Dept. UPM (XRD) are highly acknowledged. Further acknowledged are all those whom have contributed to the success of this thesis hence or otherwise. The reviewers and handling editors of American Journals of Applied Sciences, International Journal of Nanotechnology, Journal of Magnetism and Magnetic Materials, Journal of Superconductivity and Novel Magnetism for not only critically reviewing, but also accepting to publish various sections of this work in their reputable journals.

I am highly grateful to my brothers and sisters; Noraisha Akma, Noraisha Wani Azma, Ismashazly and Noraisha Asni for their warm support and prayers. The support and prayers of my parents' in-law; Haji Shamsudin and Mek Teh Ahmad are fully acknowledged.

The crowning glory goes to my beloved wife **Sakinah Shamsudin** and my three children **Zafran Hakim, Arif Amsyar** and **Hijrin Balqish** for standing by my side throughout the course of this study. Thank you very much for joining me "in sacrificing today for a better tomorrow" I LOVE YOU ALL and may Allah reward you with the best of rewards.

I cannot find the words for my parents **Haji Ismail Awang** and **Hajah Mek Esah Awang** *"my Lord! Bestow on them Thy Mercy, even as they cherished me in childhood."*

I certify that a Thesis Examination Committee has met on 3rd January 2012 to conduct the final examination of Ismayadi Ismail on his thesis entitled **"Parallel Evolving Morphology, Magnetic Properties, and Their Relationships in $Ni_{0.5}Zn_{0.5}Fe_2O_4$"** in accordance with 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 Doctor of Philosophy

Members of the Thesis Examination Committee are as follows:

Mohd. Nizar Hamidon, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Wan Mohamad Daud Wan Yusoff, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Halimah Mohamed Kamari, PhD
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Jamshid Amighian, PhD
Department of Physics
Islamic Azad University
(External Examiner)

SEOW HENG FONG, 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 fulfillment of the requirement for the degree of **Doctor of Philosophy**. The members of the Supervisory Committee were as follows:

Mansor Hashim, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Khamirul Amin Matori, PhD
Lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

Rosidah Alias, PhD
Researcher
Microelectronic and Nano Technology Program,
TM Research & Development,
TMR&D Innovation centre,
(Member)

Jumiah Hassan, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

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

Date:

DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently submitted for any other degree at Universiti Putra Malaysia or at any other institution.

____

ISMAYADI ISMAIL

Date: 3 January 2012

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

XRD	x-ray diffraction
SEM	Scanning Electron Microscopy
EDX	Energy Dispersive X-ray
TEM	Transmission electron microscopy
wt %	Weight percent
hkl	Miller indices
MUT	Material under test
JCPDS	Joint Committee on Power Diffraction Standard
BPR	Ball-to-powder weight ratio
MA	Mechanical alloying
a.u	Arbitrary unit
Fig.	Figure
χ	Magnetic susceptibility
H	Magnetic field strength
H_C	Coercivity
M	Mass magnetization
M_R	Remanent magnetization
M_S	Saturation magnetization
σ_R	Specific remanent magnetization
σ_S	Specific saturation magnetization
θ_C	Curie temperature
θ_N	Néel temperature

2θ	2 theta degree
d_m	mean grain diameter
γ	magnetic domain wall energy proportional to the global anisotropy constant
M_{sv}	magnetization per unit volume
M_{sm}	magnetization per unit mass

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Ferrites are ceramic materials with magnetic properties which are mixed metal oxides containing iron oxide as their main component. They can be formed into permanent magnets for uses in motors, speakers and other electrical-mechanical energy conversion devices. They can also be formed into soft magnetic materials which are used as core materials for transformers, inductors and in microwave communication systems. 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 field 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 desireable 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). 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 $Ni_{0.5}Zn_{0.5}Fe_2O_4$ is chosen in this study.

