UNIVERSITI PUTRA MALAYSIA

CHARACTERIZATION OF ALUMINUM-SUBSTITUTED YTTRIUM-IRON GARNET NANOPARTICLES PREPARED USING THE SOL-GEL TECHNIQUE

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

December 2006

DEDICATION


To whom their true
love and support
are behind my success
My
My
My
My
Son
Daughters
Wife
Parents
UPM
2006

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the Degree of Master of Science

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December 2006

Chairman: Associate Professor Noorhana Binti Yahya, PhD

Institute: Advanced Technology

This project presents preparation and characterization of aluminum substituted yttrium iron garnet (Al-YIG) nanocrystalline powders of compositional variation of $Y_{3.0-x}Al_xFe_5O_{12,}$ where x was 0, 0.5, 1, 1.5, 2, 2.5 and 3. The samples were synthesized using sol–gel technique. The starting raw materials used to prepare Al-YIG samples were aluminum nitrate ($Al(NO_3)_3.9H_2O$), yttrium nitrate ($Y(NO_3)_3.6H_2O$) and iron nitrate ($Fe(NO_3)_3.9H_2O$). They were weighed according to the formula above, then mixed and dissolved together in solution of citric acid ($C_6H_8O_7.H_2O$) for a month to form the gel form by using magnetic stirrer equipment at 350 r.p.m at room temperature. The sample was then dried at 110^oC in an oven for a day to remove the unneeded water before it was calcined and crushed to obtain fine particles powder. The calcined powder at 600^oC, 700^oC, 800^oC, 850^oC and 900^oC respectively, were characterized by x-ray diffraction analyzer (XRD) to confirm the garnet phase. All samples were characterized also by RF-Impedance (1 MHz-1.8 GHz) to investigate the magnetic properties. Finally, field emission scanning electron microscopy (FESEM) and energy

dispersive x-ray analyzer (EDX) were used to study the surface morphology and the elemental analysis of Al-YIG samples. The results showed that, the best garnet phase appeared when the sintering temperature was 800^{o}C and Al-YIG nano-crystalline samples with high purity and sizes ranging from 20 to 100 nm were obtained. The magnetic measurement results of Al-YIG samples prepared by sol-gel method, gave high values of real permeability, the highest value of 5.29 was given by $Y_3Fe_5O_{12}$ sample at about 80 MHz which was attributed to the large grain size, the highest magnetic permeability observed was due to easy movement of domain walls; and it shifted to the high frequency with increasing the amount of aluminum. The widest useful working frequency range appeared for $Y_3Fe_5O_{12}$ sample and, also shifted to reach high range with increasing the concentration of aluminum.

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

PENCIRIAN YTTRIUM-IRON GARNET BERPARITIKAL NANO DIGANTI DENGAN ALUMINIUM DISEDIAKAN MELALUI TEKNIK SOL-GEL

Oleh

RAMADAN MASOUD AL-HABASHI

Disember 2006

Pengerusi: Profesor Madya Noorhana Binti Yahya, PhD

Institut: Teknologi Maju

Projek ini menjalankan penyediaan dan pencirian yttrium iron garnet (Al-YIG). Berpartikal nano diganti dengan aluminium yang divariasikan komposisinya dengan $Y_{3.0-x}Al_xFe_5O_{12,}$ dimana x adalah 0, 0.5, 1, 1.5, 2, 2.5 dan 3. Sampel-sampel tersebut di sintasiskan menggunakan teknik sol-gel. Bahan mentah yang digunakan untuk menyediakan sampel Al-YIG adalah aluminium nitrat ($Al(NO_3)_3.9H_2O$), yttrium nitrat ($Y(NO_3)_3.6H_2O$) dan ferrum nitrat ($Fe(NO_3)_3.9H_2O$). Bahan-bahan mentah ini ditimbang dan kemudian dicampur dan dilarutkan di dalam larutan sitrik asid ($C_6H_8O_7.H_2O$) selama sebulan bagi membentuk gel dengan menggunakan alat pengacau bermagnet dengan putaran 350 r.p.m. pada suhu bilik. Sampel kemudiannya dikeringkan di dalam oven pada suhu 110^oC selama sehari bagi membuang air yang tidak diperlukan sebelum ianya dibakar dan dihancurkan untuk mendapatkan partikal nano. Serbuk tersebut dibakar pada suhu 600^oC, 700^oC, 800^oC, 850^oC dan 900^oC dan, kemudian dicirikan dengan analisa pembelauan sinar-x (XRD) bagi mengesahkan fasa garnet. Kesemua sampel juga dicirikan dengan RF-Impedance (1 MHz – 1.8 MHz) bagi mengkaji sifat magnetnya, akhirnya field emission scaning electron microscopy (FESEM) dan energy dispersive x-ray

