

Lead - Free Piezoelectric Based Magnetoelectric Composites

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ABSTRACT

The prime objective of this dissertation is to design, synthesize and characterize lead-free piezoelectric – magnetostrictive components based magnetoelectric (ME) composites that exhibit self-bias characteristics and high amplitude of ME coupling. The secondary goal of this thesis was to lay down the foundation for nanoscale and flexible magnetoelectric devices.

Self-biased ME effect was investigated in lead-free three-phase laminate composites. This effect is characterized by non-zero remanent ME responses at zero magnetic bias field (H_{bias}). It was revealed that the self-biased ME effects can be observed in three-phase laminate composites consisting of piezoelectric material and two dissimilar magnetostrictive materials. On applying H_{bias} to the laminates in bending mode configuration, the ME responses were found to exhibit hysteretic behaviors with remanent ME responses. The shape of hysteretic ME response could be controlled by adjusting the magnetic interactions and piezoelectric properties. Further, converse magnetoelectric (CME) responses in bending-mode three-phase laminates exhibited hysteretic behaviors with similar magnitudes during H_{bias} sweep as it was generated directly by applying ac voltage (V_{ac}) without any external H_{bias} .

Lead-free $(1 - x) [0.948 \text{ K}_{0.5}\text{Na}_{0.5}\text{NbO}_3 - 0.052 \text{ LiSbO}_3] - x \text{ Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ (KNNLS-NZF) compositions were synthesized for optimizing ME properties of particulate composites. Island-matrix microstructure was developed to improve the magnitude of ME coupling effect by

overcoming the problems found in conventional particulate composites. The structure lead to improvement of ME coefficient with maximum magnitude of 20.14 mV/cm·Oe as well as decrease of optimum H_{bias} of < 500 Oe in the composition of 0.7 KNNLS – 0.3 NZF particulate composites.

Room-temperature ME phase diagram of $(1 - x)$ BaTiO₃ – x BiFeO₃ materials (BT – x BFO, $x = 0.025 - 1.0$) was investigated for designing compositions suitable for thin film devices. The BT – x BFO compositions in narrow range of $x = 0.71 - 0.8$ were found to exhibit good piezoelectric, dielectric and magnetic properties simultaneously. The room temperature ME coefficient was found to be maximum with high magnitude of 0.87 mV/cm·Oe in the optimized composition of $x = 0.725$. This composition was found to consist of local monoclinic distortions with average rhombohedral symmetry as confirmed by detailed structural analysis through Raman spectroscopy and atomic pair distribution functions (PDFs).

MnFe₂O₄ (MFO)-Ni core-shell nanoparticles were synthesized and characterized for developing tunable devices such as memristor. The MFO nanoparticles synthesized by solvothermal method exhibited diameter of 200 nm, mean primary particle size of 15 nm, high saturation magnetization of 74 emu/g and coercivity of 89 Oe. Ni encapsulation on MFO nanoparticles was performed by aqueous ionic coating method. Ni shells with uniform thickness of 1 nm were coated on MFO nanoparticles by this method.

In order to develop future nanoscale dual phase energy harvesters and magnetic field sensors, vertically-aligned piezoelectric nanorods were synthesized. In the initial attempt, Pb(Zr_{0.52}Ti_{0.48})O₃ (PZT) was used to verify the feasibility of developing one dimensional (1D) piezoelectric nanostructures with controlled diameter and height. For the 1D nanostructure, well-ordered anodic aluminum oxide (AAO) templates were prepared by two step aluminum

anodizing. The PZT nanorods were synthesized by vacuum infiltration of PZT precursor solutions and exhibited uniform diameter of 90 nm and aspect ratio of 10 with vertical in respect to the Pt-Si substrate. The piezo-response of PZT nanorods showed good magnitude owing to the reduced clamping effect from the substrate.

Attempt towards the development of flexible tunable devices that possess magnetic field sensing and actuation ability was made in the later part of the thesis. The electroactive polymeric actuators in the form of Polypyrrole (PPy) / Au / Polyvinylidene fluoride (PVDF) / Au / Polypyrrole (PPy) were synthesized and the process flow was optimized. Pore size and thickness of PVDF layer was adjusted by changing the solvent, viscosity and drying temperature. Different types of electrolyte solutions were investigated to improve the strain and response time. The actuators exhibited high deflection of 90 % with fast response of 50% deflection per second. Dual-functional structure in the form of PPy-MFO / Au / PVDF / Au / PPy-MFO was developed by PPy polymerization including MFO nanoparticles via cyclovoltammetric method.

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TABLE OF CONTENTS

ABSTRACT.....	ii
ACKNOWLEDGEMENTS.....	v
TABLE OF CONTENTS.....	vii
LIST OF TABLES.....	ix
LIST OF FIGURES.....	x
CHAPTER 1 INTRODUCTION.....	1
1. 1 Magnetolectric multiferroics.....	1
1. 2 Lead-free magnetolectric materials.....	13
1. 3 Magnetic and piezoelectric nanostructures.....	18
1. 4 Biomimetic polymeric actuators with inherent sensing capability.....	19
CHAPTER 2 RESEARCH OBJECTIVES.....	22
2. 1 Self-biased magnetolectric effect.....	22
2. 2 Lead-free two-phase magnetolectric composites.....	25
2. 3 Lead-free single-phase magnetolectric materials.....	27
2. 4 Core-shell ferromagnetic-metal nanoparticles.....	30
2. 5 Vertically aligned piezoelectric nanorods.....	32
2. 6 Electroactive polymer actuators.....	34
CHAPTER 3 EXPERIMENTAL METHODS.....	36
3. 1 Sol-gel synthesis.....	36
3. 2 Solvothermal synthesis.....	36
3. 3 Cyclovoltammetric deposition	37
3. 4 Morphology and crystal structure characterizations.....	37
3. 5 Electric, magnetic and magnetolectric characterizations.....	38

CHAPTER 4 SELF-BIASED MAGNETOELECTRIC EFFECT.....	40
4. 1 Self-biased magnetoelectric effect in three phase laminates.....	40
4. 2 Effect of materials composition on magnetoelectric hysteretic behavior.....	57
4. 3 Direct and converse magnetoelectric effect.....	64
CHAPTER 5 LEAD-FREE TWO-PHASE MAGNETOELECTRIC COMPOSITES.....	74
5. 1 Optimization of sintered KNNLS-NZF particulate composites.....	74
5. 2 Magnetoelectric effect of KNNLS-NZF / Ni laminates.....	91
CHAPTER 6 LEAD-FREE SINGLE-PHASE MAGNETOELECTRIC MATERIALS... 	96
6. 1 Magnetoelectric phase diagram for BT-BFO solid-solutions.....	96
6. 2 Magnetoelectric effect of BT-BFO / Ni laminates.....	107
CHAPTER 7 CORE-SHELL FERROMAGNETIC-METAL NANOPARTICLES.....	110
7. 1 High performance MFO nanoparticles.....	110
7. 2 Ni encapsulation onto MFO nanoparticles.....	116
CHAPTER 8 VERTICALLY ALIGNED PIEZOELECTRIC NANORODS.....	122
8. 1 Synthesis of PZT nanorods via template transfer method	122
8. 2 Piezoelectric responses of PZT nanorods.....	131
8. 3 Synthesis of PZT nanorods via reactive ion etching..	136
CHAPTER 9 ELECTROACTIVE POLYMER ACTUATORS WITH INHERENT MAGNETIC FIELD SENSING CAPABILITY	142
9. 1 Optimization of PVDF interlayer films	142
9. 2 Electroactive performances of PPy-PVDF actuators.....	149
CHAPTER 10 CONCLUSION.....	156
CHAPTER 11 FUTURE APPLICATIONS.....	159
11. 1 Memristive ferromagnetic nanoparticles.....	159
11. 2 Lead-free magnetoelectric nanostructures.....	162
11. 3 Dual functional flexible devices.....	164
REFERENCES.....	166

LIST OF TABLES

Table 1-1. List of magnetoelectric laminate composites.....	9
Table 1-2. List of magnetoelectric laminate based on ferrite.....	10
Table 1-3. List of magnetoelectric laminate based on Terfenol-D.....	11
Table 1-4. List of magnetoelectric laminate based on Metglas.....	12
Table 1-5. List of magnetoelectric particulate composites.....	15
Table 1-6. List of lead-free piezoelectric materials.....	16
Table 1-7. List of lead-free magnetoelectric composites.....	17

LIST OF FIGURES

Figure 1-1	Schematic diagram for connectivity of multiphase ME composites: (a) 3-0 type particulate structure, (b) 2-2 type laminate structure, and (c) 1-3 type cylinder-matrix structure.....	4
Figure 1-2	Laminate ME composites operating in four-type of vibration modes.....	6
Figure 1-3	Schematic diagram for PPy / Au / PVDF / Au / PPy actuators and working principle of the redox states of PPy.....	21
Figure 2-1	Schematic diagram for ME hysteretic responses with self-bias effect in three phase laminates.....	24
Figure 2-2	Schematic diagram for the island-matrix microstructure in KNNLS-NZF composites.....	26
Figure 2-3	Schematic room-temperature ME phase diagram for BT-BFO system	29
Figure 2-4	Schematic diagram for electromagnetostrictive (EMS) effect in core-shell ceramic-metal nanoparticles.....	31
Figure 2-5	Schematic diagram for vertically-aligned PZT nanorod-arrays on a platinized silicon substrate.....	33
Figure 2-6	Schematic diagram for electroactive PPy / Au / PVDF / Au / PPy actuators.....	35
Figure 4-1	Schematic diagrams for ME laminate composites for self-biased ME effect. (a) Radial mode bilayer with two-phase magnets, (b) Radial mode bilayer with one-phase magnet, (c) Bending mode trilayer with two-phase magnets, (d) Bending mode trilayer with one-phase magnet and (e) Radial mode trilayer with two-phase magnets.....	41
Figure 4-2	M – H curves for NZF particles and Ni plates, (a) saturated magnetic hysteresis loops under high field and (b) exploded view in the low field region.....	42
Figure 4-3	ME voltage coefficients for laminate composites. (a) KNNLS-NZF / Ni radial-mode bilayer, (b) KNNLS / Ni radial-mode bilayer, (c) KNNLS-NZF / Ni / KNNLS-NZF radial mode trilayer, (d) KNNLS-NZF / Ni / KNNLS-NZF bending-mode trilayer, and (e) KNNLS / Ni / KNNLS bending mode trilayer.....	46

Figure 4-4	Impedance and phase spectra for bilayer and trilayer laminates under applied AC electric field. (a) KNNLS-NZF / Ni radial-mode bilayer, (b) KNNLS / Ni radial-mode bilayer, (c) KNNLS-NZF / Ni / KNNLS-NZF radial mode trilayer, (d) KNNLS-NZF / Ni / KNNLS-NZF bending-mode trilayer, and (e) KNNLS / Ni / KNNLS bending mode trilayer.....	48
Figure 4-5	ME voltage coefficients for bilayer and trilayer laminates as a function of frequency from 0.1 to 60 kHz. (a) KNNLS-NZF / Ni radial-mode bilayer, (b) KNNLS / Ni radial-mode bilayer, (c) KNNLS-NZF / Ni / KNNLS-NZF radial mode trilayer, (d) KNNLS-NZF / Ni / KNNLS-NZF bending-mode trilayer, and (e) KNNLS / Ni / KNNLS bending mode trilayer.....	51
Figure 4-6	ME voltage coefficients for bending-mode KNNLS-NZF / Ni /KNNLS-NZF trilayer as a function of magnetic DC bias field at frequencies of (a) 0.1 kHz, (b) 10 kHz, (c) 40.6 kHz, and (d) 55.7 kHz.....	53
Figure 4-7	ME voltage coefficients calculated by using measured values of KNNLS – NZF / Ni / KNNLS – NZF ($\alpha_{\text{bending strain} + H_{\text{bias}}}$) and KNNLS / Ni /KNNLS ($\alpha_{\text{bending strain}}$) trilayer , (a) $\alpha(H_{\text{bias}})$, (b) $\alpha_{\text{low-frequency}} = (\alpha_{\text{bending strain} + H_{\text{bias}}} + 0.5 \alpha_{H_{\text{bias}}})$, and (c) $\alpha_{\text{high-frequency}} = (\alpha_{\text{bending strain} + H_{\text{bias}}} + 2.5 \alpha_{\text{bending strain}})$	56
Figure 4-8	Schematic diagram for ME laminate composites with variation of materials composition. (1 - x) KNNLS – x NZF / Ni / (1 - x) KNNLS – x NZF with x = 0.1, 0.2 and 0.3.....	58
Figure 4-9	Magnetostrictions and piezomagnetic coefficients for Ni plate.....	59
Figure 4-10	(a) ME coefficient and sensitivity limit of dc magnetic field for bending mode laminates. (b) x = 0.1, (c) x = 0.2 and (d) x = 0.3.....	61
Figure 4-11	Longitudinal piezoelectric strain coefficient for (1 - x) KNNLS – x NZF composites as a function of atomic ratio of Fe/Nb. In sets are ME hysteresis for (1 - x) KNNLS – x NZF / Ni / (1 - x) KNNLS – x NZF bending mode laminates: (a) x = 0.1, (b) x = 0.2and (c) x = 0.3.....	63
Figure 4-12	Configuration of bending-mode for three-phase laminate of KNNLS-NZF / Ni / KNNLS-NZF and schematic diagrams for DME and CME measurements.....	67

Figure 4-13	(a) α_{DME} and (b) α_{CME} coefficients as a function of H_{bias} , (c) Integral values of α_{DME} and α_{CME} with respect to the H_{bias} , and (d) Magnetostriction of Ni, KNNLS-NZF, and bending mode KNNLS-NZF / Ni / KNNLS-NZF as a function of H_{bias}	68
Figure 4-14	(a) Impedance and phase spectra for three-phase laminate under applied AC electric field, (b) α_{DME} and (c) α_{CME} as a function of frequency under applied H_{bias} of 0 and 100 Oe.....	71
Figure 4-15	Magnetic flux density under $H_{\text{bias}} = 0$ Oe measured by periodically applying AC voltage of 1 V at 21 kHz. Inset shows the change in magnetic flux density with increasing AC voltage and sample configuration.....	73
Figure 5-1	(a) SEM image and (b) XRD patterns of KNNLS calcined at 880°C. (c) SEM image and (d) XRD patterns of NZF calcined at 1000°C.....	76
Figure 5-2	XRD patterns for (1 - x) KNNLS – x NZF composites. (a) $x = 0.1$, (b) $x = 0.2$, (c) $x = 0.3$ and (d) $x = 0.4$	77
Figure 5-3	Intensity ratio of (311)/(101) for (1 - x) KNNLS – x NZF composites as a function of sintering temperature.....	78
Figure 5-4	Piezoelectric and dielectric properties for (1 - x) KNNLS – x NZF composites, (a) longitudinal piezoelectric constant, (b) radial mode coupling factor, (c) dielectric constant, and (d) tangent loss factor.....	80
Figure 5-5	M – H curves for NZF particles and (1 - x) KNNLS – x NZF composites. (a) magnetization as a function of magnetic field for NZF particles, (b) amplified curve in the low magnetic field region shown in (a), (c) magnetization as a function of magnetic field for (1 - x) KNNLS – x NZF composites, and (d) amplified curve in the low magnetic field region shown in (c)	82
Figure 5-6	Magnetostrictions and piezomagnetic coefficients for (1 - x) KNNLS – x NZF composites. (a) $x = 0.1$, (b) $x = 0.2$, (c) $x = 0.3$ and (d) $x = 0.4$	83
Figure 5-7	Variation of (a) ME coefficient and (b) H_{bias} for (1 - x) KNNLS – x NZF composites with $x = 0.1, 0.2, 0.3$ and 0.4 as a function of sintering temperature.....	85

Figure 5-8	SEM micrographs for $(1 - x)$ KNNLS – x NZF composites sintered at 1060 °C. (a) $x = 0.1$, (b) $x = 0.2$, (c) $x = 0.3$ and (d) $x = 0.4$	89
Figure 5-9	EDS elemental mapping images for $(1 - x)$ KNNLS – x NZF composites sintered at 1060 °C. (a) – (d) SEM images for $x = 0.1 - 0.4$, (e) – (h) Nb mapping for $x = 0.1 - 0.4$, and (i) – (l) Fe mapping for $x = 0.1 - 0.4$	90
Figure 5-10	Schematic diagram for 2-2 ME laminate composites with variation of materials composition. $(1 - x)$ KNNLS – x NZF / Ni / $(1 - x)$ KNNLS – x NZF with $x = 0.1$, 0.2 and 0.3.....	92
Figure 5-11	Impedance and phase spectra for radial mode configuration trilayer laminates with $x = 0.1$, 0.2 and 0.3 under AC electric field.....	93
Figure 5-12	(a) ME coefficient and sensitivity limit of dc magnetic field for radial mode laminates. (b) $x = 0.1$, (c) $x = 0.2$ and (d) $x = 0.3$	94
Figure 6-1	XRD patterns for BT– x BFO ceramics (a) with $x = 0.025 - 1.0$ and (b) with $x = 0.710 - 0.775$ and 1.0, and (c) extended peak values for (110), (111), (210) and (211)	98
Figure 6-2	(a) Lattice parameter and rhombohedral distortion angle and (b) volume of unit cell for BT– x BFO ceramics with $x = 0.710 - 0.775$ and 1.0.....	99
Figure 6-3	Variation of magnetoelectric, piezoelectric, and dielectric properties as a function of BFO mole fraction for BT– x BFO ceramics with $x = 0.025 - 1.0$; (a) DME coefficient, (b) phase change of α_{DME} , (c) poling percent, (d) piezoelectric voltage constant, (e) piezoelectric charge constant, (f) radial mode electromechanical coupling factor, (g) dielectric constant and (h) tangent loss factor.....	101
Figure 6-4	(a) Raman spectra and (b) PDFs analysis for BT– x BFO ceramics.....	104
Figure 6-5	(a) Room-temperature $P - E$ curves and (b) Room-temperature $M - H$ curves as a function of BFO mole fraction.....	106
Figure 6-6	(a) DME coefficient and (b) CME coefficient for BT–0.725BFO/Ni laminates as a function of H_{bias} . Insets are schematic diagrams of DME and CME samples and expanded views of $\alpha_{ME}-H_{bias}$ hysteresis to show the remnant α_{DME} and α_{CME} at zero H_{bias}	108

