UNIVERSITI PUTRA MALAYSIA

STRUCTURAL, ELECTRICAL AND MAGNETIC PROPERTIES OF BISMUTH FERRITE CERAMICS SUBSTITUTED WITH YTTRIUM AND INDIUM

AMMAR ABD ALI NAJM

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By

AMMAR ABD ALI NAJM

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

October 2016

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DEDICATION

I dedicate this thesis to my father, mother, my brothers, my sisters and friends for their love and concern.

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

STRUCTURAL, ELECTRICAL AND MAGNETIC PROPERTIES OF BISMUTH FERRITE CERAMICS SUBSTITUTED WITH YTTRIUM AND INDIUM

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AMMAR ABD ALI NAJM

October 2016

Chairman : Professor Abdul Halim Bin Shaari, PhD
Faculty : Science

Multiferroic materials demonstrate the simultaneous presence of ferromagnetic, ferroelectric, or ferroelastic orderings. $BiFeO_3$ (BFO) is one of the significant multiferroic materials with high T_C ~ 1103 K and T_N ~ 643 K at room temperature. BFO suffers high leakage current and weak ferromagnetic and ferroelectric properties. This study was aimed to synthesize $BiFe_{1-x}M_xO_3$ (M = Y^{3+}, In^{3+}) samples; where x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0, investigate their phase formation due to Y^{3+} and In^{3+} substitution as well as their magnetic and electrical properties. Solid-state technique was used to synthesize $BiFe_{1-x}M_xO_3$, (M = Y^{3+}, In^{3+}) using Bi_2O_3, Fe_2O_3, Y_2O_3 and In_2O_3 as raw materials. XRD, SEM and EDX were used to determine the crystal structure, morphology of the grain size and elemental compositions respectively. Their leakage current, dielectric and magnetic properties were quantified by Keithley source measure unit, Impedance analyzer and VSM respectively.

XRD revealed the hexagonal single phase of pure BFO. The phase changed to cubic with Y^{3+} substitution and BFO remains the primary phase until x = 0.2. Substitution of In^{3+} promotes the growth of $Bi_{25}FeO_{40}$, and BFO remains the primary phase until x = 0.4. For SEM results, the average grain size of pure BFO decreased from 2.04 to 0.29 μm with Y^{3+} substitution, while it decreases to 0.32 μm for In^{3+} substitution. EDX revealed no impurities in the pure and substituted samples. From magnetic analysis, pure BFO shows antiferromagnetic behavior. A maximum M_s value of 2.9 emu/g and M_r of 0.09 were observed with Y^{3+} substitution at x = 0.2. The magnetic properties showed nonlinear dependent on In^{3+} substitution. The highest M_s value of 0.0405 emu/g and M_r of 6.22×10^{-4} emu/g was achieved at x = 0.3. The dielectric measurement showed that the ε'_r of the samples increased from 26.5 at x = 0 to 105 at x = 0.4, with Y^{3+} substitution. The values also improved with In^{3+} substitution and reached an optimum value of 372 at x = 0.6. The J-E measurement revealed that the leakage current density, J of x = 1.0 (4.6×10^{-8} A/cm^2) substituted with Y^{3+} is decreased significantly by about four order of magnitude compared to that of x = 0

(9.24 × 10^{-4} A/cm^2). Moreover, the J of x = 1.0 (1.51× 10^{-6} A/cm^2) substituted with In^{3+} is decreased significantly by about three order of magnitude compared to that of x = 0 (9.24 × 10^{-4} A/cm^2).

In conclusion, substituted BFO ceramics possess improved dielectric, magnetic properties and has reduced the leakage current. The prepared ceramics could be employed for several applications such as disk read/write heads and ceramic pressure sensor.

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

SIFAT STRUKTUR, ELEKTRIK DAN MAGNET SERAMIK BISMUT FERIT DENGAN PENGGANTIAAN ITERIUM DAN INDIUM

Oleh

AMMAR ABD ALI NAJM

Oktober 2016

Pengerusi : **Profesor Abdul Halim Bin Shaari, PhD**
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Bahan multiferoik menunjukkan kehadiran serentak sifat feromagnet, feroelektrik, dan feroelastik. Salah satu bahan multiferoik yang mempunyai suhu curie, T_C ~1103K dan suhu Neel, T_N ~643 K yang tinggi pada keadaan suhu bilik ialah $BiFeO_3$ (BFO). Walaubagaimanapun, limitasi BFO ialah kebocoran arus yang tinggi di samping mempunyai sifat feromagnetik dan feroelektrik yang lemah. Oleh itu, kajian ini bertujuan untuk mensintesis selain mengkaji sifat magnet serta elektrik bagi bahan multiferoik $BiFe_{1-x}M_xO_3$ (M = Y^{3+}, In^{3+}) dengan penggantian Y^{3+} dan In^{3+} berdasarkan perubahan pembentukan fasa (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 dan 1.0).

Teknik keadaan pepejal konvensional telah digunakan untuk mensintesis $BiFe_{1-x}M_xO_3$, (M = Y^{3+}, In^{3+}) dengan menggunakan Bi_2O_3, Fe_2O_3, Y_2O_3 dan In_2O_3 sebagai bahan mentah. XRD, SEM dan EDX telah digunakan untuk mengenal pasti struktur kristal, morfologi saiz butiran dan komposisi elemen. Manakala sifat dielektrik, sifat magnet dan kebocoran arus bahan telah diukur menggunakan penganalisis impedans VSM dan unit ukuran sumber Keithley.

Analisis XRD menunjukkan fasa tunggal heksagon bagi BFO tulen. Walaubagaimanapun, fasa tersebut berubah kepada kubik dengan penggantian Y^{3+} namun BFO kekal sebagai fasa primer sehingga x = 0.2. Manakala, penggantian In^{3+} menggalakan pertumbuhan $Bi_{25}FeO_{40}$ namun BFO turut kekal sebagai fasa primer sehingga x = 0.4. Keputusan kajian SEM menunjukkan nilai purata saiz butiran BFO tulen menurun daripada 2.04 kepada 0.29 µm dengan penggantian Y^{3+}. Berbeza dengan penggantian In^{3+} yang menurun sehingga 0.32 µm. Selain itu, analisis EDX mengesahkan tiada bendasing terdapat dalam sampel tulen mahupun sampel yang telah didopkan. Tambahan pula, BFO tulen mempunyai sifat antiferomagnetik dengan nilai maksimum M_s ialah 2.9 emu/g dan M_r ialah 0.09 emu/g apabila Y^{3+} digantikan pada x = 0.2. Sifat-sifat magnet menunjukkan kebergantungan tidak linear ke atas penggantian In^{3+}. Nilai tertinggi M_s ialah 0.0405 emu/g dan M_r ialah 6.22 ×

10^{-4} emu/g, masing-masing dicapai pada $x = 0.3$. Ukuran diaelektrik membuktikan bahawa ε'_r sampel meningkat daripada 26.5 pada $x = 0$ kepada 105 pada $x = 0.4$, dengan penggantian Y^{3+}. Nilai tersebut juga semakin bertambah baik dengan penggantian In^{3+} sehingga mencapai nilai optimum iaitu 372 pada $x = 0.6$. Pengukuran J-E mendapati bahawa kebocoran ketumpatan arus, J ialah 4.6×10^{-8} A/cm^2 pada $x = 1.0$ dengan penggantian Y^{3+} telah menurun dengan ketara kira-kira sebanyak empat turutan magnitud berbanding dengan keadaan pada $x = 0$ iaitu 9.24×10^{-4} A/cm$^{2.}$ Tambahan itu, nilai J pada $x = 1.0$ ialah 1.51×10^{-6} A/cm^2 dengan penggantian In^{3+} telah menurun dengan ketara kira-kira sebanyak tiga turutan magnitud berbanding dengan keadaan pada $x = 0$ iaitu 9.24×10^{-4} A/cm^2.

Kesimpulannya, pendopan seramik BFO dapat menambah baik sifat dielektrik, sifat magnet selain dapat mengurangkan kebocoran arus turut dapat kepada nilai yang agak rendah. Seramik yang telah disintesis boleh digunakan untuk beberapa aplikasi seperti cakera membaca/menulis atau sensor tekanan seramik.

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This thesis was 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 Supervisory Committee were as follows:

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TABLE OF CONTENTS

Page

ABSTRACT i

ABSTRAK iii

ACKNOWLEDGEMENTS v

APPROVAL vi

DECLARATION viii

LIST OF TABLES xii

LIST OF FIGURES xiii

LIST OF ABBREVIATIONS xv

CHAPTER

1 INTRODUCTION 1
- 1.1 Background of multiferroic 1
- 1.2 Multiferroic materials 2
- 1.3 Types of multiferroics 2
- 1.4 Multiferroic bismuth ferrite 3
- 1.5 Phase diagram of $BiFeO_3$ 4
- 1.6 Problem statement 5
- 1.7 Objectives of the study 5
- 1.8 Importance of the study 6
- 1.9 Thesis outline 7

2 LITERATURE REVIEW 8
- 2.1 Multiferroic materials 8
- 2.2 Perovskite structure of multiferroic materials 9
- 2.3 Bismuth ferrite and its importance as a multiferroic compound 10
  - 2.3.1 Structure of bismuth ferrite 11
  - 2.3.2 Role of Bi lone pair electrons for ferroelectricity 12
  - 2.3.3 Magnetic properties of bismuth ferrite 13
  - 2.3.4 Leakage current in bismuth ferrite 14
- 2.4 Synthesis of bismuth ferrite 15
  - 2.4.1 Solid-state reaction technique 15
- 2.5 Effect of substitution on the properties of bismuth ferrite 17

