UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF BARIUM AND STRONTIUM HEXAFERRITE EMPLOYING RECYCLED MILLScale

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PREPARATION AND CHARACTERIZATION OF BARIUM AND STRONTIUM HEXAFERRITE EMPLOYING RECYCLED MILLScale

By

RABA’AH SYAHIDAH AZIS

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, In Fulfilment of the Partial Requirement for the Degree of Master of Science

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Dedication

Special Dedication to:

My Beloved Husband & Family,
Mohd Noh Abdul Jalil & My baby...

Abah and Emak
Hj. Azis Hj Mahmud & Hjh Rukiah Hj. Jalil,

My Beloved Family,
Ratna Sita, Rahmat Sabri, Ratna Saerah, Ridha Shukri, Hasanul Mukhlis, Siti Raudha, Luqmanul Hakim, Husni Mubarak & Mohd Khairul Ariffin

Thank you very much for the support, I LOVE YOU ALL
SO MUCH.....

Kejayaan ini milik kita bersama.....
In this project work, permanent magnet barium/ strontium hexaferrite materials was prepared from millscale, using hematite derived from millscale by the Curie Temperature Separation Technique (CTST). The excellent CTST isolation and purification of wustite, FeO contained in the millscale and converted to hematite, Fe₂O₃, was confirmed by X-Ray Diffraction (XRD) pattern analysis and element analysis by Electron Dispersive X-Ray (EDAX). The sample was prepared by recycling the waste product from Malaysian steel-making factories. Using a Curie temperature separation technique, the wustite, FeO contained in the millscale was separated by this new technique using deionized water at 90°C/100°C in the presence of 1T external magnetic field. The wustite was then oxidized in air at
400°C/500°C/600°C for 10 hours. An XRD phase analysis showed that a very high percentage of Fe$_2$O$_3$ was present in the final powder preparation. A conventional ceramic powder processing method was then carried out to prepare hexagonal BaFe$_{12}$O$_{19}$ and SrFe$_{12}$O$_{19}$ pallet shaped samples. Analysis of samples was done on density, resistivity, X-Ray Diffraction (XRD), Particle Size Analysis (PSD), Electron Dispersive X-Ray (EDAX), Scanning Electron Microscopy (SEM), grain size, saturation magnetization, coercive force and remanence. The effect of prolonged milling time shows a positive tendency for the formation of needle shape microstructure (0.3μm-1μm) of barium hexaferrite. The magnetic properties were measured using an Approximation Method (APM) theory. The 3.33 kG high remanence, 0.74 kG saturation magnetisation and 2.857 kOe coercive force of the sample derived from millscale shows that recycling a waste steel-making product has a high potential to produce a low cost ferrite in the future.
Abstrak tesis yang kemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains

PENYEDIAAN DAN PENCIRIAN BARIUM DAN STRONTIUM HEXAFERIT DARI KITAR SEMULA SISIK BESI

Oleh:
RABA’AH SYAHIDAH AZIS

Mei 2003

Pengerusi : Profesor Madya Mansor Hashim, Ph.D.
Fakulti : Sains dan Pengajian Alam Sekitar

Di dalam kajian ini, kami telah menyediakan barium/ strontium hexaferit dari bahan buangan sisik besi telah disediakan, dengan menggunakan hematite yang dihasilkan dari sisik besi melalui teknik pengasingan suhu Curie (CTST). Keberkesanan proses pengasingan dan penulinan wustit,FeO di dalam bahan sisik besi di tukar kepada hematite, Fe₂O₃ telah berjaya dikenalpasti dari pembelauan sinar-x (XRD) patten dan analisis serakan electron sinar-x (EDAX). Sampel ini disediakan dari proses kitar semula bahan buangan sisik besi dari industri-industri besi di Malaysia. Dengan menggunakan teknik pengasingan suhu Curie, wustit,FeO dapat diasiking dengan teknik baru ini dengan menggunakan air pengnyahion pada suhu 90⁰/100⁰C dan 1T magnet luar yang dibekalkan. Wustit tersebut kemudiannya dioksida pada suhu 400⁰/500⁰/600⁰C selama 10 jam. Fasa XRD telah menunjukkan peratusan yang tinggi Fe₂O₃ yang terhasil. Kaedah biasa pemprosesan penyediaan serbuk seramik
dijalankan untuk menyediakan heksagon BaFe$_{12}$O$_{19}$ dan SrFe$_{12}$O$_{19}$. Analisis sample yang dijalankan adalah ketumpatan, kerintangan, Pembelauan Sinar-X (XRD), Serakan Saiz Zarah (PSD), Serakan Elektron Sinar-X (EDAX), Mikroskop Pengimbas Elektron (SEM), saiz butir, pemagnetan tepu, daya paksa dan pemagnetan baki. Kesaran pemanjangan penghancuran serbuk penyediaan menunjukkan kecenderungan positif pembentukan struktur jejarum (0.3μm-1μm). Ciri pemagnetan telah diukur dengan menggunakan kaedah penghampiran (APM). Nilai pemagnetan baki yang tinggi 3.33 kG, pemagnatan tepu yang tinggi 0.74 kG dan daya paksa sampel yang tinggi 2.857 kOe, dari bahan buagan sisik besi menunjukkan potensi yang tinggi untuk penghasilan bahan ferit berkos rendah di masa hadapan.
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For all, I would like to say “Thank you very much” to whom who have “empowered” me to complete this thesis.

