UNIVERSITI PUTRA MALAYSIA

MORPHOLOGY AND DIELECTRIC PROPERTIES OF $Ni_{0.5}Zn_{0.5}Fe_2O_4$ NANOPARTICLE PREPARED VIA MECHANICAL ALLOYING TECHNIQUE

RAFIDAH BTE HASSAN

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By

RAFIDAH BTE HASSAN

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MORPHOLOGY AND DIELECTRIC PROPERTIES OF $Ni_{0.5}Zn_{0.5}Fe_2O_4$ NANOPARTICLES PREPARED VIA MECHANICAL ALLOYING TECHNIQUE

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Chairman: Assoc. Prof. Jumiah Hassan, PhD

Faculty: Science

Ni-Zn spinel type ferrites are interesting materials due to its electrical and semiconductor properties. These materials are widely used and exploited. Nickel-zinc ferrite nanoparticles are very important soft magnetic materials for high and low frequency devices application and are good dielectric materials. The starting powders with nanoparticle-size of approximately 22 nm of as-milled $Ni_{0.5}Zn_{0.5}Fe_2O_4$ were obtained by mechanical alloying. The effect of sintering temperature on the evolving microstructural of a single sample $Ni_{0.5}Zn_{0.5}Fe_2O_4$ with the dielectric properties was investigated. The single sample pellet was subjected to repeat sintering from 600°C to 1200°C with 50°C increments. The ferrite sample was analyzed by X-Ray diffraction (XRD) to investigate the phases of the powder and Field Emission Scanning Electron Microscope (FESEM) for the morphology and microstructure analysis. The dielectric properties of the sample were measured using HP 4192A LF Impedance Analyzer in the low frequency range from 40 Hz to 1 MHz and measuring temperatures ranging from 30 °C to 250 °C. The study of dc conductivity on nickel zinc ferrite nanoparticles pellet was carried out to analyze the mechanism of conduction and temperature dependence by using a computer controlled Keithley 236 Source. The variation with temperature of dc conductivity were done from 30°C to 250°C for different sintering temperatures 600°C to 1200°C at 100°C intervals.

The results from XRD show that single phase $Ni_{0.5}Zn_{0.5}Fe_2O_4$ could not be formed during milling alone and therefore requires sintering. It also confirms that the single sample sintered Ni-Zn ferrite has single phase cubic spinel structure with lattice parameter 5.3273 Å and the formation of single phase crystallization $Ni_{0.5}Zn_{0.5}Fe_2O_4$ was detected at early sintering temperature of 600°C exhibiting the advantage of mechanical alloying. The crystallization of the ferrite sample increase with increasing sintering temperature and it was found that there is more densification or less porosity at the higher sintering temperature. The FESEM micrograph shows a significant difference in grain size distribution from 88 nm to 646 nm with increasing sintering temperature from 600°C to 1200°C. This might be an indication for different mechanisms being responsible for grain growth with respect to temperature. Evolution of the microstructure resulted in three activation energies of grain growth where above 850°C, there is a rapid grain growth in the microstructure. The activation energies of grain growth increased with rise in sintering temperature as the average grain size increased from nano-size to micron-size. The variation of the dielectric constant and dielectric loss factor as a function of frequency for the ferrites system at different temperatures show that both the dielectric constant and dielectric loss factor decreases with increasing frequency which is a normal dielectric behavior of spinel ferrites. The Cole-Cole plots are an essential tool for studying the dielectric behavior. It reveals two primary relaxation mechanisms in operation for all sintering temperatures indicating a non-debye relaxation type. Arrhenius diagram of relaxation time as a function of reciprocal temperature is used to analyze the effect of temperature on the rates of chemical reactions. The activation energies of dielectric relaxation decreased with rise in sintering temperature. The activation energy affects the hopping mechanism which correponded with the electrical energy barrier encountered by the electrons during the hopping process. The study of dc conductivity on nickel zinc ferrite nanoparticles was carried out to analyze the mechanism of conduction and the temperature dependence. The values of electrical conductivity σ_{dc} increased with increasing temperature indicating the semiconducting behavior of the sample due to the increase in the thermally activated drift mobility of the charge carriers.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains

MORFOLOGI DAN SIFAT DIELEKTRIK $Ni_{0.5}Zn_{0.5}Fe_2O_4$ NANOPARTIKEL DISEDIAKAN DENGAN KAEDAH PENGALOIAN MEKANIKAL

Oleh

RAFIDAH BTE HASSAN

Mei 2014

Pengerusi: Prof. Madya. Jumiah Hassan, PhD

Fakulti: Sains

Spinel nikel-zink ferit adalah bahan yang menarik disebabkan oleh sifat elektrik dan semikonduktor. Bahan-bahan ini digunakan secara meluas dan dieksploitasi dari abad 50 tahun yang lalu. Kini, penggunaan bahan ferit bertumbuh dengan pesat dan meneruskan trend pengecilan dalam kejuruteraan elektrik, ia adalah keperluan untuk kemajuan kaedah sintesis dan untuk melakukan pencirian terhadap bahan nano ferit. Nikel-zink ferit nanopartikel juga adalah bahan magnet lembut yang penting untuk penggunaan peranti frekuensi tinggi dan rendah dan bahan dielektrik yang baik. Serbuk aloi telah digunakan sebagai permulaan serbuk dimana nanopartikel bersaiz dengan hampir 22 nm nikel-zink ferit sebagai selepas gilingan komposisi $Ni_{0.5}Zn_{0.5}Fe_2O_4$ diperolehi dengan menggunakan electron penghantaran mikroskop (TEM). Selepas itu, sampel disediakan dengan menggunakan pengaloian mekanikal untuk menganalisis kesan suhu pensinteran ke atas perubahan mikrostructur sebagai sampel tunggal dengan sifat-sifat dielektrik. Sampel tunggal dengan pelet bersaiz nanopartikel tertakluk kepada penaikkan suhu sinteran dari 600 ^oC ke 1200 ^oC dengan kenaikan 50 °C. Sampel ferit dianalisis dengan pembelauan X-Ray (XRD) untuk menyiasat fasa serbuk dan mikroskop imbasan electron (SEM) bagi morfologi dan analisis mikrostruktur. Sifat dielektrik seperti pemalar dielektrik (ε') dan kehilangan dielektrik (ε'') telah dikaji sebagai fungsi frekuensi dan suhu untuk $Ni_{0.5}Zn_{0.5}Fe_2O_4$. Sifat-sifat dielektrik sampel diukur mengunakan HP 4192A LF Impedance Analyzer dalam julat frekuensi yang rendah dari

40 Hz sehingga 1 MHz dan suhu antara 30 °C kepada 250 °C. Kajian DC kekonduksian pada nikel zink nanopartikel ferit telah dijalankan untuk menganalisis mekanisma pengaliran dan pergantungan suhu dengan menggunakan Keithley 236 dikawal dengan sumber komputer. Perbezaan dengan pergantungan suhu kekonduksian DC untuk Ni-Zn ferit telah diteliti dari suhu 30 °C kepada 250 °C pada pengsinteran berbeza suhu 600 ^{o}C ke 1200 ^{o}C dengan kenaikan 100 °C. Hasil daripada XRD menunjukkan bahawa fasa $Ni_{0.5}Zn_{0.5}Fe_2O_4$ tidak boleh terbentuk semasa pengisaran sahaja dan oleh itu ia memerlukan proses pensinteran. Ia juga mengesahkan bahawa sampel tunggal Ni-Zn ferit disinter mempunyai struktur fasa spinel padu dengan kekisi parameter 5.3273 Å dan pembentukkan penghabluran fasa $Ni_{0.5}Zn_{0.5}Fe_2O_4$ dikesan pada suhu pensinteran awal 600 °C. Penghabluran sampel ferit meningkat dengan peningkatan suhu pensinteran, sambil mengurangkan keliangan, meningkatkan kepadatan dan purata saiz butiran. Mikrograf SEM menunjukkan perbezaan yang signifikan dalam pengedaran saiz butiran meningkat daripada 88 nm ke 646 nm dengan peningkatan suhu pensinteran. Ini mungkin menjadi petunjuk bagi mekanisme yang berbeza bertanggungjawab untuk pertumbuhan bijian dengan perubahan suhu. Evolusi mikrostruktur mengakibatkan dua tenaga pengaktifan pertumbuhan bijirin di mana, di atas 850 °C, terdapat pertumbuhan bijian yang pesat dalam mikrostruktur. Tenaga pengaktifan telah meningkat dengan kenaikan suhu pensinteran sebagai purata saiz bijian meningkat dari saiz nano ke siz micron. Perubahan pemalar dielektrik dan kehilangan dielektrik sebagai fungsi frekuensi bagi sistem ferit pada suhu berbeza menunjukkan bahawa kedua-dua pemalar dielektrik dan kehilangan dielektrik berkurangan dengan kekerapan meningkat yang merupakan tingkah laku dielektrik biasa spinel ferit. Plot Cole-Cole adalah sebagai alat penting untuk mengkaji tingkah lagu dielektrik. Ia mendedahkan dua mekanisme utama operasi kelonggaran semua suhu pensinteran menunjukkan bukan jenis Debye santai. Rajah Arrhenius untuk kelonggaran masa sebagai fungsi suhu timbale balik digunakan untuk menganalisis kesan suhu ke atas kadar tindak balas kimia. Nilai tenaga pengaktifan semakin berkurangan dengan peningkatan suhu pensinteran. Kajian kekonduksian DC pada nikel zink nanopartikel ferit telah dijalankan untuk menganalisis mekanisme pengaliran dan pergantungan suhu. Nilai-nilai kekondusian DC meningkat dengan peningkatan suhu yang menunjukkan kelakuan semikonduktor sampel.