3 THEORY 24
- 3.1 Multiferroic materials 24
- 3.2 Origin of ferromagnetism 26
  - 3.2.1 Magnetic hysteresis loop (M-H) 28
- 3.3 Origin of ferroelectricity 30
- 3.4 Leakage current 31
- 3.5 Dielectric theory and polarization 32
  - 3.5.1 Dielectric properties 32
  - 3.5.2 Dielectric polarization 35
- 3.6 Mechanisms of multiferroic 36
  - 3.6.1 Lone Pair multiferroics 36
  - 3.6.2 Magnetically driven ferroelectricity 37
  - 3.6.3 Charge order multiferroics 37

3.6.4 Geometrically driven ferroelectricity 37

4 MATERAIALS AND METHOD 38
4.1 Introduction 38
4.2 Materials and their ionic radius 38
4.3 Sample preparation 39
4.3.1 Solid state reaction method for bulk multiferroic samples 39
4.3.2 Chemical equation balancing, weighing, mixing of starting powder 40
4.3.3 Grinding process 41
4.3.4 Powder calcination process 41
4.3.5 Grinding and pelletizing 42
4.3.6 Sintering process 42
4.4 Sample characterization 43
4.4.1 X-ray diffraction 43
4.4.2 Scanning electron microscopy 45
4.4.3 Energy dispersive X-ray 45
4.4.4 Dielectric properties analysis 46
4.4.5 J-E Characteristics 47
4.4.6 Vibrating sample magnetometer (VSM) 48
4.5 Experimental errors 50

5 RESULTS AND DISCUSSION 51
5.1 X-ray diffraction pattern (XRD) of $BiFe_{1-x}M_xO_3$ ceramics 51
5.2 Microstructure analysis 60
5.3 Elemental analysis 69
5.4 Leakage current analysis 71
5.5 Dielectric properties measurement 78
5.6 Magnetic properties 82

6. CONCLUSION AND SUGGESTION 86
6.1 Conclusion 86
6.2 Suggestions 87

REFERENCES 88
APPENDICES 102
BIODATA OF STUDENT 111
LIST OF PUBLICATIONS 112

LIST OF TABLES

Table **Page**

2.1 The common multiferroic compounds with their Curie temperature (T_C), Neel temperature (T_N) and Polarization (P) 10
2.2 The literature review summary of the effect of substitution on the properties of $BiFeO_3$ 21
4.1 List of Chemicals 38
4.2 List of samples 40
4.3 The apparatus error measurement 50
5.1 Composition dependence of lattice parameters of $BiFe_{1-x}Y_xO_3$ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0) 54
5.2 Percentage of phases determined for $BiFe_{1-x}Y_xO_3$ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0) 55
5.3 Composition dependence of lattice parameters of $BiFe_{1-x}In_xO_3$ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0) 58
5.4 Percentage of phases determined for $BiFe_{1-x}In_xO_3$ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0) 59
5.5 Average grain size of $BiFe_{1-x}Y_xO_3$ sintered at 800 °C 64
5.6 Average grain size of $BiFe_{1-x}In_xO_3$ sintered at 800 °C 68
5.7 Fitting coefficient (R^2) of leakage current mechanism of Y-substituted $BiFeO_3$ for Ohmic, SCLC, Schottky and Poole-Frenkel 75
5.8 Fitting coefficient (R^2) of leakage current mechanism of In-substituted $BiFeO_3$ for Ohmic, SCLC, Schottky and Poole-Frenkel 77
5.9 Relative dielectric permittivity and loss tangent at 1 kHz for the compositions $BiFe_{1-x}Y_xO_3$ ceramics (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0) 80
5.10 Relative dielectric permittivity and loss tangent at 1 kHz for the compositions $BiFe_{1-x}In_xO_3$ ceramics (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0) 82
5.11 Magnetic parameters of $BiFe_{1-x}Y_xO_3$ ceramics (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0) 84
5.12 Magnetic parameters of $BiFe_{1-x}In_xO_3$ ceramics (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0) 85

LIST OF FIGURES

Figure		Page
1.1	Representative image of the atomic structure of $BiFeO_3$ and the direction of the polarization along [111]	3
1.2	Phase diagram of $BiFeO_3$	4
2.1	Pm-3m space group perovskite structure of $CaTiO_3$	9
2.2	Schematic diagram of $BiFeO_3$ perovskite crystal structure. The ideal material $BiFeO_3$ is displayed with Bi-ions presented in yellow, Fe-ions in red and O ions in light blue	11
2.3	Schematic of the hexagonal unit cell structure of $BiFeO_3$ and pseudo-cubic setting of R3c space group	12
2.4	(a) Schematic of a G-type antiferromagnet and the ferromagnetic order within the plane (111) was highlighted by read color (b) antiferromagnetic spins in $BiFeO_3$ lie in the plane (111) and the canting of these spins which creates sublattice magnetizations that give rise to the net magnetization M	13
2.5	Mechanism of the reaction in conventional solid-state technique of $BiFeO_3$, (a) represented the Hypothetical end of reaction (b) display the real situation	16
3.1	Schematic of hysteresis loop by applied electric field, magnetic field and stress	24
3.2	Schematic representations the relations between multiferroic and magnetoelectric materials (coexistence ferroelectricity and ferromagnetism in a typical multiferroic material)	25
3.3	Exchange energy associated with overlapping orbital	27
3.4	Schematic diagrams showing the spins of (a) ferromagnet, (b) antiferromagnet, (c) ferrimagnet and (d) canted antiferromagnetic, where the magnetic components in different directions are represented by dashed arrows	28
3.5	Magnetization dependent of the applied field for diamagnetic, antiferromagnetic and paramagnetic materials	29
3.6	A schematic representation of a generic hysteresis loop of magnetization versus applied field for ferromagnetic materials	30
3.7	(a) A charge is stored in a vacuum on conductor plats (b) shows when a dielectric material is placed between the plates, the dielectric polarizes, as well as more charge is stored.	33
3.8	Schematic representations of the principal types of mechanisms in dielectric constant versus frequency plot	36
4.1	Flow chart of the sample preparation via solid-state reaction	39
4.2	Schematic diagram of calcination temperature setting	41
4.3	Schematic molder for compacting powders using die cavity	42
4.4	Schematic diagram of sintering temperature setting	43
4.5	Schematic illustration of X-ray diffraction	44
4.6	Schematic representation of scanning electron microscopy (SEM)	45

4.7 Schematic diagram of I-V characteristic using measure unit Keithley 2400 47
4.8 Schematic diagram of VSM assembly 49
5.1 X-ray diffraction pattern for single phase $BiFeO_3$ 51
5.2 X-ray diffraction pattern of $BiFe_{1-x}Y_xO_3$ (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0) ceramics sintered at 800 °C 53
5.3 X-ray diffraction pattern of $BiFe_{1-x}Y_xO_3$ (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0) ceramics sintered at 800 °C 57
5.4 SEM micrographs of $BiFe_{1-x}Y_xO_3$: $x = 0$, $x = 0.1$, $x = 0.2$, $x = 0.3$, $x = 0.4$, $x = 0.5$, $x = 0.6$, $x = 0.8$ and $x = 1.0$ 63
5.5 Average grain sizes versus Y concentration (x) of $BiFe_{1-x}Y_xO_3$ 64
5.6 SEM micrographs of $BiFe_{1-x}In_xO_3$: $x = 0$, $x = 0.1$, $x = 0.2$, $x = 0.3$, $x = 0.4$, $x = 0.5$, $x = 0.6$, $x = 0.8$ and $x = 1.0$ 67
5.7 Average grain size versus In composition (x) of $BiFe_{1-x}In_xO_3$ 68
5.8 EDX spectrum of a) Pure $BiFeO_3$, b) $BiFe_{0.6}Y_{0.4}O_3$, c) $BiFe_{0.2}Y_{0.8}O_3$, d) $BiFe_{0.6}In_{0.4}O_3$ and e) $BiFe_{0.2}In_{0.8}O_3$. 71
5.9 (a) Leakage current density dependence applied electric field (b) $J^{1/2}$ versus E. (c) ln (J/E) versus $E^{1/2}$. (d) ln J versus $E^{1/2}$ curve for $BiFe_{1-x}Y_xO_3$ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0) samples 74
5.10 (a) Leakage current density dependence applied electric field (b) $J^{1/2}$ versus E. (c) ln (J/E) versus $E^{1/2}$. (d) ln J versus $E^{1/2}$ curve for $BiFe_{1-x}In_xO_3$ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0) samples 77
5.11 (a) Relative dielectric permittivity and (b) loss tangent as a function of frequency of $BiFe_{1-x}Y_xO_3$ ceramics (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0) measured at room temperature 79
5.12 (a) Relative dielectric permittivity and (b) loss tangent as a function of frequency of $BiFe_{1-x}In_xO_3$ ceramics (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0) measured at room temperature 81
5.13 Variation of magnetization with magnetic field for $BiFe_{1-x}Y_xO_3$ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0) ceramics measured at room temperature 83
5.14 Variation of magnetization with magnetic field for $BiFe_{1-x}Y_xO_3$ (x = 0, 0.4, 0.5, 0.6, 0.8 and 1.0) ceramics measured at room temperature. 83
5.15 Variation of magnetization with magnetic field for $BiFe_{1-x}In_xO_3$ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0) ceramics measured at room temperature 85

LIST OF ABBREVIATIONS AND SYMBOLS

BFO	$BiFeO_3$
XRD	X-ray Diffraction
SEM	Scanning Electron Microscope
EDX	Electron Dispersion X-ray
VSM	Vibrating Sample Magnetometer
Y_2O_3	Yttrium Oxide
In_2O_3	Indium Oxide
Bi_2O_3	Bismuth Oxide
Fe_2O_3	Iron Oxide
T	Temperature
T_C	Curie temperature
T_N	Neel temperature
H_c	Coercivity Field
M_r	Remnant magnetization
M_s	Saturated magnetization
ME	Magnetoelectric
FM	Ferromagnetic
FE	Ferroelectric
E	Electric field
J	Leakage current density
θ	Diffraction angle
λ	Wavelength
ICSD	Inorganic Crystal Structure Database
PVA	Polyvinylalcohol
SCLC	Space Charge Limited Current

CHAPTER 1

INTRODUCTION

1.1 Background of multiferroic

In the current age of device miniaturization, multiferroics are technologically significant. It involves the coexistence of two or more ferroic order parameters viz. ferroelectricity, ferromagnetism and ferroelasticity in a single phase (Schmid, 1994). As a logical definition to the term multiferroic, it is any material presenting two of these three ferroic properties. However, the most interesting combination was thought to be materials presenting ferroelectricity and ferromagnetism simultaneously. Nevertheless, the most significant is to involve a strong coupling interaction between these two-ferroic orders. In multiferroic materials, the coupling interaction between the different order parameters can yield additional functionalities, such as a magnetoelectric (ME) effect (Ma *et al.*, 2011). Magnetoelectric effect gives place to extra degrees of freedom, which may permit magnetization to be switched by an electric field and polarization to be switched by a magnetic field (Yatom and Englman, 1969; Eerenstein *et al.*, 2006; Chu *et al.*, 2007).

