SYNTHESIS AND CHARACTERIZATION OF COBALT BASED FERRITE

ALI A. ATI

A thesis submitted in fulfilment of the requirements for the award of the degree of
Doctor of Philosophy (Physics)

Faculty of Science
Universiti Teknologi Malaysia

FEBRUARY 2015
To my parents, with love and gratitude.
ACKNOWLEDGEMENT

First and foremost, I would like to extend my deepest gratitude to my supervisor and teacher, Prof. Dr. Zulkafli Bin Othaman, for giving me the opportunity to work in an amazing field of research. His constant encouragement, criticism and guidance were the key to bringing this project to fruitful completion, especially during the final period of the research. I have learned and gained much, not only in research skills, but also in the lessons of life, which has helped shaped my character. Thanks to him, I now talk and act with better rationale and much gained wisdom. Had we not crossed paths, I would have never realized my full potential.

I would also like to thank all those who have contributed directly and indirectly to the completion of this research and thesis. This includes my fellow postgraduate students who provided me with help and company during my study here. Otherwise, it would have been a lonely journey.

I also want to thank the original developers of the UTM thesis LATEX project for making the thesis writing process a lot easier for me. Thanks to them, I could focus on the content of the thesis, and not waste time with formatting issues.

I would also like to thank all my fellow friends and UTM staff for their contribution in giving me moral support throughout my development project period.

God bless you all.
ABSTRACT

Magnetolectric (ME) materials have the ability to convert magnetic energy into electrical energy and/or vice versa. This work involves the study of structural, electrical and magnetic properties of $(f)\text{Ni}_{(1-x)}(\text{Co/Mn}_x\text{Fe}_2\text{O}_4/\text{Pb(Mg}_{0.33}\text{Nb}_{0.67})_{0.67} \text{Ti}_{0.33}\text{O}_3$ nanocomposites, which have been successfully synthesized by chemical co-precipitation method. The presence of both phases in the composites were confirmed by using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and vibration sample magnetometer (VSM). The variations of dielectric constant and loss tangent as a function of frequency as well as temperature were studied using two-point probe impedance analyzer. Temperature dependent dielectric constant shows diffused phase transition in magnetoelectric nanocomposites. The DC electrical resistivity measurements were carried out within the temperature range of 300 – 923 K. Variation of magnetoelectric voltage coefficient traces the path of magnetostriction as a function of magnetic field. All composites show peak behavior in magnetic field dependent on magnetoelectric voltage coefficient. The magnetoelectric (ME) powder nanocomposite system of $(f)\text{Ni}_{(1-x)}(\text{Co/Mn}_x\text{Fe}_2\text{O}_4+ (1-f) \text{Pb(Mg}_{0.33}\text{Nb}_{0.67})_{0.67} \text{Ti}_{0.33}\text{O}_3$ (with $x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) and $f = 0.15$, has been successfully studied. The magnetoelectric coefficient for all the composites were measured using static magnetoelectric set up. All magnetic field dependent of magnetoelectric measurements show peak behaviour, which can be explained on the basis of magnetic field dependent variation of magnetostriction and piezomagnetic coefficient behavior. The strong compositional dependent of magnetoelectric voltage coefficient is a common feature for ferrite base nanocomposites. In this study the magnitude of the magnetoelectric coefficient is found to be higher with increasing amount of ferrite phase in nanocomposites samples. The magnetoelectric studies show that high resistive magnetic phase with high piezomagnetic coefficient in low magnetic field region is helpful to enhance the magnetoelectric coupling. The present data suggest that the magnetoelectric interaction depends on the magnetostriction behaviour, piezomagnetic coefficient, resistivity, content of constituent phases and connectivity between the phases.
ABSTRAK

Bahan magneto-elektrik (ME) mempunyai keupayaan untuk menukar tenaga magnetik kepada voltan elektrik dan/atau sebaliknya. Kajian ini melibatkan sifat-sifat struktur, elektrik dan magnetik bagi nanokomposit \((f)\text{Ni}_{1-x}(\text{Co/Mn})_x\text{Fe}_2\text{O}_4/\text{Pb(Mg}_{0.33}\text{Nb}_{0.67})_{0.67}\text{Ti}_{0.33}\text{O}_3\) yang berjaya disintesis menggunakan kaedah pemendakan kimia. Kehadiran semua fasa di dalam komposit telah dikenal pasti menggunakan kaedah pembelauan sinar-X (XRD), mikroskop electron imbasan pancaran medan (FESEM) dan magnetometer getaran sampel (VSM). Variasi pemalar dielektrik dan tangen kehilangan (\(\tan\delta\)) sebagai fungsi frekuensi serta fungsi suhu telah dikaji menggunakan penganalisis impedans dengan penduga dua titik. Kelakuan pemalar dielektrik bersandar suhu menunjukkan pembauran fasa di dalam nanokomposit magneto-elektrik. Pengukuran kerintangan elektrik DC telah dijalankan dalam julat suhu 300 – 923 K. Variasi pekali voltan magneto-elektrik telah menunjukkan magnetostriksi sebagai fungsi medan magnet. Semua komposit menunjukkan ciri-ciri puncak di dalam medan magnetik adalah bersandar kepada pekali voltan magneto-elektrik. Serbuk nanokomposit magneto-elektrik untuk sistem \((f)\text{Ni}_{1-x}(\text{Co/Mn})_x\text{Fe}_2\text{O}_4+(1-f)\ \text{Pb(Mg}_{0.33}\text{Nb}_{0.67})_{0.67}\text{Ti}_{0.33}\text{O}_3\) (dengan \(x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0\)) dan \(f = 0.15\), telah berjaya disediakan. Pekali magneto-elektrik untuk semua komposit telah diukur menggunakan aturan magneto-elektrik pegun. Semua pengukuran bagi medan magnet bersandar magneto-elektrik menunjukkan ciri-ciri puncak, yang dijelas berasaskan medan magnet bersandar terhadap kelakuun magnetostriksi dan pekali piezomagnet. Kebergantungan kuat pekali voltan magneto-elektrik terhadap komposisi adalah cirri lazim untuk nanokomposit berasas ferit. Dalam kajian ini magnitud pekali magneto-elektrik didapati meningkat dengan peningkatan aumaun fasa ferit di dalam sampel nanokomposit. Kajian magneto-elektrik menunjukkan bahawa fasa magnet kerintangan tinggi dengan pekali magnetik piezo yang tinggi di dalam medan magnet rendah dapat membantu dalam meningkatkan gandingan magneto-elektrik. Data semasa menunjukkan interaksi magneto-elektrik bergantung kepada kelakuan magnetostriksi, pekali piezomagnet, kerintangan, kandungan juzuk fasa dan hubungan antara fasa.
TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DECLARATION</td>
<td>ii</td>
</tr>
<tr>
<td></td>
<td>DEDICATION</td>
<td>iii</td>
</tr>
<tr>
<td></td>
<td>ACKNOWLEDGEMENT</td>
<td>iv</td>
</tr>
<tr>
<td></td>
<td>ABSTRACT</td>
<td>v</td>
</tr>
<tr>
<td></td>
<td>ABSTRAK</td>
<td>vi</td>
</tr>
<tr>
<td></td>
<td>TABLE OF CONTENTS</td>
<td>vii</td>
</tr>
<tr>
<td></td>
<td>LIST OF TABLES</td>
<td>xiii</td>
</tr>
<tr>
<td></td>
<td>LIST OF FIGURES</td>
<td>xiv</td>
</tr>
<tr>
<td></td>
<td>LIST OF ABBREVIATIONS</td>
<td>xx</td>
</tr>
<tr>
<td></td>
<td>LIST OF SYMBOLS</td>
<td>xxii</td>
</tr>
<tr>
<td></td>
<td>LIST OF APPENDICES</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1</td>
<td>Overview</td>
<td>1</td>
</tr>
<tr>
<td>1.2</td>
<td>Magnetoelectric (ME) Effect in Nanocomposites</td>
<td>4</td>
</tr>
<tr>
<td>1.3</td>
<td>Statement of Problem</td>
<td>6</td>
</tr>
<tr>
<td>1.4</td>
<td>Research Objectives</td>
<td>9</td>
</tr>
<tr>
<td>1.5</td>
<td>Scope of Research</td>
<td>9</td>
</tr>
<tr>
<td>1.6</td>
<td>Significance of Study</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>LITERATURE REVIEW</td>
<td>12</td>
</tr>
<tr>
<td>2.1</td>
<td>Introduction to Ferrites</td>
<td>12</td>
</tr>
<tr>
<td>2.2</td>
<td>Historical Background of Magnetic Materials</td>
<td>13</td>
</tr>
</tbody>
</table>
2.3 Classification of Magnetic Materials 15
  2.3.1 Diamagnetic Materials 15
  2.3.2 Paramagnetic Materials 17
  2.3.3 Ferromagnetic Materials 18
  2.3.4 Ferrimagnetic Materials 19

