



UNIVERSITI PUTRA MALAYSIA

***EVOLUTION OF MORPHOLOGY, MAGNETIC PROPERTIES AND THEIR
RELATIONSHIPS DURING SINTERING OF BARIUM FERITE ($BaFe_{12}O_{19}$),
COBALT FERRITE ($CoFe_2O_4$) AND COBALT NICKEL FERRITE
($Co_{0.5}Ni_{0.5}Fe_2O_4$)***

MOHD SHAMSUL EZZAD SHAFIE

ITMA 2015 16



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By

MOHD SHAMSUL EZZAD SHAFIE



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

September 2015

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**In appreciation of their love and sacrifices, this thesis is dedicated to Parents
SHAFIE BIN AWANG and NORIZAH BINTI MAT**

Beginning... PhD

Padang perahu di lautan
Padang hati di fikiran

Intermediate...PhD

Kupu-kupu terbang melintang
Hinggap menghisap bunga layu
Hati di dalam menaruh bimbang
Melihat ikan memanjang kayu

Orang selsema sakit berhingus
Lubang hidung rasa terkambus
Ibarat seperti telur kemungkus
Benci nak pandang rasa cemus

Anak ruan tidak terluang
Benang sutera di dalam tubuh
Hendak buang tidak terbuang
Sudah mesra di dalam tubuh

Ending..Phd

Murai gila jadi tekukur
Ajaib hairan hati tafakur

Kalau tuan pergi ke Kedah
Singgah lama di Kuala Muda
Kalau suatu diperolehi dengan mudah
Bagai irama hilang nada

Cahaya redup menyegar padi
Ayam berkокok mengirai tuah
Jikalau hidup tidak berbudi
Umpama pokok tidak berbuah

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

**EVOLUTION OF MORPHOLOGY, MAGNETIC PROPERTIES AND THEIR
RELATIONSHIPS DURING SINTERING OF BARIUM FERITE ($\text{BaFe}_{12}\text{O}_{19}$),
COBALT FERRITE (CoFe_2O_4) AND COBALT NICKEL FERRITE
($\text{Co}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$)**

By

MOHD SHAMSUL EZZAD SHAFIE

September 2015

Chairman: Associate Professor Mansor Hashim, PhD
Institute : Advanced Technology

In this study, the microstructural evolution during sintering of BaM, CoF and CoNiF ferrites is reported in terms of the effects of the sintering route and temperature, as well as densification behavior and grain-growth kinetics through regression coefficient plots. Three ferrite materials were selected due to outstanding properties in electronic applications and no detail study on evolution study for that material. These materials synthesized using mechanical alloying followed by sintering from 500 to 1400°C with 100°C increments. Two sintering modes were adopted: MSS and SSS. The particle size structural, microstructural and magnetic properties details of the samples were detained by appropriate use of transmission electron microscopy (TEM), X-ray diffractometry (XRD), scanning electron microscopy (SEM), vibrating sample magnetometry (VSM), and a B-H hysteresis graph.

This study proves that microstructure generally influences the magnetic properties as reflected by a threshold grain size, for the H_c , as the SD to MD magnetic transition point. At early sintering temperatures, microstructure shows widespread necking processes, proving the occurrence of densification. For hard ferrite BaM, a single phase was observed to form at a temperature of 1000°C which is higher than that for soft ferrite at 700°C. It is noted that strong magnetocrystalline anisotropy would cause significant difficulty to align magnetic moments in BaM, as indicated by H_c values for this phase. In intermediate sintering, approximately 800 to 1100°C for BaM and 700 to 1000°C for CoF and CoNiF, strong ordered magnetism is shown by the B-H loop shape. It is also believed that densification through grain boundary diffusion was dominant at this stage.

Increasing sintering temperature resulted in higher density, coarser microstructure, and further densification and grain growth. However, a substantial amount of powder surface reactivity was still preserved within the microstructure of the compact. Subsequently, during the dwell time at the highest temperature, densification and grain growth took place at higher rates resulting, finally in increased density, coarser microstructure and higher initial magnetic permeability. At this stage, grain boundary diffusion through lattice and volume diffusion dominated causing microstructure to grow abnormally with introduction of intragranular pores. Porosity was observed to increase at this stage.

The substitution of NiO into CoF enhances the sintering by increasing bulk diffusion due to the increased vacancy concentration which is accompanied by the solubility of Ni^{2+} in the ferrites. Ni^{2+} ions are cations that are soluble in the host lattice and enter regular positions on the tetrahedral or octahedral sites. The results for the MSS and SSS samples as obtained from their hysteresis magnetic loops, showed high saturation magnetization BaM ($100 < 4\pi\text{Ms} < 9800$ G), low remanence ($7 < \text{Br} < 2039$ G) and H_c ($22 < H_c < 35$ Oe) values. The relative density-grain size plot of the sintering process demonstrates a crossover between the densification mechanisms from grain boundary diffusion to lattice diffusion with increasing sintering temperature. Most importantly, the M-H loops for BaM, CoF and CoNiF were each found to belong to three families of M-H curves which correspond to different states of magnetism.