1.2 Microstructural-magnetic properties relationships of Ferrite Materials

Nanosized particles of the high-energy-milled spinel ferrites exhibit interesting physical and chemical properties markedly different from those of their bulk counterparts. The high-field magnetization irreversibility (Kodama et al., 1996), the variation of the Neel temperature with grain size (Chinnasamy et al., 2002), a high coercivity (Shi and Ding, 2001), and an altered (reduced (Lin et al., 1995) or enhanced (Oliver et al., 2000, Jiang et al., 1999 and Clark and Evans, 1997)) magnetic moments in comparison with the corresponding bulk materials have been observed in nanosize high-energy-milled ferrimagnetic spinels. Mechanical treatment of the spinel ferrites was found to be a useful activation method leading to an enhanced chemical reactivity of nanoscale powders (Sepelak et al., 1997). Nanostructured spinel ferrites prepared by high energy milling method are often inherently unstable owing to their small constituent sizes, nonequilibrium cation distribution, disordered spin configuration, and high chemical activity. Sintering of the milled spinel ferrites recrystallises the nanostructure and causes its transition from an excited metastable (activated) state into the low-energy crystalline state. During the process of sintering, the advantageous properties of the nanosize-milled spinel ferrites are mostly lost (Sepelak et al., 1998), thus an understanding of the relaxation mechanism of mechanically induced metastable states and of the thermal stability of nanostructure is necessary. A better understanding of the response of nanoscale spinel ferrites to changes in temperature is crucial not only for basic science (the development of an atomistic and microscopic theory of the mechanochemical processes) but also because of the technological high-temperature applications in catalysis, ferrofluids and information storage. To gain insight into the microstructral-magnetic property evolution relationships, this experimental work focuses on the study of the response of the fine nano-size starting powders of mechanically alloyed nickel zinc ferrite ($Ni_{0.5}Zn_{0.5}Fe_2O_4$) to changes in sintering temperature. Although extensive studies have recently been performed on the nanoscale-milled soft ferrites (Kodama et al., 1996, Chinnasamy et al., 2002, Sepelak et al., 2000, Oliver et al., 2000 and Jiang et al., 1999), no measurements, of the thermally induced structural and magnetic evolutions in this metastable solid have been reported.

1.3 Problem Statement

A fundamental line of scientific enquiry has been neglected by ferrite and garnet researchers for more than 70 years: What would be the composition-microstructure relationships at various intermediate sintering conditions during the parallel evolutions of the morphology and the material properties? This research work intends to track carefully and critically the fundamental evolutions. Do the changes of microstructure affect the magnetic properties of the materials? How do magnetic properties evolve with the microstructure changes? What would happen to the ions of the materials parallel to the microstrure changes, do they also contribute to magnetization of the materials?

1.4 Objectives

The ultimate goal of this research is to critically track the evolution of magnetic properties parallel to the microstructural changes. Previous literatures mostly based on the micron-size starting powder and gradually were grown to the bulk solid samples. It is interesting to study the evolution of the magnetic properties with the nano-size starting powders and observe transition of paramagnetic to ferromagnetic behavior. This research work embarks on the following objectives:

1) To prepare $Ni_{0.5}Zn_{0.5}Fe_2O_4$ using mechanically alloyed nanoparticles.
2) To study the phase formation and crystallite size evolution of the as-prepared ferrite using XRD.
3) To study the effect of the sintering temperature on the microstructural evolution and magnetic properties of Ni-Zn ferrites.
4) To study the evolution of magnetic properties with microstructure changes.

1.5 Thesis Outline

General introduction of ferrite, microstructural-magnetic relationships and some research questions were discussed in chapter one while related literatures of the synthesis methods, composition tailoring, mechanical alloying and its important parameters, and some microstructural consideration on magnetic properties were reported in chapter two. Chapter three reported the basic theories as they affect ferrites and sintered materials. Specifically, the chapter reports the fundamentals of magnetization, the chemistry of spinel ferrites, sintering parameters and mechanical alloying process. The preoccupations in chapter four were methodologies employed for the preparations and the characteristics measurement of the as-prepared ferrite and sintered NiZn ferrite. The discussion of the obtained results of the as-prepared ferrites and the microstructure-magnetic properties forms chapter five. Chapter six summarized and concludes the research findings, in addition to some suggested recommendations. The list of his publications was attached at the end of the thesis, preceded by the author's biography appendices and references/bibliographies respectively.

REFERENCES

Bean , C.P., (1955). Hysteresis loops of mixtures of ferromagnetic micropowders. *J. Appl. Phys*. 26, 1381–1383.

Bera, J., Roy, P.K., (2005), Effect of grain size on electromagnetic properties of $Ni_{0.7}Zn_{0.3}Fe_2O4$ ferrite, *Journal of Physica B*, 363, 128-132.

Bhosale, D.N., Verenkar, V.M.S., Rane, K.S., Bakare, P.P., Sawant, S.R. (1999). Initial susceptibility studies on Cu-Mg-Zn ferrites, *J. Mater. Chem. Phys.*, 59, 57-62.