Figure 7-1	Schematic diagram of experimental procedure for the synthesis of core-shell MnFe_2O_4 -Ni nanoparticles.....	111
Figure 7-2	(a) Zeta-potentials of MnFe_2O_4 particles for $2 \leq \text{pH} \leq 12$, (b) SEM image of MnFe_2O_4 particles, (c) XRD pattern of MnFe_2O_4 particles, and (d) M-H curve of MnFe_2O_4 particles.....	114
Figure 7-3	(a) SEM image, (b) AFM image, and (c) MFM image of MnFe_2O_4 particles onto a glass substrate.....	115
Figure 7-4	(a) SEM images and (b) Ni contents of MnFe_2O_4 -Ni core-shell particles synthesized for $2 \leq \text{pH} \leq 12$	118
Figure 7-5	M – H curves for MnFe_2O_4 and Ni-coated MnFe_2O_4 nanoparticles.....	119
Figure 7-6	TEM images of (a) MnFe_2O_4 particles and (b) MnFe_2O_4 -Ni core-shell particles, (c) HR-TEM image of MnFe_2O_4 -Ni core-shell particles, (d) EDS at Point 1 of MnFe_2O_4 -Ni core-shell particles, and (e) EDS at Point 2 of MnFe_2O_4 -Ni core-shell particles.....	120
Figure 7-7	Selected area electron diffraction patterns of (a) MnFe_2O_4 particles and (b) MnFe_2O_4 -Ni core-shell particles.....	121
Figure 8-1	Schematic diagram of experimental procedures for vertically aligned PZT nanorod-arrays on Pt-Si substrates.....	124
Figure 8-2	SEM images for (a) 1 st anodized AAO films, (b) Al films after 1 st AAO removing, (c) 2 nd anodized AAO films, (d) AAO templates after pore opening, (e) complete anodized AAO templates and (f) PZT infiltrated AAO films.....	126
Figure 8-3	XRD patterns for (a) Al, AAO and PZT-AAO films and (b) Pt-Si substrates and PZT nanorod-arrays on Pt-Si substrates.....	128
Figure 8-4	(a) - (c) Top-view SEM images for PZT nanorod-arrays on Pt-Si substrates, (d) EDS analysis for PZT nanorod arrays, (e) cross-sectional SEM image for PZT nanorod arrays and (f) TEM image of single PZT nanorod.....	130

Figure 8-5	Piezo-responses for PZT nanorods with a length of 900 nm on a Pt-Si substrate; (a) topology image, (b) amplitude image, (c) phase image, (d) ramp-mode amplitudes and (e) ramp-mode phase angles and (f) ramp-mode piezoelectric responses as a function of DC bias voltage.....	132
Figure 8-6	Piezo-responses for PZT thin films with a thickness of 120 nm on a Pt-Si substrate; (a) topology image, (b) amplitude image, (c) phase image, (d) ramp-mode amplitudes and (e) ramp-mode phase angles and (f) ramp-mode piezoelectric responses as a function of DC bias voltage.....	133
Figure 8-7	Effective piezoelectric coefficients (d_{33}) as a function of bias voltage; (a) PZT single-rod with length of 900 nm and (b) PZT thin films with a thickness of 120 nm on Pt-Si substrates.....	135
Figure 8-8	Schematic diagram of experimental procedure for PZT nanorods via direct PZT ion etching.....	137
Figure 8-9	SEM images for PZT film on platinized silicon substrate: (a) top-view and (b) cross-sectional view.....	138
Figure 8-10	Ferroelectric characteristics for PZT thin films: (a) Pt-dot patterned PZT film, (b) P – E hysteresis, (c) C – F curves, and (d) C – V curves.....	139
Figure 8-11	SEM images for Pt-patterned PZT film after reactive ion etching: (a) surface image, (b) cross-sectional image on center of Pt-patterned PZT film, and (c) cross-sectional image on edge of Pt-patterned PZT film.....	141
Figure 9-1	Surface morphologies of gold-coated PVDF films dried for 24 h at (a) 25 °C and (b) 80 °C.....	144
Figure 9-2	Cyclic voltammetry curves for 50 layers of PPy coating on (a) 25°C and (b) 80°C dried PVDF-Au films.....	146
Figure 9-3	Surface morphologies of (a) PPy / Au / PVDF dried 25°C / Au / PPy films and (b) PPy / Au / PVDF dried 80°C / Au / PPy films.....	147
Figure 9-4	Cross sectional images of (a) PPy / Au / PVDF dried 25°C / Au / PPy films and (b) PPy / Au / PVDF dried 80°C / Au / PPy films.....	148
Figure 9-5	Overlay of the initial and final states of a 6 x 20 mm PPy / Au / PVDF / Au / PPy actuator stored in 3M KCl solution actuated at 6 V _{dc} potential.....	150

Figure 9-6	MATLAB image processing techniques were used to extract actuator tip displacement.....	151
Figure 9-7	Deflection of actuator tip over time expressed as a percentage of total actuator length.....	152
Figure 9-8	Close-up photograph of the actuator showing burning due to high voltage and storage in 3M KCl.....	154
Figure 9-9	Overlay of the initial and final states of a 3.5 x 21.5 mm PPy / Au / PVDF / Au / PPy actuator stored in 0.5M KCl solution actuated at 4 V _{dc} potential.....	155
Figure 11-1	Schematic diagrams for memristive particle array (thickness of ~ 400 nm); (a) on a rigid substrate and (b) on a flexible substrate, and for single memristive particle (diameter of 200 nm); (c) on a rigid substrate and (d) on a flexible substrate.....	161
Figure 11-2	Schematic diagram for lead-free magnetoelectric nanostructures.....	163
Figure 11-3	Schematic diagram for dual-functional polymer actuator and magnetic sensor.....	165

CHAPTER 1

INTRODUCTION

1. 1 Magnetolectric multiferroics

Multiferroic materials possess two or more ferroic orders such as ferroelectric, ferromagnetic, or ferroelastic. Multiferroic magnetoelectric (ME) materials exhibit direct coupling between the ferroelectric and ferromagnetic order parameters.¹⁻³ Generally, ME materials are categorized into four groups: (i) single-phase materials, (ii) 3-0 type particulate composites, (iii) 2-2 type laminate composites, and (iv) 1-3 type cylinder-matrix composites.⁴ Single phase materials exhibiting ME effects should show two coupled-transitions: one from ferroelectric to paraelectric state, and another from ferro/ferri/antiferro-magnetic to paramagnetic state: the ME effect then arises due to coupling between the magnetic and polar sublattices.⁵ Recent investigations of single phase multiferroics have revealed that the origin of ME effect is often associated with a particular exchange mechanism for various families of compounds such as: orbital ordering, Jahn–Teller distortion, super/double exchange, and/or geometric magnetic frustration^{*}. In the single-phase ME materials, the upper limit for ME susceptibility can be given

as:

$$\alpha_{ij}^2 < (\kappa_{ii}^e \chi_{jj}^m) \quad (1-1)$$

where κ^e and χ^m are the electric and magnetic susceptibilities respectively.

^{*} In condensed matter physics, the term of frustration means a phenomenon in which the geometrical properties of the crystal lattice or the presence of conflicting atomic forces forbid simultaneous minimization of the interaction energies acting at a given site.

A similar relationship can be derived based on the thermodynamic considerations given as: ⁶

$$\alpha_{ij} < (\epsilon_{ii} \mu_{jj})^{1/2} \quad (1-2)$$

where ϵ and μ are the electric permittivity and magnetic permeability respectively. The magnetoelectric coupling coefficient has been defined as:

$$k_{ME} = \frac{U_{mutual}}{(U_{electric} \cdot U_{magnetic})^{1/2}} \quad (1-3)$$

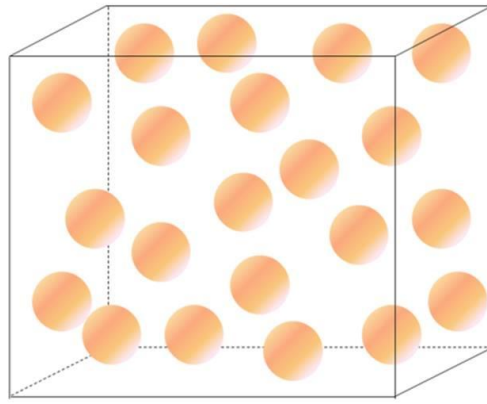
where U_{mutual} ($= \frac{1}{2} \alpha_{ij} E_i H_j$, where H_j is the magnetic field) is the mutual energy, $U_{electric}$ ($= \frac{1}{2} \epsilon_{ii} E_i E_i$) is the electric energy and $U_{magnetic}$ ($= \frac{1}{2} \mu_{jj} H_j H_j$) is the magnetic energy. In order to evaluate the efficiency of energy conversion from magnetic to electric forms, or vice-versa, a working definition of the coupling coefficient can be written as:

$$k_{me}^2 = k_{ij, piezo}^2 k_{ij, magnetic}^2 \quad (1-4)$$

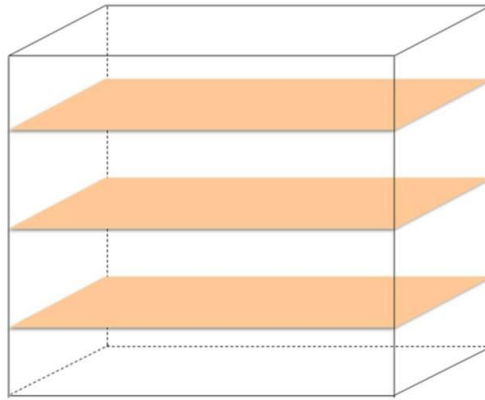
where $k_{ij, piezo}$ is the coupling coefficient of the piezoelectric phase, and $k_{ij, magnetic}$ is the coupling coefficient of the magnetic phase.

Unfortunately, single phase materials suffer from the drawback that the ME effect is extremely small at room temperature. For example, the highest ME coefficient has been reported for antiferromagnetic Cr_2O_3 crystals, which is 0.74 mV/cm·Oe at a Neel temperature of 34 °C. ^{7,8} On the other hand, multiphase ME composites were found to exhibit much higher magnitude of ME coefficient at room temperature.⁹ Composite geometry can be designed based on the connectivity. The connectivity in general can be given by the ratio $\frac{(n+3)!}{3!n!}$, where n is number

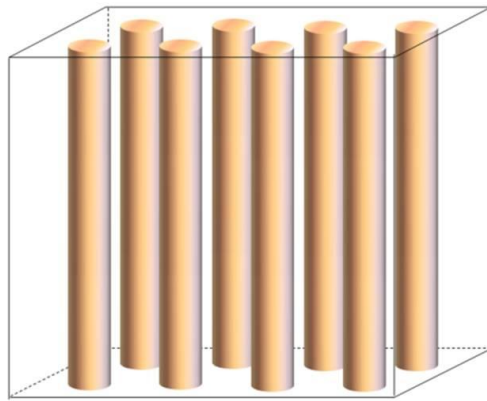
of phases. For two phase system, there are 10 types of connectivity. For three and four phase system there are 20 and 35 types of connectivity. Figure 1-1 shows three types of connectivity's for multiphase ME composites. The 3-0 type particulate ME composites were constructed by embedding one-phase particles in a matrix of another phase and found to exhibit coupling coefficient of several ten ~ hundred mV/cm·Oe at room temperature. The ME coefficient in 3-0 type particulate composites can reach up to several thousand mV/cm·Oe at resonance frequency but this magnitude is still below the theoretical magnitude due to problems related to inter-diffusion between piezoelectric and magnetostrictive phases during high-temperature sintering, thermal expansion mismatch between the two phases, and low resistivity. In order to improve the resistivity in ME composites, 2-2 type ME laminates have been synthesized by using piezoelectric and magnetostrictive layers and shown to exhibit ME coefficient of several thousand mV/cm·Oe at room temperature due to reduction of the leakage problem. The 1-3 type ME composites were investigated for high ME coefficient by exploiting contribution from both piezoelectric coefficient d_{33} and piezomagnetic coefficient q_{11} . The PZT / Terfenol-D composites were reported with ME coefficient of 500 mV/cm·Oe at off-resonance condition and 18200 mV/cm·Oe at a resonance condition by Ma et al.¹⁰ Laminate composites are generally fabricated by bonding magnetostrictive and piezoelectric layers using silver epoxy followed by annealing at lower temperature of $\sim 100^\circ\text{C}$. The most common geometry for laminate composites is “sandwich” structure where the piezoelectric layer is arranged between two magnetostrictive ones. Under applied magnetic field, the strain in magnetostrictive layer is transferred to the piezoelectric layer through bonding layer resulting in generation of electrical charge.



(a)



(b)



(c)

Figure 1-1. Schematic diagram for connectivity of multiphase ME composites: (a) 3-0 type particulate structure, (b) 2-2 type laminate structure, and (c) 1-3 type cylinder-matrix structure.

In 2-2 ME laminate composites, there can be four possible modes as shown in Figure 1-2. In L-L mode, both the applied H field and the measured E field are parallel to the principle vibration mode; in T-L mode the applied H field is perpendicular to the induced E field which is measured parallel to the principle mode; in L-T mode the applied H field is parallel and the induced E field is measured perpendicular to the principle mode; and in T-T mode the applied H field and induced E are perpendicular to the principle mode.¹¹

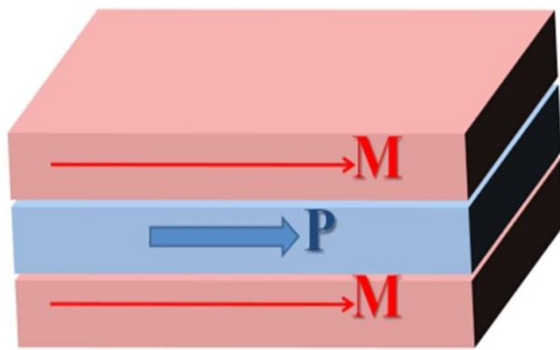
ME coefficient for 2-2 type laminate composites has been modeled by Srinivasan et al.¹² The transverse ME coefficient for the laminate composite was given as:

$$\alpha_{E31} = \frac{\delta E_3}{\delta H_1} = \frac{-2d_{31}^p q_{11}^m v^m}{(s_{11}^m + s_{12}^m) \epsilon_{33}^{T,P} v^p + (s_{11}^p + s_{12}^p) \epsilon_{33}^{T,P} v^m - 2(d_{31}^p)^2 v_m} \quad (1-5)$$

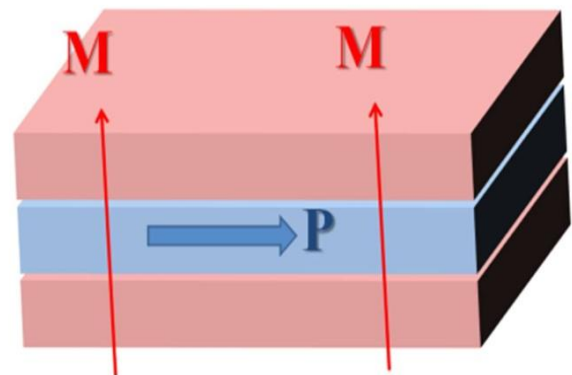
The longitudinal ME coefficient for the laminate composite was given as:

$$\alpha_{E33} = \frac{\delta E_3}{\delta H_3} = \frac{-2d_{31}^p q_{13}^m v^m}{(s_{11}^m + s_{12}^m) \epsilon_{33}^{T,P} v^p + (s_{11}^p + s_{12}^p) \epsilon_{33}^{T,P} v^m - 2(d_{31}^p)^2 v_m} \quad (1-6)$$

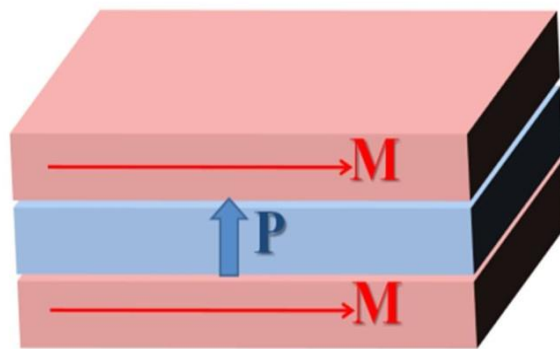
where d_{31}^p is piezoelectric coefficient, v^m and v^p are volumes of magnetostrictive and piezoelectric phases, s_{11}^p , s_{12}^p are elastic compliances for piezoelectric phase, s_{11}^m , s_{12}^m are elastic compliances for magnetostrictive phase, q_{11} is piezomagnetic coefficient of the magnetostrictive phase and $\epsilon_{33}^{T,P}$ is the permittivity of the piezoelectric phase.



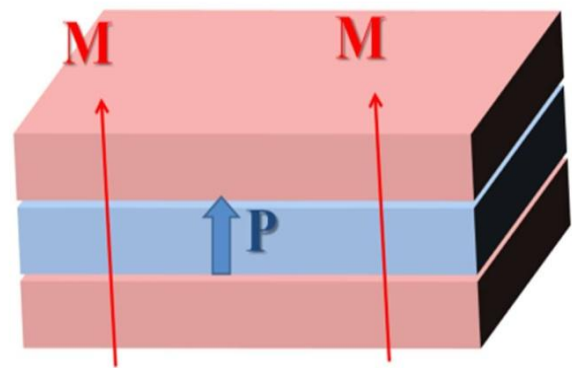
(a) L – L mode



(b) T – L mode



(c) L – T mode



(b) T – T mode

Figure 1-2. Laminate ME composites operating in four-type of vibration modes.

In the case of laminate ME composites with 2 – 2 connectivity, detailed research has been conducted in the form of bilayers, trilayers and multilayers of piezoelectric and magnetostrictive materials. Table 1-1 shows the ME properties of 2-2 type laminate ME composites. The push-pull mode ME laminates consisting of PZT, Terfenol D, and Metglas were found to exhibit ME coefficient of $\sim 20000 \text{ mV/cm}\cdot\text{Oe}$ with high magnetic sensitivity in resonance condition.¹³ Partial texturing of piezoelectric phase in 2-2 laminate composites was found to show 67 % improvement of ME coefficient compared with randomly oriented laminate.¹⁴

One of the problems related to the design of magnetic field sensors is the need for DC bias magnets. Additional magnets make the device bulky and require insulation. Thus, there is critical need for design of self-biased ME laminates. In this section, a discussion is included on the magnitude of DC bias required for the 2-2 type laminates. 2-2 type laminate ME composites can be categorized by the type of magnetostrictive material used in the design: (i) ferrite, (ii) Terfenol-D, and (iii) Metglas. Each of these ME laminate has different ME behavior due to difference in coercive field (H_c), permeability (μ), and magnetization (M). In Table 1-2, varying ferrite oxides are available to co-sinter with piezoelectric matrix and were found to exhibit different magnetostrictions due to their varying magnetic properties.¹¹ Terfenol-D in Table 1-3 has the largest magnetostriction of 1400×10^{-6} with low permeability, while Metglas in Table 1-4 has extremely high relative permeability of > 40000 and thus is quite attractive magnetostrictive material in low field ME sensors.⁹ Detailed research has been performed by the our research group exploring the 2-2 connectivity of the ME composites in the form of bilayers, trilayers and multilayers of piezoelectric and magnetostrictive materials. Islam et al. have synthesized PZT-NCZF bilayer and NCZF-PZT-NCZF trilayer using co-firing technique and found a high ME coefficient on the order of $\sim 500 \text{ mV/cm}\cdot\text{Oe}$ in trilayer structures.¹⁵ Lead-free

2-2 laminate ME composites of BaTiO₃ (BT) / (Ni_{0.8}Zn_{0.2})Fe₂O₄ (NZFO) were synthesized by co-firing and the magnitude of ME voltage coefficient reached saturation at DC bias of 1000 Oe with maximum magnitude of 152 mV/cm Oe.¹⁶ Dong et al. have studied several multilayered ME configurations by using materials PZT, Terfenol D and Metglas and have reported quite high ME coefficients on the order of 10 V/cm · Oe in resonance condition.¹⁷⁻²¹

Table 1-1. List of magnetoelectric laminate composites.