analyzer (EDX) digunakan bagi mengkaji morfologi permukaan dan analisa elemen bagi sample Al-YIG. Hasil pencirian menunjukkan bahawa fasa garnet terbaik pada suhu pensinteran 800^{o}C dan sampel kristal-nano Al-YIG dengan ketulenan tinggi dan saiz dari 20 hingga 100 nm didapati. Hasil pengukuran sifat magnet bagi sampel Al-YIG yang disediakan dengan kaedah sol-gel, memberikan nilai ketelapan yang tinggi dengan nilai tertinggi adalah 5.29 bagi sampel $Y_3Fe_5O_{12}$ pada frekuensi 80 MHz. Ini kerana saiz bijian yang besar, mengakibatkan senangnya pergerakan dinding domain dan menyebabkan. Ketelapan meningkat frekuensi fungsian manual bagi sampel $Y_3Fe_5O_{12}$ juga bertukar bagi mencapai kadar tinggi dengan penambahan kepekatan aluminium.

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my success. They were always there to strengthen my soul during the darker hours and have always lightened-up my days.

I certify that an Examination Committee has met on 21st December 2006 to conduct the final examination of Ramadan Masoud Al-Habashi on his Master of Science thesis entitled "Preparation via the Sol-Gel Technique and Characterization of Aluminum Substituted Yttrium Iron Garnet Nanoparticles" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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

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Date: 8 FEBRUARY 2007

DECLARATION

I hereby declare that the thesis is 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.

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RAMADAN MASOUD AL-HABASHI

Date: 15 JANUARY 2007

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIS OF ABBREVIATIONS

YIG	Yttrium iron garnet.
Al-YIG	Aluminum substituted yttrium iron garnet.
FIM	Ferrimagnetic material.
FM	Ferromagnetic material.
XRD	X-ray diffraction.
FESEM	Field emission scanning electron microscopy.
EDX	Energy dispersive x-ray analyzer.
B	Magnetic field.
H	Magnetic field intensity.
K	Kelvin unit.
μ_o	The permeability of free space (4π x 10^{-7} Wb/(A .m)).
M	Magnetization of solid.
μ_{ion}	Net magnetic moment of an ion.
μ	Permeability of solid.
μ_r	Relative permeability.
χ_{mag}	Magnetic susceptibility.
μ_{orb}	Orbital magnetic moment of a single electron.
ω_o	Angular frequency.
$\prod_0$	Orbital angular momentum of a single electron.
m_e	Electron mass.
l	Orbital angular momentum quantum number.
μ_B	Bohr magneton (9.27×10^{-24} A.m^2).
μ_s	Spin magnetic moment of a single electron.
$\prod_s$	Spin angular momentum of a single electron.
s	Spin quantum number (±1/2).
m_l	Orbital magnetic quantum number.
J	Total angular momentum of electrons.
L	Total orbital magnetic moment of electrons.
S	Total spin angular moment of electrons.
λ	Wavelength of the incident x-ray beam.
d_{hkl}	Distance between adjacent planes in a crystal.