Bid, S. and Phradan, S.K. (2003). Preparation of zinc ferrite by high-energy ball-milling and microstructure characterization by Rietveld's analysis, *Materials Chemistry and Physics*, 82, 27-37.

Bradley, F. N., (1971). *Materials for Magnetic Functions*. New York: Hayden Book Co.

Cahn, R.W., Haasen, P., Kramer, E.J., (1996). *Materials Science and Technology: A Comprehensive Treatment*, VCH Publishers Inc., New York, NY (USA).

Ciureanu, P. and Gavrila, H., (1990). *Studies in electrical and electronic engineering: Magnetic Heads for digital recording*, Elsevier Science Publishers, Amsterdam.

Chaudri, N.D., Kamble, R.C., Bhosale, D.N., Suryavanshi, S.S., Sawant, S.R., (2010), Thermal hysteresis and domain states in Ni-Zn ferrites synthesized by oxalate precursor method, Journal of Magnetism and Magnetic Materials, 322, 1999-2005.

Chin, Z. H., & Perng, T. P. (1991). Amorphization of Ni-Si-C ternary alloy powder by mechanical alloying. *Materials Science Froum*, 235-238(PART 1), 121-126.

Chinnasamy, C.N. Narayanasamy, A. Ponpandian, N. Justin Joseyphus, R. Jeyadevan, B. Tohji, K. Chattopadhyay, K. (2002). Grain size effect on the Néel temperature and magnetic properties of nanocrystalline $NiFe_2O_4$ spinel, *Journal of Magnetism and Magnetic Materials*, 238 (2-3), 281-287.

Clark, T.M., Evans, B.J. (1997). Enhanced magnetization and cation distributions in nanocrystalline $ZnFe_2O_4$: a conversion electron Mossbauer spectroscopic investigation, IEEE Trans. Magn. 33 (5), 3745-3747.

Coble, R.L. (1961). Sintering crystalline solids. I. intermediate and final state diffusion models, *J. Appl. Phys.* 32, 787-792.

Costa, A.C.F.M., Tortella, E., Morelli, M.R., Kiminami, R.H.G.A. (2003). Synthesis, microstructure and magnetic properties of Ni-Zn ferrites. *Journal of Magnetism and Magnetic Materials* 256, 174-182.

Ding, J., McCormick, P.G., Street, R., (1997). Formation of spinel Mn-ferrite during mechanical alloying. *Journal of Magnetism and Magnetic Materials*, 171, 309-314.

Ding, J., Miao, W.F., McCormick, P.G., Street, R., (1998). High-coercivity ferrie magnets prepared by mechanical alloying, *Journal of Alloys and Compound*, 281, 32-36.

Dunlap. R.A., Small, D.A., Mackay, G. R., O'Brien, J. W., Dahn, J. R., & Cheng, Z. H. (2000). Materials preparation by ball milling. *Canadian Journal of Physics*, 78(3), 211-229.

Fannin, P. C., Marin, C. N., & Malaescu, I. (2003). The influence of particle concentration and polarizing field on the resonant behaviour of magnetic fluids. *Journal of Physics Condensed Matter*, 15(27), 4739-4750.

Gerhardt, R., Nowick, A.S., Mochel, M.E., Dumler, I. (1986). Grain Boundary Effect in Ceria Doped with Trivalent Cations: I, Electrical Measurements, *J. Am. Ceram. Soc.*, 69, 641-646.

Gharagozlou, M. (2010). Study of the influence of ennealing temperature and ferrite content on the structural and magnetic properties of x($NiFe_2O_4$)/(100-x)SiO_2 nanocomposites, *Journal of alloys and Compounds*, 495 (1), 217-223.

Globus, A., Duplex P. and Guyot M., (1971), Determination of Initial Magnetisation Curve from Crystallite Size and effective Anisotropy Field, IEEE Trans. On Magn, 7(1):617-619.

Globus, A., (1976). Some Physical considerations about the domain wall size theory of magnetization mechanisms., *in proceeding of the 2nd international conference on ferrites*, 1-15.

Globus, A., (1997), Distance Between Magnetic Ions and Fundamental Properties in Ferrites, J. Phys. (Paris) Coll., 38, C1, 163-68.

Goldman A., *Handbook of Modern Ferromagnetic Materials*, Kluwer Academic Publishers, 1999.