Year	Compositions	DC Bias/Frequency	dE/dH (mV/cm·Oe)	Ref.
2001	Pb(Zr,Ti)O ₃ / TbDyFe ₂	4200 Oe / 1kHz	4680	22
2002	Pb(Zr _{0.5} Ti _{0.5})O ₃ / Tb _{1-x} Dy _x Fe ₂	4000 Oe/1 kHz	5900	23
2004	Pb(Mg _{1/3} Nb _{2/3})O ₃ - PbTiO ₃ / Tb _{1-x} Dy _x Fe ₂	400 Oe/1 kHz	4300	24
2004	BaTiO ₃ / Tb _{1-x} Dy _x Fe ₂	350 Oe/1 kHz	2100	25
2005	Ni / Pb(Zr _{0.5} Ti _{0.5})O ₃ / Ni	80 Oe/1 kHz	450	26
2006	BaTiO ₃ / Ni _{0.8} Zn _{0.2} Fe ₂ O ₄	1000 Oe/1 kHz	152	16
2006	Terfenol-D / Pb(Zr,TiO) ₃ / μ -metal	240 Oe/1 kHz	> 1400	27
2007	Fe-doped BaTiO ₃ / Tb _{1-x} Dy _x Fe _{2-y}	350 Oe/100 Hz	2100	28
2008	0.9 Pb(Zr _{0.52} Ti _{0.48})O ₃ - 0.1 Pb(Zn _{1/3} Nb _{2/3})O ₃ / Ni _{0.6} Cu _{0.2} Zn _{0.2} Fe ₂ O ₄	400 Oe/1 kHz	468	29
2009	BaTi _{0.99} Cr _{0.01} O ₃ / Tb _{1-x} Dy _x Fe _{2-y}	355 Oe/100 Hz	2753	30
2010	Pb(Zr,Ti)O ₃ -Pb(Mg _{1/3} Nb _{2/3})O ₃ single crystal / Terfenol-D / Metglas	1011 Oe/1 kHz	5150	31
2010	Mn-doped Na _{0.5} Bi _{0.5} TiO ₃ -BaTiO ₃ single crystal / Terfenol-D	400 Oe/1 kHz	1320	32

Table 1-2. List of magnetoelectric laminate based on ferrite.

Year	Compositions	DC Bias (Oe)	Ref.
2001	Pb(Zr, Ti)O ₃ / NiFe ₂ O ₄ - bilayer	100	12
2001	Pb(Zr, Ti)O ₃ / NiFe ₂ O ₄ - multilayer	400	12
2002	Pb(Zr, Ti)O ₃ / Ni _{0.8} Zn _{0.2} Fe ₂ O ₄	100	33
2003	Pb(Zr, Ti)O ₃ / Co _{0.6} Zn _{0.4} Fe ₂ O ₄	450	34
2003	Pb(Zr, Ti)O ₃ / Ni _{0.8} Zn _{0.2} Fe ₂ O ₄	150	34
2003	Pb(Zr, Ti)O ₃ / Li _{0.35} Zn _{0.3} Fe _{2.35} O ₄	150	35
2003	Pb(Zr, Ti)O ₃ / Ni _{0.93} Co _{0.02} Mn _{0.05} Fe _{1.95} O ₄	700	36
2006	BaTiO ₃ / Ni _{0.8} Zn _{0.2} Fe ₂ O ₄	1000	16
2006	Pb(Zr, Ti)O ₃ / Ni _{0.8} Zn _{0.2} Fe ₂ O ₄	250	37
2008	Ni _{0.6} Cu _{0.2} Zn _{0.2} Fe ₂ O ₄ / 0.9Pb(Zr _{0.52} Ti _{0.48})O ₃ – 0.1Pb(Zn _{1/3} Nb _{2/3})O ₃ / Ni _{0.6} Cu _{0.2} Zn _{0.2} Fe ₂ O ₄	400	38

Table 1-3. List of magnetoelectric laminate based on Terfenol-D.

Year	Compositions	DC Bias (Oe)	Ref.
2001	Pb(Zr,Ti)O ₃ / Terfenol-D	4200	22
2002	Pb(Zr _{0.5} Ti _{0.5})O ₃ / Terfenol-D	4000	23
2003	Pb(Zr,Ti)O ₃ / Terfenol-D	200	20
2003	Pb(Zr _{0.52} Ti _{0.48})O ₃ / Terfenol-D	700	39
2004	Pb(Mg _{1/3} Nb _{2/3})O ₃ - PbTiO ₃ / Terfenol-D	400	24
2004	BaTiO ₃ / Terfenol-D	350	25
2005	Pb(Zr _{0.52} Ti _{0.48})O ₃ / Terfenol-D	700	40
2005	Pb(Mg _{1/3} Nb _{2/3})O ₃ -PbTiO ₃ / Terfenol-D	450	13
2007	Fe-doped BaTiO ₃ / Terfenol-D	350	28
2008	Pb(Mg _{1/3} Nb _{2/3})O ₃ -PbTiO ₃ / Terfenol-D	400	41
2009	Pb(Mg _{1/3} Nb _{2/3})O ₃ -PbTiO ₃ / Tb _{0.3} Dy _{0.7} Fe _{1.92}	400	42
2009	BaTi _{0.99} Cr _{0.01} O ₃ / Tb _{1-x} Dy _x Fe _{2-y}	355	30
2009	Pb(Mg _{1/3} Nb _{2/3})O ₃ -PbTiO ₃ / Terfenol-D	400	43
2010	Pb(Zr,Ti)O ₃ / Terfenol-D	300	44
2010	Mn-doped Na _{0.5} Bi _{0.5} TiO ₃ -BaTiO ₃ single crystal / Terfenol-D	400	32

Table 1-4. List of magnetoelectric laminate based on Metglas.

Year	Compositions	DC Bias (Oe)	Ref.
2006	PVDF / Metglas	8	45
2009	Pb(Zr,Ti)O ₃ fiber / Metglas	< 10	46
2009	PVDF / Metglas	52	47
2009	PVDF / Metglas	< 10	48
2009	Pb(Zn _{1/3} Nb _{2/3}) _x (Zr _{0.5} Ti _{0.5}) _{1-x} O ₃ / Metglas	100 ~ 325	49

1. 2 Lead-free magnetoelectric materials

In composite systems, ME effect is combination of two types of materials property such as magnetostriction and piezoelectricity.⁴ On application of magnetic field, magnetostrictive phase produces strain which is transferred on to the piezoelectric phase that converts strain into electric charge. This conversion of applied magnetic field into electric field is termed as direct ME effect. On the other hand, under applied electric field piezoelectric phase produces strain which is transferred on to the magnetostrictive phase that converts it into magnetic field, termed as converse ME effect. ME effect in 3-0 particulate ME composites can be illustrated by coupling between the piezoelectric matrix and magnetostrictive dispersant or vice-versa through elastic strain.

ME coefficient (α_E) for 3-0 type particulate composites can be represented by following equation given by Zubkov.⁵⁰

$$\alpha_E = \left(\frac{dE}{dH} \right)_{comp} = \left(\frac{dS}{dH} \right)_{comp} \left(\frac{dE}{dS} \right)_{comp} = m_v \cdot \left(\frac{dS}{dH} \right)_{ferrite} (1 - m_v) \cdot \left(\frac{dE}{dS} \right)_{piezoelectric} \quad (1-7)$$

where m_v is the volume fraction of ferrite, (dE/dS) is the inverse of change in strain per unit magnetic field. Since $dE = g dX$ and $dS = dX/C$, where X is the stress, S is the strain, g is the piezoelectric voltage constant, and C is the stiffness, the equation can be demonstrated as

$$\alpha_{E33} = \left(\frac{dE}{dH} \right)_{comp} = m_v \cdot \left(\frac{dS}{dH} \right)_{ferrite} (1 - m_v) \cdot (g_{33} \cdot C_{33})_{piezoelectric} \quad (1-8)$$

Since $g_{33} = d_{33} / \epsilon_{33}^T$, the ME coefficient for 3-0 type particulate composites directly depends on the charge coefficient d_{33} and the permittivity ϵ_{33}^T of piezoelectric phase.

The ME coefficient of 3-0 particulate composites has been reported to be of the order of ~ 100 mV/cm·Oe as shown in Table 1-5, which is significantly higher than that of single-phase ME materials. However, particulate ME composites exhibit much lower ME coefficient than that theoretically predicted because of the problems related to low overall piezoelectric and magnetostrictive constants, interfacial defects, and low resistivity. Recently, investigations have focused on developing lead-free ME materials. Lead-free piezoelectric materials considered for ME laminates can be classified into three material groups (ABO_3): (i) $K_{0.5}Na_{0.5}NbO_3$ (KNN), (ii) $Na_{0.5}Bi_{0.5}TiO_3$ (NBT), and (iii) $BaTiO_3$ (BT). Table 1-6 shows piezoelectric and electromechanical properties for compositions based on KNN, NBT, and BT.

$BaTiO_3$ - $CoFeO_4$ lead-free composites were the first ones investigated by Boomgaard et al. in 1978 and found to exhibit ME coefficient of 130 mV/cm·Oe. Since that time, few studies have been conducted on lead-free ME composites as shown in Table 1-7, mainly because of the poor piezoelectric performance of lead-free materials. This problem still remains but the emphasis on developing lead-free ME composites has increased due to environmental concern.

Table 1-5. List of magnetoelectric particulate composites.

Year	Compositions	DC Bias/Frequency	dE/dH (mV/cm·Oe)	Ref.
1978	0.6 BaTiO ₃ – 0.4 Ni _{0.97} Co _{0.03} Mn _{0.1} Fe _{1.90} O ₄	500 Oe/1 kHz	80	51
2001	0.8 Pb(Zr _{0.5} Ti _{0.5})O ₃ – 0.2 NiCo _{0.02} Cu _{0.02} Mn _{0.1} Fe _{1.8} O ₄	1250 Oe/1 kHz	115	52
2004	0.41 Pb(Zr _{0.5} Ti _{0.5})O ₃ – 0.59 Ni _{1-x} Zn _x Fe ₂ O ₄	250 Oe/100 Hz	45	53
2004	0.7 Pb(Zr _{0.53} Ti _{0.47})O ₃ – 0.3 CuFe ₂ O ₄	460 Oe/100 kHz	421	54
2004	0.68 Pb(Zr _{0.57} Ti _{0.43})O ₃ – 0.32 NiFe ₂ O ₄	1000 Oe/1 kHz	80	55
2006	0.7 Sr _{0.5} Ba _{0.5} Nb ₂ O ₆ – 0.3 Ni _{0.8} Zn _{0.2} Fe ₂ O ₄	1000 Oe/100 kHz	26	56
2007	0.9 Pb(Zr _{0.52} Ti _{0.48})O ₃ – 0.1 NiFe _{1.9} Mn _{0.1} O ₄	600 Oe/1 kHz	90	57
2008	0.8 Pb(Zr _{0.52} Ti _{0.48})O ₃ – 0.2 NiFe ₂ O ₄	454 Oe/1 kHz	195	58
2008	0.8 Pb(Zr _{0.52} Ti _{0.48})O ₃ – 0.2 Ni _{0.8} Zn _{0.2} Fe ₂ O ₄	1200 Oe/1 kHz	155	59
2009	0.82 [0.69 Pb(Mg _{1/3} Nb _{2/3})O ₃ - 0.31 PbTiO ₃] – 0.18 NiMn _{0.1} Fe _{1.9} O ₄	175 Oe/1 kHz	150	60
2010	0.6 Pb(Zr _{0.5} Ti _{0.5})O ₃ – 0.4 CoFe ₂ O ₄	3000 Oe/1 kHz	70	61

Table 1-6. List of lead-free piezoelectric materials.

Year	Compositions	d_{33} (pC/N)	k_p	T_c (°C)	T_{O-T}/T_d (°C)	Ref.
1959	$(K_{0.5}Na_{0.5})NbO_3$	80	0.35	420	195	62
2005	$(K_{0.465}Na_{0.465}Li_{0.07})NbO_3$	240	0.45	460	~20	63
2006	$(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.84}Ta_{0.1}Sb_{0.06})O_3$	410	0.61	253	25	64
2006	$0.95 (K_{0.5}Na_{0.5})NbO_3 - 0.05 SrTiO_3$	200	0.37	277	27	65
2005	$0.95 (K_{0.5}Na_{0.5})NbO_3 - 0.05 LiTaO_3$	200	0.36	430	55	66
2004	$0.94 (K_{0.5}Na_{0.5})NbO_3 - 0.06 LiNbO_3$	235	0.42	460	70	67
2006	$0.95 (K_{0.5}Na_{0.5})NbO_3 - 0.05 LiSbO_3$	283	0.5	392	45	68
2006	$0.7 Bi_{0.5}Na_{0.5}TiO_3 - 0.2 Bi_{0.5}K_{0.5}TiO_3 - 0.1 Bi_{0.5}Li_{0.5}TiO_3$	216	0.401	350	160	69
2007	$x (Na_{0.5}Bi_{0.5})TiO_3 - y (K_{0.5}Bi_{0.5})TiO_3 - z BaTiO_3$, $[x + y + z = 1; y : z = 2 : 1]$	145	0.162	302	224	70
2006	$0.5 Na_{0.5}Bi_{0.5}TiO_3 - 0.5 K_{0.5}Bi_{0.5}TiO_3$	150	0.22	320	210	71
1958	$BaTiO_3$	190	0.36	115	0	72
1957	$0.95 BaTiO_3 - 0.05 CaTiO_3 - Co$	150	0.31	105	-45	73

Table 1-7. List of lead-free magnetoelectric composites.

Year	Compositions	Type	DC Bias/Frequency	dE/dH (mV/cm·Oe)	Ref.
2005	BaTiO ₃ – CoFe ₂ O ₄	Particulate	270 Oe/160 kHz	2540	74
2006	0.7 Sr _{0.5} Ba _{0.5} Nb ₂ O ₆ – 0.3 Ni _{0.8} Zn _{0.2} Fe ₂ O ₄	Particulate	1~3 kOe/100 kHz	26.6	56
2009	BaTiO ₃ – CoFe ₂ O ₄	Particulate	2000 Oe/20 kHz	17.04	75
2009	(K _{0.5} Na _{0.5})NbO ₃ -LiSbO ₃ – CoFe- ₂ O ₄	Particulate	2200 Oe/1 kHz	15	76
2010	0.75 BaZr _{0.08} Ti _{0.92} O ₃ – 0.25 Co _{1.2-y} Mn _y Fe _{1.8} O ₄ , (y = 0 ~ 0.4)	Particulate	1500 Oe/1 kHz	2.5	77
2006	BaTiO ₃ / (Ni _{0.8} Zn _{0.2})Fe ₂ O ₄	Laminate	1000 Oe/1 kHz	152	16
2010	0.885 Bi _{0.5} Na _{0.5} TiO ₃ - 0.05 Bi _{0.5} K _{0.5} TiO ₃ - 0.015 Bi _{0.5} Li _{0.5} TiO ₃ - 0.05 BaTiO ₃ / Terfenol-D	Laminate	600 Oe/131 kHz	2500	78
2010	Mn-doped Na _{0.5} Bi _{0.5} TiO ₃ –BaTiO ₃ single crystal / Terfenol-D	Laminate	400 Oe/1 kHz	1320	32

1. 3 Magnetic and piezoelectric nanostructures

The synthesis of nanostructured materials has gained considerable attention in the past two decades due to its unique size-dependent properties. Many studies on synthesis of 0 (particle), 1 (rod), 2 (thin film) and 3 (scaffold matrix) dimensional nanostructures have been conducted.⁷⁹⁻⁸³

Magnetic particles as 0D nanostructure have been used as active components of disk recording media, biomedical materials and catalysts, magnetic resonance imaging, and energy harvesting.⁸⁴⁻⁸⁷ These various technological applications are the focus of several interesting ongoing research.⁸⁵ In order to improve the functionality of magnetic sensors, various studies have been conducted on magnetic material-metal composites. The properties of magnetic nanoparticles can be determined by both the intrinsic properties of the nanoparticles and the interactions between each nanoparticles. The magnetic nanoparticles with below critical diameter maintain to be one domain which can be described as single domain. The critical diameter can be given as $2A^{1/2}/M_s$ which A is the exchange constant and M_s is the moment per unit volume.⁸⁸ The critical diameters and magnetization were reviewed with theoretical models by Zijlstra et al.⁸⁹ Several studies on ferrite nanoparticles exhibited complex depiction reflecting disordered spins and the finite size provides an effect on structural and magnetic order in nanoparticles.^{86,90}

1D nanostructures such as nanorods, nanowires, and nanotubes have received significant interest because physical properties at nanoscale are different from their bulk and film counterparts. Especially, 1D nanostructures can play important role in the electrical applications owing to their high active surface area and high flexibility. Piezoelectric nanostructures are projected to find potential applications in transducers, emitters, sensors, actuators and energy

harvesters.^{79,80,91} In order to synthesize 1D nanostructures, several fabrication methods (a: chemical syntheses, b: inducing growth, c: template-assisted syntheses, and d: template-free syntheses) have been used with various perovskite compositions (BaTiO_3 , PbTiO_3 , PbZrO_3 , SrTiO_3 , $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$, $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, and etc).⁹²⁻⁹⁹

1. 4 Biomimetic polymeric actuators with inherent sensing capability

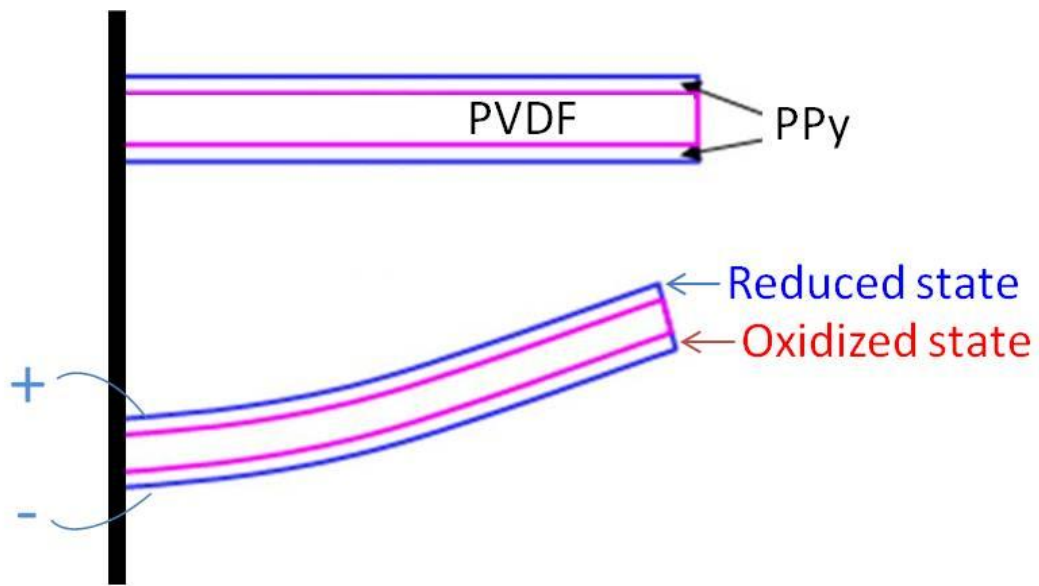
Much attention has been given to electroactive devices constructed with conducting polymers due to their low voltage requirements, high strain, and similarities to natural muscle.^{100,101} Among the reported electroactive devices, conducting polymer based actuators have been widely investigated due to their high deflection, similarities to natural muscle, and low operating voltage.^{102,103} Figure 1-3 shows the schematic diagram for Polypyrrole (PPy) / Au / Polyvinylidene fluoride (PVDF) / Au / Polypyrrole (PPy) actuators and their working principle. The electroactive polymer (EAP) can change shape in response to electrical stimulation. The large induced displacement capability of these new EAP materials is attracting the attention from many different disciplines. Practitioners in biomimetics, a field where robotic mechanisms are being developed based on biologically inspired models, are particularly excited about these materials since they can be applied to mimic the movements of animals and insects. Further, the conducting polymers have been of interest in electronic and telecommunication applications requiring shielding effect against electromagnetic interference (EMI). Many researches on EMI shielding have been conducted using conducting polymers with magnetic nanomaterials.¹⁰⁴⁻¹⁰⁸

However, conducting polymer actuators have few remaining challenges such as poor repeatability and robustness. In addition, the two most important aspects of conducting polymer

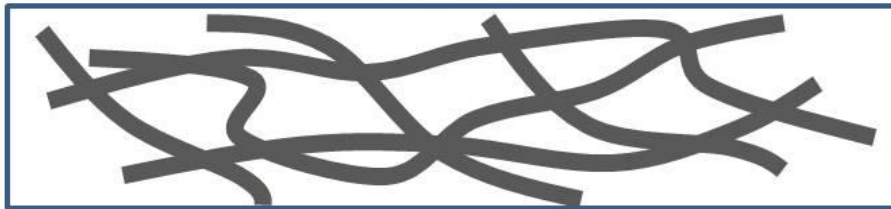
actuators that have not been addressed fully are their slow time response and low force output.