PVA	Polyvinyl alcohol.
D_0	Outer diameter of the toroidal sample.
$S_h(\%)$	Percentage shrinkage of a sample.
μ'	Real permeability.
μ''	Loss factor.
Q	Quality factor.
a.u.	Attributry unit.

CHAPTER 1

INTRODUCTION

1.1 General

Nanotechnology is considered to be the most advanced manufacturing technology and is commonly referred to as the extreme technology. This is due to the fact that as the size reduces into the nanometer range, the materials exhibit peculiar and interesting mechanical and physical properties, e.g. increased mechanical strength, enhanced diffusivity, higher specific heat and electrical resistivity compared to conventional coarse grained counterparts. This field owes its parentage to investigations of reactive species (free atoms, clusters, reactive particles) throughout the 1970s and 1980s, coupled with new techniques and instruments (Pulsed cluster beams, innovations in mass spectrometry, vacuum technology, microscopes, and more). Excitement is high and spread throughout different fields including chemistry, physics, material science, engineering, and biology. This excitement is warranted because nanoscale materials represent a new realm of matter, and the possibilities for interesting basic science as well as useful technologies for society are widespread and real (Klabunde, 2001).

A nanometer, 10^{-9} m, is about ten times the size of the smallest atoms, such as hydrogen and carbon, while a micron is barely larger than the wavelength of visible light, thus invisible to the human eye. A millimeter, the size of a pinhead, is roughly the smallest size available in present day machines. The range of scales from millimeters to nanometers is one million, which is also about the range of scales in

present day mechanical technology, from the largest skyscrapers to the smallest conventional mechanical machine parts.

The definitions of nanoscience and nanotechnology avoided the use of dimensions at all:

• Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular, and macromolecular scales, where properties differ significantly from those at a larger scale.

• Nanotechnologies are the design, characterization, production, and application of structures, devices, and systems by controlling shape and size on the nano scale.

• Nanomaterials cross the boundary between nanoscience and nanotechnology and link the two areas together, so these definitions are very appropriate. It is recognized that the size range that provides the greatest potential and, hence, the greatest interest is that below 100 nm; however, there are still many applications for which larger particles can provide properties of great interest.

Furthermore, nanomaterials cover a hugely diverse range of materials: polymers, metals, and ceramics. Nanoparticles can come in a wide range of morphologies, from spheres, through flakes and platelets, to dendritic structures, tubes, and rods. The sophistication of the production processes for some materials has reached the level in the laboratory where complex three-dimensional structures such as springs, coils, and brushes have been made.

However, the fact that these materials can be made at this scale gives them the potential to have some very interesting properties.

Materials at the nanoscale between 1 nm and 250 nm lie between the quantum effects of atoms and molecules and the bulk properties of materials. It is in this, where many physical properties of materials are controlled by phenomena that have their critical dimensions at the nanoscale. By being able to fabricate and control the structure of nanoparticles, the scientist and engineer can influence the resulting properties and, ultimately, design materials to give desired properties. The ranges of applications where the physical size of the particle can provide enhanced properties that are of benefit are extremely wide.

Nanoparticles and nanomaterials continue to attract a great deal of attention because of their potential impact on an incredibly wide range of industries and markets. Consequently, the technology is evolving rapidly and will develop faster over the coming years (Wolf, 2004).

Ultra-fine microstructures having an average phase or grain size on the order of a nanometer are classified as nanostructure materials. Currently, in a wider meaning of the term, any material that contains grains or clusters below 100 nm, or layers or filaments of that dimension, can be considered to be nanostructure. The interest in these materials has been stimulated by the fact that, owing to the small size of the building blocks (particle, grain, or phase) and the high surface to volume ratio, these materials are expected to demonstrate unique mechanical, optical, electronic, and magnetic properties. The properties of these materials depend on the following four common microstructure features: fine grain size and size distribution (<100 nm), the chemical composition of the constituent phases, the presence of interfaces (grain boundaries, hetero-phase interfaces, and so on), and interactions between the