Goldman, A. (1990). *Modern Ferrite Technology*, second ed. Springer, Pittsburg, PA, USA.

Goya, G. F. and Rechenberg, H. R. J. (1998), Reversibility of the synthesis-decomposition reaction in the ball-milled Cu-Fe-O system. *Journal of Physics: Condensed Matter*, 10, 11829-11840.

Goya, G. F. and Rechenberg, H. R. J. (1999), Magnetic properties of $ZnFe_2O_4$ synthesized by ball milling. *Journal of Magnetism and Magnetic Materials*, 203, 141-142.

Goya, G. F. and Rechenberg, H. R. J. (2002), On the magnetic properties of mechanosynthesized and ball milled spinel ferrites, *Material Science Forum*, 403, 127–132.

Guillaud, C., (1957), The Properties of Mn-Zn Ferrites and the Physical Properties Governing Them, Proc. Inst. Eng. 104(5), 165-173.

Gul, I.H., Abbasi, A.Z., Amin, F., Anis-ur-Rehman, M., Maqsood, A. (2007). Structural, magnetic and electrical properties of $Co_{1-x}Zn_xFe_2O_4$ synthesized by co-precipitation method, *J. Magn. Magn. Mater.* 311, 494-499

Hahn, H.T. (1991). The variation of permeability with ferrite tile density, *J. Appl. Phys.* 68(8) 6195-6197.

Halliday, D., Resnick, R., & Walker, J. (1997). *Fundamentals of Physics* (Extended, 5th ed ed.). New York: Wiley & Sons, Inc.

Hankare, P.P., Jadhav, S.D., Sankpal, U.B., Chavan, S.S., Waghmare, K.J. Chougule, B.K. (2009). Synthesis, characterization and effect of sintering temperat,ure on magnetic properties of MgNi ferrite prepared by co-precipitation method, *Journal of Alloys Compounds*, 475 (1-2), 926-929.

Hench, L.L. and West, j.K., (1990). *Principles of Electronic Ceramics*, John Wiley & Sons.

Huang, H., & Mc.Cormick, P. G. (1997). Effect of milling conditions on the synthesis of chromium carbides by mechanical alloying. *Journal of Alloys and Compound*, 246, 258-262.

Hong, S., Kim, C., Kim, J. (2008) Magnetic and structural properties of nitrified FINEMET powder using mechanical milling method. *Current Applied Physics*, 8, 787-789.

Hossein A.K.M.A., Mahmud, S.T., Seki, M., Kawai, T. and Tabata H., (2006). Structural, electrical transport, and magnetic properties of $Ni_{1-x}Zn_xFe_2O_4$, *Journal of Magnetism and Magnetic Materials*, 312 (1) , 210-219

Ishino, K., and Narumiya, Y. (1987). Development of magnetic ferrites: control and application of losses. *American Ceramic Society Bulletin*, 66(10), 1469- 1474.

Jalaly, M., Enayati, M. H., Karimzadeh, F., Kameli, P. (2009), Mechanosynthesis of nanostructured magnetic Ni-Zn ferrite. *Powder Technology*, 193, 150-153.

Jakubovics, J. P. (1994). *Magnetism and Magnetic Materials*. Cambridge, : The Institute of Materials.

Jarcho, M., Bolen, C.H., Thomas, M.B., Bobick, J., Kay, J.K., Doremus, R.H. (1976). Hydroxylapatite synthesis and characterization in dense polycrystalline form, *J. Mater Sci* 11, 2027-2035.

Jiang, J. Z., Goya, G. F., and Rechenberg, H. R. (1999), Magnetic properties of nanostructured CuFe2O4. *Journal of Physics: Condensed Matter*, 11, 4063-4078.

Jiles, D., (1991). *Introduction to Magnetism and Magnetic Materials*, Chapman & Hall, London, UK.

Johnson, M.T. and Visser, E.G., (1990), A coherent model for the complex permeability in polycrystalline ferrites, *IEEE Trans. Magn.*, 26, 1987-1989.

Kang, S. L. (2005). *Sintering: Densification, Grain Growth and Microstructure*, Elsevier Butterwoth-Heinemann.

Kawano, K., Hachiya, M., Iijima, Y., Sato, N., Mizuno, Y., (2009), The grain size effect on the magnetic properties in NiZn ferrite and the quality factor of the inductor. *Journal of Magnetism and Magnetic Materials* 321, 2488-2493.

