UNIVERSITI PUTRA MALAYSIA

MORPHOLOGY AND MAGNETIC PROPERTIES OF HEXAGONAL FERRITE Sr1-xMxFe12-xZnxO19 (M= La, Dy, Nd, Yb)

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By

NORLAILY MOHD SAIDEN

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Special Dedication to:

My dearest hubby, Hasri Harun,
Thanks for everything
You'll never know
How much I need you by my side
In the best of times and the worst of times
And all the times in between
It really doesn't matter
Where we are or what we're doing
As long as we're together
To share it all
I love you with all my heart and soul
You are the best husband in the world and I am blessed to have u

My sweetheart, Husna Naqeebah Hasri
You are the most beautiful flower in the garden of my existence
Having you in my life, completes and fulfills every part of me
Ummi loves you so much….

I asked God for a flower, he gave me a bouquet
I asked God for a minute, he gave me a day
I asked God for the true love, he gave me both of you…

"………..We bestowed [upon] from on high [the ability to make use of] iron, in which there is awesome power as well as [a source of] benefits for man: and [all this was given to you] so that God might mark out those who would stand up for him and His Apostle, even though He [Himself] is beyond the reach of human perception".

Surah Al-Hadid 57: 25

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Master of Science

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Chairman: Associate Professor Mansor Hashim, PhD

Faculty: Science and Environmental Studies

A permanent magnet in the form of a ring or disc is one of the components in many devices. In this project, hard magnetic ferrite with formula $Sr_{1-x}M_xFe_{12-x}Zn_xO_{19}$ (x= 0.1, 0.3, 0.5, 0.7, 0.9) (M= La, Nd, Dy, Yb) is used because of the low cost, high energy, good electrical insulation, hard to demagnetize and easy to process. Substitutions from Lanthanide group and zinc oxide (non magnetic material) are used in order to get different microstructures according to the value of hysteresis properties. Hysteresis parameters are investigated such as the remanence, B_r, energy product $(BH)_{max}$ and coercive force H_c Conventional sintering technique is used with sample being formed in disc shape. From XRD result, it was found that the substitution of Yb_2O_3, Nd_2O_3, La_2O_3, Dy_2O_3 and ZnO to the strontium ferrite magnet stabilizes the magnetoplumbite phase. The results for density, Curie temperature and grain size are better than non-substituted Sr-M. As a conclusion, improvement of the magnetic properties has been done to produce high performance of Sr-M in the future.

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

SIFAT-SIFAT MORFOLOGI DAN MAGNET FERIT HEKSAGON $Sr_{1-x}M_xFe_{12-x}Zn_xO_{19}$ (M= La, Dy, Nd, Yb)

Oleh

NORLAILY MOHD SAIDEN

Ogos 2003

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

Fakulti: **Sains Dan Pengajian Alam Sekitar**

Sebuah magnet kekal didalam bentuk cincin dan cakera merupakan salah satu komponen di dalam banyak peranti. Ia adalah sangat penting dan digunakan secara meluas di dalam sistem suara stereo. Di dalam projek ini, $Sr_{1-x}M_xFe_{12-x}Zn_xO_{19}$ (M= La, Dy, Nd, Yb), (x= 0.1, 0.3, 0.5, 0.7, 0.9) telah di gunakan kerana kos yang rendah, bertenaga tinggi, penebat elektrik yang baik, susah untuk dinyahmagnet dan mudah diproses. Penggantian dari kumpulan lanthanida dan zink oksida (bahan bukan magnet) dibuat untuk mendapatkan perbezaan mikrotsruktur berdasarkan pada ciri-ciri hysteresis. Beberapa pencirian hysteresis telah dikaji seperti B_r, $(BH)_{max}$, dan H_c. Teknik pensinteran lazim digunakan di bentuk dalam bentuk cakera. Daripada keputusan XRD, didapati bahawa penggantian Yb_2O_3, Nd_2O_3, La_2O_3, Dy_2O_3 dan ZnO terhadap magnet ferit strontium, fasa 'magnetoplumbite' tetap seimbang. Keputusan untuk ketumpatan, suhu Curie dan saiz butir bagi penggantian ferit strontium lebih baik dari tanpa penggantian. Kesimpulannya, cirri-ciri magnet telah dapat diperbaiki dan meningkat kualiti ferit strontium pada masa hadapan.

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May ALLAH bless and take care of you. In truth, Only ALLAH can reciprocate all the kindness...