¹⁰⁹ Due to the advantages of ionic electroactive devices especially those constructed with PPy, groundwork research has already been done in this area. Previously, strain has been correlated to surface area of conducting polymer, while strain or actuation rate has been correlated to PPy thickness. ¹¹⁰⁻¹¹³ Strains of 40% and strain rates of 13% per second have been shown. ^{114,115} An analytical bending model has been produced for single iteration actuators that showed the deflection is highly dependent on the modulus of the polymer substrate. ¹¹⁶ Models of the force output of polymer actuators have also been created showing mathematically and experimentally that polymer actuators can be used for small robotic grippers. ¹¹⁷

In this thesis, I made an attempt towards developing a high force – high response time conducting polymer actuators. In future, the combination of this actuator with flexible magnetostrictive layers or magnetoelectric nanoparticles will allow the capability to do sensing in conjunction with actuation. For example – the actuator will be turned on as the magnetic object comes in its vicinity.



Reduced state of PPy layer: volume contraction



Oxidized state of PPy layer: volume expansion

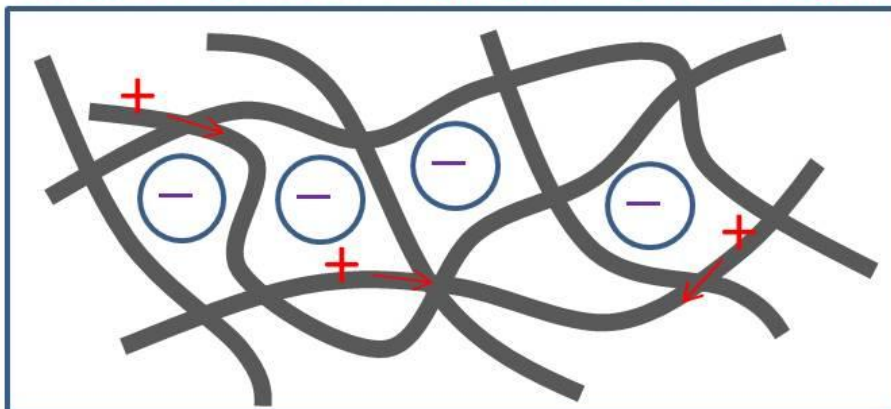


Figure 1-3. Schematic diagram for PPy / Au / PVDF / Au / PPy actuators and working principle of the redox states of PPy.

CHAPTER 2

RESEARCH OBJECTIVES

2. 1 Self-biased magnetoelectric effect

In composite systems, the ME effect can be classified as direct magnetoelectric (DME) and converse magnetoelectric (CME). DME effect is defined as change in electric polarization in response to applied magnetic field while CME effect is defined as change in magnetization in response to applied electric field.⁴

$$DME\ effect = \frac{mechanical}{magnetic} \times \frac{electric}{mechanical} \quad (2-1)$$

$$CME\ effect = \frac{mechanical}{electric} \times \frac{magnetic}{mechanical} \quad (2-2)$$

Many studies on magnetoelectric composites have revealed that bias magnetic field (H_{bias}) is essential along with ac magnetic field (H_{ac}) in order to enhance the DME effect and maximum in α_{DME} is obtained at optimum H_{bias} . The H_{bias} dependence of α_{DME} is related to the magnetostriction (λ) of ferromagnetic phase and the behavior of α_{DME} with respect to bias field has been experimentally confirmed to be very similar to that of piezomagnetic coefficient ($q = d\lambda/dH_{bias}$) of ferromagnetic phase. Depending upon the composition and dimension of the ferromagnetic material, the maximum α_{DME} is obtained at different H_{bias} ranging from few Oe to few kOe. Since the requirement of additional large H_{bias} can be problematic for device fabrication, efforts to reduce required H_{bias} have been emphasized. Most ferromagnetic materials

exhibit a very small slope in their magnetostriction curve near zero bias field ($H_{\text{bias}} = 0$) resulting in almost zero q value and consequently negligible α_{DME} .

Recently, Mandal et al. demonstrated self-biased laminate composites where ME response at zero field was correlated with presence of flexural deformation in a compositionally graded structure. However, this method of generating self-bias is dependent upon the composition grading and requires special synthesis process. In order to understand self-bias effect, three-phase laminates were designed which exhibit ME hysteretic responses and two optimum H_{bias} as shown in Figure 2-1. In this chapter, the research objectives were: (i) finding a methodology where one can achieve self-biased ME effect in composites by just changing the electrical connections on regular laminate composites, (ii) confirmation of self-biased ME effect by experimental approach such as variation of material composition, and (iii) discovering fundamental mechanisms governing this phenomenon in both direct and converse ME effects.

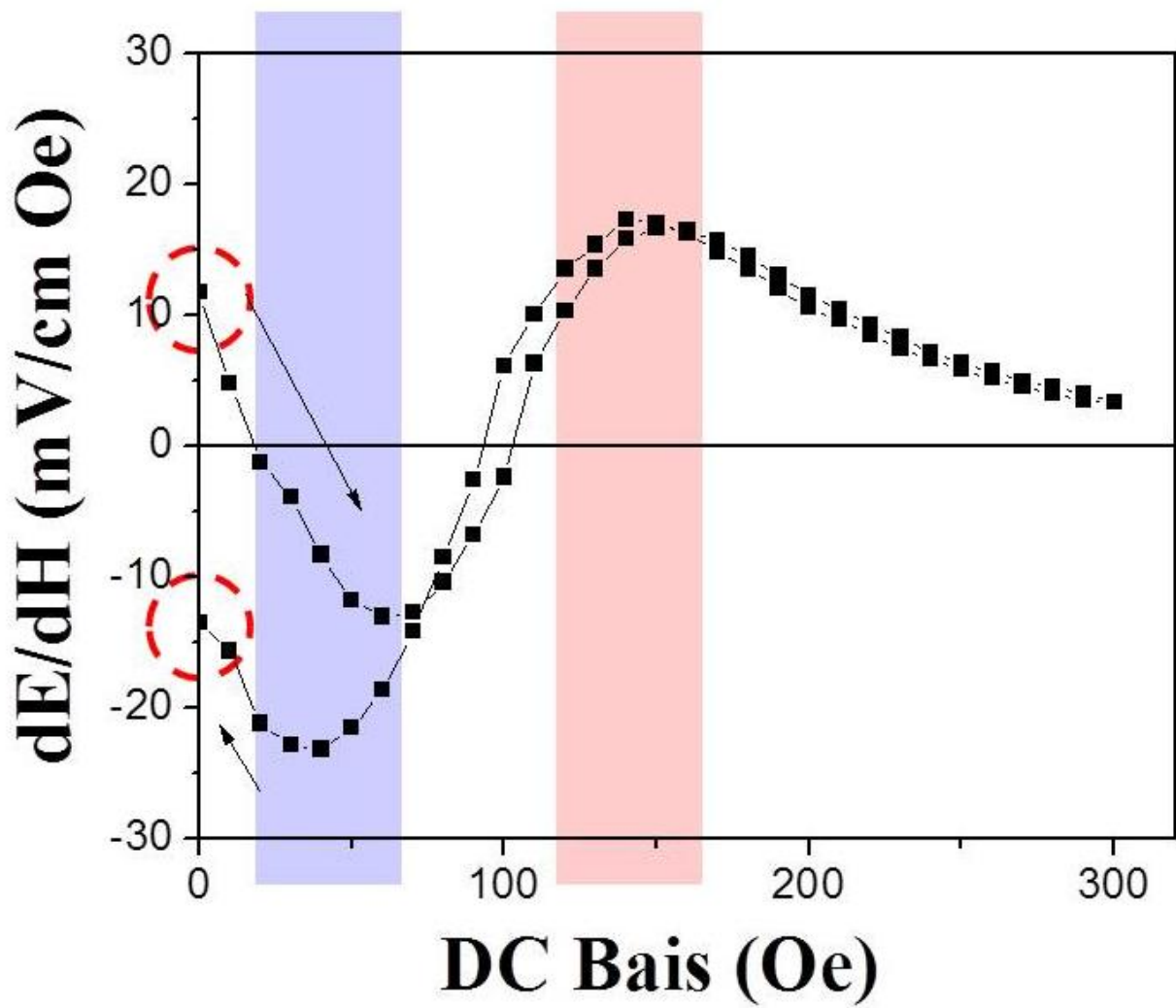


Figure 2-1. Schematic diagram for ME hysteretic responses with self-bias effect in three phase laminates.

2. 2 Lead-free two-phase magnetoelectric composites

Pb-based ME composites are attractive for various applications due to their superior piezoelectric characteristics. However, with increase in environmental concern, there has been interest in design of lead-free ME composites. 3-0 type ME particulate composites have been shown to provide enhancement in the magnitude of ME coefficient resulting from elastic coupling between piezoelectric and magnetostrictive phase.

Conventional ME particulate composites are synthesized by sintering green body consisting of piezoelectric phase, magnetostrictive phase, and sintering aid. The sintering process results in three problems that reduces the magnitude of overall ME response: (i) cross-diffusion of elements lowering the magnitude of piezoelectric and magnetostrictive constants, (ii) connectivity of ferrite phase increasing the leakage current that limits the poling, and (iii) mechanical defects due to difference in shrinkage rate of individual phases that reduces elastic coupling. To enhance the magnitude of ME coefficient of sintered composite, it is necessary to optimize the composition, microstructural features (connectivity, grain size, grain orientation), and sintering parameters.

In this chapter, island - matrix microstructure was designed and its effectiveness was demonstrated towards achieving high ME performance. Figure 2-2 shows a schematic diagram for island-matrix structure and selected materials of $K_{0.5}Na_{0.5}NbO_3LiSbO_3$ (KNNLS) and $Ni_{0.8}Zn_{0.2}Fe_2O_4$ (NZF) as piezoelectric and magnetostrictive phases respectively due to a big difference between their sintering temperatures.^{118,119} The island-matrix microstructure can overcome all the three problems mentioned above.

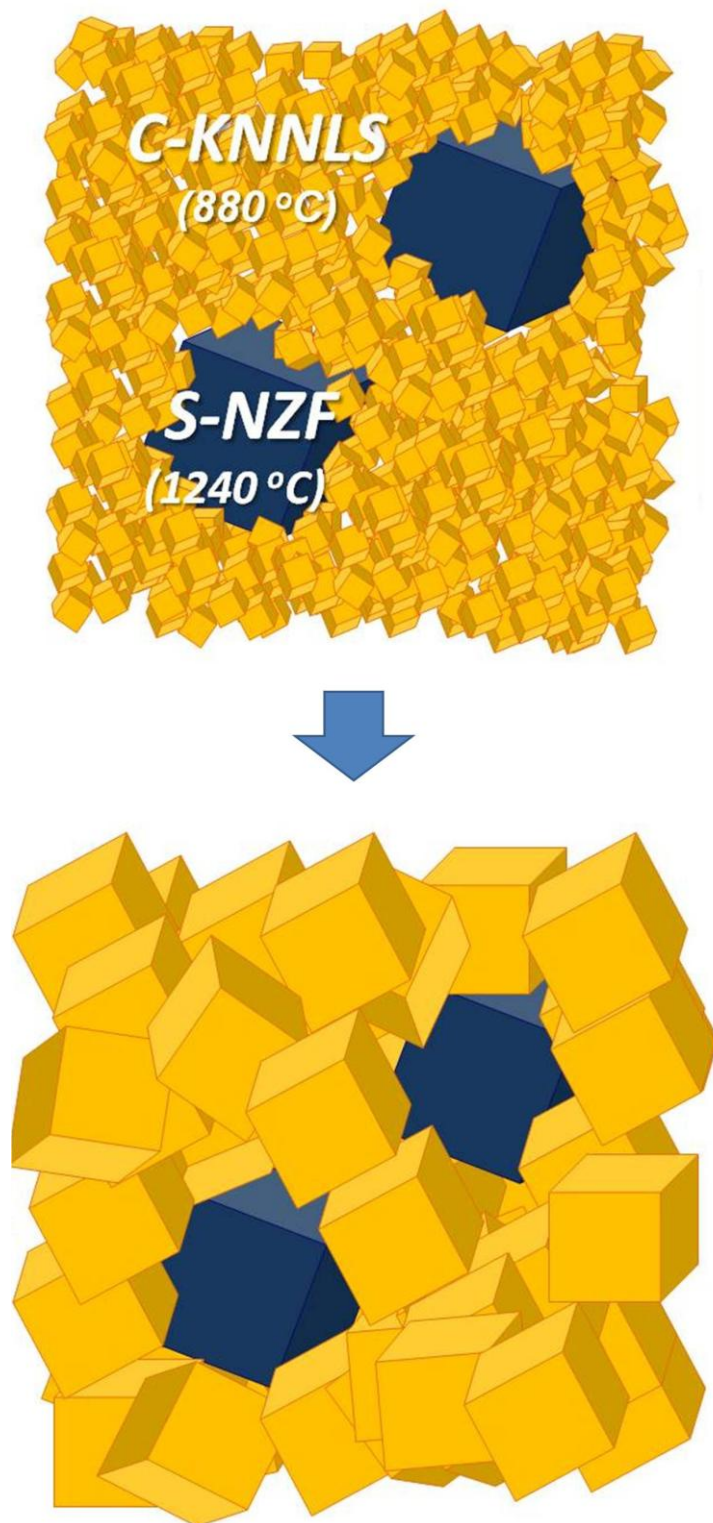


Figure 2-2. Schematic diagram for the island-matrix microstructure in KNNLS-NZF composites.

2.3 Lead-free single-phase magnetoelectric materials

In past decade, many studies have focused on single-phase multiferroic materials such as Cr_2O_3 , LiCoPO_4 , TbPO_4 , YIG, BiFeO_3 , BiMnO_3 , YMnO_3 , and BaMnF_4 .¹²⁰⁻¹²⁴ Among these multiferroic materials, BiFeO_3 has attracted most attention due to its simultaneous ferroelectric and antiferromagnetic characteristics at room temperature while exhibiting high Curie temperature and high Neel temperature.^{125,126} However, high leakage current in BiFeO_3 ceramics has been observed due to the existence of Fe ions and oxygen vacancies. To improve the ferroelectric properties, studies on solid solution of BiFeO_3 with other perovskite materials (BaTiO_3 , PbTiO_3 , CaTiO_3 , and $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$) has been performed.¹²⁷⁻¹³³ BaTiO_3 is a promising candidate in this respect, and $(1 - x) \text{BaTiO}_3 - x \text{BiFeO}_3$ solid solutions have been shown to exhibit rhombohedral ($0.7 < x \leq 1.0$), pseudo-cubic ($0.04 < x \leq 0.7$), and tetragonal ($0 \leq x \leq 0.04$) phases.¹³⁴ Substitutional doping of La, Nb, and Mn in the BaTiO_3 – BiFeO_3 have been studied to enhance the piezoelectric properties and DC resistivity.¹³⁵⁻¹³⁸ Recently, improved piezoelectric value of $d_{33} = 116 \text{ pC N}^{-1}$ with high DC resistivity of $2.7 \times 10^7 \Omega \text{ m}$ was reported in Mn-modified BaTiO_3 – BiFeO_3 ceramics by Leontsev et al.¹³⁸ On the other hand, several studies on BaTiO_3 – BiFeO_3 ceramics have shown that the solid solutions with BaTiO_3 results in enhanced magnetic properties.¹³⁹

However, identification of the precise material composition with high ME coefficient in the BaTiO_3 – BiFeO_3 system is missing. Once this composition has been identified, detailed investigation of crystal structure and phase transformation should be conducted to understand the nature of coupling between ferroelectricity and anti-ferromagnetism. In this chapter, room-temperature ME phase diagram of $(1 - x) \text{BaTiO}_3 - x \text{BiFeO}_3$ with $x = 0.025 - 1.0$ was developed as shown in Figure 2-3 for optimization of high performance composition. Piezoelectric,

dielectric and magnetic properties were measured in conjunction with detailed crystal structure analysis to determine the structure – property relationships.