Keluskar, S.H., Tangsali, R.B., Naik, G.K., Budkuley, J.S. (2006). High permeability of low loss Mn–Zn ferrite obtained by sintering nanoparticle Mn–Zn ferrite, *J. Magn. Magn. Mater.* 305, 296-303.

Kingery, W.D., Bowen, H.K. and Uhlmann, D.R. (1976). *Introduction to Ceramics (2nd edition)*. John Wiley & Sons, New York.

Kis-Varga, M., & Beke, D. L. (1996). Phase transitions in Cu-Sb systems induced by ball milling. *Materials Science Forum*, 225-227(PART 1), 465-470.

Kittel, C., (1995). *Introduction to Solid State Physics*, 7th Edition, john Wiley & Sons, New York, 1995.

Koch, C. C. (1993). The synthesis and structure of nanocrystalline materials produced by mechanical attrition: A review. *Nanostructured Materials*, 2(2), 109-129.

Kodama, R.H., Berkowitz, A.E., McNiff, E.J., Foner, S. (1996). Surface Spin Disorder in NiFe2O4 Nanoparticles, *Physical Review Letter*, 77 (2), 394-397.

Kumar, N., Kumar, A., Jha, R., Dogra, A., Pasricha, R., Kotnala, R.K., Kishan, H., Awana, V.P.S. (2010). Impact of Particle Size on Room Temperature Ferrimagnetism of $SrFe_{12}O_{19}$, *J. Supercond. Nov. Magn.*, 23, 423-427.

Lee, P. Y., Yang, J. L., & Lin, H. M. (1998). Amorphization behaviour in mechanically alloyed Ni-Ta powders. *Journal of Materials Science*, 33(1), 235-239.

Lee, C. H., Mori, M., Fukunaga, T., & Mizutani, U. (1990). Effect of ambient temperature on the MA and MG processes in Ni-Zr alloy system. *Japanese Journal of Applied Physics*, Part 1: Regular Papers and Short Notes and Review Papers, 29(3), 540-544.

Le Floc'h, M., Konn, A.M., (1997) Some of the magnetic properties of polycrystalline soft ferrites : Origins and developments of a model for the description of the quasistatic magnetization, *J. Phys. IV France*, 07, C1-187-C1-190.

Levinson. L.M., (1988), Electronic Ceramics: Properties, Devices and Applications, General Electric Company Schenectady, New York.

Lezhong, L., Zhongwen, L., Zhong, Y., Ke, S., Haining, J. (2007). Influence of quencher on microstructure and magnetic properties of manganese-zinc ferrites. *Journal of Magnetism and Magnetic Materials*, 318, 39-43.

Li, X. and Wang, G. (2009). Low-temperature synthesis and growth of superparamagnetic $Zn_{0.5}Ni_{0.5}Fe_2O_4$ nanosized particles. *J. Magn. Magn. Mater.* 321, 1276-1279.

Lima, U.R., Nasar, M.C., Rezende, M.C., Araujo, J.H. (2008). Ni–Zn nanoferrite for radar-absorbing material. *J. Magn. Magn. Mater.* 320, 1666-1670.

Lin, D., Nunes, A.C., Majkrzak, C.F., Berkowitz, A.E. (1995). Polarized neutron study of the magnetization density distribution within a $CoFe_2O_4$ colloidal particle II, *Journal of Magnetism and Magnetic Materials*, 145 (1995) 343.

Lopez, G. P., Silvetti, S. P., Uretta, S. E., Cabanillas, E. D. (2007), Magnetic interactions in high-energy ball-milled $NiZnFe_2O_4/SiO_2$ composites. *Journal of Physica B*, 398, 241-244.

Louh, R, Reynolds III, T.G and Buchanan, R.C.,(2003). "Ferrite Ceramics" in Ceramic Materials for Electronics, edited by Buchanan, R.C., 3rd Edition, Marcel Dekker Inc., New York.

Maisnam, M., Phanjoubam, S., Sarma, H. N. K., Devi, L. R., Thakur, O. P. and Prakash, C. (2004). Hysteresis and initial permeability behavior of vanadium-substituted lithium–zinc–titanium ferrite. *Physica B*, 352, 86-90.

Marrero-López, D., Martín-Sedeño, M.C., Peña-Martínez, J., Ruiz-Morales, J.C., Núñez, P., Aranda, M.A.G. and Ramos-Barrado, J.R. (2010). Evaluation of apatite silicates as solid oxide fuel cell electrolytes, *Journal of Power Sources*, 195, 2496-2506.