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π	Pi
ϕ	magnetic flux
λ	length of wave
ρ^*	density
μ_B	Bohr magneton
θ_B	half the 2θ angle at the center of the peak
$(BH)_{max}$	maximum B XH product in the demagnetizing quadrant
χ_m	magnetic susceptibility
μ_o	permeability of vacuum
σ_s	spontaneous magnetization
A	cross sectional area
A	lattice constant a axis
B	induction
B	width of half maximum
B_r	remanent induction
B_s	saturated induction
C	lattice constant c-axis
D	demagnetizing factor
d_{hkl}	d-spacing
DW	domain wall
F	force
H	applied filed
H_c	coercive force

iH_c	intrinsic coersive force
L	inductance
l	length
M	magnetization
m	magnetic moment
M_s	saturation magnetization
PVA	polyvinyl alcohol
q	electric charge
SDP	single domain particle
SEM	Scanning electron microscope
SQUID	Superconducting Quantum Interference Devices
T	Scherrer formula
T_c	Curie temperature
v	volume
VSM	Vibrating sample magnetometer
W	weight
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

Introduction

Permanent magnets are based on a wide class of magnetic materials, which are identified as "hard magnetic materials". The magnetic "hardness" of the material is its capability to be spontaneously magnetized to a high degree and to retain its magnetization in opposing magnetic fields for long time. A permanent magnet can be regarded as a means of generating a virtually zero-cost electric current. The recent advances in the field of hard magnetic materials are among the best examples of how technology depends to a great extent upon the continuous progress in scientific knowledge of the materials (Asti and Solzi, 1994).

The greatly improved properties have allowed magnets to solve many device problems and today the world market value for magnets is in excess of US$1,000,000,000 (Far, 1999). The interest in pennanent magnet is international and magnets are being developed and produced in every industrialized nation. For so many sophisticated devices and s ystems, w e find t hat p erformance p arameters a re limited by available pennanent magnet properties. This has prompted investment in permanent magnet research and development by government and leading industrial companies all over the world (Parker, 1989).

During an international conference on ferrite (ICF5) held in Bombay, India in 1989, Malaysia was anticipated to manufacture 1000-ton metric soft ferrite beyond 1990 but apparently there was no estimate on the permanent magnet at all. On the other hand, our neighbours, Indonesia, the Philippines and Singapore are scheduled to be capable of manufacturing soft and hard magnet with a higher amount beyond 1990.

Research on permanent magnet preparation is not yet active in Malaysia. At UPM itself, more attention is given to soft ferrite research compared to hard ferrite although research on ferrite was started in 1989 in Physics Department, UPM. Barium ferrites are going on to be substituted more and more by strontium ferrites (although these are more expensive), because barium generates environmental problems and strontium provides an approximately 25 percent higher resistance to demagnetizing field.

Compared to soft ferrite cores, the hard ferrites products have relatively simple shapes. Concerning application, 45 per cent of hard ferrite magnets are used in permanent magnet motors, 30 % in loudspeaker and the rest in many other applications. During the last ten years, the typical product began to shift from the simple to produce loudspeaker magnets to a growing content of complex segments as the applications for magnetic motors grew.

Most of these products are magnetically oriented. Meanwhile, 30% of all hard magnetic products are polymer-bonded magnets; partly anisotropic, partly oriented.

History of Magnetic Research

Magnetism is one of the oldest phenomena in the history of science (Chikazumi and Charap, 1964; Robert, 1988). The 'magnetism', probably more than any other scientific term, has widened its meaning to such an extent that it has invaded fields that do not have anything in common with physics (Long and Grandjean, 1990). It is said that the magnetite or lodestone had already been found to be a natural magnet several centuries before Christ. (Chikazumi and Charap, 1964; Parker, 1989; Wolfarth, 1982; Robert, 1988). Since this mineral was found mostly in Magnesia of Asia minor, it was called magnetite, from which the word magnetism was derived. Earlier texts on permanent magnets have opened with historical review of these materials (McCaig, 1967; Parker 1989; Parker and Studders, 1962).

What is the reason for the success of the word, magnetism? Einstein gave an excellent answer to this question, when he wrote,

"*What I felt as a child of four or five years, when my father showed me a compass, was wonderful! The fact that the magnetized needle behaved in such a precise way is not included in the nature of events that are part of the unconscious world of concept. I still remember that the experience had a deep and indelible effect to me.*"

(Long and Grandjean, 1990).