Finally for the evolution study, it is strongly believed that there are a few factors found to sensitively influence the samples content of ordered magnetism: their ferrite-phase crystallinity degree, the fraction of grains above the critical grain size and large enough grains for domain wall accommodation.

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

**EVOLUSI RUPABENTUK, SIFAT MAGNETIK DAN HUBUNGAN
MEREKA SEMASA PENSINTERAN BARIUM FERIT ($BaFe_{12}O_{19}$), KOBALT
FERIT ($CoFe_2O_4$) KOBALT NIKEL FERIT ($Co_{0.5}Ni_{0.5}Fe_2O_4$)**

Oleh

MOHD SHAMSUL EZZAD SHAFIE

September 2015

Pengerusi: Profesor Madya Mansor Hashim, PhD
Institut : Teknologi Maju

Dalam kajian ini, evolusi mikrostruktur semasa pensinteran BAM, COF dan CoNiF ferrites dilaporkan dari segi kesan laluan pensinteran dan suhu, serta juga keadaan pemanasan dan kinetik pertumbuhan bijirin melalui plot pekali regresi. Tiga bahan ferit dipilih kerana sifat cemerlang dalam aplikasi elektronik dan tiada kajian terperinci mengenai kajian evolusi untuk bahan tersebut. Bahan-bahan ini dihasilkan menggunakan pengaloian mekanikal diikuti oleh pensinteran dari 500-1400°C dengan 100°C kenaikan. Dua mod pensinteran telah diterima pakai : MSS dan SSS. Saiz zarah sifat-sifat struktur , mikrostruktur dan magnet butiran sampel telah diperolehi dengan penggunaan yang sesuai alat mikroskop pemancaran elektron (TEM) ,Pembelauan sinar- X (XRD) , mikroskop imbasan elektron (SEM) , magnetometry sampel bergetar (VSM) dan BH histerisis graf.

Kajian ini membuktikan bahawa mikrostruktur umumnya mempengaruhi sifat-sifat magnet seperti yang ditunjukkan oleh saiz ambang bijirin, untuk H_c , kerana titik peralihan magnet dari SD kepada MD. Pada suhu pensinteran awal, mikrostruktur menunjukkan proses perleheran yang meluas , membuktikan berlakunya pemanasan . Untuk ferit keras BaM , fasa tunggal diperhatikan terbentuk pada suhu 1000 °C yang lebih tinggi daripada itu untuk ferit lembut pada suhu 700 °C. Ia menyatakan bahawa anisotropi hablur magnetic kukuh akan menyebabkan kesukaran besar untuk menyelaraskan momen magnet di BaM , seperti yang ditunjukkan oleh nilai-nilai H_c untuk fasa ini. Dalam pensinteran pertengahan, kira-kira 800-1100 °C untuk BaM dan 700 1000 °C untuk COF dan CoNiF , kemagnetan kuat terarah ditunjukkan oleh bentuk gelung BH. Ia juga dipercayai bahawa pemanasan melalui sempadan bijian penyebaran adalah dominan pada peringkat ini.

Peningkatan suhu pembakaran menghasilkan ketumpatan yang lebih tinggi, mikrostruktur kasar, dan pemedatan serta pertumbuhan bijian. Walau bagaimanapun, sejumlah besar kereaktifan permukaan serbuk masih dikekalkan dalam mikrostruktur padat . Selepas itu , pada masa suhu dikekalkan, pemedatan dan bijirin pertumbuhan tertinggi berlaku pada kadar yang lebih tinggi, akhirnya ketumpatan meningkat, mikrostruktur lebih kasar dan kebolehtelapan magnet di permulaan yang lebih tinggi. Pada peringkat ini , penyebaran sempadan bijian melalui kekisi dan jumlah penyebaran dikuasai menyebabkan mikrostruktur berkembang secara biasa dengan kemunculan liang intraganular . Keliangan diperhatikan meningkat pada peringkat ini.