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APPROVAL

I certify that a Thesis Examination Committee has met on 15 May 2014 to conduct the final examination of Rafidah binti Hassan on her thesis entitled “Morphology And Dielectric Properties Of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ Nanoparticles Prepared Via Mechanical Alloying Technique” 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:

Azmi bin Zakaria, PhD
Physics Department
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Zulkifly bin Abbas, PhD
Physics Department
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Zaidan bin Abdul Wahab, PhD
Physics Department
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Rosli Hussin, PhD
Physics Department
Faculty of Science
Universiti Teknologi Malaysia
(External Examiner)

NORITAH OMAR, PhD
Associate Professor Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 21 July 2014

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

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

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

Suriati Paiman, PhD
Lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

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

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Signature:___________________
Name of
Chairman of
Supervisory Committee: Prof. Madya Dr. Jumiah Hassan

Signature:__________________
Name of
Member of
Supervisory
Committee: Prof. Madya Dr. Mansor Hashim

Signature:__________________
Name of
Member of
Supervisory
Committee: Dr. Suriati bt Paiman

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LIST OF SYMBOLS AND ABBREVIATIONS

XRD	X-ray diffraction
FESEM	Field Emission Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
wt %	Weight percent
hkl	Miller indices
BPR	Ball-to-powder weight ratio
MA	Mechanical alloying
HEBM	High energy ball milling
2θ	2 theta degree
ε’	Dielectric constant
ε’’	Dielectric loss factor
°	Degree
ρ	Density
ρ_{xrd}	X-ray density
σ	Conductivity
nm	Nanometre
Hz	Hertz
MHz	MegaHertz
DC	Direct current
eV	Electron volt
T	Temperature
k	Boltzmann constant
E_a	Activation energy for conductivity
τ	Relaxation time
f	frequency
D	Grain size
Q	Activation energy for grain growth

CHAPTER 1

INTRODUCTION

1.1 Background of the study

The extreme progress in the evolution and growth of electronic ceramics since the time of post Second World War II has played a crucial role in the transformation of the society from Steel Age to the Information Age. Practically instantaneous satellite communications from coast to coast and all over the world would not be possible without simultaneous advances in semiconductors, dielectrics, ferroelectrics, ferrites and optical electronics. The continued developments in these fields have corresponds, and possible eventually superseded, with advances in superconducting ceramics, photonics, optical waveguides and potentially in optical computing and information processing (Hench and West, 1990). Properties of materials are substantially modified with reduction in their size. This has been an extensive area of research with regard to the family of ferrites. Novel methodologies for the development of nanoferrites and investigation of their properties has gained much attention owing to their numerous needs for application in areas like magnetic recording media, targeted drug delivery, magnetic resonance imaging, sensors, heterogenous catalysis, repulsion suspension for use in levitated railway systems, ferrofluids, microwave devices, RF frequency tune circuits and antennas. Ferrites have technological importance due to their high frequency applications. They are good dielectric materials whose properties vary with the method of preparation, sintering condition and amount of constituents. When size of ferrite particles gets reduced to nanoscale, they exhibit unique properties quite different from their bulk counterparts. This opens up several questions regarding the fundamental physics and chemistry of ferrite materials. Nickel zinc ferrite belonging to the class of soft magnetic materials is one such candidate which has wide application potential. In this study, nickel zinc ferrite in the nano regime was prepared by employing both top-down as well as bottom up approaches. It is well known that nanostructured materials can be synthesized based on two general principles as strategies for designing molecular systems. A top-down approach describes the breaking down, or decomposing, of a system to construct the material of interest or to gain apprehension into its compositional subunits. In contrast, a bottom up approach describes the piercing together, or synthesis, of fragments to form the larger molecular system. In the most fundamental sense, nanotechnology refers to the ability to construct molecular assemblies from the bottom up, using current methods and tools to make useful products. The chemical reactions with sufficient driving force can build up particles (bottom up approach) of the material from atomic scale to micron level and above. Here constituent atomic clusters are assembled to form the required nano sized materials by various processes. The dielectric properties of ferrites are susceptible to the cation distribution and microstructure which are successively responsive to the synthesis condition. Therefore, selection of appropriate process is crucial in order to obtain desirables properties. Modern research aims at developing simple low temperature techniques for delivering ferrite nanoparticles in large quantities, having improved properties than those produced by conventional techniques. Among these, an ideal method would be the one which could be carried out at low temperatures with minimal energy consumption, having better yield and to produce ferrites at low cost with improved electrical and mechanical properties.