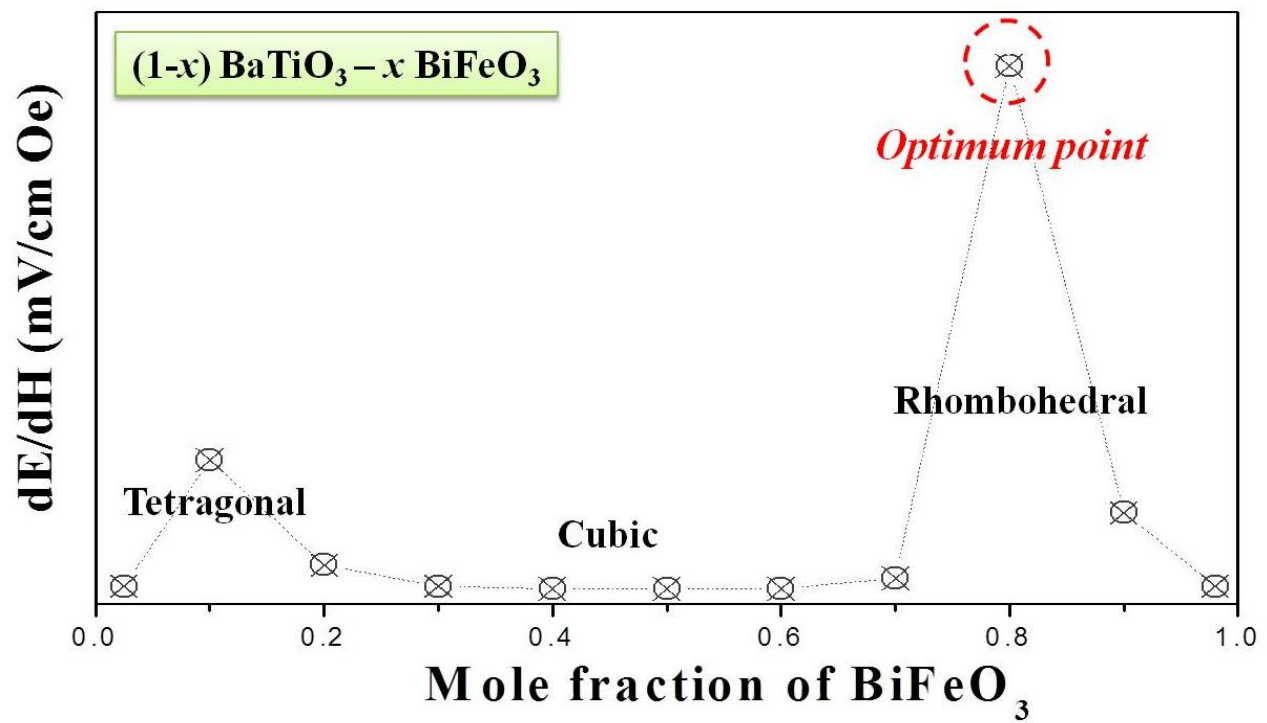


Figure 2-3. Schematic room-temperature ME phase diagram for BT-BFO system.

2. 4 Core-shell ferromagnetic-metal nanoparticles

Magnetic nanoparticles have been of significant interest for various applications such as data information storage, biomedical drug delivery, magnetic resonance imaging and energy harvesting due to their unique characteristics as a function of size. In order to improve the functionality of magnetic sensors various studies are being conducted on magnetic material-metal composites.^{84,140-142} Iron and cobalt nanoparticles can occur in multiple crystal phases, which can result in large differences in the magnetic moment and crystalline anisotropy.^{143,144} This appears to be a size effect related to the balance of surface and bulk free energies for the different possible crystal structures, and therefore depends on the particle size and matrix material.

The objective of this chapter was to develop new concepts of core-shell electromagnetostrictive (EMS) nanoparticles for realizing better magnetic field sensor and memristor. The sensor utilizes thermal detection to quantify the changes in external magnetic field. An oscillating electric field in the surrounding will induce eddy current through the conductive shells that could result in the joule heating of the core. Furthermore, the oscillating electric field will induce strain in the core due to magnetostriction which will create deformation in the matrix. The result of these two effects will be to create a finite temperature difference with the surrounding. Figure 2-4 shows the schematic diagram for EMS effect resulting in an induced strain in the grains through electromagnetoelastic coupling.

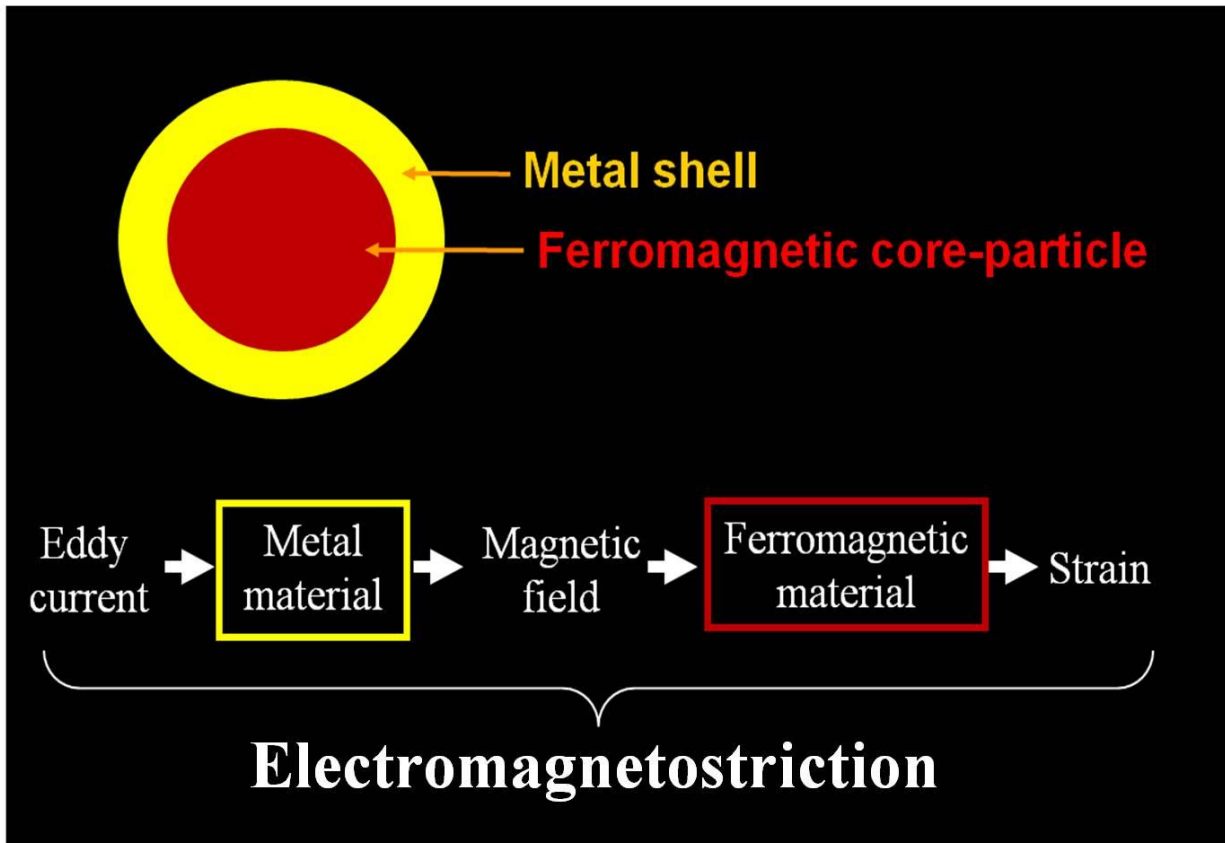


Figure 2-4. Schematic diagram for electromagnetostriuctive (EMS) effect in core-shell ceramic-metal nanoparticles.

2. 5 Vertically aligned piezoelectric nanorods

In prior studies on one dimensional (1D) nanostructures, finite size effect in nanostructures has been focused with respect to the electrical and mechanical boundary conditions and domain configuration.^{145,146} Recently, well-ordered 1D nanostructures on conductive substrates have been developed to achieve unique characteristics given by its high active surface area.¹⁴⁷⁻¹⁵⁰ Several fabrication methods have been used to acquire high resolution nano-patterns through focused ion beam patterning or electron beam lithography.¹⁵¹⁻¹⁵⁴ However, these patterning methods are very slow and expensive to be developed on large area.

In order to develop high performance piezoelectric nano-devices with thickness of < 1 μm , free-standing 1D piezoelectric nanostructures on conductive substrate were designed as shown in Figure 2-5. To prove feasibility of process for synthesizing 1D piezoelectric nanostructures, vertically aligned nanorods using lead-based PZT were synthesized on wide area of conductive substrate via transfer method using porous templates. This method has several advantages such as low price, large area fabrication and good control on dimensions. Further, the porous alumina template synthesized by two-step aluminum anodizing exhibited straight cylindrical pores with ordered patterns.^{155,156}

High performance PZT nanorod-arrays

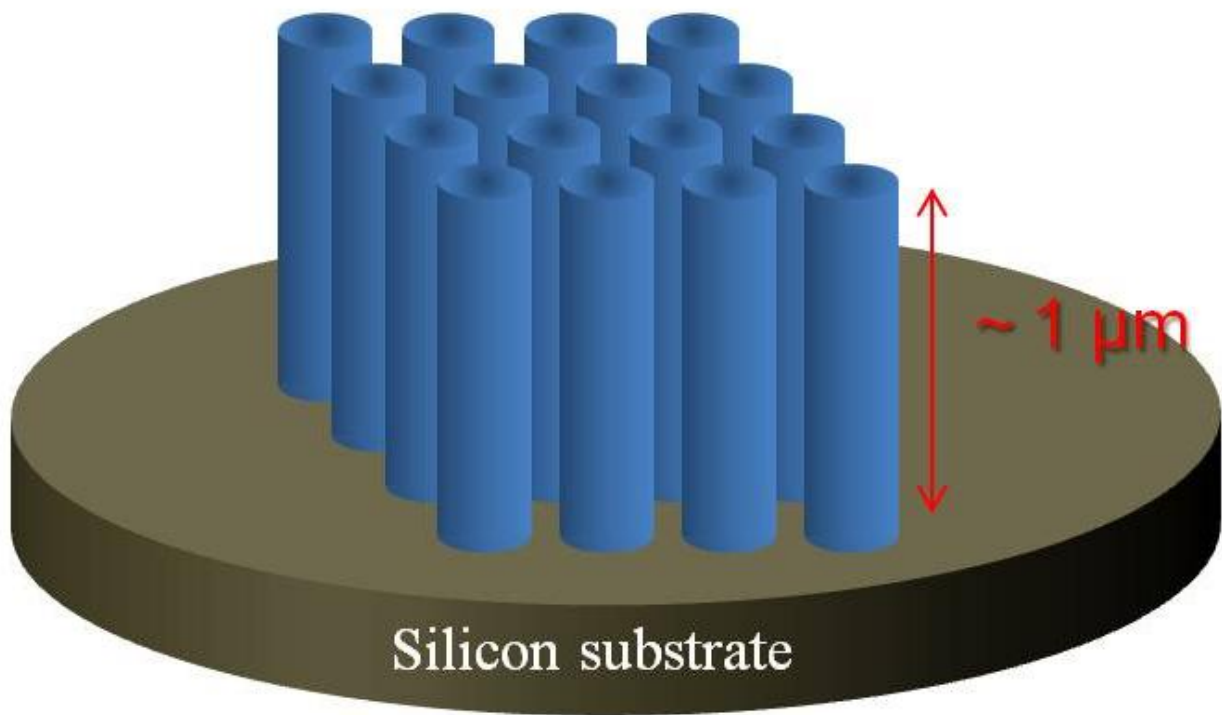


Figure 2-5. Schematic diagram for vertically-aligned PZT nanorod-arrays on a platinized silicon substrate.

2. 6 Electroactive polymer actuators

Actuators with high force output, large strain and fast response are desired to be used in a variety of applications. Such application can take the form of a biomimetic robotic jellyfish, expressive robotic face or braille displays for the visually impaired.^{157,158} All of these applications are limited by the small force output of conducting polymer actuators. Actuation characteristics are dominantly dependent upon structure of polymer actuators and rate of ionic diffusion. In the ionic electroactive polymer actuators using PDVF-PPy structure, various electrolyte solutions consisting of different ionic dopants exhibit fast response time up to 0.25 sec and high strain of 30 % in water or polycarbonate solutions.

The objective of this chapter was to create a monolithic actuator, operable in air, with fast actuation times and increased force generation. For improvement of actuation properties, two approaches were performed in the electroactive polymer structure of PPy / Au / PVDF / Au / PPy as shown in Figure 2-6. First approach was to make good channels for ion movement by optimizing pore size and thickness of PVDF inter layer in PPy / Au / PVDF / Au / PPy system. Second approach was to optimize electrolyte solution for fast response time in air by using different electrolytes and adjusting the molality of electrolyte solutions.

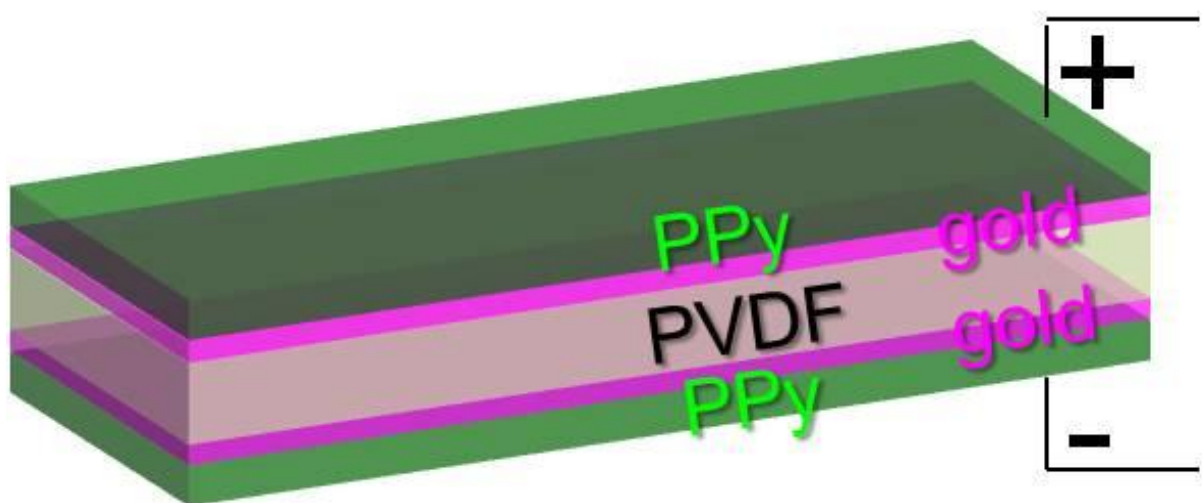


Figure 2-6. Schematic diagram for electroactive PPy / Au / PVDF / Au / PPy actuators.

CHAPTER 3

EXPERIMENTAL METHODS

3. 1 Sol-gel synthesis

For development of nanostructure and thin film piezoelectric materials, sol-gel synthesis was used as a wet-chemical method. Sol-gel method provides good control over stoichiometry and reduced sintering temperature. The sol is a stable suspension of colloidal solid particles or polymers in a liquid and the gel is a three-dimensional network surrounding a liquid phase. Therefore, the sol-gel process can be demonstrated as formation of an oxide network via condensation of precursor in a liquid. Piezoelectric nanostructure and thin film materials via sol-gel synthesis can be found to exhibit good piezoelectric characteristics due to strong adhesion of oxide surfaces on both the individual crystallites during sol-gel process.

3. 2 Solvothermal synthesis

For high performance ferromagnetic nanoparticles, solvothermal method was used to synthesize nano-size magnetic particles. The solvothermal synthesis is commonly used for nanocrystalline materials. In this process, a solvent under moderate to high pressure between 1 atm and 10000 atm and temperature between 100 °C and 1000 °C are used to facilitate interactions of precursors during synthesis. The method can be used to prepare thermodynamically stable and metastable states including novel materials that cannot be easily formed from other synthetic methods. The magnetic permeability of ferromagnetic materials dominantly depends on its grain

size so that the enhanced magnetic properties were observed in nanocrystalline materials with small grain size.¹⁵⁹

3.3 Cyclovoltammetric deposition

For thin film coating of polypyrrole on conductive substrate, cyclovoltammetric (CV) deposition was conducted as electrochemical method. The advantages of CV electrochemical deposition are simple preparation using one-step procedure and fine control of film thickness. Optimization of CV conditions was performed by variation of applied current, applied potential and composition of electrolyte solutions. Further, the adhesion of PPy deposition is a main factor to provide high actuation performances in electroactive polymer actuators. The CV method especially can be used to deposit nanoparticles in conductive polymers.¹⁶⁰

3.4 Morphology and crystal structure characterizations

Microstructures of piezoelectric, magnetic and magnetoelectric materials were investigated using field emission scanning electron microscope (FE-SEM, LEO/Zeiss 1550, Zeiss) in conjunction with energy dispersive spectroscopy (EDS). Detailed structural and microstructural analyses were performed using high-resolution transmission electron microscopy (HRTEM, Titan 300, FEI) with point energy dispersive spectroscopy (point-EDS). Selected area electron diffraction (SAED) patterns were determined to investigate the crystal structure.

Crystal structures of piezoelectric, magnetic and magnetoelectric materials were investigated using X-ray diffraction patterns (D/MAX-2500, Rigaku) at room temperature. Local structures were also investigated by Raman spectroscopy (JY Horbia LabRam HR 800, Horiba Ltd., Japan) and atomic pair distribution function (PDF) analysis. Raman spectra were recorded in the wave number range of 50 – 1000 cm^{-1} equipped with a CCD detector and Labspec software package. The light source was a 514.5 nm argon laser at 50 mW power and 400s exposure time.

3.5 Electric, magnetic and magnetoelectric characterizations

Piezoelectric characteristics were examined using APC YE 2730A d_{33} meter. Dielectric characteristics were investigated using HP 4194A impedance analyzer (Hewlett Packard Co. USA). Ferroelectric polarization-electric field measurement was performed using modified Sawyer-Tower Bridge Precision II (Radiant Technologies, Albuquerque, NM). Dielectric characteristics were determined by using the HP 4194A impedance analyzer (Hewlett Packard Co. USA). The piezoelectric characteristics for nanostructure were examined using piezo-response force microscopy (PFM, Dimension Icon, Bruker) in the contact- and ramp- modes.

Surface charges of nanoparticles under colloidal solutions were investigated using Zeta-potential measurement (Zetasizer Nano, Malvern instruments Ltd., UK). Zeta potential was measured using a combination of electrophoresis and velocimetry. This method measures how fast a particle moves in a liquid when an electrical field is applied.

Magnetization-magnetic field measurement was performed using the vibrating sample magnetometer (VSM 7304, Lake Shore Cryotronics). Magnetic properties for nanostructure were measured by magnetic force microscopy (MFM, Vecoo DI 3100a). Magnetostriction was measured using a strain measurement method based on micro-strain gauges with Wheatstone bridge.

Magnetoelectric (ME) measurements were conducted by applying H_{bias} . For direct magnetoelectric (DME) measurement, H_{ac} was provided by Helmholtz coil (DME-Input) to the laminate and then the induced voltage was measured from the sample (DME-Output). For converse magnetoelectric (CME) measurement, V_{ac} (CME-Input) was applied directly on the sample and then the induced magnetic flux density was measured by using Helmholtz coil (CME-Output).