Mendelson, M.I. (1969). Average Grain size in Polycrystalline Ceramics, *Journal of the American Ceramic Society*, (52), 443-446.

Mitoff, S.P. (1966). *“Electrical Conduction mechanisms in oxides” in Progress in Ceramic Science*, 1st Edition, Pergamon Press, Oxford.

Moulson, A.J. and Herbert, J.M., (1990). *Electroceramics: Materials, Properties, Applications*, 1st Edition, Chapman & Hall, London.

Moustafa, S.F. and Morsi, M.B. (1998), The formation of Mg ferrite by mechanical alloying and sintering. *Materials Letter,* 34, 241–247.

Naumann, R. J. (2009). *Introduction to the Physics and Chemistry of Materials*. New York: CRC Press.

Neel, L. (1948). Magnetic properties of ferrites: ferrimagnetism and antiferromagnetism. *Ann. Phys*. Paris 3, 137–198.

Newnham, R.E. (1989). Electroceramics, *Reports on Progras in Physics*, 52, 123-156.

Oliver, S.A., Harris, V.G., Hamdeh, H.H., Ho, J.C. (2000). Large zinc cation occupancy of octahedral sites in mechanically activated zinc ferrite powders, *Applied Physics Letters*, 76 (19), 2761-2764.

Padella, F., Alvani, C., La Barbera, A., Ennas, G., Liberatore, R., Varsano, F. (2005), Mechanosynthesis and process characterization of nanostructured manganese ferrite. *Materials Chemistry and Physics*, 90, 172-174.

Pannarayil, T., Morande R., Komarneni, S., (1991), Magnetic Properties of High Density Mn-Zn Ferrites, J. Appl. Phys. 69 (8), 5349-5341.

Pankert, J., (1994), Influence of grain boundaries on complex permeability in MnZn ferrites, Journal of Magnetism and Magnetic Materials, 138, 45-51.

Pedzich, Z., Bucko, M.M., Krolokowski, M., Bakalarska, M., Babiarz,. J. (2004). Microwave sintering of $(Bi_{0.75}Ca_{1.2}Y_{1.05})(V_{0.6}Fe_{4.4})O_{12}$ Microwave Magnetic Materials, *J. Eur. Ceram. Soc.* 24, 1053-1056.

Perduijin, D.J. Peloschek, H.P. (1968). MnZn ferrites with very high permeabilities, *Proc. Br. Ceram. Soc.*, 10, 263-273.

Rabanal, M.E., Varez, A., Levenfeld, B., Torralba, J.M. (2003), Optimization of the synthesis of soft magnetic materials by mechanochemical process at room temperature. *Materials Science Forum*, 426-432, 4349-4354.

Rafferty, A., Prescott, T and Brabazon, D. (2008). Sintering behavior of cobalt ferrite ceramic, *Ceramic International*, 34, 15-21.

Raghavender , A.T., Zadro, K., Pajic, D., Skoko, Z., Biliskov, N., (2010), Effect of grain size on the Neel temperature of nanocrystalline nickel ferrite, *Journal of Materials Letters*, 64, 1144-1146.

Rao, B.P.. Rao, S.V.S. Prao K.H. (1997). Densification, grain growth and microstructure of Ni-Zn Ferrites. *J. PHYS. Iv FRANCE* 07, C1-241-C1-242.

Rao, B. P., Caltun, O., Dunitru, I., Spinu, L. (2006), Ferromagentic resonance parameters of ball-milled Ni-Zn ferrite nanoparticles. *Journal of Magnetism and Magnetic Materials*, 304, e752-e754.

Reddy, M. P., Madhuri, W. Venkata Ramana, M., Ramamanohar Reddy, N., Siva Kumar, K.V., Murthy, V.R.K., Siva Kumar, K. and Ramakrishna Reddy, R. (2010). Effect of sintering temperature on structural and magnetic properties of NiCuZn and MgCuZn ferrites, *Journal of Magnetism and Magnetic Materials*, 322 (19), 2819-2823.

Rezlescu, E., Sachelarie, L., Popa, P.D., Rezlescu, N. (2000). Effect of substitution of divalent ions on the electrical and magnetic properties of Ni-Zn-Me ferrites, *IEEE Transactions on Magnetics*. 36, 3962.

