



UNIVERSITI PUTRA MALAYSIA

**MICROSTRUCTURAL, MAGNETIC AND DIELECTRIC PROPERTIES
OF $\text{Bi}_{1-x}\text{Sm}_x\text{FeO}_3$ MULTIFERROIC MATERIALS**

SITI NOR AIN BINTI RUSLY

FS 2013 30



UPM
UNIVERSITI PUTRA MALAYSIA
BERILMU BERBAKTI

**MICROSTRUCTURAL, MAGNETIC AND
DIELECTRIC PROPERTIES OF $\text{Bi}_{1-x}\text{Sm}_x\text{FeO}_3$
MULTIFERROIC MATERIALS**

SITI NOR AIN BINTI RUSLY

**MASTER OF SCIENCE
UNIVERSITI PUTRA MALAYSIA**

2013



**MICROSTRUCTURAL, MAGNETIC AND DIELECTRIC PROPERTIES OF
 $\text{Bi}_{1-x}\text{Sm}_x\text{FeO}_3$ MULTIFERROIC MATERIALS**

By

SITI NOR AIN BINTI RUSLY

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

February 2013

The image features a large, semi-transparent watermark of the Universiti Putra Malaysia (UPM) logo in the background. The logo is a shield-shaped emblem with a red and white color scheme. At the top left of the shield, the letters 'UPM' are written in white on a red rectangular background. In the center, there is a stylized white book with a red cover. Below the book, there are several vertical white lines of varying heights, and at the bottom, a series of horizontal white lines. The entire shield is set against a light gray background.

DEDICATION

I dedicate this thesis to my beloved husband, parent, family and friends.

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

**MICROSTRUCTURAL, MAGNETIC AND DIELECTRIC PROPERTIES OF
 $\text{Bi}_{1-x}\text{Sm}_x\text{FeO}_3$ MULTIFERROIC MATERIALS**

By

SITI NOR AIN BINTI RUSLY
February 2013

Chairman: Professor Abdul Halim Bin Shaari, PhD

Faculty: Science

BiFeO_3 (BFO) is a most common type of multiferroic materials that exhibits antiferromagnetic and ferroelectric order at room temperature. Based on previous reports, it was rather difficult to synthesize BFO in form of pure single phase due to narrow range of temperature stabilities. Hence, in this thesis, we report some research findings on the effect of different small ranges of calcinations and sintering temperature for preparing BFO. The best BFO sample could be determine by analyzing the phase transformation, magnetic and dielectric properties using XRD, VSM and impedance analyzer respectively. The effect of Sm substitution in the BFO system also has been studied. Samples of $\text{Bi}_{1-x}\text{Sm}_x\text{FeO}_3$ (BSFO) with $x = 0.0, 0.1, 0.2, 0.3, 0.4$ and 0.5 were prepared using solid state reaction method. There are three series of samples that have been prepared which are Sample A (both calcinations and sintering temperature at $800\text{ }^\circ\text{C}$), Sample B (calcinations temperature at $800\text{ }^\circ\text{C}$ and sintering temperature at $825\text{ }^\circ\text{C}$) and Sample C (both calcinations and sintering

temperature at 825 °C). The XRD pattern showed an improvement of crystallinity in pure BFO with the lower unwanted secondary phases by increasing the calcinations and sintering temperature at 825 °C. However, the unwanted secondary phases disappeared in BSFO sample implying that Sm^{3+} substitution can stabilize the perovskite structure. SEM micrograph showed a well defines grain structures with clear grain boundaries in BFO sample. A larger grain sizes were observed as the calcinations and sintering temperature increase. However, BSFO have smaller average grain size than BFO sample. As the Sm composition increases from $x = 0.0$ to $x = 0.5$, the density values decreased for all series. The density increases proportionally with sintering temperature caused by elimination pores. The magnetization analysis showed that BFO compound have very narrow hysteresis loop exhibits antiferromagnetic behavior ($H_c = 191$ Oe and $M_r = 1.81 \times 10^{-3}$ emu/g) at room temperature. The result showed magnetic properties were enhanced with higher calcinations and sintering temperature at 825 °C. Larger hysteresis loop were obtained in BSFO indicates weak ferromagnetic behavior and the magnetization values increases when Sm composition increases. Sample C5 have highest magnetic properties with $H_c = 3589.9$ Oe and $M_r = 7.52 \times 10^{-2}$ emu/g. The dielectric permittivity, ϵ' and dielectric loss, ϵ'' decreased with increasing of frequency. The higher calcinations and sintering temperature, Sample C has the higher value of ϵ' and ϵ'' . The value of ϵ' and ϵ'' increased with Sm composition and dielectric measuring temperature. The dispersion of ϵ' and ϵ'' are maximum for Sample C5 with $\epsilon' \sim 141$ and $\epsilon'' \sim 5$ at room temperature. Hence BSFO with $x = 0.5$ with higher calcinations and sintering (825 °C) is formed to be a better multiferroic material than pure BFO sample by resulting enhancement in magnetic and dielectric properties.