CHAPTER 4

SELF-BIASED MAGNETOELECTRIC EFFECT

4. 1 Self-biased magnetoelectric effect in three phase laminates

0.948 $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3 - 0.052 \text{LiSbO}_3$ (KNNLS) and $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ (NZF) ceramics were synthesized by mixed oxide sintering method. KNNLS-NZF / Ni bilayer and KNNLS-NZF / Ni / KNNLS-NZF trilayer laminates were fabricated by bonding Ni plates with dimension of $15 \times 15 \text{ mm}^2$ with KNNLS-NZF disks of diameter 10 mm, using epoxy with curing temperature of 80°C . Each layer had a thickness of 0.5 mm and the ME composite operated in L-T mode. Figure 4-1 shows schematic diagrams for configurations of 2-2 ME laminates studied in this chapter.

Figure 4-2 shows the $M - H$ curves for NZF particles and Ni plates. NZF particles had saturation magnetization (M_s) of 64.6 emu/g under an applied magnetic field of 3000 Oe. The magnetic susceptibility (χ) was calculated to be $3.3 \times 10^{-2} \text{ emu/g} \cdot \text{Oe}$ in the magnetic field range of -1000 to 1000 Oe, as shown in Figure 4-2(a). Nickel plates were found to possess the saturation magnetization (M_s) of 50.2 emu/g at an applied magnetic field of 4000 Oe. The magnetic susceptibility (χ) was calculated to be $1.6 \times 10^{-2} \text{ emu/g} \cdot \text{Oe}$ in the magnetic field range of -1000 to 1000 Oe, as shown in Figure 4-2(a). Using Figure 4-2(b), the coercive field (H_c) of NZF particles was found to be 5 Oe and the H_c for Ni was found to be 14 Oe. The remnant magnetizations (M_r) for Ni and NZF particles was of the same amplitude, 0.29 emu/g. These results indicate that the composite fabricated by using Ni and NZF phase will have built-in bias field (H_{bias}) which is related to difference in the magnitude of susceptibility and coercivity.

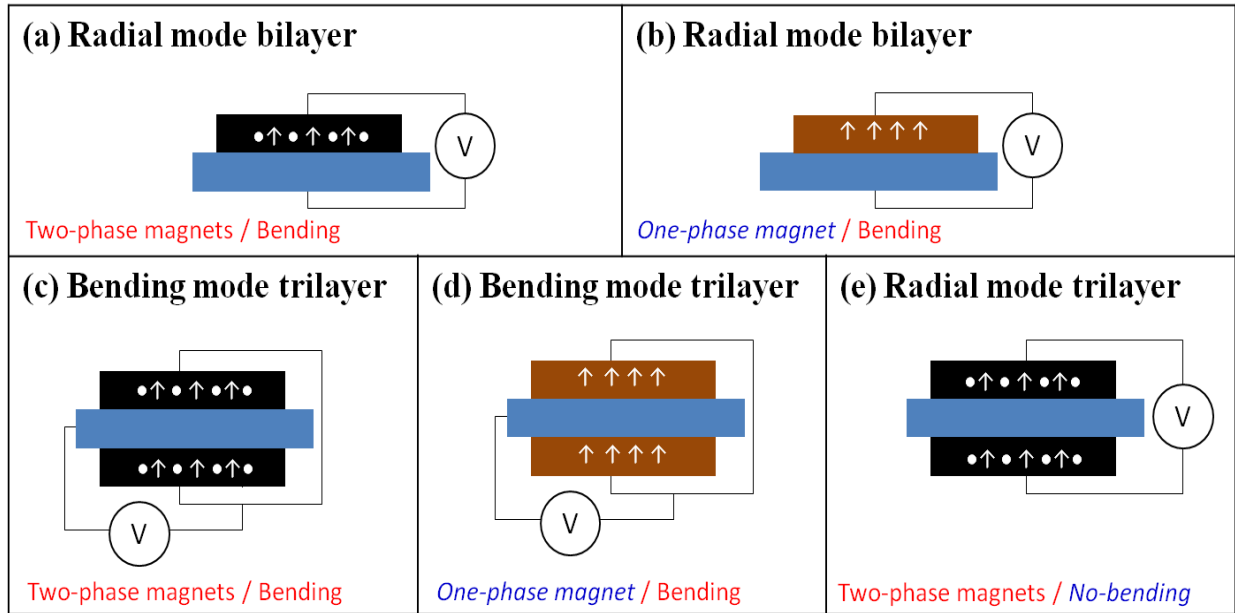


Figure 4-1. Schematic diagrams for ME laminate composites for self-biased ME effect. (a) Radial mode bilayer with two-phase magnet, (b) Radial mode bilayer with one-phase magnet, (c) Bending mode trilayer with two-phase magnets, (d) Bending mode trilayer with one-phase magnet and (e) Radial mode trilayer with two-phase magnets.

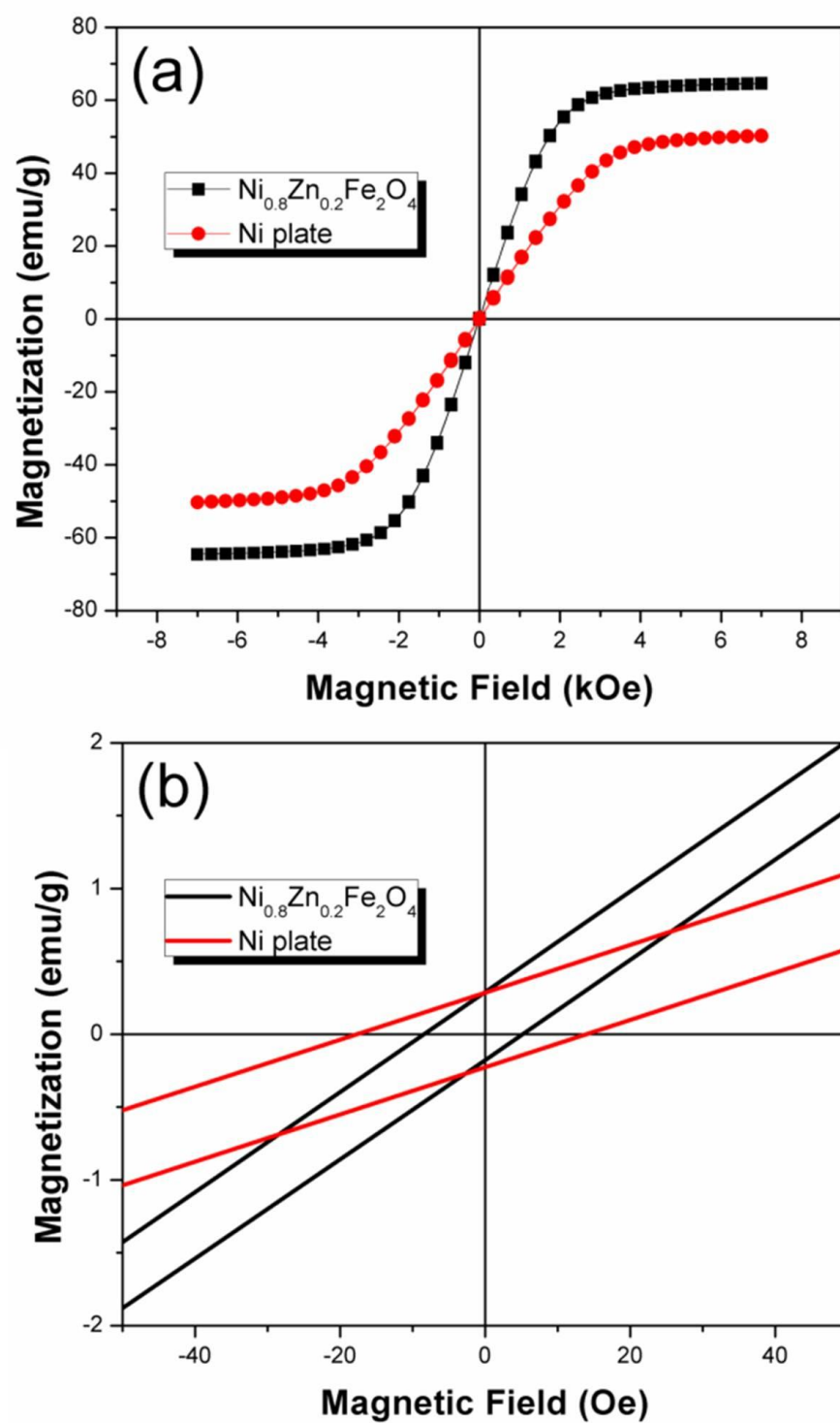


Figure 4-2. M – H curves for NZF particles and Ni plates, (a) saturated magnetic hysteresis loops under high field and (b) exploded view in the low field region.

Figure 4-3 shows the ME voltage coefficient (α_E) for bilayer and trilayer laminates. All the measurements were conducted at 1 kHz. It can be seen in Figure 4-3(a) that KNNLS-NZF / Ni bilayer had maximum α_E of 166 mV/cm·Oe at an applied magnetic DC bias of 120 Oe and remanent ME coefficient α_{ER} of 30 mV/cm·Oe at zero magnetic DC bias. It should be noted here that in these structures, Ni plays three roles, as: (i) it acts as electrode, (ii) it induces bending modes in the composite at low frequencies by lowering the overall stiffness, and (iii) it magnetically couples with the NZF phase. In bilayer, there is structural asymmetry and mismatch of coercive force induced by differences in χ and H_c of two ferromagnetic materials given by H_{bias} . This asymmetry is further enhanced at higher magnetic DC bias owing to mismatch in the magnetostrictive strain of NZF and Ni. Thus, the ME response is summation of three effects, one related to the H_{bias} , second related to the resultant of applied magnetic DC bias field (H_{appl}) and H_{bias} given as $\sum \vec{H}_{appl} + \vec{H}_{bias}$ which is frequency dependent term, and third related to structural asymmetry which induces bending modes. The data in Figure 4-3(b) and (c) further strengthens this argument. Figure 4-3(b) shows that KNNLS / Ni bilayer exhibited maximum α_E of 120 mV/cm·Oe at an applied magnetic DC bias of 150 Oe without any α_{ER} . The low α_E and zero α_{ER} could be related to absence of magnetic interaction between Ni and NZF. A comparison of Figure 4-3(a) and (b) indicates that hysteresis is related to the magnetic interaction between Ni and NZF. The NZF phase was absent in Figure 4-3(b) and the ME behavior was similar to that obtained for conventional laminates with linear response. The magnitude of α_E for KNNLS-NZF / Ni / KNNLS-NZF trilayer exhibited maximum α_E of 385 mV/cm·Oe at an applied magnetic DC bias of 96 Oe without any α_{ER} as shown in Figure 4-3(c). This configuration in Figure 4-3(c) will be referred to as “radial-mode trilayer (RMT)”. High α_E of trilayer and zero α_{ER} was related to structural symmetry which reduces in-plane strain and maximizes the out-of-plane strain. The

peak position in this curve corresponds with the maximum in gradient of the magnetostriction vs. magnetic DC bias curve. Note the electrical connection in Figure 4-3(c) which will generate charge on the piezoelectric layer due to symmetric deformation in top and bottom layer. In contrast, Figure 4-3(d) shows the ME response of KNNLS-NZF / Ni / KNNLS-NZF trilayer composite with modified electric connections to excite the bending mode, and will be referred as “bending-mode trilayer (BMT)”. In this case, there was clear hysteresis in the forward and backward sweep of ME response with zero cross-over points. The region defined by $-50 < H_{DC} < 50$ Oe represents the switchable states by changing the applied DC bias. In the forward sweep, the minimum in α_E was found to occur at ~ 16.6 mV/cm·Oe and maxima was found at ~ 20 mV/cm·Oe. In the backward sweep, the maxima was found at 23.1 mV/cm·Oe with minimum occurring at ~ 10 mV/cm·Oe. The magnitude of α_{ER} was 11.78 mV/cm·Oe at zero DC bias. BMT has clear α_{ER} as well as two zero cross-over points at magnetic DC bias of 17.7 Oe and 92.8 Oe. The behavior was not exactly symmetric in the positive and negative quadrants of applied magnetic field with slight shift towards negative Y-axis. I think that this shift is related to the magnitude of $\sum \vec{H}_{appl} + \vec{H}_{bias}$ which may have different magnitude during the forward and backward sweep.

In order to understand the ME response of Figure 4-3(d), I present data on BMT without any NZF phase. Figure 4-3(e) shows the ME response of KNNLS / Ni / KNNLS trilayer without any NZF. A maximum α_E of 15.5 mV/cm·Oe was obtained at magnetic DC bias field of 72 Oe without any α_{ER} . Further, the magnitude of α_E was quite small as compared to ME behavior shown for RMT. This result clearly shows that interaction between NZF and Ni is important to achieve high α_E and finite α_{ER} with zero cross-over points. This also confirms the hypothesis that

BMT ME response is governed by $\sum \vec{H}_{appl} + \vec{H}_{bias}$. Comparing the data of Figure 4-3(d) and (e), the magnitude of H_{bias} was estimated to be in the region of -92.8 to 92.8 Oe. Higher magnitude of α_{ER} in Figure 4-3(a) has some contribution from the lower stiffness of the bilayer structure.

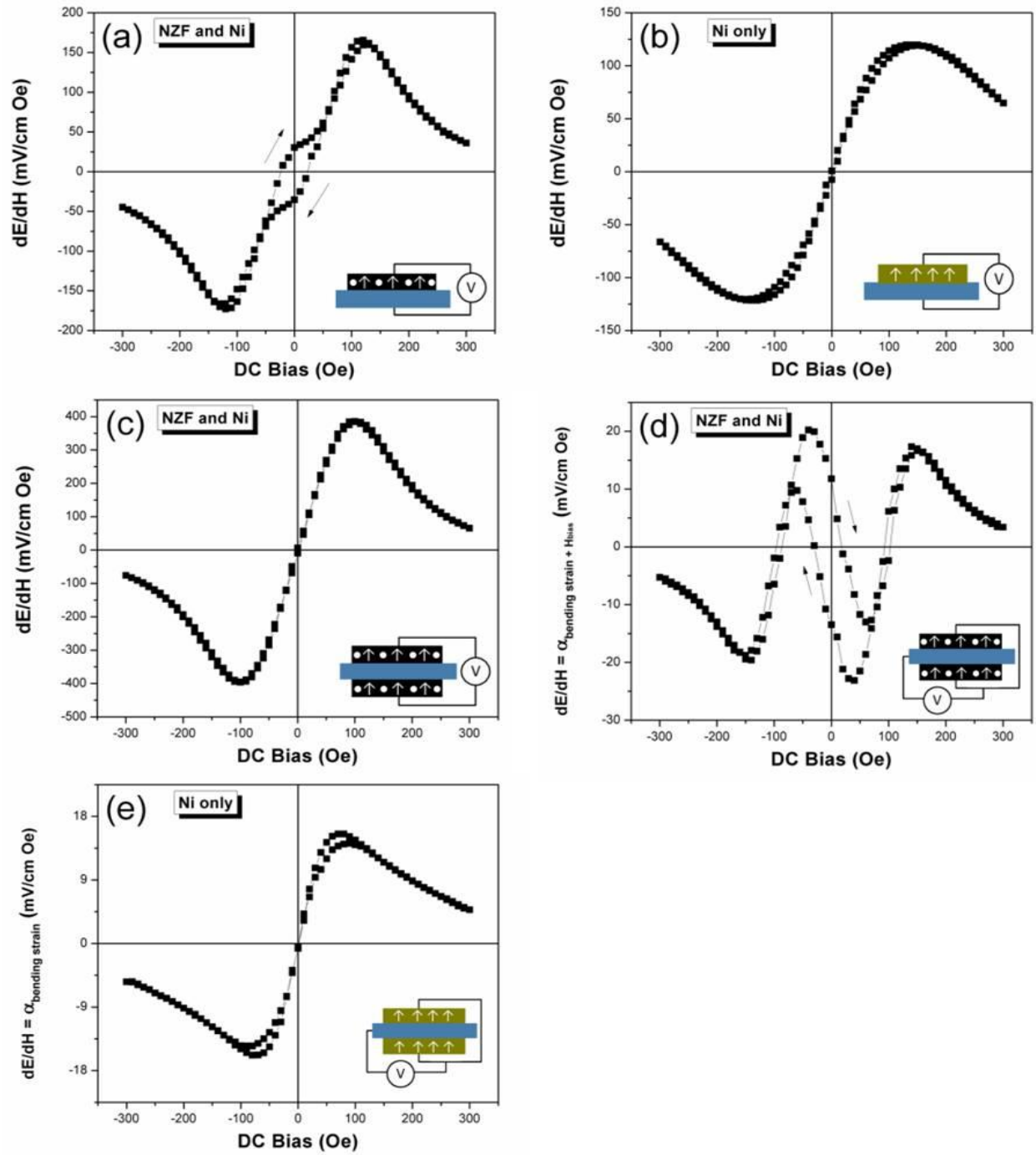


Figure 4-3. ME voltage coefficients for laminate composites. (a) KNNLS-NZF / Ni radial-mode bilayer, (b) KNNLS / Ni radial-mode bilayer, (c) KNNLS-NZF / Ni / KNNLS-NZF radial mode trilayer, (d) KNNLS-NZF / Ni / KNNLS-NZF bending-mode trilayer, and (e) KNNLS / Ni / KNNLS bending mode trilayer.

In order to illustrate the role of radial and bending vibration modes, impedance and phase spectra for bilayer and trilayer laminates under a small applied AC electric field are shown in Figure 4-4. It was found that KNNLS-NZF / Ni bilayer exhibited resonance peaks at 17.2, 35.9, and 55.8 kHz which were related to bending modes. KNNLS / Ni bilayer exhibited resonance peaks at 18.9, 38.9, and 60.0 kHz which were related to bending modes due to structural asymmetry. This structure represents the conventional unimorph. However, KNNLS-NZF / Ni / KNNLS-NZF RMT did not exhibit any peaks in the same range. The impedance measurements indicate that RMT composite had dominant radial mode at low frequencies. BMT exhibited low frequency resonance peaks at 18.4, 22.2, 40.9, 55.8, and 58.3 kHz. BMT without any NZF, given by KNNLS / Ni / KNNLS also exhibited resonance peaks at 18.8, 22.5, 41.3, and 58.8 kHz. Thus, both the BMT composites shown in Figure 4-3(d) and 1-7(e), exhibited bending resonance peaks but only the structure shown in Figure 4-3(d) had the self-bias magnetic response with zero-cross over points. This result confirms that the self-biased ME effect has prime contribution from the magnetic interaction between the NZF and Ni, or H_{bias} .