Rikugawa, H., (1982), Relationship between microstructures and magnetic properties of ferrites containing closed pores, IEE Trans. Magn. 18, 1535-1537.

Roess, E. Hanke, I. and Moser, E. (1964). Mangan-Zink-Ferrite mit Anfangspermeabilitaten bis uber 20 000 und ihr Gefuge, *Z. Angew. Phys.*, 17, 504-508.

Sameshima, S., Higashi K., and Hirata, Y. (2000). Sintering and grain growth of rare-earth-doped ceria particles. *Journal of Ceramic Processing Resources*. 1, 27-33.

Sankaranayanan, V.K., Pankhurst, Q.A., Dickson, D.P.E., Johnson, C.E. (1993). An investigation of particle size effects in ultrafine barium ferrite. *Journal of Materials Science Letters*. 125. 199-208.

Sankpal, A.M., Suryavanshi, S.S., Kakatkar, S.V., Tengshe, G.G, Patil, R.S., Chaudri, N.D., Sawant, S.R., (1998), Magnetization studies on aluminium and chromium substituted Ni-Zn ferrites, *Journal of Magnetism and Magnetic Materials*, 186, 349-356.

Santos, C, Koizumi, M.H., Daguano, J.K.M.F., Santos, F.A., elias, C.N., Ramos, A.S. (2009). *Properties* of Y-TZP/Al2O3 ceramic nanocomposites obtained by high-energy ball milling, *Mater. Sci. Eng. A*, 502, 6-12.

Sepelak, V. Steinike, U. Uecker, D.Chr. Trettin, R. Wibmann, S. Becker, K.D. (1997). High-temperature reactivity of mechanosynthesized zinc ferrite, *Solid State Ionics*, 101–103 (2), 1343-1349.

Sepelak, V., Wibmann, S., Becker, K.D. (1998). A temperature-dependent Mössbauer study of mechanically activated and non-activated zinc ferrite, *Journal of Materials Science*, 33 (11), 2845-2850.

Sepelak, V. and Becker, K.D. (2000). Mossbauer Studies in the Mechanochemistry of Spinel Ferrites, *Journal of Materials Synthesis and Processing*. 8, 155.

Sepelak, V., Menzel, M., Bergmann, I., Wiebcke, M., Krumeich, F., Becker, K.D. (2004), Structural and magnetic properties of nanosize mechanosynthesized nickel ferrite. *Journal of Magnetism and Magnetic Materials*, 272-276, pp. 1616-1618.

Sepelak, V., Bergmann, I., Kips, S., Becker, K.D., Anorg, Z. (2005), Nanocrystalline ferrites prepared by mechanical activation and mechanosynthesis. *Journal of Inorganic and General Chemisry*, 631, 993-1003.

Shinde, T.J., Gadkari, A.B., & Vasambekar, P.N., (2008). DC resistivity of Ni-Zn ferrites prepared by oxalate precipitation method. *Materials Chemistry and Physics*, 111(1), 87-91.

Shokrollahi, H., and Janghorban, K., (2007), Influence of additives on the magnetic properties, microstructure and densification of Mn-Zn soft ferrites, Materials Science & Engineering B, 141, 91-107.

Sivakumar, N., Narayanasamy, A., Ponpandian, N., Greneche, J-M., Shinoda, K., Jeyadevan, B., Tohji, K. (2006), Effect of mechanical milling on the electrical and magnetic properties of nanostructured $Ni_{0.5}Zn_{0.5}Fe_2O_4$. *Journal of Physics D: Applied Physics*, 29, 4688-4694.

Snelling, E.C., (1969). *Soft Ferrites: Properties and applications*, 1st Edition, Iliffe Books Ltd, London.

Sun, K., Ian, Z., Chen, S., Sun, Y., Yu, Z., (2006). Effect of sintering process on microstructure and magnetic properties of high frequency power ferrite, *Rare Metals*, 25, 509-514.

Suryanarayana, C., Chen, G. H., & Froes, F. H. (1992). Milling maps for phase identification during mechanical alloying. *Scripta Metallurgica et Materiala*, 26(11), 1727-17732.

Suryanarayana, C. (1995). Nanocrystalline materials. *International Materials Reviews*, 40(2), 41-64.

Suryanarayana, C. (2001). Mechanical alloying and milling. *Progress in Materials Science*, 46(1-2), 1-184.

