UNIVERSITI PUTRA MALAYSIA

EVOLUTION OF MORPHOLOGY AND MULTIFERROIC PROPERTIES OF POLYCRYSTALLINE ERBIUM MANGANITE SYNTHESIZED VIA MECHANICAL ALLOYING

MUHAMMAD AIZAT BIN NOOR ISMAIL

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By

MUHAMMAD AIZAT BIN NOOR ISMAIL

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Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

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Chairman: **Assoc. Prof. Mansor Hashim, PhD**
Institute: **Institute of Advance Technology**

In this research work, the goal is to establish the parallel evolution stages of microstructure development and properties development and their relationship. This kind of observation is absent in the literature since for several past decades, studies of the relationship between morphological properties and ferroelectric and dielectric properties of multiferroic materials have been focusing only on the product of the final sintering temperature, largely neglecting the parallel evolutions of morphological and properties and their relationship at various sintering temperatures. Erbium manganese oxide was prepared via high-energy ball milling (HEBM) in a hardened steel vial for 12 hours using a SPEX8000D mill. To get the evolving series of temperature, the pellet samples went through multi-sample sintering, where the samples were sintered from 600°C to 1200°C with 50°C increments, for any one sample being subjected to only one sintering temperature. The x-ray diffraction (XRD) results confirm the formation of the crystalline sample in an evolution series of $ErMnO_3$. The evolution of microstructural properties was studied using FEI NovaNano 230 FeSEM. The dielectric studies were carried out by using an Agilent Impedance Analyzer Model 4291B. For ferroelectric transition temperature and P-E hysteresis loop was measured using a typical LCR meter induced 4284A with VECSTAR furnace and a Precision LC from Radiant Technologies respectively. The XRD patterns showed an improvement of crystallinity with increasing sintering temperature. At 700°C sintering temperature, single phase material ($ErMnO_3$) starting to appear until 950°C and as at 950°C sintering temperature was known as the optimum crystallization temperature for $ErMnO_3$. As degree of crystallinity increase with increasing sintering temperature, at final sintering temperature 1200°C, $ErMnO_3$ peaks were the only observed with no other second phase peaks. SEM micrographs showed larger grain size as the sintering temperature increased, consequently increasing the multi-domain grains. For Polarization-Electric field (P-E) plot reveals $ErMnO_3$ is highly leaky ferroelectrics with P-E curve shape drastically different from the normal shape of highly insulating ferroelectrics. It shows the remanent polarization, the coercive field and dielectric constant generally decreased with increasing grain size. The dielectric studies on evolution

microstructure for $ErMnO_3$ showed that the resonant frequency increasing with grain size. However the ferroelectric transition temperature (T_{FE}) which is intrinsic properties did not change during microstructure evolution. The value estimates by experimentally is ~ 580°C.