In the second century the south-seeking property of the magnetic needle was revealed and it was utilized as a compass in voyages (Long and Grandjean, 1990; Chikazumi and Charap, 1964; Parker 1989; Mc Caig, 1967). Scientific investigations were first made in the sixteenth century by W. Gilbert, who studied terrestrial magnetism, magnetic induction and so on, and found that magnet loses its magnetism at high temperature (Long and Grandjean, 1990; Chikazumi and Charap, 1964; Parker 1989).

The most fruitful period in the study of electricity and magnetism came at the end of the eighteenth century and continued through the nineteenth century. The Coulomb law of magnetic interaction between two magnetic poles was discovered at the end of the eighteenth century. Magnetism due to electric currents was investigated by Oersted, Ampere, Biot and Savart at the beginning of the nineteenth century. Arago tried to magnetize a magnetic substance by using an electric current. Discoveries of diamagnetism by Faraday, of magnetostriction-deformation due to magnetization-by joule, of the Curie law by P. Curie, of hysteresis by Ewing were all made during this period (Chikazumi and Charap, 1964).

Ewing may have been the first person to study magnetic phenomena from the atomistic point of view. He tried to explain the phenomenon of hysteresis in terms of the magnetic interaction between molecular magnets. In this sense he was succeeded by Langevin and P. Weiss, who gave the correct interpretations of Para and ferromagnetism, respectively, from the atomistic standpoint (Mc Caig, 1967, Chikazumi and Charap, 1964).

The invention of hexagonal ferrites magnets (Kojima, 1982) such the barium and strontium ferrite magents by Went et al. (1952) or the completion of ferroxplana-type hexagonal ferrites by Jonker et al. (1957) is a very important event in the history of ferrites (Sugimoto, 1989, 1999). Figure 1 shows that soft and hard ferrites as well as ferrites for xerographic printing have experienced an increase in output.

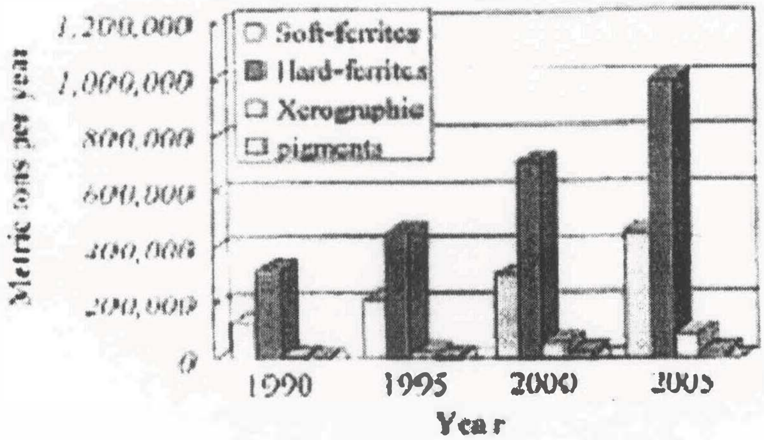

Figure 1: Estimated world wide ferrite production (Sugimoto, 1999)

The main current of magnetic research dated from the beginning of the twentieth century. A number of papers on magnetism began to appear at this time- a rate of about 10 papers per year until 1920. Since then, the development has been accelerated; 120 papers per year were recorded by 1939, and after the World War II this number rapidly increased to more than 500 papers per year. There are so many varieties involved in this development that we can hardly describe the general history of magnetic research in this limited space (Chikazumi and Charap, 1964)

A look ahead

The spinel-type ferrite magnet with the composition $Fe_3O_4.3CoFe_2O_4$ was mass-produced as a commercial magnet but was discontinued about 1955. This magnet was replaced by the hexagonal-type barium ferrite magnet and strontium ferrite magnet, which have been mass-produced worldwide since about 1953. Figure 2 shows the development of the output of hexagonal type ferrite magnets with respect to country over 20 years. Figure 2 shows that the output of the individual countries, except that of Japan, has increased each year. This due to the fact that the production cost of ferrite magnets is lower than of the other alloy magnets (Sugimoto, 1999).

Clearly, there are some compelling reasons to use permanent magnets over electromagnets. The growth of permanent magnets in industry is at least as rapid as the electrical manufacturing industry (Parker, 1989).

It is not easy to develop novel, attractive and epoch-making ferrite material. However, research and development of some types of promising materials are under investigation, and their future development is anticipated (Sugimoto, 1999).