Standley, K.J. (1972). Oxide Magnetic Materials 2nd. Ed. Northern Ireland Clerendon press. Oxford.

Stuijts, A.L., Verwell, J. and Peloscheck, H.P. (1964). Dense ferrites and their applications, *IEEE Transactions on Communications and Electronics*, 83, 726-736.

Shi, Y. and Ding, J. (2001). Strong unidirectional anisotropy in mechanically alloyed spinel ferrites, *Journal of Applied Physics*, 90, 4078-4085.

Shinde, T.J. Gadkari, A.B. and Vasambekar, P.N. (2008). DC resistivity of Ni-Zn ferrites prepared by oxalate precipitation method. *Mater. Chem. Phy*. 111(1), 87-91.

Tang, X. L., Wu Zhang, H., Su, H., Jing, Y. L., & Zhong, Z. Y. (2009). Improving exchange-coupling field in the same thickness of pinned magnetic layer. *Journal of Magnetism and Magnetic Materials*, 321(18), 2855-2858.

Tashtoush, N., Hemeda., O.M., Tawfik., A. (2003). Effect of the soaking time on the diffusion and resonant frequency of CoZn ferrite transducer, *Journal of Magnetism and Magnetic Materials*, 256 (1-3), 168-173.

Van der Zaag, P.J., Ruigrok, J.J.M., Noordermeer, A., van Delden, M.H.W.M., Por, P.T., Rekveldt, M.Th., Donnet, D.M., Chapman, J.N., (1993), The initial permeability of polycrystalline MnZn ferrites: The influence of domain and microstructure, *Journal of Applied Physics*, 74, 4085-4095.

Van der Zaag, P.J. (1999). New views on the dissipation in soft magnetic ferrites, *J. Magn. Magn. Mater*. 315, 196-197.

Van Groenou, A. B., Bongers, P.F. and Stuijts, A.L. (1969). Magnetism, Microstructure and Crystal Chemistry of Spinel Ferrites, *Materials Science and Engineering*, (3), 317-392.

Verma, A., Goel, T.C, Mendiratta, R.G., Kishan, P. (2000). Magnetic properties of nickel–zinc ferrites prepared by the citrate precursor method, *J. Magn. Magn. Mater.* 208, 13-19.

Verma, A., Thakur, O.P., Prakash, C., Goel, T.C., and Mendiratta, R.G. (2005). Temperature dependence of electrical properties of nickel-zinc processed by citrate precursor technique. *Materials Science and Engineering B*, 116(1), 1-6.

Viswanathan, B. and Murthy, V.R.K., (1990). *Ferrite Materials: Science and Technology*, Narosa Publishing House.

Waje, S. B., Hashim, M., Wan Yusoff, W. D., Abbas, Z. (2010), X-ray diffraction studies on crystallite size evolution of $CoFe_2O_4$ nanoparticles prepared using mechanical alloying and sintering. *Applied Surface Science*, 256, 3122-3127.

Wang, L. and Jiang J. (2007), Preparation of α-Fe_2O_3 nanoparticles by high-energy ball milling. *Journal of Physica B*, 390, 23-27.

Wang, X., Gui, Y., Wang, Y., Hao, S., Liu, C., (2006). Sintering process and grain growth of Mn-Zn ferrite nanoparticles, *Rare Metals*, 25, 526-530.

Winkler, G. (1981). *Magnetic garnets* (Vol. 5). Braunschweig/Weisbaden: Friedr Vieg &Sons.

Yu, L., Zhang, J., Liu, Y., Jing, C., Cao, S. (2005), Fabrication, structure and magnetic properties of nanocrystalline NiZn-ferrite by high-energy milling. *Journal of Magnetism and Magnetic Materials*, 288, 54-59.

Zalich, M. A. (2005). *Physical Properties of Magnetic Macromolecule-Metal and Macromolecule-Metal Oxide Nanoparticle Complexes*. Virginia Polytechnic Institute and State University Virginia

Zhou, P. H., Deng, L. J., Xie, J. L., Liang, D. F., Chen, L., Zhao, X. Q. (2005) Nanocrystalline structure and particle size effect on microwave permeability of FeNi powders prepared by mechanical alloying. *Journal of Magnetism and Magnetic Materials,* 292, 325-331.

Znidarsic, A and Drofenik, M., (1999), High resistivity grain boundaries in CaO-doped MnZn ferrites for high-frequency power applications, J. Am. Ceram. Soc., 82, 359-365.