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

EVOLUSI MORFOLOGI DAN SIFAT MULTIFEROIK POLIHABLUR MANGANIT ERBIUM DISINTESIS MELALUI PENGALOIAN MEKANIKAL

Oleh

MUHAMMAD AIZAT BIN NOOR ISMAIL

Jun 2014

Pengerusi: **Prof. Madya Mansor Hashim, PhD**
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Dalam kerja-kerja penyelidikan ini, matlamatnya adalah untuk mewujudkan tahap evolusi yang selari dengan pembentukan mikrostruktur dan perkembangan sifat dan hubungan yang wujud diantara mereka. Pemerhatian jenis ini tidak hadir dalam literatur kerana selama beberapa dekad yang lalu, kajian tentang hubungan antara ciri-ciri morfologi dan sifat feroelektrik dan dielektrik bahan multiferoik memberi tumpuan hanya pada produk suhu pensinteran akhir, dengan mengabaikan evolusi sifat-sifat mikrostruktur dan multiferoik yang selari pada pelbagai suhu pensinteran yang rendah. Mangan erbium oksida telah disediakan melalui pengisar bebola berkuasa tinggi (HEBM) di dalam bekas keluli keras selama 12 jam menggunakan pengisar SPEX8000D. Untuk mendapatkan siri evolusi yang berubah dengan kenaikan suhu, sampel berbentuk pelet telah melalui proses pensinteran iaitu pensinteran pelbagai sampel, di mana sampel disinter dari 600°C hingga 1200°C dengan kenaikan 50°C, dengan menggunakan sampel berlainan bagi setiap suhu. Data daripada pembelauan sinar-x (XRD) mengesahkan pembentukan sampel kristal dalam siri evolusi $ErMnO_3$. Sifat mikrostruktur evolusi dikaji menggunakan FEI NovaNano 230 FeSEM. Kajian sifat-sifat dielecktrik telah dijalankan dengan menggunakan Penganalisis Impedan/Bahan model Agilent 4291B. Pengukuran untuk suhu peralihan sifat feroelektrik dan P-E gelung histeresis telah dibuat dengan menggunakan meter LCR biasa teraruh 4284A dengan relau VECSTAR dan Precision LC masing-masing daripada Radiant Technologies. Corak-corak pembelauan sinar-x menunjukkan peningkatan kehabluran dengan meningkatnya suhu pensinteran. Pensinteran pada suhu 700°C, fasa tunggal bahan manganit erbium mula muncul sehingga 950°C, dan pada suhu pensinteran 950°C dikenali sebagai suhu optimum bagi penghabluran untuk manganit erbium. Apabila suhu pensinteran meningkat tahap kehabluran akan meningkat, pada suhu akhir pensiteran, 1200°C, hanya fasa $ErMnO_3$ dilihat dan tiada kehadiran fasa lain. Gambar SEM menunjukkan, butiran saiz meningkat dengan peningkatan suhu pensinteran, menyebabkan butiran pelbagai-domain meningkat. Bagi graf pengutuban-medan elektrik (P-E) mendedahkan $ErMnO_3$ adalah bahan feroelektrik yang mempunyai kebocoran tinggi dengan perubahan bentuk lengkung P-E berbeza daripada bahan

penebat feroelektri biasa. Ia menunjukkan pengutuban kekal, medan paksa dan pemalar dielektrik umumnya akan menurun dengan peningkatan saiz butiran. Kajian dielektrik dengan evolusi mikrostruktur bagi $ErMnO_3$ menunjukkan bahawa frekuensi resonan meningkat dengan saiz butiran. Walau bagaimanapun suhu peralihan feroelektrik (T_{FE}) adalah merupakan sifat intrinsik yang tidak berubah dengan evolusi mikrostruktur. Nilai anggaran secara uji kaji adalah ~ 580 ° C.

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I certify that a Thesis Examination Committee has met on 16 June 2014 to conduct the final examination of Muhammad Aizat bin Noor Ismail on his thesis entitled "Evolution of Morphology and Multiferroic Properties of Polycrystalline Erbium Manganite Synthesized via Mechanical Alloying" 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.

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DECLARATION

Declaration by graduate student

I hereby confirm that:

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LIST OF ABBREVIATIONS AND SYMBOLS

XRD	X-ray diffraction
SEM	Scanning electron microscopy
FeSEM	Field emission scanning electron microscopy
HRTEM	high resolution transmission electron microscopy
EDX	Energy-dispersive X-ray
TEM	Transmission electron microscopy
PVA	Polyvinyl alcohol
EMO/$ErMnO_3$	Erbium manganese oxide
HEBM	High-energy ball milling
BPR	Ball to powder weight ratio
Eq.	Equation
a.u	Arbitrary unit
2θ	2 theta degree
wt%	Weight percent
hkl	Miller indices
MPa	Megapascal
W_a	Weight of the sample in air
W_w	Weight of the sample in water
ρ_{xrd}	X-ray diffraction density

ρ_x	Experimental density
M	Molecular weight
N	Avogadro's constant
ρ	Percentage porosity
λ	Wavelength
T_{FE}	Ferroelectric transition temperature
ΔV_{gb}	Percentage of the amorphous phase
P-E	Polarization-electric field
P_r	Polarization remanent
Q_{sb}	surface bound charges
Q_b	bound charges
Q_f	free charges
ε_r'	Dielectric constant
γA	Total interfacial energy of a powder compact
γ	Specific surface (interface) energy
A	Total surface (interface) area of the compact
$\Delta\gamma$	The change in interfacial energy
μ	Diffusion potential
C	Capacitance
C_o	Capacitance without dielectric
Q	Magnitude of charge stored