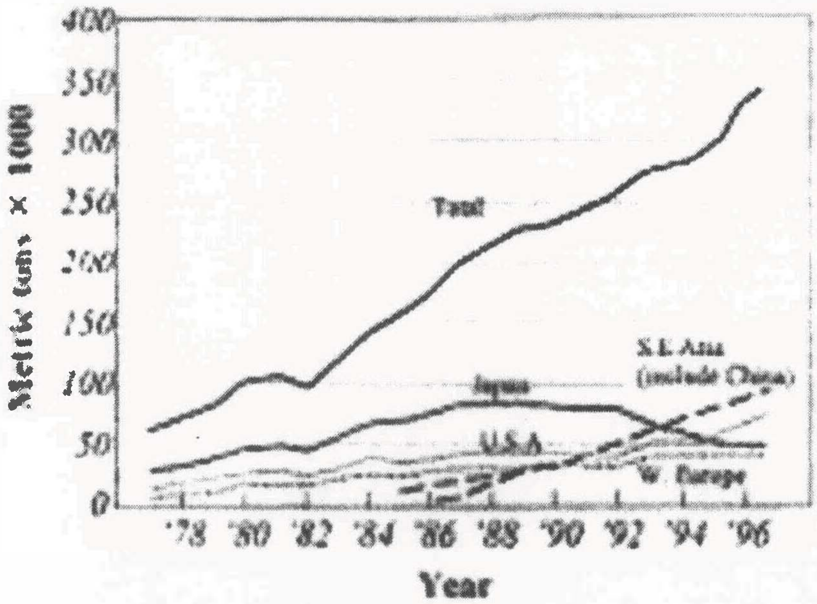

Figure 2: Estimated sintered hard ferrites production by country during a 20 years (Sugimoto, 1999).

Application of hard magnetic ferrites

Permanent magnets are used in a great variety of devices in modern technology, such as electric motors, loudspeakers, actuators and many others (Asti and Solzi, 1994). In our everyday life we encounter surprisingly numerous examples of equipment containing permanent magnet devices: computers and peripherals, radio and TV, recorders, telephones, watt-hour meters, refrigenerator doors, various portable appliances in which low voltage dc motors are used, such as electric knives and automobile accessories. In the industrial world we find permanent magnets in various instruments, microwave devices, magnetic elevators and coupling, magnetic separators, and so on.

On the whole, the driving force behind the development of permanent magnet materials came from the electrical and electronic industries rather than from makers of mechanical devices. The bread and butter of the permanent magnet industry have been earned by providing magnets for telephones, measuring instruments, small dynamos, radar and above all, loudspeakers (Mc Caig, 1967).

Significance of studies

The growth of the hard ferrite market in the past was heavily influenced by the exorbitant increase of the Cobalt price. This causes the replacement of Alnico magnets by ferrite materials.

Magnetic properties of hard ferrites are known to depend on their microstructural characteristics such as grain size, porosity, second phase and growth anisotropy (Lee et al., 1999). Furthermore their magnetic properties can be tailored for different applications by the partial substitution of divalent-tetravalent, trivalent metal elements, or rare earth ions (Wang et al., 2001). In order to improve the fundamental magnetic properties of hexaferrite, many studies have also been carried out concerning cationic substitution. Some experiments used light rare earth ions such as La, Pr and other metal cations in substitution for Sr and Fe, respectively, taking into account the ionic radius of the elements (Liu et al., 2002). Owing to the large ion size difference between the rare-earth element and iron, the Dy^{3+} would not occupy the Fe^{3+} sites. The only real possibility is the substitution of rare earth element for Sr. As the ion size of the rare-earth elements is smaller than that of Sr^{2+}, the Fe^{3+} (ions) would be closer in the O-Fe-O lattice and a stronger interaction might be anticipated, which would result in changed magnetic properties in rare-earth-element doped SrM particle (Wang et al., 2001).

The most important factors in the production of strontium ferrite apart from the processing method are the cost and availability of the raw materials (Stablein , 1982). Due to environmental problems connected with barium, the production of strontium ferrites became more important, in spite of the somewhat higher strontium price (Far, 1999).

Expert predicts a major increase of hard ferrite application in cars and trucks, for example for permanent magnetic starter motors, electronic mufflers, magnetic gaskets, for further PM motor types, etc. Also, the replacement of low efficiency AC motors to highly efficient and versatile permanent magnet motors will generate more