Penggantian NiO ke dalam COF menambahbaik pembakaran dengan meningkatkan penyebaran pukal kerana kekosongan kepekatan meningkat yang disertai oleh kebolehlarutan Ni^{2+} dalam ferrites. Ni^{2+} ion adalah kation yang larut dalam kekisi perumah dan memasuki kedudukan biasa pada tapak tetrahedron atau oktahedron. Keputusan bagi MSS dan SSS sampel yang diperolehi daripada gelung magnet histerisis mereka, menunjukkan tingginya nilai-nilai pemangnetan tenu BaM ($100 < 4\pi Ms < 9800$ G), remanence rendah ($7 < Br, < 2039$ G) dan H_c ($22 < Hc < 35$ Oe). Plot pemedatan saiz bijirin relatif untuk proses pensinteran menunjukkan salingkaitan antara mekanisma pemedatan dari penyebaran sempadan bijian kepada kekisi penyebaran dengan peningkatan suhu pembakaran. Paling utama, gelung M-H untuk BaM, COF dan CoNiF telah didapati setiapnya memiliki tiga keluarga lengkung M-H yang sesuai dengan keadaan-keadaan yang berbeza kemagnetan. Akhir sekali dalam kajian evolusi, amat dipercayai bahawa terdapat beberapa faktor yang didapati dengan secara sensitif mempengaruhi kandungan sampel kemagnetan terarah: darjah fasa penghaburan ferit, sebahagian kecil daripada biji-bijian melampaui saiz butiran kritis dan bijirin cukup besar untuk pengisian dinding domain.

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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 are as follows:

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LIST OF ABBREVIATIONS

XRD	X-ray diffraction
SEM	Scanning Electron Microscopy
EDX	Energy Dispersive X-ray
STEM	Scanning 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_a	Anisotropy field
H_C	Coercivity
M	Mass magnetization
M_R	Remanent magnetization
M_S	Saturation magnetization
σ_R	Specific remanent magnetization
σ_S	Specific saturation magnetization
T_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
MSS	Multisample sintering
SSS	Single sample sintering
BaM	Barium hexaferrite
CoF	Cobalt ferrite
CoNiF	Cobalt nickel ferrite
T_s	Sintering temperature
T_c	Curie temperature
PVA	Polyvinyl Alcohol
Q_a	Activation energy
D_{RD}	Relative density
G	Grain size
HEBM	High Energy Ball Milling
SP	Superparamagnetic
SPM	Superparamagnetic material
MD	Multi-Domain
SD	Single-Domain
PSD	Pseudo Single-Domain
D	Diffusion
G	Grain size
r_p	Pore radius
ρ_{xrd}	XRD density
ρ_{exp}	Experimental density

CHAPTER 1

INTRODUCTION

1.1 Current trend of magnetic nanomaterials research

Magnetic materials nowadays have been of great interest for their technological applications. The changing of grain size would adjust magnetic properties of ferrite (Ismail et al., 2014). The systematic studies on the correlations between magnetic properties and microstructure evolution of ferrite will provide fundamental understanding of magnetic properties. This study is focused on investigating the underlying mechanisms and correlating these to changes in structure and magnetic properties of the ferrite as a function of processing characteristics, sintering route and initial state starting powders. In this study, we apply two routes of sintering known as single sample sintering (SSS) and multi sample sintering (MSS). SSS has one compaction of nanoparticles and one sintering route while the MSS has different sample compaction of nanoparticles and different routes of sintering. It should be carefully noted from the beginning that the MSS scheme yields evolution changes statistically assumed to occur subsequently after the previous lower temperature. However, the SSS scheme yields evolution changes which are tone, not statistically assumed, changes occurring after the previous lower temperature. This is because in the MSS scheme there is only one sintering temperature for each sample, which in the SSS scheme there is only one sample which goes through the entire sequence of sintering temperatures.

1.2 Scope of this study

In this study, we describe synthesis of hard magnetic material via mechanical alloying processing. The chosen of material are confined to hard magnetic materials which are probably representative of hard magnetic ceramics. The all-important crystal structure, microstructure and the major hysteresis loop parameters of the materials are the main study focus in this work.

In particular, a considerable effort was made to understand the details of the evolution of microstructure and magnetic properties during the grain growth and subsequent sintering treatment. By studying the key mechanisms associated with the formation of grain evolution in the course of the sintering routes investigated in this work we hope to develop well-tailored and micro structurally guided approaches to the large scale production of ferrite magnetic material. However, very little attention has been paid to this aspect in the literature. Williamson-hall analysis adopted in this study for observing the nanoscale features such as strain broadening present inside the mechanically alloyed powder particles.

1.3 Problem Statement

The control of the magnetic properties relies on the control of the microstructure development in sintering. To control the microstructure development, the understanding of the relation between densification, grain and pore growth is clearly necessary. Thus, to have a good understanding of the behavior of ferrites, it is imperative to perform systematic investigations of their properties, in particular, the microstructural evolution during sintering (or their densification and grain growth). The microstructures developed during sintering are determined to a large extent by the powder characteristics (crystallite size and shape, size distribution, porosity, state of agglomeration, and chemical and phase composition) and by the green microstructure, which are intimately related to the processing method. The effects of these parameters on the microstructural evolution are reported and qualitatively discussed in terms of the densification and grain growth kinetics.