1.2 Ferrites

Ferrites are well explored in the micron and nano regime. They are mixed metal oxides with iron (III) oxides as their main component and the general chemical formula of spinel ferrites may be written as $MeFe_2O_4$ where 'Me' stands for the divalent metal cation, Me^{+2}. It is very hard and brittle which appears as dark grey or black. A mixture of powders is pressed to form a ferrite core consisting of the component raw materials and subsequently turning it into a ceramic component by sintering process. Crystal types of ferrites can be categorized into three groups where the first group is hexagonal ferrites which have been distinguished due to their high uni-axial magneto-crystalline anisotropy and used for permanent or hard ferrites applications. The second group is the garnet type (soft) ferrites that are unique magnetic ceramics that gives the transparency needed for magnetic optical applications. The third group is spinel ferrites which exhibit soft magnetic behavior that can be magnetized or demagnetized rather easily by externally applied magnetic fields and indeed is the majority of present day magnetically soft ferrites, with cubic crystal structure in the form of the mineral spinel. Nickel zinc ferrites and manganese zinc ferrites are the major members of the spinel ferrite family and the two most popular soft ferrites due to their high electrical resistivity and possible modification of basic properties over a wide spectrum (Hench and West, 1990).

Mn-Zn ferrites have higher initial magnetic permeability and saturation induction than Ni-Zn ferrites but the use of Mn-Zn ferrites cause problems as the premature dielectric breakdown or mal-functioning due to their high electrical conductivity when operating under high frequencies and also overheating by eddy currents. Meanwhile, Ni-Zn ferrites proved to be the chosen ceramic material for high frequency applications where they are more acceptable for frequencies above 1 MHz and exhibit higher resistivity than Mn-Zn ferrites (MnZnFe). It was also found to be very useful in high frequency technological applications in which eddy current suppression is of primary consideration (Kulikowski, 1984). The electrical properties of this particular group of ferrites determined the microstructural characteristics such as grain size, grain boundaries and the nature of porosity that is present in the materials. These aspects are influenced by the chemical composition and high sintering temperature process required in the production of nickel zinc ferrites (NiZnFe). The sintering of NiZnFe is simpler than MnZnFe due to the atmosphere control as operations of NiZnFe are managed in air while MnZnFe needed a redox conditions induced in the sintering chamber during the firing and cooling process. Low losses of NiZnFe controlled by the grain size also give an effect on NiZnFe to be mostly used at high frequency. At the tetrahedral and octahedral sites, nickel and zinc has very firm priority respectively which makes Ni-Fe a model inverse ferrite and Zn-Fe a normal ferrite. Despite that, they are known to occur as mixed spinel structures. Ni-Zn ferrites also have high electrical resistivity to prevent eddy current and moderate magnetic permeability compared to other ferrites. They are also more stable than the other ferrites, easily manufactured, low cost and have excellent desirable magnetic properties. Spinel ferrites nanoparticle have great importance in nano science and nanotechnology for technological applications because of their outstanding properties such as nanometer size and large surface area to volume ratio. Current interest has been made for nano sized nickel zinc ferrite in order to reduce energy losses associated with bulk properties to be more efficient and cost effective.

1.3 Dielectric phenomena

Phenomena of dielectric is like the other natural phenomena which been discovered long time ago. In early 600 BC, the Greek philosopher Thales develops that there is an attractive light objects like bits of chaff on “amber” which is known as electricity in Greek, when rubbed with cloth. Nevertheless, it is well known that many materials have this kind of properties to some scale. The attraction phenomenon where a light piece of paper being pull by metal rod after rubbing with a polyester sheet occurred because of the polarization of paper due to the charge on the rod tip. An opposite charge on the paper surface near the charge rod tip resulted in this attraction cause by electric polarization. In dielectric material, polarization is influence by any electromagnetic wave that also creates their own field which interacts with the external fields, results in an extensive width of dielectric phenomena.