V	voltage
ε	permittivity
ε_o	permittivity of free space
P_T	Total electric dipole
V	Volume
E_c	Coercive field
T_c	Curie temperature
χ	Electrical susceptibility

CHAPTER 1

INTRODUCTION

1.1 General Introduction

Over the last few decades, studies on the relationship between morphology and magnetic properties in polycrystalline material have become a great interest and widely investigated. Few materials such as Nickel Zinc Ferrite (Ismail et al., 2012), Yttrium Iron Garnet (Rodziah et al., 2012) and $Co_{0.2}Ni_{0.3}Zn_{0.5}Fe_2O_4$ (Waje et al., 2010) show a significant increase in magnetic response by manipulating their microstructure growth with the influence of sintering temperature

Multiferroic materials exhibit more than one primary ferroic order such as ferromagnetic, ferroelectric and ferroelastic. They have many potential applications in the oxide electronics, spintronics and even the green energy devices for reducing the power consumption. Since there exists giant magneto-resistance in rare-earth manganese oxide $REMnO_3$, it has attracted special attention due to the coexistence of ferroelectric and magnetic orders. For rare-earth elements with a small ionic radius, RE= Ho, Er, Tm, Yb, and Lu, they exhibit ferroelectromagnets' properties where these hexagonal manganese oxides have a ferroelectric transition at high temperature and an antiferromagnetic transition at low temperature (Park et al., 2002). Thus, it is important to correlate the microstructure and multiferroic properties of $ErMnO_3$ relating them from nanometer grain-size microstructure until they have evolved to their final forms at their last evolution stage.

1.2 Problem Statement

Researchers nowadays and in the past have neglected a fundamental line of scientific enquiry: What would be the composition-microstructure relationships at various intermediate sintering conditions during the parallel evolutions of the morphology and the properties of a sintered ferroelectric material? Do the changes of microstructure affect the dielectric and ferroelectric properties of the materials? How do dielectric and ferroelectric properties evolve with the microstructure changes? What would happen to the ions of the materials parallel to the microstructure changes, do they also contribute to polarization of the materials? Thus this work intends to observe carefully and the fundamental evolutions and their relationships.

1.3 Project objective and workstep objectives

The main goal of this research is to critically track the evolution of the ferroelectric and dielectric properties parallel to the microstructural changes. Previous literature has shown little evidence of synthesis work via high energy ball milling to reach nanometer grain-size region and critically track the microstructural grain growth to micron size. Thus due to the significant amount of material required mechanical alloying seems to be the only practical technique in studies involving the evolution of the microstructure of the material. Thus this research embarks on the following objectives: to study the evolution of dielectric and ferroelectric properties with microstructure changes.

The work steps of the project are to ensure the successful attainment of the project objective. These are:

1) To prepare $ErMnO_3$ using mechanically alloyed nanoparticles
2) To study the phase formation and crystallite size evolution using XRD.
3) To study the effect of the sintering temperature on the microstructural evolution for dielectric and ferroelectric properties of erbium manganite.

1.4 Thesis Outline

This thesis comprises 6 chapters. In the introduction, general introduction of evolution and material study, microstructural- dielectric and ferroelectric properties and some research questions are discussed.

The second chapter deals with literatures of the synthesis methods, mechanical alloying and important material properties, multiferroic theory and material properties, some microstructural consideration on ferroelectric and dielectric properties and some overview about material evolution studies.

The third chapter presents the basic theories on manganites and sintered materials. In some aspects of the theory, the chapter describes the basic crystal structure that controls the ferroelectric behavior of the multiferroic material.

Experimental and measurement techniques which include sample preparation and the apparatus used for both microstructural-ferroelectric and dielectric analysis will be discussed in the fourth chapter.

The fifth chapter presents the results of microstructural-ferroelectric and dielectric analysis. The ceramics analysed using XRD, SEM, EDX, and TEM will lead to the understanding of the microstructure evolution observed. Data obtained from dielectric and ferroelectric measurements are also discussed.

The sixth or final chapter summarizes and concludes the research findings and comments on the $ErMnO_3$ ceramics in relation to microstructural-ferroelectric and dielectric properties. Recommendations for further work are also given. The author's biography, appendices and references/bibliographies are on the last part of this thesis.

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