Although there are multiferroic materials that are not magnetoelectric and vice versa, for fundamental reasons, the magnetoelectric coupling in single-phase materials is largest in multiferroic materials. For this reason, the development of these classes of materials is intimately related. Ferroelectric and ferromagnetic materials are characterized by their spontaneous polarization (electric or magnetic, respectively).

However, most materials do not exhibit a spontaneous order, but they do interact with applied fields. An electric field (E) produces an electric dipole moment and hence electric polarization (P) in the material. Conversely, a magnetic field (H) produces magnetization (M) and stress (s) produces stain (ε) (Velev *et al.*, 2011).

Multiferroism is observed in very few naturally available single-phase multiferroic systems. Moreover, commercial device engineering considerations impose further restrictions on the materials to exhibit ferroelectric/magnetic ordering at room temperature (RT) or close to RT. Boracites were possibly the first multiferroics materials identified (Khomskii, 2006), while others were soon to be found in nature, or synthesized artificially. Initially, most of the focus was on materials such as $BiFeO_3$, which have ferroelectric and magnetic transition temperatures close to or above RT (Roy *et al.*, 2012).

1.2 Multiferroic materials

Complex oxide materials display a varied range of properties especially due to various interactions that occur among the electronic degrees of freedom, structural and magnetic properties. H. Schmidt initially invented the expression “multiferroic” in 1994 to define multiferroic as a single phase material that has either two or three order parameters of ferroic which coexistence at the same phase, such ferroic are ferroelectricity, ferromagnetism, ferroelasticity and ferrotoroidic order which shows a strong coupling between the two ferroic orders (Schmid, 1994; Fiebig, 2005). Specifically, ferroelectric and ferromagnetic are materials with high technological relevance, and can be used in magneto-electric sensors driven magnetic data storage and recording devices (Spaldin and Fiebig, 2005).

Considering materials performing multiferroic properties, a coupling interaction that arises between ferroic parameters which yield additional characteristics, include magnetoelectric (ME) effect (Ma *et al.*, 2011). The incidence of ferromagnetic and ferroelectric orders in a material with a single-phase crystal structure is based on three conditions namely:

i. Symmetry conditions.
ii. The existence of sufficient structural building blocks which allows off-center ion displacement, related to the ferroelectric spontaneous polarization or other different mechanism for ferroelectricity lone pair: $BiFeO_3$, $BiMnO_3$ or geometric thwarting e.g.$YMnO_3$ (Hill, 2000).
iii. Magnetic-interaction pathways for the magnetic order, more commonly of super-exchange type (Gheorghiu *et al.*, 2013).

The expression “magnetoelectric”, has lately become widespread, this term consists of not only ferroelctromagnets, but also with the materials upon which any two ferroic parameters coexist such as ferroelectric materials, antiferroelectric materials, ferromagnetic materials, antiferromagnetic materials, ferrimagnetic materials, ferroelastic materials and ferrotoroidic materials (Eerenstein *et al.*, 2006).

1.3 Types of multiferroics

To comprehend all fundamental phenomena in the multiferroic field, it is important to classify multiferroics according to the different basic mechanisms into two types. Recently, multiferroic materials have been categorized into two sorts: Type I and Type II (Khomskii, 2009). The magnetism and ferroelectricity in Type I resulted from different sources and the influence independent of each other, but unfortunately the degree of coupling between the magnetism and ferroelectricity, is often weak. The spontaneous polarization (P) of such materials is usually large of the order (10 - 100 $\mu C/cm^2$) and the best example of such materials is bismuth ferrite ($BiFeO_3$) ($T_C \approx 1103K$, $T_N \approx 643$ K, $P \sim 88 - 100$ $\mu C/cm^2$) (Xie *et al.*, 2014), Yttrium manganite

($YMnO_3$) ($T_C \approx 914$ K, $T_N \approx 76$ K, P ~ 6 μC/cm^2). In type II multiferroic materials such as $TbMnO_3$, $Ni_3V_2O_6$ and $MnWO_6$, magnetism causes coexistence of ferroelectricity, which implies a strong coupling between the two. A much smaller polarization (10^{-2} μC/cm^2), is displayed in the presence of its magnetized state (Kimura *et al.*, 2003).

1.4 Multiferroic bismuth ferrite

Bismuth ferrite ($BiFeO_3$: BFO) is a prototype multiferroic among all the novel multiferroic materials that are currently in use. $BiFeO_3$ has been widely considered in the form of ceramics, thin films and nano-powders (Simões *et al.*, 2011). Generally, $BiFeO_3$ is denoted by BFO in the field of materials science. BFO consists of bismuth (Bi), iron (Fe) and oxygen (O) which is considered an inorganic compound. BFO displays multiferroic properties especially at room temperatures. In addition, BFO also shows high transition temperature (1103 K) and in particular, a single crystal of BFO displays high electric polarization (~ 100 μC/cm^2) when compared to other ferroelectric materials. It is often a great challenge to produce a single phase BFO. Previously, the difficulties of preparing single phases of BFO has been reported elsewhere (Xie *et al.*, 2014), where the characteristic single phase of BFO with ferroelectric Curie temperature (T_C) of 1103 K and Neel temperature (T_N) of 653 K has been reported (Xie *et al.*, 2014). The special arrangement of R3c group in the crystal lattice of BFO, which has rhombohedrally distorted perovskite structure, allows spontaneous ferroelectric polarization that can be either any of the eight diagonal [111] directions as revealed in Figure 1.1**.** Usually BFO polarization comes from A-site which is mainly due to the lone pair of Bi ions ($6s^2$ orbital), in the same manner the magnetization result from Fe^{3+} at B-site.

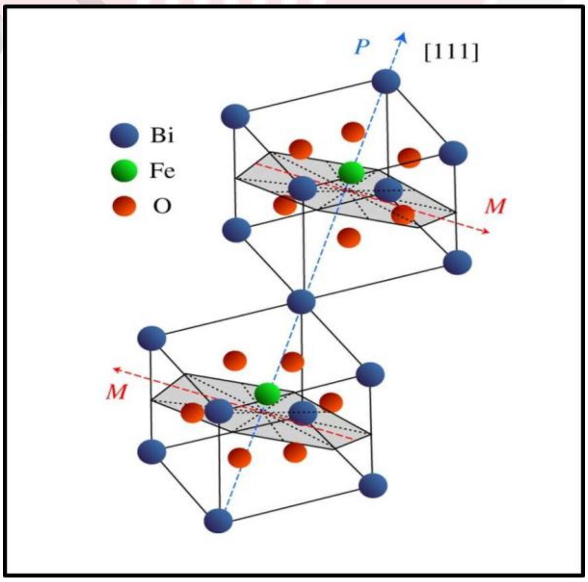

Figure 1.1: Representative image of the atomic structure of $BiFeO_3$ and the direction of the polarization along [111]. Source: Adapted from (Velev *et al.*, 2011).

1.5 Phase diagram of $BiFeO_3$

Figure 1.2 shows the phase diagram of bismuth oxide (Bi_2O_3)/iron oxide (Fe_2O_3) (Morozov *et al.*, 2003; Palai *et al.*, 2008). The preparation of bismuth ferrite ($BiFeO_3$) is always from the equal mixtures of raw materials i.e., Bi_2O_3 + Fe_2O_3 (1:1), at high temperatures, the mixture has the tendency to decompose back to its starting (raw) materials based on the following equation (1.1).