Prior to the mid of the 18th century, the attention in dielectric phenomena is not wide despite the fact that Leyden jar condenser which could store charge was found in 1745 (Skilling, 1948). Faraday was the person in 1837 that introduced the capacitance of a condenser that depends on the condenser with material inside it. It was known as correlation of the capacitance and condenser occupied with a dielectric material with the same condenser, free space and the specific inductive capacity which is known as permittivity. The development of new dielectrics especially the ferroelectric ones, as well as the growth of the area of application of some of their special features has led to the creation of new types of dielectric devices for radio-electronic and optical equipment, and has induced large number of research in this field. Dielectric behavior is the most significant of ferrites which obviously relied on the preparation conditions such as sintering atmosphere, temperature, type of material and technique of the process. The nano crystalline ferrites have many applications which provide useful information on the response of localized electric charge carriers influential to substantial understanding of the mechanism of dielectric polarization and its varied from microwave to radio frequencies

1.4 Problem statement

The primary focus of the thesis work was the production of dense and microstructurally tailored Ni-Zn ferrite sample of composition $Ni_{0.5}Zn_{0.5}Fe_2O_4$ which could be sintered at relatively low sintering temperatures. Currently, many branches of communication and electronic engineering have been established in applications of ferrites. Common applications include audio and video recording tapes, motors, generators, recorders, computer disks and high frequency inductor and transformer cores (Moulson et al., 1990). Concurrently, there are fast developments of electronic industry, electronic components which require higher density circuit in electronics while largely accelerated with multifunctional and high performance, smaller size and cost effective of miniaturization of electronic chip components. Dielectric and electrical properties of materials have wide attention lately and a lot of operation has been conducted for analyzing dielectric materials to encounter the essential for multifunctional components (Mantese et al., 1996). It can exhibit both high inductive and capacitive properties which have been determined to be an enabling solution to fabricate miniature filter and antenna, electro-magnetic interference (EMI) devices and others.

The composition and microstructure of material give impact on the properties of ferrite materials susceptible to the processing methods used in the synthesis. It suggests investigating the microstructure-dielectric properties relationships at various intermediate sintering conditions in the parallel evolutions of the morphology and material properties. Do the changes of microstructure affect the dielectric properties of the material? This research work intends to track the evolution of dielectric properties parallel to the microstructural changes with only one single sample being sintered at different sintering temperatures and which is the best sintering temperature for this composition.

1.5 Research Objectives

The purpose of the current thesis study is to investigate the parallel evolution of microstructural and dielectric properties of a single sample from lower sintering temperature of 600 °C to 1200 °C. Nickel zinc ferrite with the composition $Ni_{0.5}Zn_{0.5}Fe_2O_4$ was chosen in this study and it has been proved to be the preferred ceramic material for high frequency applications. It was proposed to make high performance ferrites which have high electrical resistivity, improved dielectric properties, densities and less porosity. The description of ferrites composition needed different analyses such as surface analysis, phase analysis and their properties. NiZn ferrite are more stable than the other ferrites, easier in the sintering process due to the simplicity of the atmosphere control, easily manufactured, low cost, have excellent and desirable dielectric properties.

The electrical and dielectric properties of this particular group of ferrites depend strongly on the microstructural features such as grain size, the nature of grain boundaries and the extent and nature of porosity. This study embarks on the following objectives:

1. To prepare a single sample $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticle using mechanical alloying method to refine its microstructure-dielectric properties to produce high purity sample.

2. To determine the dielectric properties of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ at low frequency from 40 Hz to 1 MHz at measuring temperatures from room temperature to 250 ^{o}C.

3. To analyze the effect of the sintering temperature 600^{o}C to 1200°C on the microstructural evolution and dielectric properties of Ni-Zn ferrite.

REFERENCES

Adnan, A., Gul, S., and Ali, M. (2008). Content based image retrieval using geometrical shape of objects in image, *International Conference on Technology*. Peshawar, p. 222-225.

Alvani C., Ennas G., La Barbera A., Marongiu G., Padella F., Varsano F. (2005). Synthesis and characterization of nanocrystalline $MnFe_2O_4$ advances in thermochemical water splitting, *International Journal Hydrogen Energy*. 30(13-14), p. 1407-1411.

Amador, D. R. and Torralba, J. M. (2003). Morphological and microstructural characterization of low alloying Fe powder obtained by mechanical attrition, *Journal Material Technology*, Vol. 143-144, p. 776-780.

Benjamin, J. S. and Violin, T. E. (1934). The Kinetics of Composite Particle Forming during Mechanical Alloying, *Metallic Transcript.*, Vol. 5, p. 1929-1934.

Benjamin J. S. (1970). Dispersion Strengthened Superalloys by Mechanical Alloying, *Metalic Transcript.*, Vol. 1, p. 2943.

Benjamin S. and Gilman P. S. (1983). *Metals Handbook.* (9^{th} ed.). ASM International, Ohio, Chapter 7, p. 722.