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

**MIKROSTRUKTUR, SIFAT MAGNET DAN DIELEKTRIK BAGI BAHAN
MULTIFEROIK $\text{Bi}_{1-x}\text{Sm}_x\text{FeO}_3$**

Oleh

SITI NOR AIN BINTI RUSLY

Februari 2013

Pengerusi: Professor Abdul Halim Bin Shaari, PhD

Fakulti: Sains

BiFeO_3 (BFO) merupakan salah satu bahan multiferroik yang menunjukkan sifat antiferromagnet dan ferroelektrik pada suhu bilik. Kajian lepas menunjukkan agak sukar untuk mensintesis BFO dalam bentuk fasa tulen tunggal disebabkan oleh julat suhu kestabilan yang kecil. Maka, dalam tesis ini kami melaporkan beberapa penemuan penyelidikan tentang kesan perbezaan julat kecil suhu pengkalsinan dan pensinteran bagi penyediaan BFO. Sampel BFO yang terbaik dapat ditentukan dengan menganalisis pembentukan fasa, sifat magnet dan sifat dielektrik masing-masing dengan menggunakan XRD, VSM dan penganalisis impedans analyzer. Kesan penggantian Sm dalam sistem BFO juga telah dikaji. Sampel $\text{Bi}_{1-x}\text{Sm}_x\text{FeO}_3$ (BSFO) dengan $x = 0.0, 0.1, 0.2, 0.3, 0.4$ and 0.5 telah disediakan menggunakan kaedah tindakbalas keadaan pepejal. Tiga siri sampel telah disediakan dalam kajian ini, iaitu Sampel A (Kedua-dua suhu pengkalsinan dan pesinteran pada $800\text{ }^\circ\text{C}$), Sampel B (Suhu pengkalsinan pada $800\text{ }^\circ\text{C}$ dan suhu pesinteran pada $825\text{ }^\circ\text{C}$) dan Sampel C (Kedua-dua suhu pengkalsinan dan pesinteran pada suhu $825\text{ }^\circ\text{C}$). Corak

pembelauan sinar-X menunjukkan penambahbaikan penghabluran dalam BFO dengan kandungan fasa sekunder tidak dikehendaki yang rendah dengan kenaikan suhu pengkalsinan dan pensinteran pada suhu 825 °C. Walaubagaimanapun, fasa sekunder tidak dikehendaki tidak dikesan dalam sampel BSFO memperlihatkan bahawa penggantian ion Sm dapat menstabilkan struktur perovskit. Mikrograf SEM telah menunjukkan struktur butiran sempurna dengan sempadan butiran yang jelas bagi sampel BFO. Saiz butiran yang lebih besar diperolehi apabila suhu pengkalsinan dan pesinteran meningkat. Walaubagaimanapun, BSFO mempunyai saiz purata butiran yang lebih kecil daripada BFO. Dengan bertambahnya kandungan Sm daripada $x = 0.0$ kepada $x = 0.5$, nilai ketumpatan bahan berkurangan bagi semua siri. Nilai ketumpatan meningkat berkadaran dengan suhu pensinteran disebabkan oleh penyingkiran liang-liang. Analisis kemagnetan menunjukkan bahawa sebatian BFO mempunyai gelung histeresis yang sempit mempamerkan sifat antiferomagnetik ($H_c = 191$ Oe and $M_r = 1.81 \times 10^{-3}$ emu/g) pada suhu bilik. Hasil kajian menunjukkan sifat magnet meningkat dengan peningkatan suhu pengkalsinan dan suhu pesinteran pada 825 °C. Gelung histeresis yang lebih besar diperolehi dalam BSFO menunjukkan sifat feromagnetik lemah dan nilai kemagnetan bertambah apabila komposisi Sm bertambah. Sampel C5 mempunyai sifat magnet yang tertinggi dengan $H_c = 3589.9$ Oe dan $M_r = 7.52 \times 10^{-2}$ emu/g. Nilai ketelusan dielektrik, ϵ' dan dielektrik lesapan, ϵ'' meningkat dengan kenaikan frekuensi. Sampel BSFO yang dikalsin dan disinter pada suhu tinggi 825 °C mempunyai nilai ϵ' dan ϵ'' yang tinggi. Nilai ϵ' dan nilai ϵ'' bertambah dengan kenaikan komposisi Sm dan suhu pengukuran dielektrik. Penyebaran ϵ' dan ϵ'' adalah maksimum untuk Sampel C5 dengan nilai $\epsilon' \sim 141$ dan $\epsilon'' \sim 5$ pada suhu bilik. Maka, BSFO dengan $x = 0.5$ dengan pengkalsinan dan pesinteran pada suhu tertinggi (825 °C) merupakan bahan multiferroik yang lebih