$$Bi_2O_3 + Fe_2O_3 \rightarrow 2BiFeO_3 \tag{1.1}$$

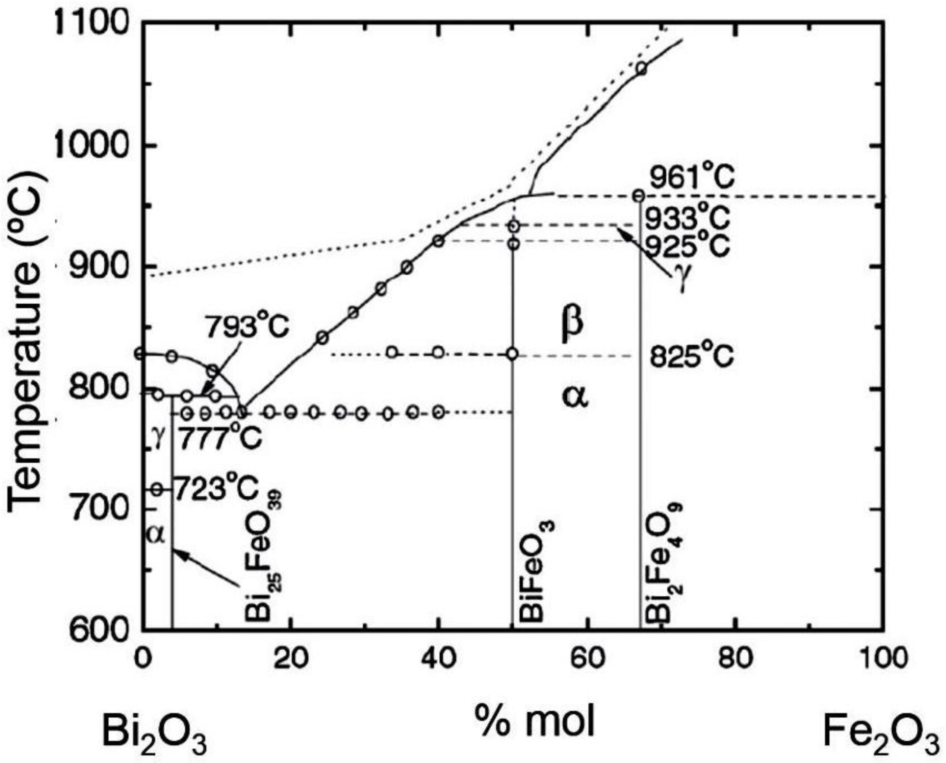

Figure 1.2: Phase diagram of $BiFeO_3$. Source: Adapted from (Catalan and Scott, 2009)**.**

BFO is likely to show parasitic phases in which they nucleate together in the form of impurities at grain boundaries (Valant *et al.*, 2007). Previously, BFO has been reported to be truly metastable in atmospheric air, especially due to its optically visible impurity that are commonly found well below the melting point (Catalan and Scott, 2009). The remnant magnetization artificially improves due to the impurities and oxygen vacancies (Bea *et al.*, 2005; Lou *et al.*, 2007). When 200 kV/cm of electric field are applied, the BFO decomposes to produce a by-product Fe_3O_4 (magnetite) at room temperature (Leontsev and Eitel, 2009) as shown in the equation (1.2) below:

$$6\mathrm{BiFeO_3} \rightarrow 2\mathrm{Fe_3O_4} + 3\mathrm{Bi_2O_3} + \mathrm{O} \qquad (1.2)$$

The phase Bi_2O_3 was possibly undetectable due to its known glass-forming compound, or because of its vaporizing capability within thermal decomposition. In addition, Bi_2O_3 reaches a melting point at temperature above 800 °C (Palai *et al.*, 2008).

1.6 Problem statement

There are some problems associated with $BiFeO_3$. The major problem in the preparation of bismuth ferrite ($BiFeO_3$) is the presence of impurities, non-perovskite phases such as $Bi_{25}FeO_{39}$ (sillenite) and $Bi_2Fe_4O_9$ (mullite) using solid-state reaction techniques (Muneeswaran *et al.*, 2014). These secondary phases (impurities) occur due to volatility and the dynamics phase formation. $BiFeO_3$ also has high leakage current because of oxygen vacancies and the oxidation status of Fe (ions) is fluctuation that appears (Fe^{2+}, Fe^{3+}) inside the perovskite matrix (Adhlakha *et al.*, 2013). In addition, $BiFeO_3$ also exhibits weak ferromagnetic (FM) properties due to the deformation of structure of spin spiral with G-type antiferromagnetism (Pradhan *et al.*, 2005; Godara *et al.*, 2015).

To overcome these difficulties, a modification has been employed, which is the substitution of B-site of BFO with rare-earth and transitional element, yttrium (Y^{3+}) and Indium (In^{3+}) using solid state reaction method. This is due to their larger ionic radius than iron, which can alter the crystal structure and improve their electrical and magnetic properties. Moreover, this will result in the reduction of high leakage current as well as remove the impurities. The following questions may arise for further research from the above-mentioned phenomenon:

1. At which percentage of substitution can one have an excellent reduction of leakage current?
2. At which specific phase formation of samples is a better substitution?
3. Will the influence of substitution increase/decrease the magnetic and electric properties of the materials?

1.7 Objectives of the study

General objective

The aim of this research is to study the influence of substitution of yttrium (Y^{3+}) and indium (In^{3+}) at the Fe-site of $BiFeO_3$ ceramics prepared via conventional solid-state reaction method. The effects of various concentrations on the structural, electrical and magnetic properties are investigated.

Specific objectives

The specific objectives are as follow

1. To synthesize $BiFe_{1-x}M_xO_3$ (M = Y^{3+} and In^{3+}) where (0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1).
2. To study the phase formation of samples due to Y^{3+} and In^{3+} substitution.
3. To investigate the effect of substitution of Y^{3+}, with ionic radius of (1.04 Å) and In^{3+}, with ionic radius of (0.94 Å) on magnetic and electric properties of $BiFeO_3$.

1.8 Importance of the study

Multiferroics including $BiFeO_3$ are materials with high attractive interest subjects that have been deeply investigated in the field of material science research, due to their physical-chemical properties and numerous applications such as information storage devices, disk read/write heads, spin valves that are used in magnetic sensors and microelectronic devices. The material usually produces an enormous magnetoelectric coupling response above the room temperature. Moreover, it grants basic control of the electric polarization with a magnetic field or controlling charge by an electric field, which makes them valuable in the area of technological applications (Nan *et al.,* 2008). These applications include spintronics, data storage, sensors and microelectronic devices (Arnold *et al.*, 2010). The magnetoelectric (ME) influence is relatively significant for data storage applications that would allow magnetic information to be composed electrically and for the magnetic utility later (Smolenskiĭ and Chupis, 1982; Eerenstein *et al.*, 2006; Bibes and Barthélémy, 2008). $BiFeO_3$ is a possible candidate for magnetoelectric and spintronic application. In spintroncs devices, information is written electrically and read magnetically (Chen *et al.*, 2006). $BiFeO_3$ is found to be essential as a tunneling barrier layer, where the magnetic field can control the ferroelectric states, while the tunneling resistance controls the direction of polarization as well (Yin *et al.*, 2015).

Given these evidences, multiferroics are currently being employed in several commercial applications, such as magnetic memory systems, sensor, spintronics (Béa *et al.*, 2005; Gajek *et al.*, 2005) and tunable microwave devices (Kadomtseva *et al.*, 2006): thus rendering the potential to revolutionize electromagnetic material's applications.

In this research study, the result obtained from yttrium and indium substituted BFO have added new contribution that can be adapted in many devices as mentioned above. Moreover, these new result can be considered new acknowledgments for researchers working in this field of research. In addition, the work conducted here using Y^{3+} and In^{3+} substitution on Fe-site of BFO has not been conducted by any other researcher and are not available in the literature.

1.9 Thesis outline

Synthesis and characterization of $BiFe_{1-x}M_xO_3$ (M = Y^{3+}, In^{3+}) by conventional solid-state reaction is the main feature of evaluation in this research. Summary of multiferroic materials and bismuth ferrite in addition to the problem statement, importance and objectives of the study were presented in Chapter 1. A brief discussion on the general background of multiferroic materials, perovskite structure, magnetic and electrical properties of $BiFeO_3$, methods followed to synthesize $BiFeO_3$ and the effect of substitution on $BiFeO_3$ are presented in Chapter 2. Chapter 3 explains multiferroics, ferromagnetism, hysteresis loop, ferroelectrics, leakage current and dielectric properties. Information on the clarification of the procedures involved in the synthesis of $BiFe_{1-x}M_xO_3$ ceramics by solid-state synthesis technique were described in Chapter 4. The results and discussion of all the characterizations scanning electron microscopy (SEM), energy dispersive X-ray (EDX), X-ray diffraction (XRD), vibrating sample magnetometer (VSM), Impedance Analysis and Keithley source measure unit were explained in Chapter 5. Summary of all-important results presented in the dissertation with recommendations for future research were presented in Chapter 6. Finally, Chapter 6 was followed by list of references, appendices, list of publications (research articles, conferences papers/posters by the author) and bio-data of the student.

REFERENCES

Abe, N., Taniguchi, K., Ohtani, S., Takenobu, T., Iwasa, Y., and Arima, T. (2007). Polarization reversal in multiferroic $TbMnO_3$ with a rotating magnetic field direction. *Physical Review Letters,* 99(22): 7206-7210.

Ablat, A., Wu, R., Mamat, M., Li, J., Muhemmed, E., Si, C., Wu, R., Wang, J., Qian, H., and Ibrahim, K. (2014). Structural analysis and magnetic properties of Gd doped $BiFeO_3$ ceramics. *Ceramics International,* 40(9): 14083-14089.

Achenbach, G., James, W., and Gerson, R. (1967). Preparation of Single‐Phase Polycrystalline $BiFeO_3$. *Journal of the American Ceramic Society,* 50(8): 437-437.

Adhlakha, N., Yadav, K., and Singh, R. (2013). Implications of La and Y codoping on structural, multiferroic, magnetoelectric and optical properties of $BiFeO_3$. *Science of Advanced Materials,* 5(8): 947-959.

Ahn, K. H., Kim, S. S., and Baik, S. (2002). Change of conduction mechanism by microstructural variation in Pt/(Ba, Sr) TiO_3/Pt film capacitors. *Journal of applied physics,* 92(1): 421-425.

Anderson, P. (1950). Antiferromagnetism. Theory of superexchange interaction. *Physical Review,* 79(2): 350-356.