2.4 Types of Ferrites 20
  2.4.1 Simple Spinel Ferrites 20
  2.4.2 Mixed Spinel Ferrites 21
  2.4.3 Substitutional Spinel Ferrites 21

2.5 The Structure of Spinel Ferrite 21

2.6 Classification of Spinel Ferrites on the Basic of Cation Distribution 23
  2.6.1 Normal Spinel Ferrite 23
  2.6.2 Inverse Spinel Ferrite 24
  2.6.3 Random Spinel Ferrite 24

2.7 Magnetic Properties of Ferrites 25

2.8 Ferroelectrics Materials 26

2.9 Perovskites Ferroelectric Materials (ABO3) 28

2.10 Methods for Ferrite Synthesis 29
  2.10.1 Dry Method 29
  2.10.2 Decomposition Method 29
  2.10.3 Solid State Reaction Method 30
  2.10.4 Sol-Gel Method 30
  2.10.5 Co-precipitation Method 31

2.11 Properties of Magnetoelectric (ME) Composites 32
  2.11.1 Morphological Studies of Magnetoelectric (ME) Composites 33
  2.11.2 Electrical Properties of Magnetoelectric Composites 36
  2.11.3 Dielectric Properties of Magnetoelectric (ME) Composites 37
  2.11.4 Magnetic and Ferroelectric Properties of ME Composites 38
2.12 Dipole Moment and Polarization 40
2.13 The Concept of Polarization 40
  2.13.1 Electronic Polarization (\(P_E\)) 40
  2.13.2 Ionic Polarization (\(P_I\)) 42
  2.13.3 Dipole of Orientational Polarization (\(P_O\)) 42
  2.13.4 Interface or Space Charge Polarization (\(P_S\)) 42
2.14 Dielectrics in Alternating Fields 43
2.15 Koop’s Model 44
2.16 Dielectric Losses 45
2.17 X-ray Diffraction (XRD) 47
  2.17.1 Determination of Lattice Parameter 49
  2.17.2 Determination of Particle Size 49
  2.17.3 Lattice Strain 50
  2.17.4 Determination of Phase Percentage 51
2.18 Determination of Density 51
2.19 Fourier Transform Infrared Spectroscopy (FT-IR) 52
2.20 Morphological Studies by Field Emission Scanning Electron Microscope (FE-SEM) 55
  2.20.1 Image Formation in the FE-SEM 58
2.21 Electrical Resistivity 60
2.22 Dielectric Measurement 64
2.23 Ferroelectric Hysteresis Loop 65
2.24 Magnetic Characterization 67
  2.24.1 Magnetic Hysteresis Loop 67
  2.24.2 Vibrating Sample Magnetometer (VSM) Principle 68
2.25 Magnetoelectric Measurements 70
  2.25.1 Static Method 70
  2.25.2 Dynamic Method 71

3 RESEARCH METHODOLOGY 73
3.1 Introduction 73
3.2 Synthesis of (Ni-Co, Co-Mn) Ferrites using Co-precipitation Method 74
3.2.1 Actual Method of Precipitation 74
3.2.2 Mixing of Oxides 74
3.2.3 Formation of Precipitate 75
3.2.4 Synthesis of Pb(Mg$_{1/3}$Nb$_{2/3}$)$_{0.67}$Ti$_{0.33}$O$_3$ (PMN-PT) Phase 78
3.2.5 Synthesis of Ni$_{1-x}$Co$_x$Fe$_2$O$_4$ /PMN-PT Nanocomposite Phase 81
3.2.6 Preparation of Samples 82

3.3 Experimental 83
3.3.1 Electric Polling 83
3.3.2 Magnetic Polling 85

4 STRUCTURAL AND MORPHOLOGICAL STUDIES 87
4.1 Structural 87
4.1.1 XRD Analysis of Ni$_{1-x}$Co$_x$Fe$_2$O$_4$ Ferrite Phase 89
4.1.2 XRD Analysis of Co$_{1-x}$Mn$_x$Fe$_2$O$_4$ Ferrite Phase 93
4.1.3 XRD Analyses of Ferroelectric Phase Pb(Mg$_{0.33}$Nb$_{0.67}$)$_{0.67}$Ti$_{0.33}$O$_3$ [PMN-PT] 94
4.1.4 X-ray Analysis of Magnetoelectric (ME) Nano-composite 95
4.2 FT-IR Analysis 102
4.2.1 FT-IR Analysis of Ni$_{1-x}$Co$_x$Fe$_2$O$_4$ Ferrite Phase 102
4.2.2 FT-IR Analysis of Pb(Mg$_{0.33}$Nb$_{0.67}$)$_{0.67}$Ti$_{0.33}$O$_3$ [PMN-PT] Ferroelectric Phase 104
4.3 Morphology and EDX Analysis 105
4.3.1 Morphology and EDX Analysis of Ni$_{1-x}$Co$_x$Fe$_2$O$_4$ Ferrite Phase 105
4.3.2 Morphology and EDX Analysis of Co\textsubscript{(1-x)}Mn\textsubscript{x}Fe\textsubscript{2}O\textsubscript{4} Ferrite Phase 108
4.3.3 Morphology and EDX Analysis of Co\textsubscript{(1-x)}Mn\textsubscript{x}Fe\textsubscript{2}O\textsubscript{4} Ferrite Phase 111
4.3.4 Morphology and EDX Analysis of Magnetoelectric (ME) Nanocomposites 113
4.4 Lattice Strain Analysis 118