Borner I. and Eckert J. (1997). Nanostructure formation and steady state grain size of ball-milled iron powders. *Material Science Engineering*, 541, p. 226-228.

Broese Van Groenev A., Bongers P. F. and Stuyts A. L. (1968). Magnetism, microstructure and crystal chemistry of spinel ferrites, *Material Science Engineering*, 3, p. 317.

Chougule S. S. and Chougule B. K. (2008). Response of dielectric behavior on ferroelectric rich (x) $Ni_{0.8}Zn_{0.2}Fe_2O_4$+(1-x) PZT ME composites. *Material Chemistry Physics*, 108, p. 408.

Chen D. G., Tang X. G.,Tong J. J., Wu J. B., Jiang Y. P., Liu Q. X. (2011). Dielectric relaxation of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ Ceramics, *Journal Solid State Communications.*, 151, p. 1042-1044.

Coble R. L. (1961). Sintering crystalline solids. II. Experimental test of diffusion models in powder compact, *Journal Applied Physics*, 32, p. 793-799.

Cole K. S. and Cole R. H. (1941). Dispersion and Absorption in Dielectrics and Alternating Current Characteristics, *Journal Chemistry Physics*, 9, p. 341.

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 Magnetic. Material*, 256, p. 174.

Cullity, B. D., (1978). *Elements of X-Ray Diffraction*, (2nd ed.). Addison Wesley, UK.

Dias A. and Moreira R. L. (1999). Chemical, mechanical and dielectric properties after sintering of hydrothermal NiZn ferrites, *Material Letter*, 39, p. 69.

Dunitz J. D. and Orgel L. E. (1957). Electronic properties of transition metal oxides, Cation distribution amongst octahedral and tetrahedral sites, *Journal Physics Chemistry Solids,* 3, 318.

El-Sayed, A. M. (2002). Influence of zinc content on some properties of Ni-Zn ferrites, *Ceramic International*. 28, 363-367.

F. de Boer, Van Santen, J. H., and Verwey, E. J. W. (1937). Cation arrangement in spinels ferrites, *Procedure Royal Society,* London, 49, 59.

Fang H., Chen B., Jiang K., Sha J., Jiao Z., Zhang Q. and Zhang L. (1995). *Physics Status Solidi*, b 192, K11.

Fecht H. J., (1994). Proceedings of the NATO Advanced study institute on Nanophase materials-syntheses, properties and applications, *Kluwer academic publishers*, p. 125.

Forestier, H., Ann. Chemie Xe Series Tome. (1928). 9, 353.

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

Haijun Z. L., Zhichao L., Chenliang M., Xi Y., Liangying Z. and Mingzhong W. (2003). Preparation and microwave properties of Co-and Ti- doped barium ferrite by citrate sol-gel process, *Material Chemistry Physics*, 80, p. 129.

Hench, L. L. and West, J. K. (1990). Principles of electronic ceramics. *John Wiley & Sons.*

Heiks R. R. (1955). Relation of magnetic structure to electrical conductivity in NiO and related compounds, *Phyics Revision,* 99, 1232.

Heinicke G. (1984). Akademie Verlag, Berlin, Vol. 36, p. 400-401.

Homes C. C., Vogt T., Shapiro S. M., Wakimoto S., and Ramirez A. P. (2001). Optical response of high dielectric constant perovskite related oxide, *Science,* 293, p. 673.

Igarashi, H., Okazaki, K. (1977). Effects of porosity and grain size on the magnetic properties of NiZn ferrites, *Journal Ceramic Society*, 51(60).

Ismail, I., Hashim M. (2011). The Effect of Milling Time on $Ni_{0.5}Zn_{0.5}Fe_2O_4$ Compositional Evolution and Particle Size Distribution. *America Journal Applied Sciece,* p. 1548-1552.

Ismail, I.,Hashim M. (2014).Evolving microstructure, magnetic properties and phase transition in a mechanically alloyed $Ni_{0.5}Zn_{0.5}Fe_2O_4$ single sample, *Journal Magnetism and Magnetic Materials.*, 351, p. 16-24.

Iwauchi K. (1971). Interface Properties of Al_2O_3 Structure and Chararcteristics, *Journal Applied Physics,* 10, p. 1520.

Jonker G. H. (1959). Ferromagnetic compounds of manganese with perovskite structure, *Journal Physics Chemistry Solids,* 9, p. 165.

Jonscher A. K. (1983). Dielectric relaxation in solids, *Chelsea, Dielectric Press,* London. 3, 231.