Truly,

Raba’ah Syahidah Azis

University Putra Malaysia

I certify that an Examination Committee met on                to conduct the final examination of Raba’ah Syahidah Azis on her Master of Science thesis entitled “Preparation and Characterization of Barium and Strontium Hexaferrite Employing Recycled Millscale” in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate to awarded the relevant degree. Members of the Examination Committee are as follows:

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DECLARATION

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

RABA’AH SYAHIDAH AZIS

Date:
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63. Resistivity value for SFM samples sintered at different sintering temperature
LIST OF ABBREVIATION/ GLOSSARY OF TERMS

CTST  Curie temperature separation technique
IMS  Impurity separation technique
APM  Approximation technique
SFM  strontium ferrite (millscale derived sample)
BFM  barium ferrite (millscale derived sample)
SFP  strontium ferrite (high purity iron oxide)
BFM  barium ferrite (high purity iron oxide)
SEM  scanning electron microscopy
XRD  x-ray diffraction
EDAX  electron dispersive x-ray
PSD  particle size analysis
$T_c$  Curie temperature
H  applied field
$\rho$  density
$f$  frequency
B  induction
$\mu_B$  Bohr magneton
A  cross section
L  induction
$l$  length
PVA  polyvinyl alcohol
$B_r$  remanence induction
R  resistance
$\rho$  resistivity
$H_c$  coercive force
$B_s$  saturation induction
$(BH)_{\text{max}}$  energy product
CHAPTER 1

INTRODUCTION

General

Ferrites are magnetic materials, which have been studied for several decades due to their wide range of applications in the field of telecommunications, microwave telecommunication system, transformers, inductors, audio and video electronics, power transformer, EMI suppression, antennas and many others involving electric signals with frequencies normally not exceeding a few hundreds Megahertz. A very important use of ferrites have occurred in electric mortar and loudspeakers. Ferrite is a member of a class of mixed oxides MO.\(\text{Fe}_2\text{O}_3\), where M is metal such as Ba, Sr, Mn, Co, etc. Ferrite materials have been produced with strong magnetic properties, high electrical resistivity, and low hysteresis loss [31]. These materials are ceramic materials and are ferromagnetic, but not electrical conductors. For this reason, ferrites are used in high-frequency circuits as magnetic cores [26].

Ferrites are hard, brittle, ceramic-like materials with magnetic properties that make them useful in many electrical devices [18]. They are polycrystalline and are
generally gray or black in color. They can be formed into permanent magnets uses in motors, speakers and other electrical-mechanical energy conversion devices as well as devices requiring the simple use at attraction or repulsion by a dc magnetic field. Normally, they have a very high electrical resistance and can be operated at high frequencies (MHz) without excessive losses.

**Hard Ferrite and Soft Ferrite**

Ferrites can be classified according to crystal structure, ie, cubic versus hexagonal, or magnetic behavior, soft versus hard ferrites [20]. A soft ferrite is easy to magnetize and easy to demagnetize. Soft magnetic ferrites have a high electrical resistivity and they permit eddy current losses in a-c applications and have largely replaced the iron-based core materials in the radio frequency range. An example of soft ferrites is MnZn ferrite (frequencies up to about 1 MHz) and NiZn ferrites (frequencies >> 1 MHz).

The main composition for hard ferrites is BaFe$_{12}$O$_{19}$, SrFe$_{12}$O$_{19}$ and PbFe$_{12}$O$_{19}$, and some rare earth elements that is a W,X, and Z type compounds. But mostly W,X and Z type are not interesting economically because of relative difficulty of the processing. A hard ferrite is hard to magnetize and hard to demagnetize. The magnetization of the hard ferrite is strongly bound to its hexagonal axis, which is the reason it exhibits a hard magnet behaviour, that is high permeability in the plane and low permeability in other directions. Hard ferrites have a wide application in the tape
recording market for their highly useful magnetic properties. According to Stuijts (1964), the most straightforward relation between microstructure and properties of permanent magnet materials are based on single domain behavior of their constituent particles [21].

Permanent Magnet

Hard Magnetic Materials

* High coercivity
* High remanent magnetism
* Wide hysterisis loop
* Difficult to demagnetize

Soft Magnetic Materials

* Low coercivity
* High saturation flux density
* Narrow hysterisis loop
* High relative permeability
* Easy to magnetize and demagnetize

Figure 1: The comparison between soft ferrite and hard magnetic ferrite [30].
Permanent magnet

Permanent magnets play an important role and are spread in daily-life applications. Due to their very low cost, large availability of the raw materials and their high chemical stability, hard ferrites are still dominant in the permanent magnet market although their relatively poor magnetic properties are a distinct disadvantage. Today’s high-performance magnets are mostly made from Nd$_2$Fe$_{14}$B. The aim of this research is to combine the large spontaneous magnetization of 3d metals with strong anisotropy fields known from rare-earth transition-metal compounds and at the same time, to maintain a high value of the Curie temperature [1].

Permanent magnet materials have found many application in a wide variety of areas [2]. Ferrite-based magnetic materials, especially BaFe$_{12}$O$_{19}$ and SrFe$_{12}$O$_{19}$, are still the most widely used starting materials as permanent magnets. They have excellent chemical stability and are relatively cheap to produce [3]. Ferrite magnetic materials with high coercivity due to the relatively high magnetocrystalline anisotropy field exhibit important properties for permanent magnet applications. [4]. Advanced magnetic material permanent magnet now underpin the data storage, telecommunications, consumer electronics and appliance industries [5].

Among the different classes of magnetic materials, hexagonal hard ferrites such as barium ferrite have attracted much attention because of their potential applications in permanent magnet, microwave devices and magnetic recording media [6,7,8]. The