Arnold, D. C., Knight, K. S., Catalan, G., Redfern, S. A., Scott, J. F., Lightfoot, P., and Morrison, F. D. (2010). The β‐to‐γ Transition in $BiFeO_3$: A Powder Neutron Diffraction Study. *Advanced Functional Materials,* 20(13): 2116-2123.

Ascher, E., Rieder, H., Schmid, H., and Stössel, H. (1966). Some Properties of Ferromagnetoelectric Nickel‐Iodine Boracite, $Ni_3B_7O_{13}I$. *Journal of Applied Physics,* 37(3): 1404-1405.

Azough, F., Freer, R., Thrall, M., Cernik, R., Tuna, F., and Collison, D. (2010). Microstructure and properties of Co-, Ni-, Zn-, Nb-and W-modified multiferroic $BiFeO_3$ ceramics. *Journal of the European Ceramic Society,* 30(3): 727-736.

Béa, H., Bibes, M., Sirena, M., Herranz, G., Bouzehouane, K., Jacquet, E., Fusil, S., Paruch, P., Dawber, M., and Contour, J. (2005). Combining half-metals and multiferroics into epitaxial heterostructures for spintronics. *Applied Physics Letters,* 88(6): 2502-2505.

Bea, H., Bouzehouane, K., Jacquet, E., Khodan, A., Contour, J. P., Fusil, S., Wyczisk, F., and Forget, A. (2005). Influence of parasitic phases on the properties of $BiFeO_3$ epitaxial thin films. *arXiv preprint cond-mat/0504631,* 87(7): 2508-25011.

Belik, A. A., Stefanovich, S. Y., Lazoryak, B. I., and Takayama-Muromachi, E. (2006). $BiInO_3$: A polar oxide with $GdFeO_3$-type perovskite structure. *Chemistry of materials,* 18(7): 1964-1968.

Benedek, N. A., and Fennie, C. J. (2013). Why are there so few perovskite ferroelectrics? *The Journal of Physical Chemistry,* 117(26): 13339-13349.

Bernardo, M., Jardiel, T., Peiteado, M., Caballero, A., and Villegas, M. (2011). Reaction pathways in the solid state synthesis of multiferroic $BiFeO_3$. *Journal of the European Ceramic Society,* 31(16): 3047-3053.

Bhalla, A., Guo, R., and Roy, R. (2000). The perovskite structure–a review of its role in ceramic science and technology. *Material Research Innovations*, 4(1): 3-26.

Bibes, M., and Barthélémy, A. (2008). Towards a magnetoelectric memory. *Nat. Mater,* 7: 425-426.

Biswal, M., Nanda, J., Mishra, N., Anwar, S., and Mishra, A. (2014). Dielectric and impedance spectroscopic studies of multiferroic $BiFe_{1-x}Ni_xO_3$. *Adv. Mat. Lett,* 5(9): 531-537.

Blasse, G. (1965). Ferromagnetic interactions in non-metallic perovskites. *Journal of Physics and Chemistry of Solids,* 26(12): 1969-1971.

Catalan, G., and Scott, J. (2009). Physics and applications of bismuth ferrite. *Advanced Materials,* 21(24): 2463-2485.

Chakrabarti, K., Das, K., Sarkar, B., and De, S. (2011). Magnetic and dielectric properties of Eu-doped $BiFeO_3$ nanoparticles by acetic acid-assisted sol-gel method. *Journal of Applied Physics,* 110(10): 3905-39014.

Chang, F., Zhang, N., Yang, F., Wang, S., and Song, G. (2007). Effect of Cr substitution on the structure and electrical properties of $BiFeO_3$ ceramics. *Journal of Physics D: Applied Physics*, 40(24): 7799–7803.

Chen, X., Hochstrat, A., Borisov, P., and Kleemann, W. (2006). Magnetoelectric exchange bias systems in spintronics. *Applied Physics Letters,* 89(20): 2508-2511.

Cheng, Z., Wang, X., Du, Y., and Dou, S. (2010). A way to enhance the magnetic moment of multiferroic bismuth ferrite. *Journal of Physics D: Applied Physics*, 43(24): 2001-2006.

Chu, Y. H., Martin, L. W., Holcomb, M. B., and Ramesh, R. (2007). Controlling magnetism with multiferroics. *Materials Today,* 10(10): 16-23.

Dahiya, R., Agarwal, A., Sanghi, S., Hooda, A., and Godara, P. (2015). Structural, magnetic and dielectric properties of Sr and V doped $BiFeO_3$ multiferroics. *Journal of Magnetism and Magnetic Materials,* 385: 175-181.

Dai, H., Xue, R., Chen, Z., Li, T., Chen, J., and Xiang, H. (2014). Effect of Eu, Ti co-doping on the structural and multiferroic properties of $BiFeO_3$ ceramics. *Ceramics International,* 40(10): 15617-15622.

Di Domenico, M., Eibschütz, M., Guggenheim, H., and Camlibel, I. (1969). Dielectric behavior of ferroelectric $BaMF_4$ above room temperature. *Solid State Communications,* 7(16): 1119-1122.

Dietz, G. W., Antpöhler, W., Klee, M., and Waser, R. (1995). Electrode influence on the charge transport through $SrTiO_3$ thin films. *Journal of Applied Physics,* 78(10): 6113-6121.

Dutta, D. P., Jayakumar, O., Tyagi, A., Girija, K., Pillai, C., and Sharma, G. (2010). Effect of doping on the morphology and multiferroic properties of $BiFeO_3$ nanorods. *Nanoscale,* 2(7): 1149-1154.

Ederer, C., and Spaldin, N. (2005). Recent progress in first-principles studies of magnetoelectric multiferroics. *Current Opinion in Solid State and Materials Science,* 9(3): 128-139.

Eerenstein, W., Mathur, N., and Scott, J. F. (2006). Multiferroic and magnetoelectric materials. *Nature,* 442(4): 759-765.

Feng, B., Xue, H., and Xiong, Z. (2010). Structure and multiferroic properties of Y-doped $BiFeO_3$ ceramics. *Chinese Science Bulletin,* 55(4-5): 452-456.

Fiebig, M. (2005). Revival of the magnetoelectric effect. *Journal of Physics D: Applied Physics,* 38(8): R123.

Filip'ev, V., Smolyaninov, N., Fesenko, E., and Belyaev, I. (1960). Synthesis of $BiFeO_3$ and determination of the unit cell. *Kristallografiya,* 5(6): 958-961.

Fischer, P., Polomska, M., Sosnowska, I., and Szymanski, M. (1980). Temperature dependence of the crystal and magnetic structures of $BiFeO_3$. *Journal of Physics C: Solid State Physics,* 13(10): 1931-1940.

Fox, D. L., Tilley, D., Scott, J., and Guggenheim, H. (1980). Magnetoelectric phenomena in $BaMnF_4$ and $BaMn_{0.99}Co_{0.01}F_4$. *Physical Review B,* 21(7): 2926-2936.

Fukumura, H., Matsui, S., Harima, H., Kisoda, K., Takahashi, T., Yoshimura, T., and Fujimura, N. (2007). Raman scattering studies on multiferroic $YMnO_3$. *Journal of Physics: Condensed Matter,* 19(36): 5239-5248.

Gajek, M., Bibes, M., Barthélémy, A., Bouzehouane, K., Fusil, S., Varela, M., Fontcuberta, J., and Fert, A. (2005). Spin filtering through ferromagnetic $BiMnO_3$ tunnel barriers. *Physical Review B,* 72(2): 0406-0410.

Gautam, A., Uniyal, P., Yadav, K., and Rangra, V. (2012). Dielectric and magnetic properties of $Bi_{1-x}Y_xFeO_3$ ceramics. *Journal of Physics and Chemistry of Solids,* 73(2): 188-192.

Gheorghiu, F., Calugaru, M., Ianculescu, A., Musteata, V., and Mitoseriu, L. (2013). Preparation and functional characterization of $BiFeO_3$ ceramics: A comparative study of the dielectric properties. *Solid State Sciences,* 23: 79-87.

Ghosh, S., Dasgupta, S., Sen, A., and Sekhar Maiti, H. (2005). Low‐temperature synthesis of nanosized bismuth ferrite by soft chemical route. *Journal of the American Ceramic Society,* 88(5): 1349-1352.

Godara, P., Agarwal, A., Ahlawat, N., and Sanghi, S. (2015). Crystal structure refinement, dielectric and magnetic properties of Sm modified $BiFeO_3$ multiferroic. *Journal of Molecular Structure*, 1097: 207-213.

Goodenough, J. B. (1958). An interpretation of the magnetic properties of the perovskite-type mixed crystals $La_{1-x}Sr_xCoO_{3-\lambda}$. *Journal of Physics and Chemistry of Solids,* 6(2-3): 287-297.

Goodenough, J. B., Wold, A., Arnott, R., and Menyuk, N. (1961). Relationship between crystal symmetry and magnetic properties of ionic compounds containing Mn^{3+}. *Physical Review,* 124(2): 373-384.

Hasan, M., Hakim, M., Basith, M., Hossain, M. S., Ahmmad, B., Zubair, M., Hussain, A., and Islam, M. F. (2016). Size dependent magnetic and electrical properties of Ba-doped nanocrystalline $BiFeO_3$. *AIP Advances,* 6(3): 5314-5327.

Heron, J., Schlom, D., and Ramesh, R. (2014). Electric field control of magnetism using $BiFeO_3$-based heterostructures. *Applied Physics Reviews,* 1(2): 1303-13021.

Hill, N. A. (2000). Why are there so few magnetic ferroelectrics? *The Journal of Physical Chemistry B,* 104(29): 6694-6709.

Hill, N. A. (2002). Density functional studies of multiferroic magnetoelectrics. *Annual Review of Materials Research,* 32(1): 1-37.