5 ELECTRICAL AND MAGNETIC PROPERTIES 121
5.1 Introduction 121
5.2 Dielectric Properties 122
  5.2.1 Frequency Dependent Dielectric of Ni\textsubscript{(1-x)}Co\textsubscript{x}Fe\textsubscript{2}O\textsubscript{4} (NCFO) 122
  5.2.2 Temperature Dependent Variation of Dielectric Constant 125
  5.2.3 Electrical Properties 128
  5.2.4 Dielectric Properties of Co\textsubscript{(1-x)}Mn\textsubscript{x}Fe\textsubscript{2}O\textsubscript{4} 130
  5.2.5 Dielectric Properties of PMN-PT 131
  5.2.6 Frequency Dependent Variation of Dielectric Constant of nano-composite Y\textsubscript{1}, Y\textsubscript{2} and Y\textsubscript{3} 133
  5.2.7 Temperature Dependent Variation of nano-composite Y\textsubscript{1}, Y\textsubscript{2} and Y\textsubscript{3} 137
5.3 Resistivity Measurements of nano-composite Y\textsubscript{1}, Y\textsubscript{2} and Y\textsubscript{3} 142
  5.3.1 DC Resistivity 142
  5.3.2 AC Resistivity for Y\textsubscript{2} nano-composite 144
5.4 Ferroelectric Properties of nano-composite Y\textsubscript{1}, Y\textsubscript{2}, Y\textsubscript{3} and PMN-PT 145
5.5 Magnetic Properties of nano-composite Y\textsubscript{1}, Y\textsubscript{2} and Y\textsubscript{3} 147
5.6 Magnetoelectric Effect of nano-composite Y\textsubscript{1}, Y\textsubscript{2} and Y\textsubscript{3} 152
5.7 Temperature Dependent Variation of Dielectric Constant nano-composites of S₁, S₂ and S₃ 154
5.8 DC Resistivity of nano-composites of S₁, S₂ and S₃ 157
5.9 Magnetic Properties of nano-composites of S₁, S₂ and S₃ 158
5.10 Magnetoelectric Effect of nano-composites of S₁, S₂ and S₃ 160

6 CONCLUSION 162
6.1 Further Work 165

REFERENCES 166
Appendices A 190
# LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE NO</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>The compositions for Ni-Co ferrite and Co-Mn ferrite series</td>
<td>78</td>
</tr>
<tr>
<td>4.1</td>
<td>The characteristic parameters for each Ni_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4 composition at room temperature</td>
<td>92</td>
</tr>
<tr>
<td>4.2</td>
<td>Data of obtained characteristic parameters for each composition \text{Mn}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4 at room temperature</td>
<td>94</td>
</tr>
<tr>
<td>4.3</td>
<td>Lattice parameters and porosity data for ME nano-composite</td>
<td>100</td>
</tr>
<tr>
<td>4.4</td>
<td>Structural parameters and percentage of the constituent phases of S_1, S_2 and S_3 nano-composite</td>
<td>101</td>
</tr>
<tr>
<td>5.1</td>
<td>Comparison of electrical and dielectric properties of Ni-Co ferrite and Co-Mn ferrites system</td>
<td>131</td>
</tr>
<tr>
<td>5.2</td>
<td>Activation energies in the ferroelectric and paraelectric regions for all sample series</td>
<td>143</td>
</tr>
<tr>
<td>5.3</td>
<td>Ferroelectric, magnetic and magnetoelectric properties of the constituent phase and their nano-composites</td>
<td>146</td>
</tr>
<tr>
<td>5.4</td>
<td>The room temperature magnetic properties for each composition</td>
<td>150</td>
</tr>
<tr>
<td>5.5</td>
<td>Electric data for S_1, S_2 and S_3 nanocomposites</td>
<td>158</td>
</tr>
</tbody>
</table>
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE NO</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>A sketch representation of ferroelectricity and ferromagnetism integration as well as the mutual control between them in multi-ferroics (ferrite and ferroelectric materials)</td>
<td>3</td>
</tr>
<tr>
<td>1.2</td>
<td>Schematic representation of particulate ME nanocomposites</td>
<td>4</td>
</tr>
<tr>
<td>1.3</td>
<td>Block diagram indicating sequential steps of magnetoelectric effect in nanocomposites</td>
<td>5</td>
</tr>
<tr>
<td>2.1</td>
<td>Pictorial representation of the origin of the (a) orbital magnetic moment and (b) spin magnetic moment in an atom</td>
<td>15</td>
</tr>
<tr>
<td>2.2</td>
<td>Schematic representation of orientations of magnetic moments in (a) diamagnetic (b) paramagnetic, (c) ferromagnetic, (d) antiferromagnetic and (e) ferrimagnetic materials</td>
<td>18</td>
</tr>
<tr>
<td>2.3</td>
<td>Schematic representation of spinel cubic lattice with ionic distribution in two upper left octants with tetrahedral A site and Octahedral B site</td>
<td>22</td>
</tr>
<tr>
<td>2.4</td>
<td>Magnetic hysteresis loop showing different orientation of magnetic moments</td>
<td>26</td>
</tr>
<tr>
<td>2.5</td>
<td>Interrelationship of piezoelectric and subgroup on the basis of symmetry</td>
<td>27</td>
</tr>
<tr>
<td>2.6</td>
<td>The cubic Perovskites structure (ABO3)</td>
<td>28</td>
</tr>
</tbody>
</table>
2.7 SEM images of free surface of the (1-x)NZCF/x PNN-PZN-PNWPT grain ceramic composites sintered at 950 °C for 2 hours after thermal etching at 825 °C for 30 mins

2.8 Images of SEM micrographs of CMFO+BZT magnetoelectric (ME) composites

2.9 SEM micrograph of a composite containing 45% ferrite phase

2.10 Schematic representation of different mechanisms of polarization

2.11 (a) Schematic representation of Braggs X-ray diffraction and (b) Geometry of an X-ray diffractometer (Bruker, model D8 Advance)

2.12 Fourier Transform Infrared Spectroscopy (FT-IR) (Thermo fisher Scientific Nicolet 50)

2.13 A photograph of (JEOL, JSM-6360A) FE-SEM machine

2.14 Pictorial representation of resistivity of a material in cylindrical shape

2.15 (a) Circuit diagram for the electrical resistivity measurements, (b) Two probe sample holder and (c) Actual two-probe sample holder fabricated in physics department

2.16 Sawyer-Tower method for the measurement of polarization-electric field (P-E) characteristics (LCR Hi-TESTER)

2.17 Photograph of the vibrating sample magnetometer

2.18 Pictorial representation of static magnetoelectric (ME) setup

2.19 Schematic representation of longitudinal and transverse modes of magnetoelectric (ME) measurement
3.1 Flow chart representing steps involved in synthesis of \( \text{Co}_{(1-x)}\text{Mn}_x\text{Fe}_2\text{O}_4 \) ferrite phase 76

3.2 Flow chart representing steps involved in synthesis of \( \text{Ni}_{(1-x)}\text{Co}_x\text{Fe}_2\text{O}_4 \) ferrite phase 77