Josyulu O. S. and Sobhanadri J. (1976). DC conductivity and dielectric behavior of cobalt zinc ferrites, *Journal Physics Statistic Solid,* 36K, p. 133.

Kulikowski, J. (1984). Soft magnetic ferrites development or stagnation, *Journal Magnetic Material,*41, 56

Koop C. G. (1951). On the dispersion of resistivity and dielectric constant of some semiconductors at audio frequencies, *Physics Revision*, 83, p. 121.

Kuhn E., (1984). "*Powder Metallurgy", ASM Handbook,* Vol. 7, ASM International: Material Park, OH. p. 56-70.

Louh, R., Reynolds III, T. G. and Buchanan, R. C. (2004). *Ferrite Ceramics in Ceramic materials for electrocnics* (3rd ed.). Marcel Dekker inc., New York.

Maensiri, S., Masingboon, C., Boomchom, B., Seraphin, S. (2007). A simple route to synthesize nickel ferrite ($NiFe_2O_4$) nanoparticles using egg white, *Scripta Materialia*, vol. 56, p. 797.

Mantese, J. V., Micheli, A. L., Dungan, D.F., Geyer, R.G., BakerJarvis & Grosvenor, J. (1996). Applicability of effective medium theory to ferroelectric/ferrimagentic composites with composition and frequency-dependent complex permittivities and permeabilities. *Journal Applied Physics.* 79(3):1655-1660.

Mangalaraja R. V., Ramam K. V. S., Ravi J., Carlos P., Camurri. (2008). Synthesis of nanocrystalline yttria by microwave assisted citrate gel decomposition technique, *Journal Material Process Technology,* 197, p. 292-295.

Mathur R. B.,Chatterjee S., and Singh B. P. (2008). Growth of carbon nanotubes on carbon fibre substrates to produce hybrid/phenolic composites with improved mechanical properties. *Compos Science Technology*, 68, p. 1608-1615.

Maxwell J. C. (1982). A Treatise on Electricity and Magnetism, *Clarendon Press*, Oxford. Vol. 2, (3rd ed.).

McClure D. S., (1957). First Singlet-Singlet transition, *Journal Physics. Chemistry. Solids,* 3, 311.

Mohan R. M., Amara C. E., Cunningham D. A., Duffin J. (1999). Department of Physiology, Universiti of Toronto,Ontario, Canada, 115, 23-33.

Mohan G. R., Ravinder D., (1999). Dielectric properties of polycrystalline mixed nickel-zinc ferrites, *Material Letter*, 40, p. 39-45.

Moltgen S. (1952). *Z. Angew. Physics*, 4, 216.

Moulson, A. J. and Herbert, J.M. (1990). *Electroceramics: Material Process Applied*, (1st ed.). Chapman & Hall, London.

Mu C., Chen N., Pan X., Shen X. and Gu X. (2008). Preparation and microwave absorption properties of barium ferrite nanorods, *Material Letter* 62, p. 840.

Murr L. E. (1982). Electron and Ion Microscopy and Microanalysis, Principles and Applicatons, *Mc. Graw Hill Inc.* New York. 544.

Naik A. B. and Powar J. I. (1985). Electric and magnetic behavior of ferrites, *Indian Journal Pure and Applied Physics*, 23, 436.

Nazlan R., Ismail I., (2014). Complex permeability, Curie temperature and activation energy as a function of microstructure evolution in a mechanically alloyed $Y_3Fe_5O_{12}$ single sample, *Journal Basic and Applied Science* 8(3), p. 474-482.

Ozdemir I., Ahrens S., Mucklich S., Bemhard W., (2008). Nanocrystalline Al_2O_3 and SiC composites produced by high energy ball milling. *Journal Material Process Technology*, 205, p. 111-118.

Parvatheeswara Rao B., Subba Rao P. S. V. and Rao K. H. (1977). *IEEE Transnational. Magnetic*, 33, 4454.

Plocharski J. and Wieczorek W. (1988). PEO based composite solidelectrolyte containing Nasicon, *Solid State Ionics*, 28-30, p. 970-983.

Pradhan, A. K., Hammel, K. R., Deramus, R., Pollatsek, A., Noyce, D. A., Fisher, D. L. (2005). *Human Factors*, 47(4), 840-852.

Ponpandian N., Balaya P., and Narayanasamy A. (2002). *Journal Physics Condenser. Matter*, 14, 3221.

Ramalho, M. A. F., Gama, L., Antonio, S. G., Paiva-Santos, Miola, E. J., Kiminami, R. H. G. A., and Costa, A. C. F. M. (2007). X-Ray diffraction and Mossbauer spectra of nickel ferrite prepared by combustion reaction. *Journal of Material Science*, 42, 3603-3606.