Ismailza, I., and Kizhaev, S. (1965). Determination of the curie point of the ferroelectrics ymno sub 3 and ybmno sub 3(High temperature X-ray examination of yttrium manganate and ytterbium manganate to determine Curie point). *Soviet Physics-Solid State,* 7: 236-238.

Jangid, S., Barbar, S., Bala, I., and Roy, M. (2012). Structural, thermal, electrical and magnetic properties of pure and 50% La doped $BiFeO_3$ ceramics. *Physica B: Condensed Matter,* 407(18): 3694-3699.

Jayakumar, O., Achary, S., Girija, K., Tyagi, A., Sudakar, C., Lawes, G., Naik, R., Nisar, J., Peng, X., and Ahuja, R. (2010). Theoretical and experimental evidence of enhanced ferromagnetism in Ba and Mn cosubstituted $BiFeO_3$. *Applied Physics Letters,* 96(3): 2903-2906.

Jeon, N., Rout, D., Kim, I. W., and Kang, S. J. L. (2011). Enhanced multiferroic properties of single-phase $BiFeO_3$ bulk ceramics by Ho doping. *Applied Physics Letters,* 98(7): 2901-2904.

Jiang, Y.-P., Tang, X.-G., Liu, Q.-X., Chen, D.-G., and Ma, C.-B. (2014). Improvement of electrical conductivity and leakage current in co-precipitation derived Nd-doping $BiFeO_3$ ceramics. *Journal of Materials Science: Materials in Electronics,* 25(1): 495-499.

Johnsson, M., and Lemmens, P. (2007). Crystallography and chemistry of perovskites. *Handbook of magnetism and advanced magnetic materials*.

Jonscher, A. (1983). Dielectric relaxation in solids. 1983. *Chelsea Dielectric, London*.

Jonscher, A. K. (1977). Theuniversal'dielectric response. *Nature,* 267: 673-679.

Jun, Y., Moon, W., Chang, C., Kim, H., Ryu, H., Kim, J., Kim, K., and Hong, S. (2005). Effects of Nb-doping on electric and magnetic properties in multi-ferroic $BiFeO_3$ ceramics. *Solid State Communications,* 135(1): 133-137.

Kadomtseva, A., Popov, Y. F., Pyatakov, A., Vorob'ev, G., Zvezdin, A., and Viehland, D. (2006). Phase transitions in multiferroic $BiFeO_3$ crystals, thin-layers, and ceramics: enduring potential for a single phase, room-temperature magnetoelectric 'holy grail'. *Phase Transitions,* 79(12): 1019-1042.

Kanamori, J. (1959). Superexchange interaction and symmetry properties of electron orbitals. *Journal of Physics and Chemistry of Solids,* 10(2-3): 87-98.

Kazhugasalamoorthy, S., Jegatheesan, P., Mohandoss, R., Giridharan, N., Karthikeyan, B., Joseyphus, R. J., and Dhanuskodi, S. (2010). Investigations on the properties of pure and rare earth modified bismuth ferrite ceramics. *Journal of Alloys and Compounds,* 493(1): 569-572.

Khomchenko, V., Kiselev, D., Kopcewicz, M., Maglione, M., Shvartsman, V., Borisov, P., Kleemann, W., Lopes, A., Pogorelov, Y., and Araujo, J. (2009). Doping strategies for increased performance in $BiFeO_3$. *Journal of Magnetism and Magnetic Materials,* 321(11): 1692-1698.

Khomchenko, V., Paixao, J., Shvartsman, V., Borisov, P., Kleemann, W., Karpinsky, D., and Kholkin, A. (2010). Effect of Sm substitution on ferroelectric and magnetic properties of $BiFeO_3$. *Scripta Materialia,* 62(5): 238-241.

Khomskii, D. (2006). Multiferroics: Different ways to combine magnetism and ferroelectricity. *Journal of Magnetism and Magnetic Materials,* 306(1): 1-8.

Khomskii, D. (2009). Trend: Classifying multiferroics: mechanisms and effects. *Physics,* 2: 20.

Kim, J. K., Kim, S. S., Kim, W.-J., Bhalla, A. S., and Guo, R. (2006). Enhanced ferroelectric properties of Cr-doped BiFeO3 thin films grown by chemical solution deposition. *Applied Physics Letters*, 88(13): 2901-2904.

Kimura, T. (2007). Spiral magnets as magnetoelectrics. *Annu. Rev. Mater. Res.*, 37: 387-413.

Kimura, T., Goto, T., Shintani, H., Ishizaka, K., Arima, T., and Tokura, Y. (2003). Magnetic control of ferroelectric polarization. *Nature*, 426(6962): 55-58.

King-Smith, R., and Vanderbilt, D. (1993). Theory of polarization of crystalline solids. *Physical Review B*, 47(3): 1651-1654.

King-Smith, R., and Vanderbilt, D. (1994). First-principles investigation of ferroelectricity in perovskite compounds. *Physical Review B*, 49(9): 5828-5844.

Koval, V., Skorvanek, I., Reece, M., Mitoseriu, L., and Yan, H. (2014). Effect of dysprosium substitution on crystal structure and physical properties of multiferroic $BiFeO_3$ ceramics. *Journal of the European Ceramic Society*, 34(3): 641-651.

Kuang, D., Tang, P., Ding, X., Yang, S., and Zhang, Y. (2015). Effects of Y doping on multiferroic properties of sol–gel deposited $BiFeO_3$ thin films. *Journal of Materials Science: Materials in Electronics*, 26(5): 3001-3007.

Kubel, F., and Schmid, H. (1990). Structure of a ferroelectric and ferroelastic monodomain crystal of the perovskite $BiFeO_3$. *Acta Crystallographica Section B: Structural Science*, 46(6): 698-702.

Kumar, K. S., Aswini, P., and Venkateswaran, C. (2014). Effect of Tb–Mn substitution on the magnetic and electrical properties of $BiFeO_3$ ceramics. *Journal of Magnetism and Magnetic Materials*, 364: 60-67.

Kumar, M. M., Palkar, V., Srinivas, K., and Suryanarayana, S. (2000). Ferroelectricity in a pure $BiFeO_3$ ceramic. *Applied Physics Letters*, 76(19): 2764-2766.

Kumar, P., and Kar, M. (2014). Effect of structural transition on magnetic and optical properties of Ca and Ti co-substituted $BiFeO_3$ ceramics. *Journal of Alloys and Compounds*, 584: 566-572.

Lawes, G., Kenzelmann, M., and Broholm, C. (2008). Magnetically induced ferroelectricity in the buckled kagome antiferromagnet $Ni_3V_2O_8$. *Journal of Physics: Condensed Matter*, 20(43): 4205-4214.

Lazenka, V., Zhang, G., Vanacken, J., Makoed, I., Ravinski, A., and Moshchalkov, V. (2012). Structural transformation and magnetoelectric behaviour in $Bi_{1-x}Gd_xFeO_3$ multiferroics. *Journal of Physics D: Applied Physics*, 45(12): 5002-5009.

Lebeugle, D., Colson, D., Forget, A., Viret, M., Bataille, A., and Gukasov, A. (2008). Electric-field-induced spin flop in $BiFeO_3$ single crystals at room temperature. *Physical Review Letters,* 100(22): 7602-7606.

Leontsev, S. O., and Eitel, R. E. (2009). Dielectric and Piezoelectric Properties in Mn‐Modified (1− x)$BiFeO_3$–x$BaTiO_3$ Ceramics. *Journal of the American Ceramic Society,* 92(12): 2957-2961.

Li, P., and Lu, T.-M. (1991). Conduction mechanisms in $BaTiO_3$ thin films. *Physical Review B,* 43(17): 14261-14264.

Lottermoser, T., Lonkai, T., Amann, U., Hohlwein, D., Ihringer, J., and Fiebig, M. (2004). Magnetic phase control by an electric field. *Nature,* 430(6999): 541-544.

Lou, X., Yang, C., Tang, T., Lin, Y., Zhang, M., and Scott, J. (2007). Formation of magnetite in bismuth ferrrite under voltage stressing. *Applied Physics Letters,* 90(26): 2908-2911.

Luo, L., Wei, W., Yuan, X., Shen, K., Xu, M., and Xu, Q. (2012). Multiferroic properties of Y-doped $BiFeO_3$. *Journal of Alloys and Compounds,* 540(2012): 36-38.

Ma, J., Hu, J., Li, Z., and Nan, C. W. (2011). Recent progress in multiferroic magnetoelectric composites: from bulk to thin films. *Advanced Materials,* 23(9): 1062-1087.

Markiewicz, E., Hilczer, B., Błaszyk, M., Pietraszko, A., and Talik, E. (2011). Dielectric properties of $BiFeO_3$ ceramics obtained from mechanochemically synthesized nanopowders. *Journal of Electroceramics,* 27(3-4): 154-161.

Maurya, D., Thota, H., Nalwa, K. S., and Garg, A. (2009). $BiFeO_3$ ceramics synthesized by mechanical activation assisted versus conventional solid-state-reaction process: a comparative study. *Journal of Alloys and Compounds,* 477(1): 780-784.

Mazumder, R., and Sen, A. (2009). Effect of Pb-doping on dielectric properties of $BiFeO_3$ ceramics. *Journal of Alloys and Compounds,* 475(1): 577-580.

Medina, L. M. S., Jorge, G. A., and Negri, R. M. (2014). Structural, dielectric and magnetic properties of $Bi_{1-x}Y_xFeO_3$ ($0 \le x \le 0.2$) obtained by acid–base co-precipitation. *Journal of Alloys and Compounds,* 592(2014): 306-312.

Medina, L. M. S., Jorge, G. A., and Negri, R. M. (2014). Structural, dielectric and magnetic properties of $Bi_{1-x}Y_xFeO_3$ obtained by acid–base co-precipitation. *Journal of Alloys and Compounds,* 592: 306-312.