3.3 Flow chart representing steps involved in synthesis of ferroelectric phase 80

3.4 Flow chart represents the steps involved in synthesis of magnetoelectric nanocomposites 81

3.5 Schematic representation of orientation of dipole moments (a) before electric poling, (b) during electric poling and (c) after electric poling 84

3.6 Photograph sample holder used for electric poling 85

3.7 Experimental set up for magnetoelectric effect measurement 86

3.8 Photo of sample holder for magnetoelectric measurements 86

4.1 X-ray diffraction patterns of synthesized \( \text{Ni}_{(1-x)}\text{Co}_x\text{Fe}_2\text{O}_4 \) ferrite 91

4.2 X-ray diffraction patterns of \( \text{Co}_{(1-x)}\text{Mn}_x\text{Fe}_2\text{O}_4 \) ferrites 93

4.3 X-ray diffraction pattern for \( \text{Pb}(\text{Mg}_{0.33}\text{Nb}_{0.67})_{0.67}\text{Ti}_{0.33}\text{O}_3 \) sintered at 1250 °C 95

4.4 X-ray diffraction patterns of (f)NFO+ (1-f) PMN-PT sintered at 1200 °C (B group) and 1100 °C (A group). The additional peaks are indicated by ‘#’, and ‘*’ symbols 97

4.5 X-ray diffraction patterns of (f) \( \text{Ni}_{0.2}\text{Co}_{0.8}\text{Fe}_2\text{O}_4 \) + (1-f) PMN-PT sintered at 1200 °C (B group) and 1100 °C (A group) 99

4.6 X-ray diffraction patterns for (f) \( \text{Ni}_{0.4}\text{Co}_{0.6}\text{Fe}_2\text{O}_4 \) + (1-f) PMN-PT sintered at 1200 °C (B group) and 1100 °C (A group) 99
4.7 X–ray diffraction pattern of PMN-PT phase, CMFO phase nano-composite sintered at 1200 °C (S₁, S₂ group) and S₃ at 1100 °C

4.8 FT-IR spectra of Niₙ₋ₓCoₓFe₂O₄ samples sintered at 600 °C

4.9 FT-IR spectra of Coₙ₋ₓMnₓFe₂O₄ samples sintered at 600 °C

4.10 FT-IR spectra of PMN-PT at room temperature

4.11 FE-SEM micrographs for Niₙ₋ₓCoₓFe₂O₄ ferrite phase consist of nanoparticles

4.12 Quantitative analysis of elemental distribution using EDX pattern in FE-SEM for Ni₀.₈Co₀.₂Fe₂O₄ ferrite phase

4.13 FE-SEM micrographs for Coₙ₋ₓMnₓFe₂O₄ ferrite phase

4.14 Quantitative analysis of elemental distribution using EDX pattern in FE-SEM for Co₀.₈Mn₀.₂Fe₂O₄ ferrite phase

4.15 SEM (a) and FE-SEM (b) micrograph of the PMN-PT sample

4.16 Quantitative analysis of elemental distribution using EDX for ferroelectric phase

4.17 SEM micrographs of (a) S₁, (b) S₂, (c) S₃ and (d) S₄ nano-composites

4.18 Quantitative analysis of elemental distribution using EDX pattern in SEM for white grain

4.19 Quantitative analysis of elemental distribution using EDX pattern in SEM for black grain

4.20 Lattice strain calculations for (a) PMN-PT phase and (b) CMFO phase present in S₁, S₂ and S₃ ME nano-composites

5.1 Frequency dependent variations of a) dielectric constant b) loss tangent and c) AC resistivity for Ni-Co ferrite samples
<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2</td>
<td>Plot of $\log (\sigma_{ac} - \sigma_{dc})$ versus $\log \omega^2$ for Ni-Co ferrite</td>
</tr>
<tr>
<td>5.3</td>
<td>Variation of dielectric constant with temperature for samples A1, A2, A3 and</td>
</tr>
<tr>
<td>5.4</td>
<td>Variation of loss tangent with temperature for samples A1, A2, A3 and A4</td>
</tr>
<tr>
<td>5.5</td>
<td>Variation of DC resistivity with inverse temperature for Ni-Co ferrite</td>
</tr>
<tr>
<td>5.6</td>
<td>Frequency dependent variation of dielectric constant and dielectric loss for sample A</td>
</tr>
<tr>
<td>5.7</td>
<td>Frequency dependent variation of dielectric constant and dielectric loss for sample B</td>
</tr>
<tr>
<td>5.8</td>
<td>Frequency dependent variation of (a) dielectric constant (b) loss tangent and (c) AC resistivity for nano-composite Y1, Y2 and Y3 at room temperature</td>
</tr>
<tr>
<td>5.9</td>
<td>Plot of $\log (\sigma_{ac} - \sigma_{dc})$ versus $\log \omega^2$ for nano-composites Y1, Y2 and Y3</td>
</tr>
<tr>
<td>5.10</td>
<td>The variation of dielectric constant with temperatures for the nano-composites (a) Y1, (b) Y2 and (c) Y3, respectively</td>
</tr>
<tr>
<td>5.11</td>
<td>Variation of loss tangent with temperature for the Y1, Y2 and Y3 nano-composites</td>
</tr>
<tr>
<td>5.12</td>
<td>Variation of DC resistivity with inverse temperature for Y1, Y2 and Y3 nano-composite</td>
</tr>
<tr>
<td>5.13</td>
<td>Variation of $\log \rho_{ac}$ with inverse temperature for Y2 nano-composite</td>
</tr>
<tr>
<td>5.14</td>
<td>P-E hysteresis loop of PMN-PT and Y1, Y2 and Y3 nano-composites</td>
</tr>
<tr>
<td>5.15</td>
<td>Hysteresis of NCFO, Y1, Y2 and Y3 nanocomposites</td>
</tr>
<tr>
<td>5.16</td>
<td>The room temperature M–H curves of Ni$_{1-x}$Co$_x$Fe$_2$O$_4$ nanoparticles</td>
</tr>
<tr>
<td>Section</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>5.17</td>
<td>Variation of longitudinal ME voltage coefficient ((dE/dH)_H) with applied magnetic field for nano-composites (Y_1, Y_2) and (Y_3)</td>
</tr>
<tr>
<td>5.18</td>
<td>Variation of dielectric constants with temperature for (S_1, S_2) and (S_3) nano-composites</td>
</tr>
<tr>
<td>5.19</td>
<td>Variation of loss tangent with temperature for nano-composites (S_2)</td>
</tr>
<tr>
<td>5.20</td>
<td>Variation of DC resistivity with temperature for (S_1, S_2,) and (S_3) nano-composites</td>
</tr>
<tr>
<td>5.21</td>
<td>Hysteresis of pure CMFO, (S_1, S_2) and (S_3) composites</td>
</tr>
<tr>
<td>5.22</td>
<td>Variation of ME voltage coefficient with applied magnetic field for nano-composites (S_1 S_2,) and (S_3)</td>
</tr>
</tbody>
</table>
### LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC Resistivity</td>
<td>Electric resistivity measurements</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray</td>
</tr>
<tr>
<td>E-P</td>
<td>Electric poling</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field emission scanning electron microscopy</td>
</tr>
<tr>
<td>FT-IT</td>
<td>Fourier transform Infrared</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full with at half maximum</td>
</tr>
<tr>
<td>LCR</td>
<td>Inductance capacitance resistance</td>
</tr>
<tr>
<td>ME</td>
<td>Magnetoelectric Measurements</td>
</tr>
<tr>
<td>P-E</td>
<td>Polarization electric field measurement</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>VSM</td>
<td>Vibrating sample magnetometer</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
</tbody>
</table>
### LIST OF SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>(dE/dH)</td>
<td>Magnetoelectric voltage coefficient</td>
</tr>
<tr>
<td>(dE/dH)_H</td>
<td>Magnetoelectric voltage coefficient</td>
</tr>
<tr>
<td>ΔE</td>
<td>Activation energy</td>
</tr>
<tr>
<td>μ₀</td>
<td>Permeability</td>
</tr>
<tr>
<td>A</td>
<td>Area</td>
</tr>
<tr>
<td>a</td>
<td>Area</td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>a, c</td>
<td>Lattice parameter</td>
</tr>
<tr>
<td>Ba</td>
<td>Barium</td>
</tr>
<tr>
<td>Bi</td>
<td></td>
</tr>
<tr>
<td>BSTO</td>
<td>Barium strontium titanate</td>
</tr>
<tr>
<td>C</td>
<td>Capacity</td>
</tr>
<tr>
<td>C₀</td>
<td>Capacitance of condenser</td>
</tr>
<tr>
<td>Ca</td>
<td>Calcium</td>
</tr>
<tr>
<td>CBH</td>
<td>Correlated barrier hopping</td>
</tr>
<tr>
<td>Co</td>
<td>Cobalt</td>
</tr>
<tr>
<td>C₀</td>
<td>Stander capacitor</td>
</tr>
<tr>
<td>Cp</td>
<td>Capacity</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>Chromium(III) oxide</td>
</tr>
<tr>
<td>Cu Kα</td>
<td>Copper K-alpha line</td>
</tr>
<tr>
<td>CuFe₂O₄</td>
<td>Copper ferrite</td>
</tr>
<tr>
<td>d</td>
<td>Interplaner distance</td>
</tr>
<tr>
<td>D</td>
<td>Vertical distance</td>
</tr>
<tr>
<td>d</td>
<td>Thicknesses of grain boundary</td>
</tr>
<tr>
<td>d₃₃</td>
<td>Piezoelectric coefficient</td>
</tr>
</tbody>
</table>
## LIST OF APPENDICES