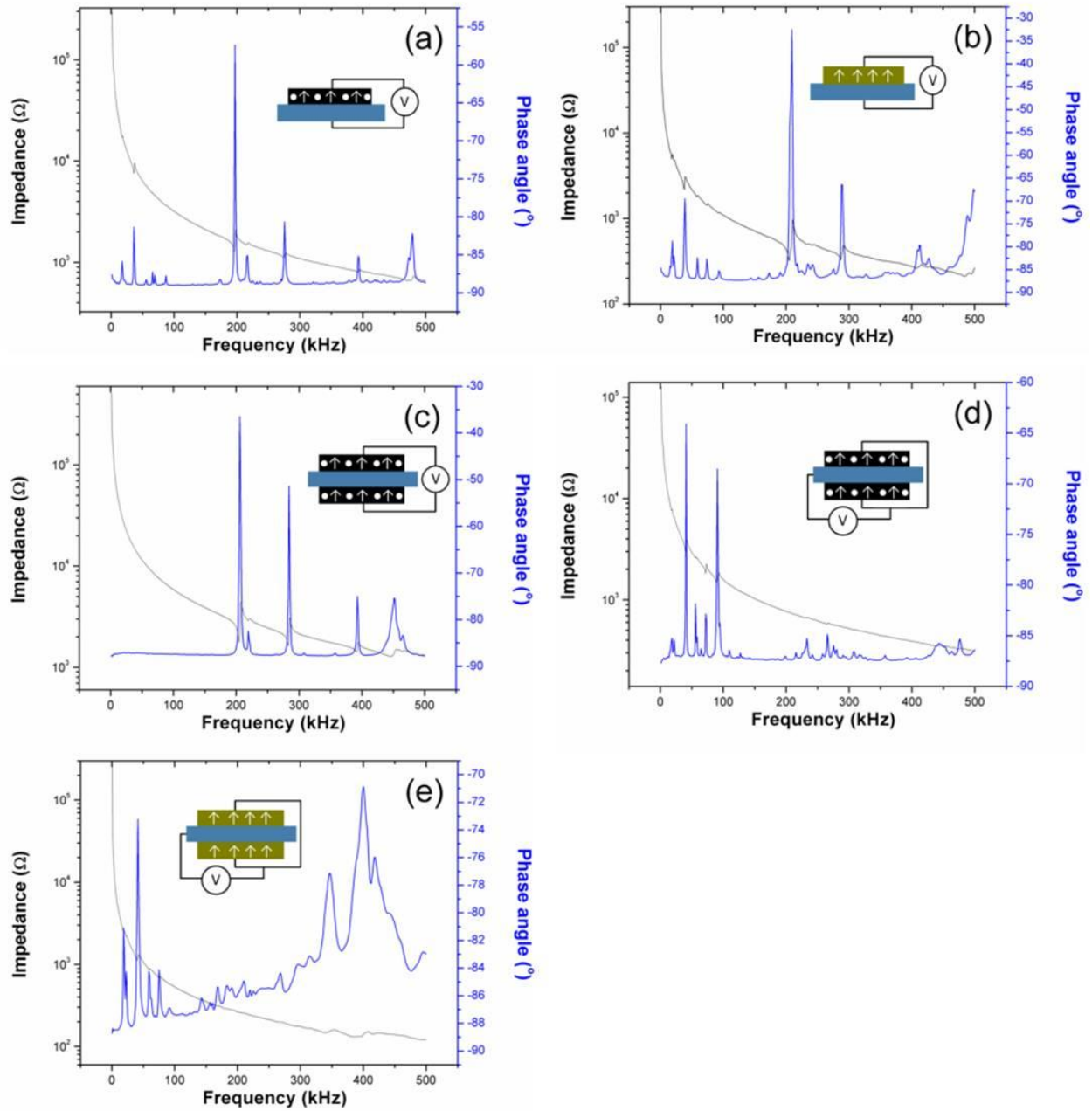


Figure 4-4. Impedance and phase spectra for bilayer and trilayer laminates under applied AC electric field. (a) KNNLS-NZF / Ni radial-mode bilayer, (b) KNNLS / Ni radial-mode bilayer, (c) KNNLS-NZF / Ni / KNNLS-NZF radial mode trilayer, (d) KNNLS-NZF / Ni / KNNLS-NZF bending-mode trilayer, and (e) KNNLS / Ni / KNNLS bending mode trilayer.

Figure 4-5 shows the variation of α_E for bilayer and trilayer laminates as a function of frequency from 0.1 to 60 kHz. ME response of KNNLS-NZF / Ni bilayer is shown in Figure 4-5(a), exhibiting peaks at bending mode frequencies of 17.2, 17.8, and 35.9 kHz under applied magnetic DC bias of $H_{\text{appl}} = 120$ Oe with an superimposed AC magnetic field of 1 Oe. Figure 4-5(b) shows that KNNLS / Ni bilayer without any NZF phase exhibited peaks at bending mode frequencies of 16.0 and 38.9 kHz under applied magnetic DC bias of $H_{\text{appl}} = 150$ Oe with an superimposed AC magnetic field of 1 Oe. In comparison to Figure 4-5(a), the ME peak near 35 kHz was reduced significantly in the absence of NZF. Thus, the ME peak at 35.9 kHz in Figure 4-5(a) is related to both magnetic interaction between Ni and NZF, and bending related to structural asymmetry. ME response of the RMT composite remained almost constant over the whole frequency range at magnetic DC bias of $H_{\text{appl}} = 96$ Oe with an AC magnetic field of 1 Oe, as shown in Figure 4-5(c). The magnitude of applied DC bias was determined from the ME peak obtained in Figure 4-3 for the corresponding laminate structures. ME response of BMT exhibited peaks at frequencies of 17.0, 18.2, 21.9, and 40.6 kHz under applied magnetic DC bias of $H_{\text{appl}} = 34$ Oe, and 17.0, 18.2, 21.9, 40.2 and 55.7 kHz under magnetic DC bias of $H_{\text{appl}} = 145$ Oe as shown in Figure 4-5(d). Near 40.6 kHz, the ME response at magnetic DC bias of $H_{\text{appl}} = 34$ Oe was higher than that at magnetic DC bias of $H_{\text{appl}} = 145$ Oe. Further near 55.8 kHz, there is a peak in ME response at magnetic DC bias of $H_{\text{appl}} = 145$ Oe which was not observed at magnetic DC bias of $H_{\text{appl}} = 34$ Oe. This result shows that in BMT composite the magnitude of H_{bias} changes with frequency and the magnitude of summation $\sum \vec{H}_{\text{appl}} + \vec{H}_{\text{bias}}$ determines the magnitude of α_E . The ME response of BMT without any NZF phase exhibited peaks at frequencies of 18.5, 23.3, 41.5, and 59.5 kHz under magnetic DC bias of $H_{\text{appl}} = 72$ Oe, as shown in Figure 4-5(e). These peak ME frequencies are related to bending only, quite similar to that

obtained for BMT with NZF phase at $H_{dc} = 145$ Oe in Figure 4-5(d). Therefore, magnetic interaction dominates the ME response in BMT with NZF phase at $H_{dc} = 35$ Oe and bending strain dominates the ME response in BMT with NZF phase at $H_{dc} = 134$ Oe.

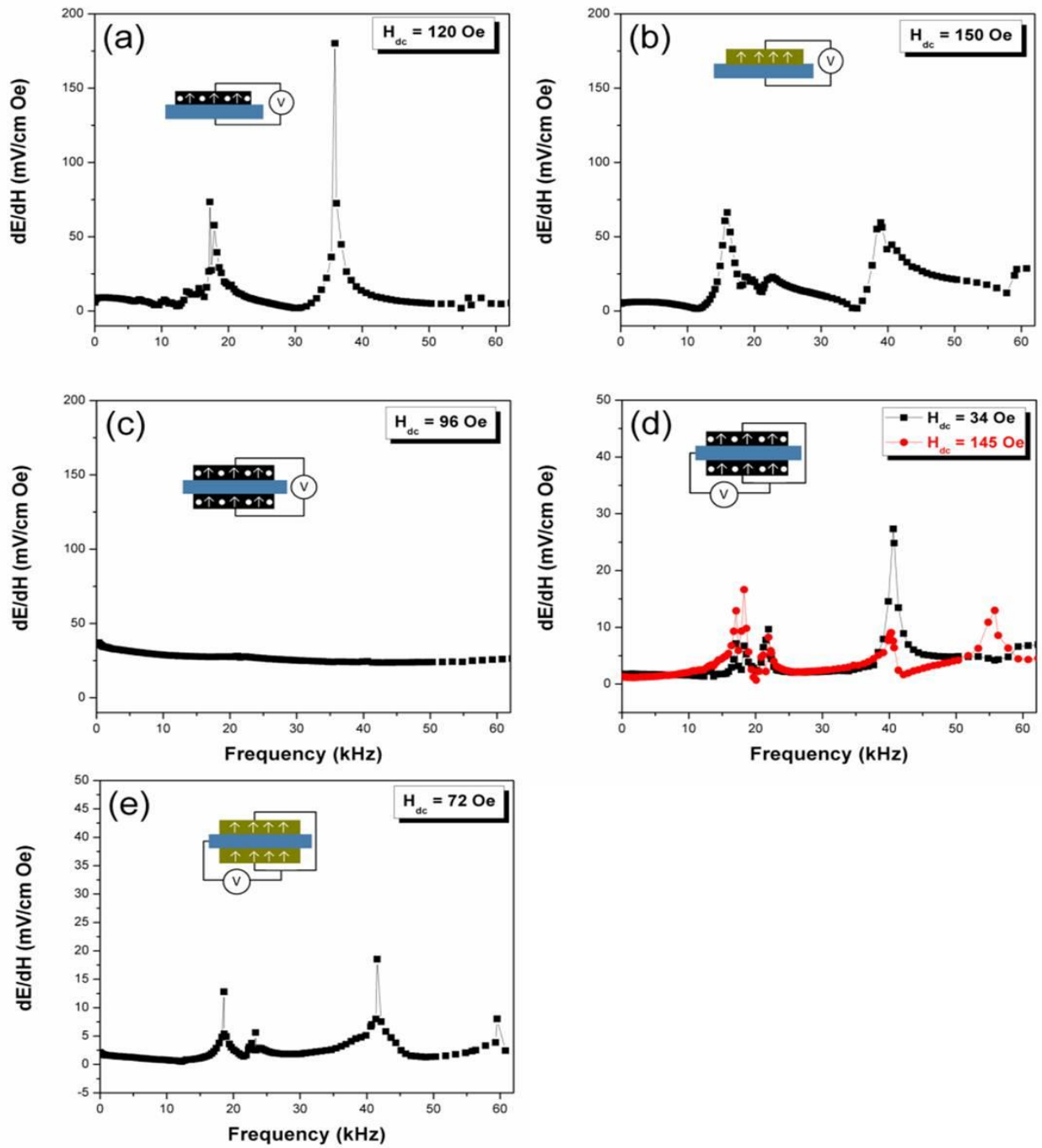


Figure 4-5. ME voltage coefficients for bilayer and trilayer laminates as a function of frequency from 0.1 to 60 kHz. (a) KNNLS-NZF / Ni radial-mode bilayer, (b) KNNLS / Ni radial-mode bilayer, (c) KNNLS-NZF / Ni / KNNLS-NZF radial mode trilayer, (d) KNNLS-NZF / Ni / KNNLS-NZF bending-mode trilayer, and (e) KNNLS / Ni / KNNLS bending mode trilayer.

Figure 4-6 shows the ME voltage coefficient for BMT as a function of magnetic DC bias at frequencies of 0.1, 10, 40.6, and 55.7 kHz under applied AC magnetic field of 1 Oe. At the non-resonance frequencies of 0.1 and 10 kHz, BMT has small remanent α_{ER} and two zero cross-over points of α_E , as shown in Figure 4-6(a) and 1-10(b). Further, at the frequency of 10 kHz, BMT has wide hysteresis near zero DC bias than that of BMT at the frequency of 0.1 kHz. At the resonance frequency of 40.6 kHz in Figure 4-6(c), BMT has high remanent α_{ER} of 147.3 mV/cm·Oe and one zero cross-over point of α_E . This data illustrates that increased ME coefficient at low DC bias magnetic field of 34.5 Oe leads to one zero cross-over point of α_E by reducing relative change of ME coefficient at high DC bias magnetic field of 134.2 Oe. At the resonance frequency of 59.5 kHz, BMT has remanent α_{ER} of 24.4 mV/cm·Oe and one zero cross-over point of α_E , as shown in Figure 4-6(d). It also illustrates that increased ME coefficient at magnetic DC bias of 169.3 Oe leads to only one zero cross-over point of α_E . This figure clearly shows the promise of this structure in providing the possible electrically tuned memory states, and leads us to the possibility of designing a magnetic field controlled memristor element.

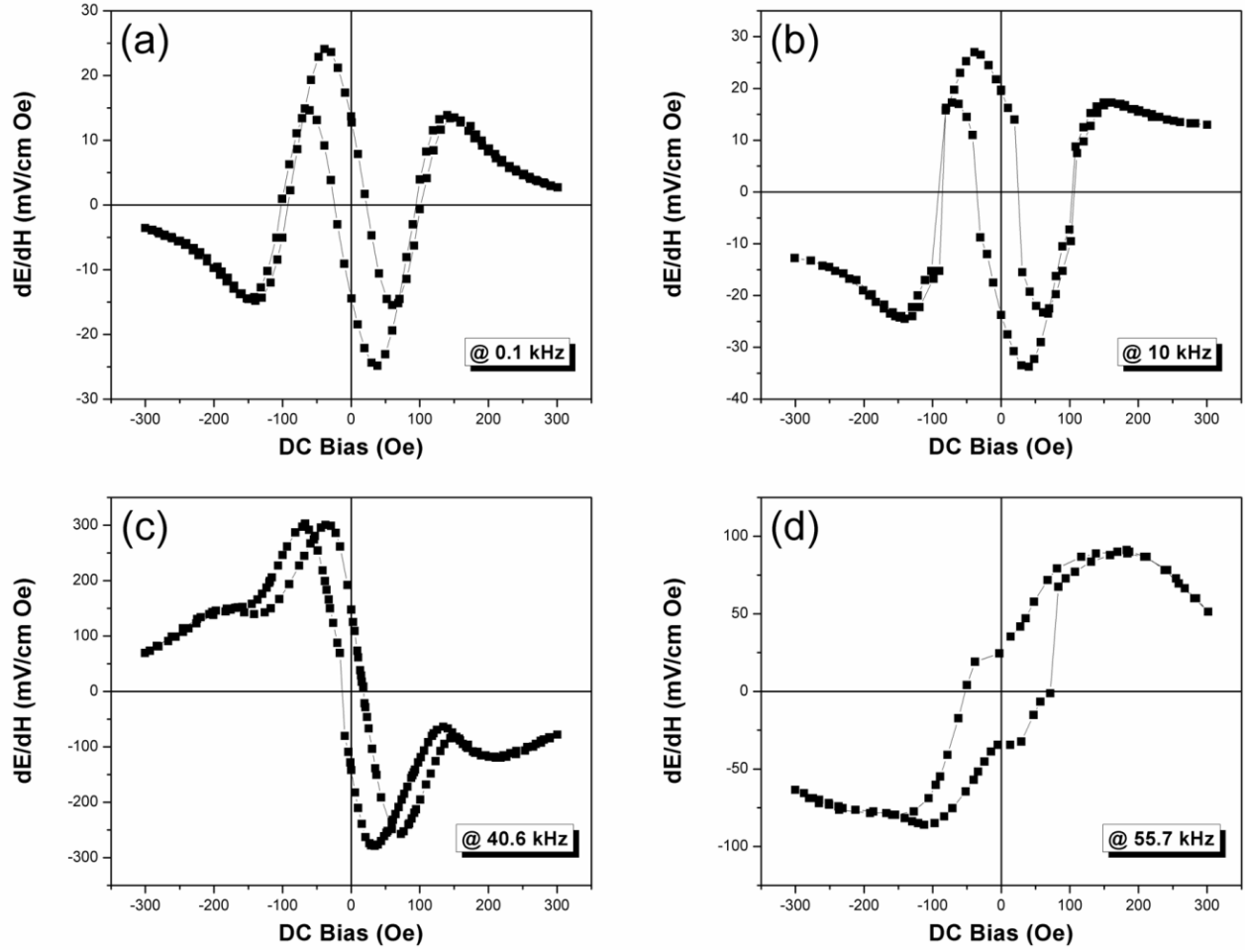


Figure 4-6. ME voltage coefficients for bending-mode KNNLS-NZF / Ni /KNNLS-NZF trilayer as a function of magnetic DC bias field at frequencies of (a) 0.1 kHz, (b) 10 kHz, (c) 40.6 kHz, and (d) 55.7 kHz.

The ME response of BMT as a function of frequency can be calculated from the measured values of α_E for the KNNLS-NZF / Ni / KNNLS-NZF BMT and KNNLS / Ni / KNNLS BMT laminates. Figure 4-7(a) – (c) summarizes the role of magnetic interaction and bending strain on the hysteresis in ME voltage coefficients (α_E). Figure 4-3(d) and (e) show the measured values of α_E for KNNLS-NZF / Ni / KNNLS-NZF BMT and KNNLS / Ni / KNNLS trilayer. Please note that the structure in Figure 4-3(d) has NZF phase so there is magnetic interaction with Ni, while that in Figure 4-3(e) does not have any NZF phase. Besides this difference, the electrical connections and layer dimensions are exactly similar in both the cases. Comparing Figure 4-3(d) and (e), one can immediately notice that magnetoelectric hysteretic response requires the presence of magnetic interaction. Subtracting the magnitude of magnetoelectric coefficient in Figure 4-3(e) ($\alpha_{\text{bending strain}}$) from that in Figure 4-3(d) ($\alpha_{\text{bending strain} + H_{\text{bias}}}$), one can delineate the contribution arising from the magnetic interaction, or $\alpha(H_{\text{bias}})$ as shown in Figure 4-7(a). Next, the role of H_{bias} can be understood by increasing its contribution to the overall magnetoelectric response. Figure 4-7(b) plots the magnetoelectric coefficient given as $\alpha_{\text{low-frequency}} = (\alpha_{\text{bending strain} + H_{\text{bias}}} + 0.5 \alpha_{H_{\text{bias}}})$, which resembles the data shown in Figure 4-6(a) and (b) at low frequencies. This indicates that by increasing the contribution related to magnetic interaction in proportion to that of bending strain, high remanent α_{ER} and narrow hysteresis near zero DC bias were induced. Figure 4-7(c) plots the magnetoelectric coefficient given as $\alpha_{\text{high-frequency}} = (\alpha_{\text{bending strain} + H_{\text{bias}}} + 2.5 \alpha_{\text{bending strain}})$, which resembles the behavior obtained at resonance frequency of 55.7 kHz as shown in Figure 4-6(d). These calculations show that a linear relation between the contributions from the magnetic interaction and bending strain leads to emergence of remanent α_{ER} and zero cross-over point of α_E . The increase in contribution from the bending strain leads to increase in the magnitude of α_E and suppresses the peaks at higher

magnetic DC bias. As a result, the BMT's hysteresis and remanent α_{ER} with first cross-over point of α_E dominantly depend on magnetic interaction than bending strain. On the contrary, bending strain is dominant than magnetic interaction for magnitude of α_E at high DC bias with second cross-over point of α_E .