The investigations of the sintering phenomena are mainly concentrated on densification and microstructure development of ferrites. Although the densification process is one of the main phenomena in the sintering process, however, coarsening process, involving grain growth, pore growth, and diminution, is also an important process in sintering, and more importantly, the coarsening process will affect the densification. Therefore, in order to understand the sintering process well, the relationship between the densification and the growth of pore and grain should also be understood. To understand it, in this study we provide knowledge to answer the composition-microstructure relationships at various intermediate sintering conditions during the parallel evolutions of the morphology and the material properties. We also attempt to answer the following questions; do the changes of microstructure affect the magnetic properties? What would the magnetic properties evolve with the microstructure changes? what would happen to the ions of the materials during and parallel to the microstructure changes? do they also rearrange to contribute to magnetization of the materials?

1.4 Objectives

Based on reviews throughout publication from other researchers, no studies on the detail magnetic-properties relationship in barium hexaferrites, cobalt ferrite and cobalt nickel ferrite synthesized by mechanical alloying method have been carried out. The ultimate goal of this research is to critically track the evolution of magnetic properties parallel to the microstructural changes. Our objective in this study is to understand the evolution of magnetic properties parallel to the microstructural changes. The specific objectives are:

- 1) To prepare $\text{BaFe}_{12}\text{O}_{19}$, CoFe_2O_4 and $\text{Co}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ prepared by mechanical alloying process.
- 2) To study the evolution of magnetic properties with microstructure changes involving mechanical alloying effect.
- 3) To study microstructure changes arising from mechanical alloying effects.

- 4) To study the effect of the sintering route on the microstructural evolution and magnetic properties of $\text{BaFe}_{12}\text{O}_{19}$, CoFe_2O_4 and $\text{Co}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ ferrites.
- 5) To study the influence of microstructural changes of magnetic properties when the cobalt in cobalt ferrite is partially substituted by a partially nickel amount.

1.5 Significant of Study

Ferrite materials are known to provide the best combination of magnetic properties necessary for applications in the magnet industry. High performance ferrites materials, offering a high magnetization with a large H_c , exhibit outstanding magnetic behavior at room temperature. $\text{BaFe}_{12}\text{O}_{19}$, CoFe_2O_4 and $\text{Co}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ materials have become the ideal candidates, as they possess a many applications nowadays. These materials are characterized by the relation magnetic-microstructure evolution, which bears the fundamental importance for structural and magnetic properties. Presently, the preparation and production of these materials are generally not yet fully systematic.

Thus, the enhancement of magnetic properties can be tailored by systematically controlling the sintering process through microstructural modifications, which depend on the formation of the specific atomic sublattices governed by establishment of the proper phase relationship in the materials systems. A lack of fundamental understanding of phase formation in the ferrite material with respect to temperature is a detriment to magnetic materials research and is a driving force for this work.

In this thesis we will derive the sintering path beginning with phenomena that happen in mechanical alloying related to strains as discussed using the Williamson-hall plot, diffusion mechanism by introducing activation energy, magnetic properties detailed behavior as exhibited by M-H (fundamental study) and B-H (potential practical study) loops and the trajectory path in sintering as explained by the regression coefficient of relative density. Finally the conclusions are based on the data analysis.

1.6 Thesis Outline

Chapter 1 introduces the objectives of the thesis, summarizes the main contributions, and outlines the thesis arrangement. Chapter 2 describes different experimental techniques used in these studies and microstructure-evolution study by other researchers. Chapter 3 discusses the basic theories as they affect ferrites and sintered materials. Specifically, the chapter reports the fundamentals of magnetization, the chemistry of spinel and hexagonal ferrites, sintering parameters and the mechanical alloying process. In Chapter 4, the characteristics measurement of the as-prepared ferrite and sintered ferrite is described. The discussion of the results obtained for the as-prepared ferrites and the microstructure-magnetic properties forms chapter five. Chapter 5 covers the discussion of the results obtained of the as-prepared ferrites and the microstructure-magnetic properties. Chapter 6 summarizes and concludes the

research findings, in addition to some suggested recommendations. A list of the author's publications is attached at the end of the thesis, sequentially preceded by the author's biography appendices and references/bibliographies.



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- Shafie, M. S. E.**, Hashim, M., Ismail, I., Kanagesan, S., Fadzidah, M. I., Idza, I. R., Sabbaghizadeh, R. (2014). Magnetic M – H loops family characteristics in the microstructure evolution of BaFe₁₂O₁₉. *Journal of Materials Science: Materials in Electronics*, (25), 3787–3794.
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