baik daripada sampel asli BFO dengan penambahbaikan sifat magnet dan sifat dielektrik.



© COPYRIGHT UPM

ACKNOWLEDGEMENTS

Alhamdulillah, all praises to Allah for the strengths and His blessing in completing this thesis. I would like to convey my gratitude and sincere thanks to my supervisor Prof. Dr. Abdul Halim Shaari, and my co supervisor Assoc. Prof. Dr. Mansor Hashim for their constant monitoring, supporting, encouragement and sponsoring from the beginning to the end of this thesis. Thank you for helping me to solve the problem and for providing insights towards the solution.

I would like to thank to my lecturer Dr Mustapha Awang Kechik for providing me information how to produce a great thesis. I want to thank all my lab-mates; Fadhilah, Amalina Hafiza, Amir, Arlina, Aima and Nurul Ain Shaaidi, for their tremendous assistance and support throughout this study. I also like to express my gratitude to all Faculty of Science staff especially to Pn. Norhaslinda, Pn. Kamsiah, En. Razak for their technical guidance throughout this project.

Finally, most appreciation I would like to express is to my mother Maimon Binti Abu, my father Rusly Bin Md Tan, my sisters Rusmymah Binti Rusly, Rusmailiza Binti Rusly, Siti Asmah Binti Rusly and my youngest brother Mohd Ridhuan Bin Rusly for their support, encouragement and prayer. Not forgotten my appreciations also go to my husband Mohd Azizul Bin Abu Kassim for his moral support, undying love and prayers. This thesis would have been impossible without their perpetual moral support. I love all of you.

.

I certify that a Thesis Examination Committee has met on **1 FEBRUARI 2013** to conduct the final examination of **SITI NOR AIN BINTI RUSLY** on her Master thesis entitled “**MICROSTRUCTURAL, MAGNETIC AND DIELECTRIC PROPERTIES OF $\text{Bi}_{1-x}\text{Sm}_x\text{FeO}_3$ MULTIFERROIC MATERIALS**” 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 relevant degree.

Members of the Thesis Examination Committee were as follows:

Zulkifly Abbas, PhD

Professor
Faculty
Universiti Putra Malaysia
(Chairman)

Name of Examiner 1, PhD

Professor
Faculty
Universiti Putra Malaysia
(Internal Examiner)

Name of Examiner 2, PhD

Professor
Faculty
Universiti Putra Malaysia
(Internal Examiner)

Name of External Examiner, PhD

Professor
Faculty
(External Examiner)