Mitchell, R. (2002). Perovskites: Modern and Ancient Almaz. *Thunder Bay, ON.*

Moreau, J., Michel, C., Gerson, R., and James, W. (1971). Ferroelectric $BiFeO_3$ X-ray and neutron diffraction study. *Journal of Physics and Chemistry of Solids,* 32(6): 1315-1320.

Morozov, M., Lomanova, N., and Gusarov, V. (2003). Specific features of $BiFeO_3$ formation in a mixture of bismuth (III) and iron (III) oxides. *Russian Journal of General Chemistry,* 73(11): 1676-1680.

Muneeswaran, M., Jegatheesan, P., Gopiraman, M., Kim, I.-S., and Giridharan, N. (2014). Structural, optical, and multiferroic properties of single phased $BiFeO_3$. *Applied Physics A,* 114(3): 853-859.

Nalwa, K., Garg, A., and Upadhyaya, A. (2008). Effect of samarium doping on the properties of solid-state synthesized multiferroic bismuth ferrite. *Materials Letters,* 62(6): 878-881.

Nan, C., Bichurin, M., Dong, S., Viehland, D., and Srinivasan, G. (2008). Multiferroic magnetoelectric composites: historical perspective, status, and future directions. *Journal of Applied Physics,* 103(3): 1101-1136.

Neaton, J., Ederer, C., Waghmare, U., Spaldin, N., and Rabe, K. (2005). First-principles study of spontaneous polarization in multiferroic $BiFeO_3$. *Physical Review B,* 71(1): 4113-4121.

Neusel, C., Jelitto, H., and Schneider, G. (2015). Electrical conduction mechanism in bulk ceramic insulators at high voltages until dielectric breakdown. *Journal of Applied Physics,* 117(15): 4902-4910.

Niazi, A., Poddar, P., and Rastogi, A. (2000). A precision, low-cost vibrating sample magnetometer. *Current Science,* 79(1): 99-109.

Ortega, N., Kumar, A., Scott, J., and Katiyar, R. S. (2015). Multifunctional magnetoelectric materials for device applications. *Journal of Physics: Condensed Matter,* 27(50): 4002-4025.

Pabst, G. W., Martin, L. W., Chu, Y.-H., and Ramesh, R. (2007). Leakage mechanisms in $BiFeO_3$ thin films. *Applied physics letters,* 90(7): 2902-2906.

Palai, R., Katiyar, R., Schmid, H., Tissot, P., Clark, S., Robertson, J., Redfern, S., Catalan, G., and Scott, J. (2008). β phase and γ−β metal-insulator transition in multiferroic $BiFeO_3$. *Physical Review B,* 77(1): 4110-4121.

Palkar, V., John, J., and Pinto, R. (2002). Observation of saturated polarization and dielectric anomaly in magnetoelectric $BiFeO_3$ thin films. *Applied Physics Letters,* 80(9): 1628-1630.

Pandit, P., Satapathy, S., and Gupta, P. (2011). Effect of La substitution on conductivity and dielectric properties of $Bi_{1-x}La_xFeO_3$ ceramics: An impedance spectroscopy analysis. *Physica B: Condensed Matter,* 406(13): 2669-2677.

Patel, P., Yadav, K., Singh, H., and Yadav, A. (2014). Origin of giant dielectric constant and magnetodielectric study in Ba($Fe_{0.5}Nb_{0.5}$)O_3 nanoceramics. *Journal of Alloys and Compounds,* 591: 224-229.

Patel, R., and Sawadh, P. (2015). Capitalizing multiferroic properties of $BiFeO_3$ for spintronics. *Journal of Applied Physics* 7(1): 31-35.

Peng, C., and Krupanidhi, S. (1995). Structures and electrical properties of barium strontium titanate thin films grown by multi-ion-beam reactive sputtering technique. *Journal of materials research,* 10(03): 708-726.

Perejón, A., Gil-González, E., Sánchez-Jiménez, P. E., Criado, J. M., and Pérez-Maqueda, L. A. (2015). Structural, optical, and electrical characterization of Yttrium-substituted $BiFeO_3$ ceramics prepared by mechanical activation. *Inorganic Chemistry,* 54(20): 9876-9884.

Pradhan, A., Zhang, K., Hunter, D., Dadson, J., Loiutts, G., Bhattacharya, P., Katiyar, R., Zhang, J., Sellmyer, D. J., and Roy, U. (2005). Magnetic and electrical properties of single-phase multiferroic $BiFeO_3$. *Applied Physics Letters,* 97(9): 3903-3907.

Pradhan, S., and Roul, B. (2012). Electrical behavior of high resistivity Ce-doped $BiFeO_3$ multiferroic. *Physica B: Condensed Matter,* 407(13): 2527-2532.

Qi, X., Dho, J., Tomov, R., Blamire, M. G., and MacManus-Driscoll, J. L. (2005). Greatly reduced leakage current and conduction mechanism in aliovalent-ion-doped $BiFeO_3$. *Applied Physics Letters,* 86(6): 2903-2903.

Ramirez, A. (1997). Colossal magnetoresistance. *Journal of Physics: Condensed Matter,* 9(39): 8171.

Rao, T., Karthik, T., and Asthana, S. (2013). Investigation of structural, magnetic and optical properties of rare earth substituted bismuth ferrite. *Journal of Rare Earths,* 31(4): 370-375.

Resta, R. (1994). Macroscopic polarization in crystalline dielectrics: the geometric phase approach. *Reviews of modern physics,* 66(3): 899-915.

Rojac, T., Bencan, A., Malic, B., Tutuncu, G., Jones, J. L., Daniels, J. E., and Damjanovic, D. (2014). $BiFeO_3$ ceramics: Processing, electrical, and electromechanical properties. *Journal of the American Ceramic Society,* 97(7): 1993-2011.

Roy, A., Gupta, R., and Garg, A. (2012). Multiferroic memory. *Advances in Condensed Matter Physics,* 926290: 2011.

Sahoo, S., Mahapatra, P., and Choudhary, R. (2015). The structural, electrical and magnetoelectric properties of soft-chemically-synthesized $SmFeO_3$ ceramics. *Journal of Physics D: Applied Physics,* 49(3): 5302-5313.

Sati, P., Arora, M., Chauhan, S., Kumar, M., and Chhoker, S. (2014). Effect of Dy substitution on structural, magnetic and optical properties of $BiFeO_3$ ceramics. *Journal of Physics and Chemistry of Solids,* 75(1): 105-108.

Sati, P. C., Kumar, M., Chhoker, S., and Jewariya, M. (2015). Influence of Eu substitution on structural, magnetic, optical and dielectric properties of $BiFeO_3$ multiferroic ceramics. *Ceramics International*, 41(2): 2389-2398.

Schmid, H. (1994). Multiferroic magnetoelectrics. *Ferroelectrics,* 162(1): 317-338.

Schmid, H. (2008). Some symmetry aspects of ferroics and single phase multiferroics*. *Journal of Physics: Condensed Matter,* 20(43): 434201.

Schmidt, R., Eerenstein, W., Winiecki, T., Morrison, F. D., and Midgley, P. A. (2007). Impedance spectroscopy of epitaxial multiferroic thin films. *Physical Review B,* 75(24): 5111-5119.

Scott, J., Araujo, C., Melnick, B., McMillan, L., and Zuleeg, R. (1991). Quantitative measurement of space ‐ charge effects in lead zirconate ‐ titanate memories. *Journal of Applied Physics,* 70(1): 382-388.

Seshadri, R., and Hill, N. (2001). Visualizing the role of Bi 6s “lone pairs” in the off-center distortion in ferromagnetic $BiMnO_3$. *Chemistry of Materials,* 13(9): 2892-2899.

Shannon, R. (1976). Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography,* 32(5): 751-767.

Sharma, P., Varshney, D., Satapathy, S., and Gupta, P. (2014). Effect of Pr substitution on structural and electrical properties of $BiFeO_3$ ceramics. *Materials Chemistry and Physics,* 143(2): 629-636.

Sharma, S., Mishra, A., Saravanan, P., Pandey, O., and Sharma, P. (2016). Effect of Gd-substitution on the ferroelectric and magnetic properties of $BiFeO_3$ processed by high-energy ball milling. *Journal of Magnetism and Magnetic Materials*.

Shen, H., Xu, J., Wu, A., Zhao, J., and Shi, M. (2009). Magnetic and thermal properties of perovskite $YFeO_3$ single crystals. *Materials Science and Engineering: B,* 157(1): 77-80.

Shukla, D., Mollah, S., Kumar, R., Thakur, P., Chae, K., Choi, W., and Banerjee, A. (2008). Effect of Ti substitution on multiferroic properties of $BiMn_2O_5$. *Journal of Applied Physics,* 104(3): 707-712.

Silva, J., Reyes, A., Esparza, H., Camacho, H., and Fuentes, L. (2011). $BiFeO_3$: a review on synthesis, doping and crystal structure. *Integrated Ferroelectrics,* 126(1): 47-59.

Simões, A., Cavalcante, L., Moura, F., Longo, E., and Varela, J. (2011). Structure, ferroelectric/magnetoelectric properties and leakage current density of $(Bi_{0.85}Nd_{0.15})FeO_3$ thin films. *Journal of Alloys and Compounds,* 509(17): 5326-5335.

Singh, H., and Yadav, K. (2015). Structural, dielectric, vibrational and magnetic properties of Sm doped $BiFeO_3$ multiferroic ceramics prepared by a rapid liquid phase sintering method. *Ceramics International,* 41(8): 9285-9295.