Ranga Mohan G. and Ravinder D. (1999). *Material Letter*, 40, 39-45.

Rahman, M. N. (2003). Ceramic Processing and Sintering. *CRC Press.*

Ravindranathan, P., Patil, K. C. (1987). *Journal Material Science*, 3261(22).

Rao, B. P., S. V. S. Rao and K. H. Prao. (1997). Densification, grain growth and microstructure of Ni-Zn ferrites, *Journal Physics* Iv France.

Rao P. B.C., Setty S. P., Paldouglas S., Venkateswara rao B. (2011). *International Journal Engineering Technology Science*, Vol 2(3), 238-240.

Rezlescu N. and Rezlescu E. (1974). Dielectric properties of copper containing ferrites, *Journal Physics Status Solid*, 23, 575.

Rezlescu N., Sachelarie L., Rezlescu E., C-L., SavaandP. Popa, D. (2003). Influence of PbO on microstructure and properties of a NiZn ferrite. *Ceramics International*, 29, pp. 107-111.

Samokhvalov, A. A. and Rustamov, A. G. (1964). *Soviet Physics Solid State*, *6*, *749.*

Shenoy S. D., Joy P. A., Anantharaman M. R. (2004). Effect of mechanical milling on the structural, magnetic and dielectric properties of coprecipitated ultrafine zinc ferrite, *Journal Magnetic Magnet Material*, 269, p. 217-226.

Shingu, P. H. (1991). Mechanical alloying, *Transcript Technology Publication, Switzerland*, Vol. 1992, p. 816.

Sivakumar, N., Narayanasamy, A., Jeyadevan, B., Justin Joseyphus, R., and Venkateswaran, C. (2008). *Journal Physics D: Applied Physics*, 41**,** 2451.

Skilling, H.H. (1948). *Fundamental of electric waves* (2nd ed.). J. Wiley &Son Incorporated.

Smith J. and Wijn H. P. J. (1959). Ferrite, Philips Technical Library, Eindhoven, The Netherlands, p, 137.

Snelling, E. C. (1969). *Soft Ferrites: Properties and Application* (1st ed.). Life Books Ltd., London.

Snoek, J. L. (1947). New developments in ferromagnetic materials. *Elsevier Publishing Co.* New York-Amsterdam.

Soohoo R. F. (1960). Theory and Application of Ferrites, *Prentice-Hall*, p. 30.

Tayal D. C. (1988). Electricity and Magnetism, *Himalaya Publishers.* 5, p. 372.

Thakur, A. and Singh, M. (2003). Preparation and characterization of nanosize $Mn_{0.4}Zn_{0.6}Fe_2O_4$ ferrite by citrate precursor method, *Ceramics International,* Vol. 29, p. 505.

Trivedi U. N.,Chantbar M. C., Modi K. B. and Joshi H. H. (2005). *India Journal Pure Applied Physics,* Vol. 43, p. 668-690.

Upadhyay Trupti, Upadhyay R. V. & Mehta R. V. (1997). Characterization of temperature sensitive magnetic fluid, *Physics Revision Book,* 55(9), 5585.

Verma, A., Goel, T. C., Mendiratta, R.G., Alam, M. I. (1999). Dielectric properties of nizn ferrites prepared by the citrate precursor, *Material Science Engineering Book*, 60, p. 156.

Van Uitert, L. G. (1956). High resistivity nickel ferrites the effect of minor additions, *Process IRE,* 44, 1294.

Verwey E. J. W., De Boer F., and Van Santen J. H. (1948). Cation arrangement in spinels, *Journal Chemistry Physics.* 16, 1091.

Watt I. M. (1997). *The principles and practice of electron microscopy.* (2nd ed.). Cambridge University Press, p. 263-302.

Wagner K. W. (1913). On the theory of imperfect dielectrics, *Journal Physics* Vol. 345, p. 817-855.

West A. R. (2005). Solid State Chemistry and its applications. *John Wiley Sons,* India, p. 1973-1978.

Yang H., Zhang Z., Tang A. and Qiu G. (2004). Cobalt ferrite nanoparticles prepared by co-precipitationor mechanical treatment. *Chemistry Letter*, 33(7): 826.

Yavari, A. R., Desre, P. J. and Benameur, T. (1992). Mechanical driven alloying of immiscible elements, *Physics Revision Letter*, Vol. 68, p. 2235-2238.

Xu G., Zhang X., He W., Liu H., Li H., Boughton R. I. (2006). Synthesis of nanodisperse and spherical YAG nanopowder by a mixed solvothermal method, *Material Letter*, 60, p. 962-965.