SEOW HENG FONG, PhD

Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

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

Abdul Halim Shaari, PhD

Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Mansor Hashim, PhD

Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

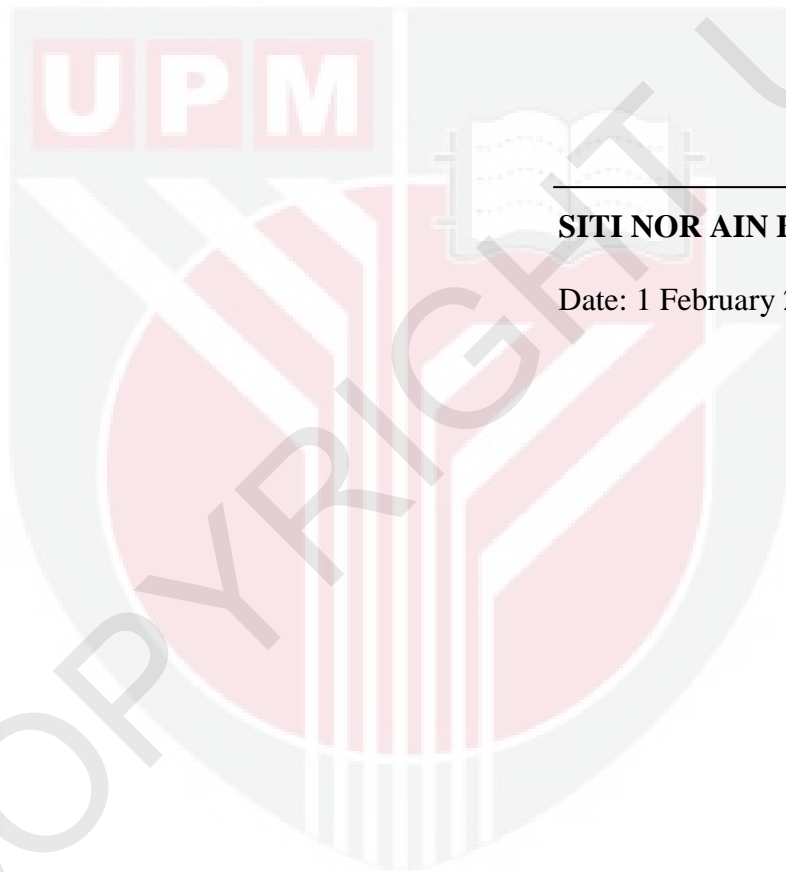
BUJANG BIN KIM HUAT, PhD

Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.



SITI NOR AIN BINTI RUSLY

Date: 1 February 2013

TABLE OF CONTENTS

	Page
DEDICATION	ii
ABSTRACT	iii
ABSTRAK	v
ACKNOWLEDGEMENTS	viii
APPROVAL	ix
DECLARATION	xi
LIST OF TABLES	xiv
LIST OF FIGURES	xv
LIST OF ABBREVIATIONS AND SYMBOLS	xix
CHAPTER	
1 INTRODUCTION	1
1.1 General Introduction	1
1.2 Overview of Multiferroics	2
1.3 Problem Statement	3
1.4 Research Objectives	5
1.5 Chapter Organization	6
2 LITERATURE REVIEW	7
2.1 BiFeO ₃ Multiferroic Ceramic	7
2.2 Structure of BiFeO ₃	7
2.3 Electrical Properties of BiFeO ₃	9
2.4 Magnetic Properties of BiFeO ₃	10
2.5 Preparation Method of BiFeO ₃	11
2.6 BiFeO ₃ Doping	13
3 THEORY	16
3.1 Theory of Multiferroics	16
3.2 Origin of Magnetism	17
3.3 Magnetization and Classification of Magnetic Material	18
3.3.1 Diamagnetism and Paramagnetism	20
3.3.2 Ferromagnetism	21
3.3.3 Antiferromagnetism	22
3.3.4 Ferrimagnetism	23
3.4 M-H Hysteresis Loop	24
3.5 The Effect of Temperature on Magnetic Properties	26
3.6 Origin of Ferroelectricity	27
3.7 Dielectric Polarization Mechanism	28
3.8 Mechanisms of Multiferroics	32
3.8.1 Lone Pairs Multiferroics	32
3.8.2 Magnetically Driven Ferroelectricity	32
3.8.3 Charge Order Multiferroics	33

	3.8.4	Geometrically Driven Ferroelectricity	33
4		METHODOLOGY	35
	4.1	Introduction	35
	4.2	Sample Preparation	35
	4.3	Characterization Process	40
	4.3.1	X-Ray Diffraction (XRD)	40
	4.3.2	Scanning Electron Microscope (SEM)	41
	4.3.3	Energy Dispersive X-Ray (EDX)	41
	4.3.4	Vibrating Sample Magnetometer (VSM)	42
	4.3.5	Impedance Analyzer	42
	4.4	Experimental Errors	43
5		RESULTS AND DISCUSSION	44
	5.1	Phase Analysis, Structure and Lattice Parameter	44
	5.2	Elemental Composition Analysis	56
	5.3	Scanning Electron Microscope Microstructure	60
	5.4	Grain Size Distribution	67
	5.5	Density by Archimedes Principle	71
	5.6	Magnetic Study	73
	5.6.1	M-H Magnetic Hysteresis for Different Sm Compositions	73
	5.6.2	M-H Magnetic Hysteresis for Different Sintering Temperatures	79
	5.7	Dielectric Study	84
	5.7.1	Dielectric Properties for Different Preparation Temperatures	84
	5.7.2	Dielectric Properties at Different Temperatures	93
6		CONCLUSIONS AND SUGGESTION	100
	6.1	Conclusion	100
	6.2	Suggestions	102
		REFERENCES	103
		APPENDICES	108
		BIODATA OF STUDENT	110
		LIST OF PUBLICATION	111