Singh, V., Sharma, S., Jha, P. K., Kumar, M., and Dwivedi, R. (2014). Effect of Y^{3+} substitution on structural, electrical and optical properties of $BiFeO_3$ ceramics. *Ceramics International,* 40(1): 1971-1977.

Singhal, R., Samariya, A., Xing, Y., Kumar, S., Dolia, S., Deshpande, U., Shripathi, T., and Saitovitch, E. B. (2010). Electronic and magnetic properties of Co-doped ZnO diluted magnetic semiconductor. *Journal of Alloys and Compounds,* 496(1): 324-330.

Smolenskiĭ, G., and Chupis, I. (1982). Ferroelectromagnets. *Soviet Physics Uspekhi,* 25(7): 475-493.

Sosnowska, I., Neumaier, T., and Steichele, E. (1982). Spiral magnetic ordering in bismuth ferrite. *Journal of Physics C: Solid State Physics,* 15(23): 4835-4846.

Sosnowska, I., Przeniosło, R., Fischer, P., and Murashov, V. (1996). Neutron diffraction studies of the crystal and magnetic structures of $BiFeO_3$ and $Bi_{0.93}La_{0.07}FeO_3$. *Journal of Magnetism and Magnetic Materials,* 160: 384-385.

Spaldin, N., and Fiebig, M. (2005). The renaissance of magnetoelectric multiferroics. *Science,* 309(5733): 391-392.

Srivastava, A., Garg, A., and Morrison, F. D. (2009). Impedance spectroscopy studies on polycrystalline $BiFeO_3$ thin films on Pt/Si substrates. *Journal of Applied Physics,* 105(5): 4103-4109.

Staykov, A., Téllez, H., Akbay, T., Druce, J., Ishihara, T., and Kilner, J. (2015). Oxygen activation and dissociation on transition metal free perovskite surfaces. *Chemistry of Materials,* 27(24): 8273-8281.

Stoner, E. C. (1933). Atomic moments in ferromagnetic metals and alloys with non-ferromagnetic elements. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science,* 15(101): 18-34.

Su, W., Wang, D., Cao, Q., Han, Z., Yin, J., Zhang, J., and Du, Y. (2007). Large polarization and enhanced magnetic properties in $BiFeO_3$ ceramic prepared by high-pressure synthesis. *Applied Physics Letters,* 91(9): 2905-2908.

Tang, Z., Tang, M., Lv, X., Xiao, Y., Cai, H., Jiang, B., Cheng, C., Li, L., and Zhou, Y. (2013). Microstructure, magnetoelectric properties and leakage mechanisms of $La_{0.7}Ca_{0.3}MnO_3/Bi_{3.15}Nd_{0.85}TiO_3$ composite thin films. *Solid State Sciences,* 17: 35-39.

Teague, J., Gerson, R., and James, W. (1970). Dielectric hysteresis in single crystal $BiFeO_3$. *Solid State Communications,* 8(13): 1073-1074.

Tokunaga, Y., Furukawa, N., Sakai, H., Taguchi, Y., Arima, T., and Tokura, Y. (2009). Composite domain walls in a multiferroic perovskite ferrite. *Nature Materials,* 8(7): 558-562.

Valant, M., Axelsson, A., and Alford, N. (2007). Peculiarities of a solid-state synthesis of multiferroic polycrystalline $BiFeO_3$. *Chemistry of Materials,* 19(22): 5431-5436.

Van Minh, N., and Thang, D. (2010). Dopant effects on the structural, optical and electromagnetic properties in multiferroic $Bi_{1-x}Y_xFeO_3$ ceramics. *Journal of Alloys and Compounds,* 505(2): 619-622.

Vanderbemden, P., Rivas-Murias, B., Lovchinov, V., and Vertruyen, B. (2010). Measurement of dielectric properties at low temperatures: application to the study of magnetoresistive manganite/insulating oxide bulk composites. Paper presented at the Journal of Physics: Conference Series.

Velev, J., Jaswal, S., and Tsymbal, E. (2011). Multi-ferroic and magnetoelectric materials and interfaces. *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences,* 369(1948): 3069-3097.

Venevtsev, Y. N., and Gagulin, V. (1994). Search, design and investigation of seignettomagnetic oxides. *Ferroelectrics,* 162(1): 23-31.

Wang, Liu, H., and Yan, B. (2009). Enhanced ferroelectric properties of Ce-substituted $BiFeO_3$ thin films on $LaNiO_3$/Si substrates prepared by sol–gel process. *Journal of the European Ceramic Society,* 29(6): 1183-1187.

Wang, D., Goh, W., Ning, M., and Ong, C. (2006). Effect of Ba doping on magnetic, ferroelectric, and magnetoelectric properties in mutiferroic $BiFeO_3$ at room temperature. *Applied Physics Letters,* 88(21): 2907-2910.

Wang, J., Fu, Z., Peng, R., Liu, M., Sun, S., Huang, H., Li, L., Knize, R. J., and Lu, Y. (2015). Low magnetic field response single-phase multiferroics under high temperature. *Materials Horizons,* 2(2): 232-236.

Wang, Y., Zhou, L., Zhang, M., Chen, X., Liu, J., and Liu, Z. (2004). Room-temperature saturated ferroelectric polarization in $BiFeO_3$ ceramics synthesized by rapid liquid phase sintering. *Applied Physics Letters,* 84(10): 1731-1733.

Weiss, P. (1907). L'hypothèse du champ moléculaire et la propriété ferromagnétique. *J. Phys. Theor. Appl.,* 6(1): 661-690.

Xie, J., Feng, C., Pan, X., and Liu, Y. (2014). Structure analysis and multiferroic properties of Zr^{4+} doped $BiFeO_3$ ceramics. *Ceramics International,* 40(1): 703-706.

Xie, J., Liu, Y., Feng, C., and Pan, X. (2013). Preparation and characterization of Zr^{4+}-doped $BiFeO_3$ ceramics. *Materials Letters,* 96: 143-145.

Yan, F., Lai, M., Lu, L., and Zhu, T. (2010). Enhanced multiferroic properties and valence effect of Ru-doped $BiFeO_3$ thin films. *The Journal of Physical Chemistry C,* 114(15): 6994-6998.

Yang, H., Jain, M., Suvorova, N., Zhou, H., Luo, H., Feldmann, D., Dowden, P., DePaula, R., Foltyn, S., and Jia, Q. (2007). Temperature-dependent leakage mechanisms of $Pt/BiFeO_3/SrRuO_3$ thin film capacitors. *Applied Physics Letters,* 91(7): 2911-2911.

Yao, Y., Liu, W., Chan, Y., Leung, C., Mak, C., and Ploss, B. (2011). Studies of Rare‐Earth‐Doped $BiFeO_3$ Ceramics. *International Journal of Applied Ceramic Technology,* 8(5): 1246-1253.

Yao, Y., Ploss, B., Mak, C., and Wong, K. (2010). Pyroelectric properties of $BiFeO_3$ ceramics prepared byááámodified solid-state-reaction method. *Applied Physics A,* 99(1): 211-216.

Yatom, H., and Englman, R. (1969). Theoretical methods in the magnetoelectric effect. I. Formal treatment. *Physical Review,* 188(2): 793-802.

Yin, Y., Raju, M., Hu, W., Burton, J., Kim, Borisevich, A., Pennycook, S., Yang, S., Noh, T., and Gruverman, A. (2015). Multiferroic tunnel junctions and ferroelectric control of magnetic state at interface. *Journal of Applied Physics,* 117(17): 2601-2608.

Yu, B., Li, M., Liu, J., Guo, D., Pei, L., and Zhao, X. (2008). Effects of ion doping at different sites on electrical properties of multiferroic $BiFeO_3$ ceramics. *Journal of Physics D: Applied Physics,* 41(6): 5003-5007.

Yuan, G., and Or, D. (2006). Enhanced piezoelectric and pyroelectric effects in single-phase multiferroic $Bi_{1-x}Nd_xFeO_3$ (x= 0–0.15). *Applied Physics Letters,* 88(6): 2905-2908.

Yuan, G., Or, D., and Chan, H. (2007). Raman scattering spectra and ferroelectric properties of $Bi_{1-x}Nd_xFeO_3$ (x = 0-0.2) multiferroic ceramics. *Journal of Applied Physics,* 101(6): 1-5.

Yuan, G., Or, S., Wang, Y., Liu, Z., and Liu, J. (2006). Preparation and multi-properties of insulated single-phase $BiFeO_3$ ceramics. *Solid State Communications,* 138(2): 76-81.

Yuan, X., Tang, Y., Sun, Y., and Xu, M. (2012). Structure and magnetic properties of $Y_{1-x}Lu_xFeO_3$ ($0\leq x\leq 1$) ceramics. *Journal of Applied Physics,* 111(5): 3911-3915.

Zaghrioui, M., Greneche, J., Autret-Lambert, C., and Gervais, M. (2011). Effect of Fe substitution on multiferroic hexagonal $YMnO_3$. *Journal of Magnetism and Magnetic Materials,* 323(5): 509-514.

Zhang, D., Shi, P., Wu, X., and Ren, W. (2013). Structural and electrical properties of sol–gel-derived Al-doped bismuth ferrite thin films. *Ceramics International,* 39: S461-S464.

Zhang, S., Luo, W., Wang, D., and Ma, Y. (2009). Phase evolution and magnetic property of $Bi_{1-x}Dy_xFeO_3$ ceramics. *Materials Letters,* 63(21): 1820-1822.

Zhao, T., Scholl, A., Zavaliche, F., Lee, K., Barry, M., Doran, A., Cruz, M., Chu, Y., Ederer, C., and Spaldin, N. (2006). Electrical control of antiferromagnetic domains in multiferroic $BiFeO_3$ films at room temperature. *Nature Materials,* 5(10): 823-829.