<table>
<thead>
<tr>
<th>APPENDIX</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>List of Publications</td>
<td>190</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

1.1 Overview

The identification of novel materials with better properties or new dispensation techniques to improve the performance of existing materials, along with the inexpensive advantages, is always a substance of attention to researchers. The desire to produce novel smart materials is strongly dependent on the availability of suitable materials with enhanced properties [1, 2]. Each ceramic material has its own properties, which makes it useful for human beings. There are certain classes of materials such as, magnetic and ferroelectric materials, which infuse many aspects of modern science and technology. In this case, these materials are prepared today by various techniques in different form. Therefore, it is essential to know the origin and mechanism of magnetic and electrical for every combination and form of the magnetic and electrical materials, which is used for specific applications [3-5]. As mentioned before, each material has its unique property, which increases its importance in useful applications of these materials.

It is known that, a piezoelectric material has ability to convert mechanical energy into electrical energy and vice versa. Similarly, magnetostrictive materials
can convert magnetic energy into mechanical energy [6, 7]. New generation of devices need such type of smart materials, which can convert magnetic energy into electrical energy or vice versa. Such a conversion is possible in a new category of materials called magneto-electric (ME) materials [8, 9]. Very few naturally occur single phase materials like Cr$_2$O$_3$, show magneto-electric phenomena, whereas a combination of ferro-electric-ferrite materials generate ME effect extrinsically. Such a combination of individual phases having its own characteristic properties shows a new material property, which is absent in their parent phases. The demerit of the single phase magneto-electric materials is that, it’s magneto-electric effect at room temperature is very weak and not usable in practical applications [10]. The main advantage of composite material is that, one can improve the magneto-electric phenomena by a combination of the best characteristics of ferrite-ferroelectric materials.

Recently, many research groups paid attention for the improvement of magneto-electricity in different composites, to fulfill the necessary requirements for device applications. As for the trend towards advanced technology, a good addition of multi-functions into a single material organization then becomes very attractive. It is expected that new generation of devices using composite materials that combine magnetic, ferro-electric and magneto-electric (ME) properties in an effective and intrinsic manner have broad potential applications. The co-existence of magnetism and electricity will produce new physical phenomena (magneto-electric effect), which offer possibilities for new device functions [11-13].
**Figure 1.1** A sketch representation of ferroelectricity and ferromagnetism integration as well as the mutual control between them in multi-ferroics (ferrite and ferroelectric materials)

Multi-ferroic (ferrite and ferroelectric materials) offers excellent ferroelectric polarization (electric field hysteresis) and magnetization (magnetic field hysteresis) [13-15]. It is represented in Figure 1.1 where all magnetoelectric (ME) materials are multi-ferroics in nature, and hence the coupling interaction between the two order parameters becomes prime important. The coupling of the ferroelectricity and magnetism (either ferromagnetic or ferrimagnetic) in magneto-electricity indicates an option that influences the magnetic properties over electric fields in vice versa manner. Thus, the material is suited for many state memory parts or unique memory requests.

In the case of magnetoelectric (ME) nanocomposites, despite of many materials mixtures and structures surveyed, poor performances on the magnetoelectric (ME) yields were due to the reduced dielectric, electrical and ferroelectric features. In addition, there are poor reproducibility and large scattering of functional properties data [16, 17]. Comprehensive investigations considering the different aspects such as, the influence of nanocomposition, preparation routes,
nanostructural properties such as interface doping and degree of connectivity, magnetic/ferroelectric properties of the parent phases are still lacking.

1.2 Magnetoelectric (ME) Effect in Nanocomposites

Neither ferroelectric nor magnetic phase has the magnetoelectric (ME) influence except in the composites of these two phases, which can be used to create magnetoelectric (ME) behavior from materials, which do not show the magnetoelectric (ME) outcome. This is conveniently achieved by using a mixture of magnetic and ferroelectric composites.

Consider a particulate of ME nanocomposites as shown in Figure 1.2, where the magnetostrictive particles are distributed in the ferroelectric grains.

![Figure 1.2 Schematic representation of particulate ME nanocomposites](image)

The magneto-electric influence on nanocomposites material term a product property [18, 19], was from the results of cross interaction on different orderings of
two separate composite phases. This two-step process was observed from the ME effect in nanocomposites, which is explained using block diagram in Figure 1.3.

![Figure 1.3](image)

**Figure 1.3** Block diagram indicating sequential steps of magnetoelectric effect in nanocomposites

When a magnetic field is applied to ferrite-ferroelectric composites, the magnetic phase changes its shape magnetostrictively i.e. ferrite grains are strained. The strain is then transferred to the ferroelectric phase, which exerts stress on it, resulting in an electric polarization due to piezoelectric effect. Thus, the magnetoelectric effect in composites is extrinsic (i.e. in product, unlike in single phase, where it is intrinsic), depending on the composite nanostructure and coupling interaction across ferromagnetic-ferroelectric interfaces. The magneto-electric is a response from an electric polarization (P) upon magnetic field (H) application (i.e. the ME direct effect is denoted as ME$_H$ effect: $P=\alpha H$) and/or the appearance of a magnetization $M$ upon applying an electric field $E$ (i.e., the converse ME effect, or ME$_E$: $M=\alpha E$). The product properties of the composites can be mathematically represented as follows:

$$ME_H \text{ effect} = \left( \frac{\text{magnetic}}{\text{mechanical}} \right)_{\text{magnetostriction}} \times \left( \frac{\text{mechanical}}{\text{electrical}} \right)_{\text{piezoelectric}} \quad (1.1)$$

$$ME_E \text{ effect} = \left( \frac{\text{electrical}}{\text{mechanical}} \right)_{\text{piezoelectric}} \times \left( \frac{\text{mechanical}}{\text{magnetic}} \right)_{\text{piezomagnetic}} \quad (1.2)$$
The ME effect is a product of the magnetostrictive effect in the magnetic field i.e. magnetic/mechanical effect and the piezoelectric effect in the ferroelectric type i.e. electrical/mechanical effect. Thus, the ME outcome is a product property referring to unique effects which initiate the interaction within ME nanocomposites. The magnetostrictive effect on the magnetic phase and piezoelectric effects in the ferroelectric phase are included [20]. This trend is related to the concentration of individual phases present in the ME nanocomposites. The conceptual points to enhance the ME effect in composites are:

i. Two different phases should be in equilibrium.
ii. Mismatching between grains ought to be minimum.
iii. The magnitude of the magnetostriction coefficient of magnetic phase ought to be as high as possible.
iv. The magnitude of the piezoelectric coefficient of the ferroelectric phase should be high.
v. The accumulated charges must not leak through the magnetic phase, i.e. resistivity of both phases must be comparable and sufficiently large.
vi. The ferroelectric/magnetic transition temperatures need to be higher than the room temperature, near achieving electric and magnetic ordering respectively at room temperature.
vii. Proper electrical poling of the magnetoelectric (ME) nanocomposites is required in order to improve piezoelectricity in ferroelectric phase.

1.3 Statement of Problem

The nanocomposites materials of ferrite and ferroelectric phase show interesting properties that are superior to conventional ferrite and ferroelectric materials. The magnetoelectric (ME) effect observed in such composites is absent in its constituent phases and magnetoelectric (ME) output is small as compared to single phase material.
It has been seen from previous discussion, selection of a suitable ferrite and ferroelectric materials with high piezomagnetic coefficient and piezoelectric coefficient can enhance the magnetoelectric effect in nanocomposites. Where $\mu$ is the permeability of magnetic phase and $\varepsilon$ is the dielectric permittivity of ferroelectric phase. Thus, the primary criterion for selection of individual phases in the nanocomposite is to identify materials having similar crystallographic symmetry and possesses large magnetic permeability and dielectric permittivity.

In nanocomposites the individual phases are mixed, milled, shaped and sintered in order to obtain very dense samples. The reaction between the individual phases limits the high value of the sintering temperature for nanocomposites. The problem of high leakage current for such systems arises due to the magnetic phases. It has been found that, both the perovskite $A^{2+}B^{4+}O_3$ and spinel $M^{2+}Fe_2O_4$ are appropriate to enhance the magnetoelectric effect in nanocomposite form. Hence it is necessary to select suitable nanocomposite system which will fulfill all the necessary requirements.

Terfenol-D, an alloy of terbium, dysprosium, and iron, is known to exhibit highest magnetostriction. However, Terfenol has many limitations such as its poor mechanical properties, a single crystal is required for many applications, the high costs of Tb and Dy, and the presence of eddy currents when high frequencies are involved. In order to overcome these problems, current research has been focused to obtain an oxide based magnetostrictive material that will exhibit higher magnetostrictive strains at lower magnetic field strengths. The advantages of an oxide based magnetic material are that it would be much cheaper than the commercial alloys and can prevent the generation of eddy currents. Naturally ferrites have very large resistivity (MΩ cm) than the $R$-Fe compounds (µΩ cm) and thus compatible with the ferroelectric materials (GΩ cm) in high frequency applications. They are also known to have saturation in their magnetostriction at low bias magnetic fields due to small magnetic anisotropy. It is known that, CoFe$_2$O$_4$ exhibits highest magnetostriction among all the known ferrites. Cobalt ferrite in single crystalline form exhibits high anisotropic magnetostrictive strain depending on the
composition. Similarly, Nickel ferrite has attracted considerable attention because of its large permeability at high frequency, remarkable high electrical resistivity, mechanical hardness, chemical stability and cost effectiveness. The appropriate choice of substituents in nickel ferrite has made it possible to tailor the materials properties for a variety of diverse requirements of electronic and magnetic devices. [Ni–Co(Mn)] mixed ferrites are highly resistive and magnetostrictive. Thus in this study, nanocomposition for ferrimagnetic phase was varied to change the magnetic properties such as magnetization, permeability, and resistivity. $\text{Ni}_{1-x}(\text{Co/Mn})_x\text{Fe}_2\text{O}_4$ ferrite provides high resistivity and magnetostriction coefficient which favors the magnetoelectric effect, and is suitable as one of the phases used for the magnetoelectric biphasic composite. Hence $\text{Ni}_{1-x}(\text{Co/Mn})_x\text{Fe}_2\text{O}_4$ with $x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$ is suitable as piezomagnetic phase used for the magnetoelectric biphasic composite. Large piezoelectric responses have been observed in these perovskites near structural phase boundary, the so-called morphotropic phase boundary (MPB). The Pb based ferroelectrics such as Lead-Magnesium-Niobium–Lead Titanium (PMN-PT) is selected to be a good choice as ferroelectric phase. Hence in this case PMN-PT is selected as the ferroelectric phase. The selection of PMN-PT as a ferroelectric phase in magnetoelectric nanocomposites shows enhancement in magnetoelectric voltage coefficient compared to other magnetoelectric nanocomposites. Hence PMN-PT in morphotropic phase boundary (MPB) region is selected as a ferroelectric phase due to its strongest piezoelectric property among various piezoelectric materials.

It is expected that, the selected individual phases will fulfill all the necessary requirements. Microscopic studies of composites also shows leakage of relevance structure of composites, which may be due to mismatching between grains of ferrite and ferroelectric phase in the composites materials. Since physical properties of multiphase nanocomposites depend critically on nanostructure, it is desirable to know the distribution of the constituent phases. A more precise way of morphological analysis required for understanding of nanostructural dependent properties of magnetoelectric nanocomposites.
1.4 Research Objectives

The objectives of this study are to:

1. synthesize magneto-electric composite of \([\text{Co}_{(1-x)}\text{Mn}_x\text{Fe}_2\text{O}_4, \text{Ni}_{(1-x)}\text{Co}_x\text{Fe}_2\text{O}_4]\) nanoparticles ferrite and Lead-Magnesium-Niobium–Lead Titanium (PMN-PT) ferroelectric materials by using chemical co-precipitation technique.
2. determine the structure of the ferrite, ferroelectric and nanocomposites studies using X-ray diffraction technique.
3. determine lattice strain of nanocomposites using X-ray diffraction technique data.
4. determine morphology of magneto-electrical nanocomposites by scanning electron microscopy (SEM).
5. determine the electrical properties of \(\text{Co}_{(1-x)}\text{Mn}_x\text{Fe}_2\text{O}_4, \text{Ni}_{(1-x)}\text{Co}_x\text{Fe}_2\text{O}_4\) and PMN-PT.
6. determine the magnetoelectric characteristics\([(dE/dH)_H]\) as a function of magnetic field at room temperature for nanocomposites samples \([(f) \text{Ni}_{(1-x)}\text{Co}_x\text{Fe}_2\text{O}_4 + (1-f) \text{PMN}-\text{PT}]\) and \([(f) \text{Co}_{(1-x)}\text{Mn}_x\text{Fe}_2\text{O}_4+ (1-f)\text{PMN}-\text{PT}]\).

1.5 Scope of Research

In this work, ferrites nanoparticles phase of \(\text{Ni}_{(1-x)}\text{Co}_x\text{Fe}_2\text{O}_4, \text{Co}_{(1-x)}\text{Mn}_x\text{Fe}_2\text{O}_4\) and ferroelectric nanoparticles phase of PMN-PT were synthesized using chemical method. The two phases were mixed together to obtain the nanocomposites. Morphology and structure of nanocomposites were studied by field emission scanning electron microscopy (FE-SEM) and X-ray diffraction. The dielectric properties were determined using impedance analyzer at room temperature and well above room temperature in frequency range of 100 Hz to 5 MHz.
Temperature dependence of electrical resistivity \((\rho_{dc})\) and the effect of ferrite phase addition on the conductivity were also determined. Magnetic and ferroelectric hysteresis loop were determined using vibrating sample magnetometer (VSM) and polarization versus electric field (P-E) loop tracer system. Chemically synthesized samples will be used to prepare nanocomposites and subjected at a different sintering temperature of 600 °C, 1100 °C, 1200 °C, 1250 °C in order to study the effect of sintering on various properties of ME nanocomposites.

1.6 Significance of Study

The nanocomposite materials (magneticoelectric nanocomposition) were synthesized in particulate form using hydroxide co-precipitation method. All of these samples are carefully processed further in order to obtain a high purity product. Since the physical properties of multiphase (nanocomposites) strongly dependent on the structural, it is desirable to know the distribution of the constituent phases. A more precise way of morphological analysis is required for understanding of nanostructural dependent properties of ME nanocomposites. Since there are tremendous technical demands for large dielectric constant materials, it is significant to study systematically the dielectric properties of the magnetoelectric nanocomposites, which certainly will cast light on the origin of the high dielectric constant in multiphase materials. The detailed analysis of temperature dependent dielectric constant behaviour, especially in the transition temperature region, is useful to understand the diffuse phase transition behaviour. In the present work, we have highlighted the nature of the dielectric peak in the vicinity of phase transition temperature region. For this a modified Curie-Weiss law used which seems to be more suitable than the standard Curie-Weiss law. The Curie–Weiss law describes the magnetic susceptibility \(\chi\) of a ferromagnet in the paramagnetic region above the Curie point: \([\chi = C / (T-T_C)]\), where \(C\) is a material-specific Curie constant, \(T\) is absolute temperature, measured in kelvins, and \(T_C\) is the Curie temperature, measured in kelvin. The law predicts a singularity in the susceptibility at \(T=T_C\). Below this
temperature the ferromagnet has a spontaneous magnetization. It is also necessary to analyze the temperature dependent dielectric constant behaviour of magnetoelectric composites for different contents of individual phases at room temperature and at temperatures well above the transition temperature of both phases. The electrical and magnetic properties of this material as a unique substance in the electrical, electronics and magnetic applications are important in microwave communication, data processing devices, electrical device, circulators and magnetic recording. Additionally, tremendous technical demand for large dielectric material constant is important.

A broad literature reviews on magnetoelectric nanocomposites show wide variation in magnetoelectric (ME) voltage coefficient in bulk nanocomposites. It can be observed that the magnetoelectric (ME) voltage coefficient is affected by the number of factors such as the method of synthesis, grain size of individual phases, nanostructure of the samples, selection of individual phases, porosity, resistivity, dielectric and magnetoelectric properties of the nanocomposites.
REFERENCES


8. Guzdek, P., The Magnetostrictive and Magnetoelectric Characterization of \( \text{Ni}_{0.3}\text{Zn}_{0.62}\text{Cu}_{0.08}\text{Fe}_{2}\text{O}_4-\text{Pb(FeNb)}_{0.5}\text{O}_3 \) Laminated Composite, *Journal of Magnetism and Magnetic Materials*, 2014. 349: p. 219-223.


13. Kanamadi, C.M., Pujari, L.B. and Chougule, B.K., Dielectric Behaviour and Magnetoelectric Effect in \((x)\text{Ni}_{0.8}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4+(1-x)\text{Ba}_{0.9}\text{Pb}_{0.1}\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_3\) ME Composites, *Journal of Magnetism and Magnetic Materials*, 2005. 295: p.139-144.


15. Pahuja, P., Sharma, R., Prakash, C. and Tandon, R.P., Synthesis and Characterization of \( \text{Ni}_{0.8}\text{Co}_{0.2}\text{Fe}_2\text{O}_4-\text{Ba}_{0.98}\text{Sr}_{0.05}\text{TiO}_3\) Multiferroic Composites, *Ceramics International*, 2013. 39(8): p. 9435-9445.

16. Ahmed, M.A., Mansour, S.F. and Afifi, M., Structural, Electric and Magnetoelectric Properties of \( \text{Ni}_{0.85}\text{Cu}_{0.15}\text{Fe}_2\text{O}_4/\text{BiFe}_0.7\text{Mn}_{0.3}\text{O}_3\) Multiferroic Nanocomposites, *Journal of Alloys and Compounds*, 2013. 578: p. 303-308.


18. Kumar, M. and Yadav, K.L., Magnetoelectric Characterization of \( x\text{Ni}_{0.75}\text{Co}_{0.25}\text{Fe}_2\text{O}_4-(1-x)\text{BiFeO}_3\) Nanocomposites, *Journal of Physics and Chemistry of Solids*, 2007. 68(9): p. 1791-1795.


25. Kumar, P., Juneja, J.K., Prakash, C., Singh, S., Shukla, R.K. and Raina, K.K., High DC Resistivity in Microwave Sintered Li$_{0.40}$Zn$_{0.02}$Mn$_{0.06}$Fe$_{2.43}$O$_4$ Ferrites, *Ceramics International*, 2014. 40 (1): p. 2501-2504.


28. Tangcharoen, T., Ruangphanit, A. and Pecharapa, W., Structural and Magnetic Properties of Nanocrystalline Zinc-Doped Metal Ferrites


68. Chougule, S.S. and Chougule, B.K., Response of Dielectric Behavior and Magnetoelectric Effect in Ferroelectric Rich (x) Ni_{0.9}Zn_{0.1}Fe_{2}O_{4}+ (1-x) PZT ME Composites, *Journal of Alloys and Compounds*, 2008. 456(1-2). p.441-446.


71. Bammannavar, B.K., Chavan, G.N., Naik, L.R. and Chougule, B.K., Magnetic Properties and Magnetoelectric (ME) Effect in Ferroelectric Rich Ni_{0.2}Co_{0.8}Fe_{2}O_{4} + PbZr_{0.8}Ti_{0.2}O_{3} ME Composites, *Materials Chemistry and Physics*, 2009. 117 (1): p. 46-50.


77. Sun, R., Fang, B., Dong, X., Liu, J., Magnetoelectric and Electrical Properties of WO$_3$-doped(Ni$_{0.8}$Zn$_{0.1}$Cu$_{0.1}$)Fe$_2$O$_4$/Pb(Ni$_{1/3}$Nb$_{2/3}$)O$_3$–Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$–PbTiO$_3$ Composites, *Journal of Materials Science*, 2009. 44 (20): p. 5515-5523.


82. Kulkarni, S.R., Kanamadi, C.M. and Chougule, B.K., Magnetic and Dielectric Properties of Ni$_{0.8}$Co$_{0.1}$Cu$_{0.1}$Fe$_2$O$_4$+PZT Composites, *Journal of Physics and Chemistry of Solids*, 2006. 67 (8): p. 1607-1611.


85. Devan, R.S., Deshpande, S.B. and Chougule, B.K., Ferroelectric and Ferromagnetic Properties of (x)BaTiO$_3$+(1-x)Ni$_{0.94}$Co$_{0.01}$Cu$_{0.05}$Fe$_2$O$_4$ Composite, *Journal of Physics D: Applied Physics*, 2007. 40 (7): p. 1864-1870.


108. Kanamadi, C. M., Pujari, L. B. and Chougule, B. K. Dielectric Behaviour and Magnetoelectric Effect in (x) Ni$_{0.8}$Cu$_{0.2}$Fe$_2$O$_4$+ (1-x) Ba$_{0.9}$Pb$_{0.1}$Ti$_{0.9}$Zr$_{0.1}$O$_3$ ME Composites. *Journal of Magnetism and Magnetic Materials*, 2005. 295: p. 139-144.

109. Zhang, H. and Mak, C-L., Impedance spectroscopic characterization of fine-grained magnetoelectric Pb(Zr$_{0.53}$Ti$_{0.47}$)O$_3$–(Ni$_{0.5}$Zn$_{0.5}$)Fe$_2$O$_4$ Ceramic Composites, *Journal of Alloys and Compounds*, 2012. 513: p. 165-171.


113. Sartale, S.D., Bagde, G.D., Lokhande, C.D. and Giersig, M., Room Temperature Synthesis of Nanocrystalline Ferrite (MFe$_2$O$_4$, M = Cu, Co and


118. Kadam, S.L., Kanamadi, C.M., Patankar, K.K. and Chougule, B.K., Dielectric Behaviour and Magnetoelectric Effect in Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$+Ba$_{0.8}$Pb$_{0.2}$TiO$_3$ ME composites, *Materials Letters*, 2005. 59 (2-3): p. 215-219.

119. Babu, S. N., Suryanarayana, S.V. and Bhimasankaram, T., Magnetic and Magnetoelectric Characterization of Ni$_{0.95}$Co$_{0.02}$Mn$_{0.03}$Fe$_{1.95}$O$_4$ and PZT Composites, *Journal of Alloys and Compounds*, 2009. 473 (1-2): p. 418-422.


139. Lokare, S.A., Patil, D.R., Devan, R.S., Chougule, S.S., Kolekar, Y.D., Chougule, B.K., Electrical Conduction, Dielectric Behavior and Magnetoelectric Effect in (x)BaTiO_3&Ni_{0.94}Co_{0.01}Mn_{0.05}Fe_{2}O_{4} ME Composites, *Materials Research Bulletin*, 2008. 43(2): p. 326-332.


153. Ashiq, M.N., Naz, F., Malana, M.A., Gohar, R.S. and Ahmad, Z., Role of Co–Cr Substitution on the Structural, Electrical and Magnetic Properties of


220. Sharma, A., Kotnala, R.K., Negi, N.S., Observation of Multiferroic Properties and Magnetoelectric Effect in (x)CoFe$_2$O$_4$–(1-x)Pb$_{0.7}$Ca$_{0.3}$TiO$_3$ Composites, *Journal of Alloys and Compounds*, 2014. 582: p. 628-634.

221. Devan, R., Kanamadi, C., Lokare, S. and Chougule, B., Electrical Properties and Magnetoelectric Effect Measurement in (x) Ni$_{0.8}$Cu$_{0.2}$Fe$_2$O$_4$+(1– x) Ba$_0$. 
$\text{Pb}_0.1\text{Ti}_0.9\text{Zr}_0.1\text{O}_3$ Composites, *Smart Materials and Structures*, 2006.15: p. 1877-1881.

222. Bammannavar, B. K., Naik, L. R., Pujar, R. B., Chougule, B. K., Resistivity Dependent Magnetoelectric Characterization of $(x)\text{Ni}_{0.2}\text{Co}_{0.8}\text{Fe}_2\text{O}_4+(1-x)\text{Ba}_{0.8}\text{Pb}_{0.2}\text{Zr}_{0.8}\text{Ti}_{0.2}\text{O}_3$ composites, *Journal of Alloys and Compounds*, 2009.477:p. L4-L7.


228. Gupta, A. and Chatterjee, R., Dielectric and Magnetoelectric Properties of $\text{BaTiO}_3$–$\text{Co}_{0.6}\text{Zn}_{0.4}\text{Fe}_{1.7}\text{Mn}_{0.3}\text{O}_4$ Composite, *Journal of the European Ceramic Society*, 2013. 33(5): p. 1017-1022.


234. Zhang, H.-f., Or, S.W. and Chan, H.L.W., Electrical, Magnetic, and Magnetoelectric Characterization of Fine-Grained Pb(Zr$_{0.53}$Ti$_{0.47}$)O$_3$–(Ni$_{0.5}$Zn$_{0.5}$)Fe$_2$O$_4$ Composite Ceramics, *Journal of Alloys and Compounds*, 2011. 509(21): p. 6311-6316.


236. Reddy, N.R., Rajagopal, E., Sivakumar, K.V., Patankar, K.K., Murthy, V.R.K., Effect of Temperature on the Elastic and Anelastic Behaviour of Magneto-Ferroelectric Composites Ba$_{0.8}$Pb$_{0.2}$TiO$_3$+Ni$_{0.93}$Co$_{0.02}$Mn$_{0.05}$Fe$_{1.95}$O$_{4-x}$ in the Ferroelectric Rich Region, *Journal of Electroceramics*, 2003. 11(3): p. 167-172.


240. Kanamadi, C.M., Raju, G. S. R., Yang, H.K., Choi, B.C., Jeong, J.H., Conduction Mechanism and Magnetic Properties of \( (x)\text{Ni}_{0.8}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4+(1-x)\text{Ba}_{0.8}\text{Pb}_{0.2}\text{Ti}_{0.8}\text{Zr}_{0.2}\text{O}_3 \) Multiferroics, *Journal of Alloys and Compounds*, 2009.479:p. 807-811.