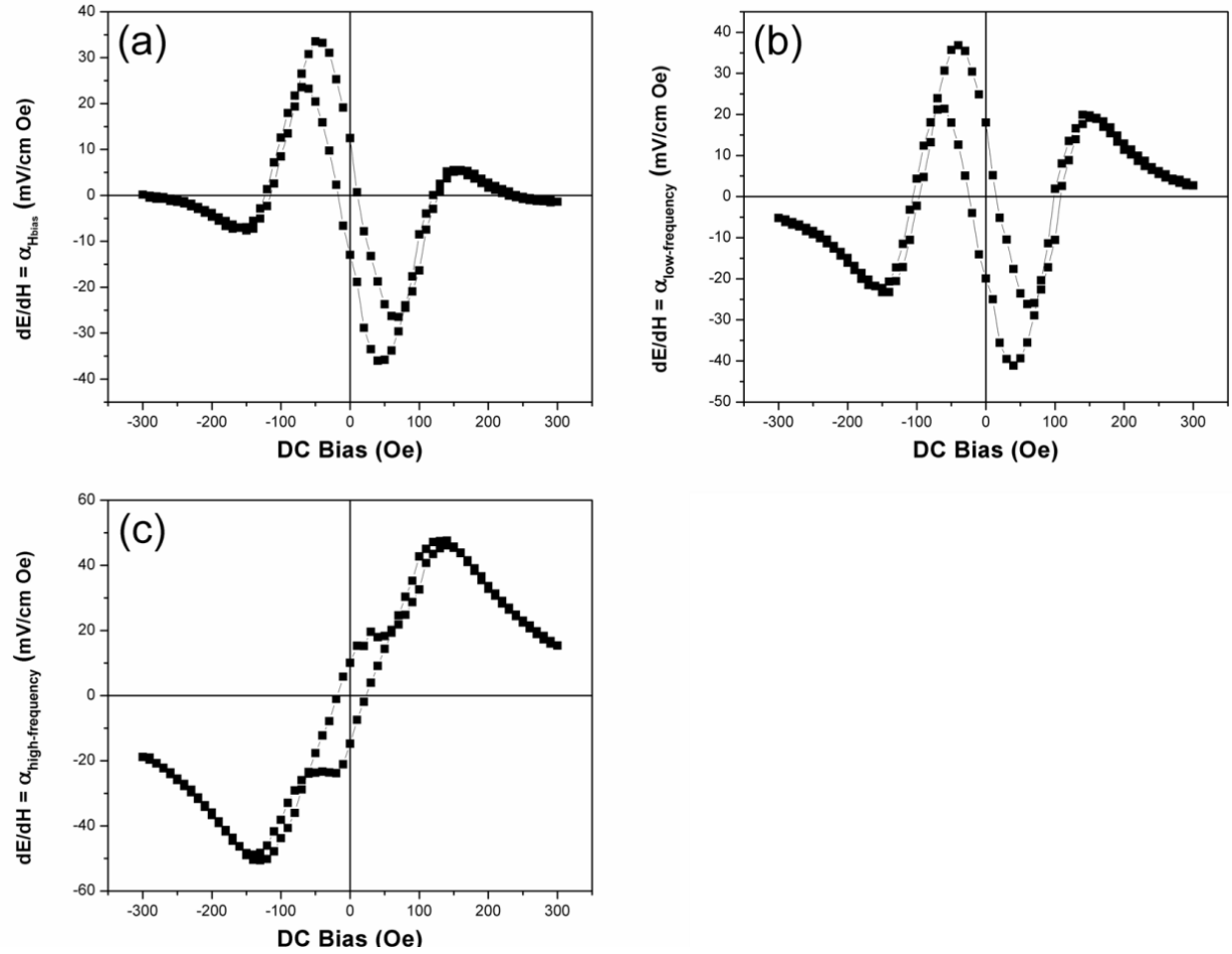


Figure 4-7. ME voltage coefficients calculated by using measured values of KNNLS – NZF / Ni / KNNLS – NZF ($\alpha_{bending\ strain + H_{bias}}$) and KNNLS / Ni / KNNLS ($\alpha_{bending\ strain}$) trilayer , (a) $\alpha(H_{bias})$, (b) $\alpha_{low-frequency} = (\alpha_{bending\ strain + H_{bias}} + 0.5 \alpha_{H_{bias}})$, and (c) $\alpha_{high-frequency} = (\alpha_{bending\ strain + H_{bias}} + 2.5 \alpha_{bending\ strain})$.

4. 2 Effect of materials composition on magnetoelectric hysteretic behavior

For experimental approach in self-biased ME laminates, variation of material composition of x KNNLS – $(1 - x)$ NZF was conducted with $x = 0.9, 0.8$, and 0.7 in the laminate configuration as shown in Figure 4-8. KNNLS-NZF / Ni / KNNLS-NZF bimorph laminates were fabricated by bonding Ni foils with dimension of $15 \times 15 \text{ mm}^2$ between two KNNLS-NZF disks with diameter of 10 mm. Each layer of Ni and KNNLS- NZF had a thickness of 0.5 mm and the bimorph laminates were operated in L-T mode. Magnetic properties of λ and q for Ni plate were measured in the range of 0 – 1000 Oe as shown in Figure 4-9. It can be seen that Ni plate exhibited high strain of $\lambda_{11} = -29 \text{ ppm}$ and $\lambda_{12} = 22 \text{ ppm}$ and peak piezomagnetic coefficient of $q_{11} = -0.14 \text{ ppm/Oe}$ and $q_{12} = 0.14 \text{ ppm/Oe}$ below applied H of 100 Oe.

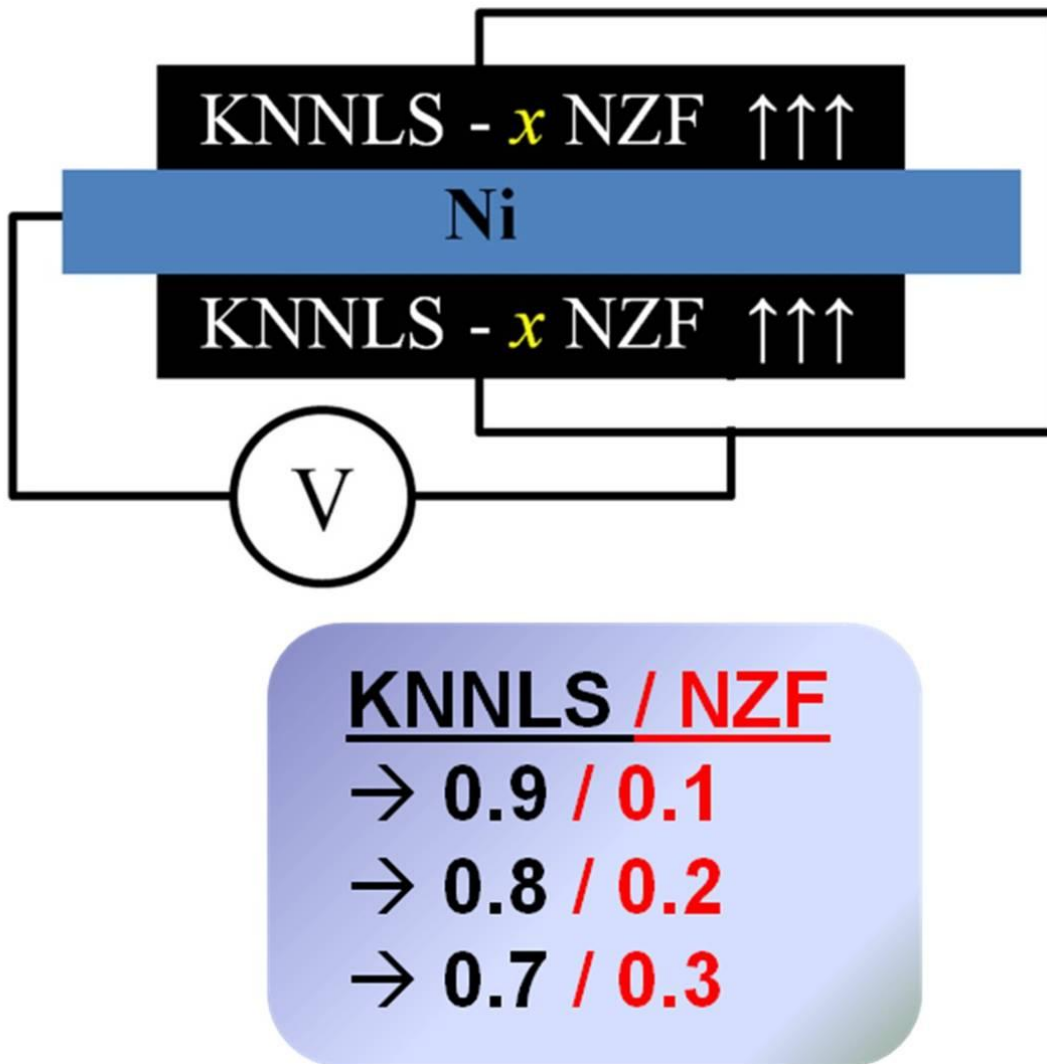


Figure 4-8. Schematic diagram for ME laminate composites with variation of materials composition. $(1 - x)$ KNNLS – x NZF / Ni / $(1 - x)$ KNNLS – x NZF with $x = 0.1, 0.2$ and 0.3 .

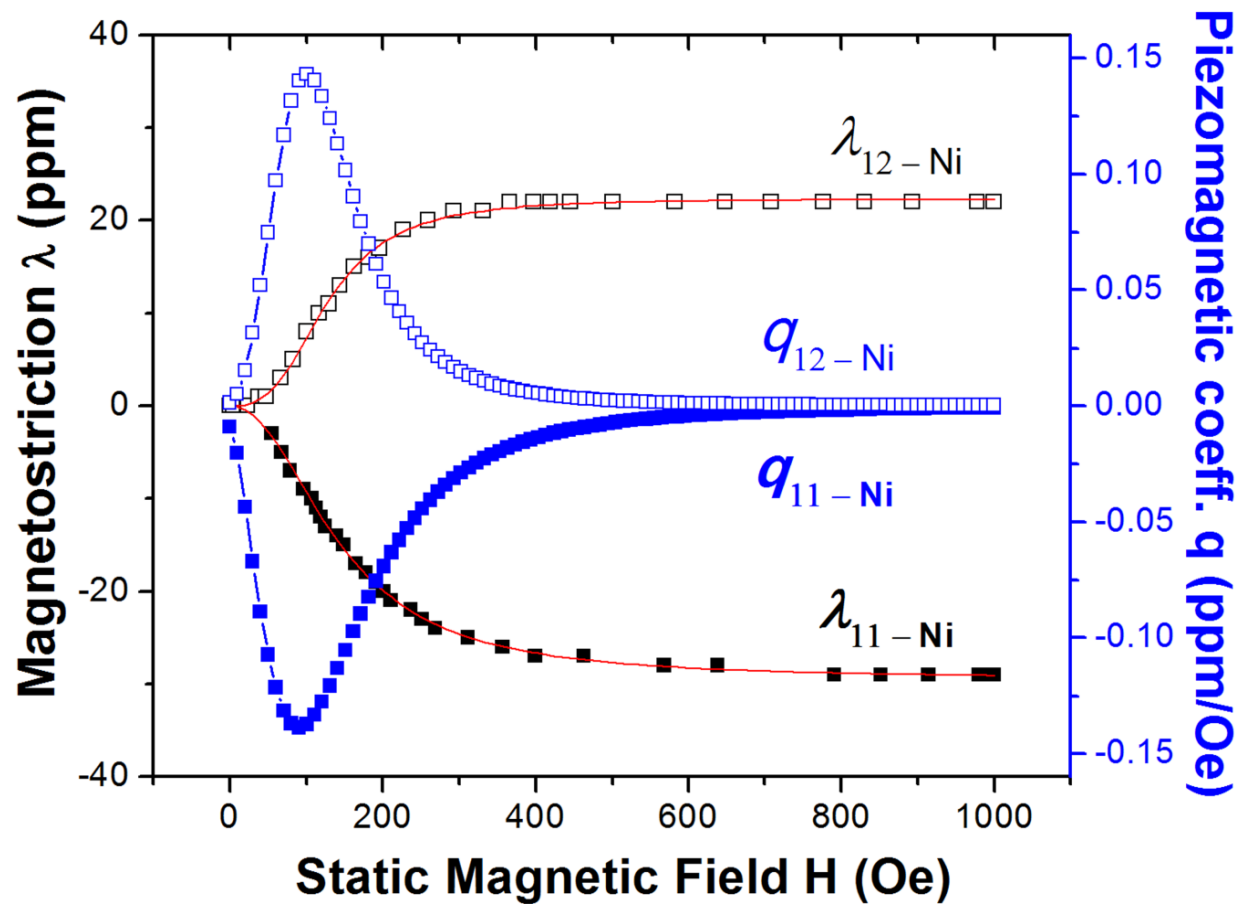


Figure 4-9. Magnetostrictions and piezomagnetic coefficients for Ni plate.

Figure 4-10 (a) shows the variation of α_E for BM laminates measured by applying H_{bias} with $H_{ac} = 1$ Oe at 1 kHz. The changes in the shape of ME hysteresis could be associated with increase of the magnetic interactions between NZF islands and Ni and decrease of the bending effect. The BM laminate with $x = 0.1$ was found to exhibit ME hysteresis with sharp slope, maximum α_E of 35.1 mV/cm·Oe, high remanent ME coefficient α_{ER} of 21.4 mV/cm·Oe, and constant α_E in the wide range of magnetic field $0 \sim 75$ Oe. This ME behavior with sharp slope and wide band-width can provide the possibility for low-field high sensitivity magnetic sensors and electrically tuned memory states. As NZF concentration increases, the magnitude of α_E in the range of $H_{bias} > 100$ Oe was found to decrease while the magnitude of α_{ER} initially decreases and then slightly increases. The sensitivity of the BM laminates shown in Figure 4-10(b) – (d) was smaller than the RM laminates. This is mainly related to the fact that the measurement are confined in the small magnetic field region near origin where the slope in the output voltage curve is smaller and also the noise factor for bending vibrations is higher.

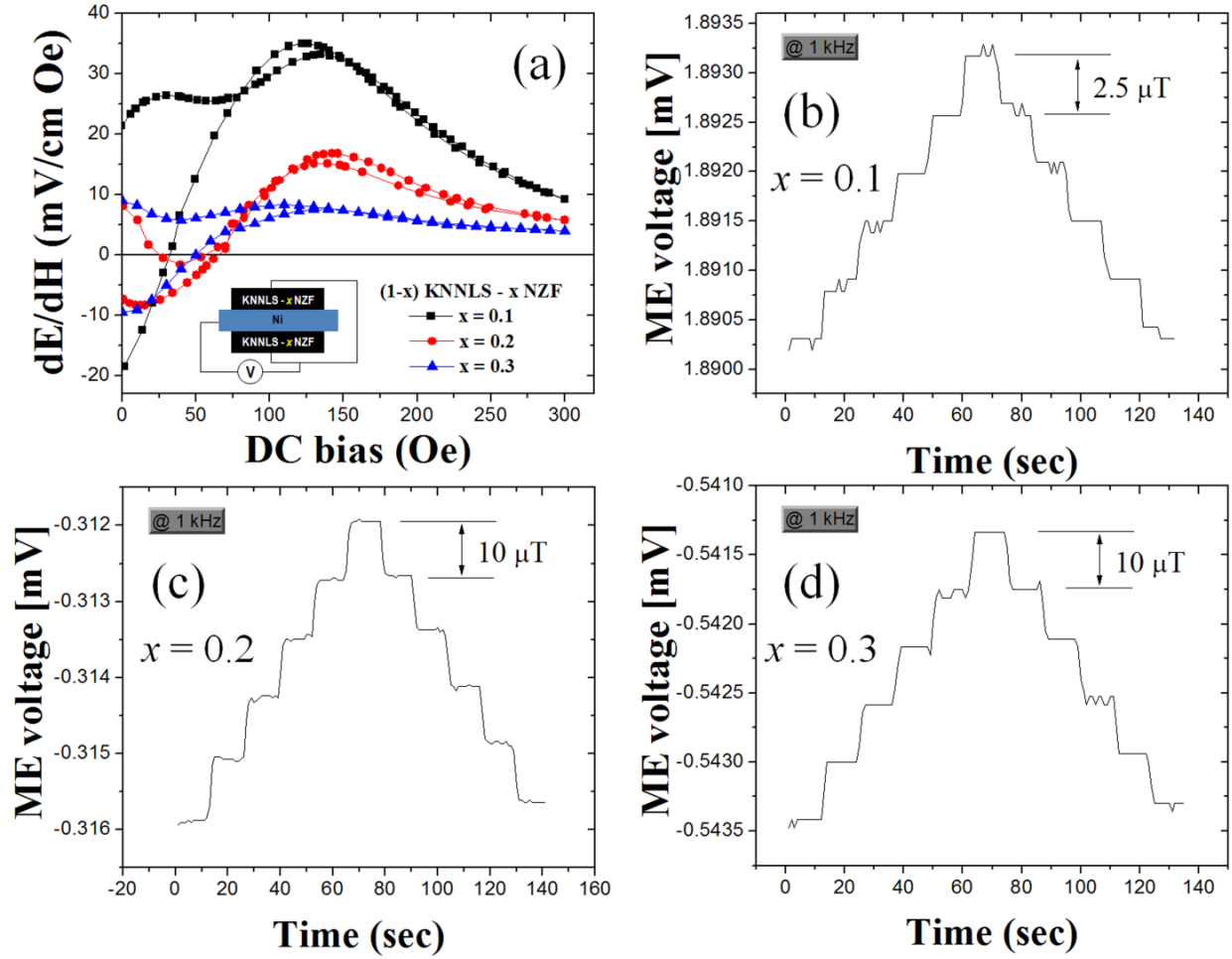


Figure 4-10. (a) ME coefficient and sensitivity limit of dc magnetic field for bending mode laminates. (b) $x = 0.1$, (c) $x = 0.2$ and (d) $x = 0.3$.

The effect of material composition on ME hysteresis in the BM laminates is shown in Figure 4-11. The magnitude of α_{ER} and α_E in the range of $H_{bias} > 100$ Oe were mainly dependent on piezoelectric property and bending strain while the shape of ME hysteresis was dependent on magnetic interactions between Ni and NZF. The limit of DC magnetic field sensitivity for BM laminates at 1 kHz was found to be: 2.5 μ T for $x = 0.1$, and 10 μ T for $x = 0.2$ and 0.3 as shown in Figure 4-10(b) – (d). It can be seen in this Figure that BM laminates with $x = 0.2$ and 0.3 were found to exhibit negative values of ME voltage while the laminate with $x = 0.1$ was found to exhibit positive values at the zero DC bias. This change is mainly related to the magnetic interactions occurring between Ni and NZF leading to hysteresis between the forward and backward sweeps. From Figure 4-11(a) – (c), it can be seen that there is transition from positive bias (+ve ME coefficient at zero H) to negative bias. This transition cannot be solely explained in terms of the combination of bending strain and magnetic interaction (quantified by the bias field arising from difference in susceptibility of nickel and NZF). Rather, the NZF island shape, size and distribution in the KNNLS matrix should play an important role. This is expected as the shape of the pseudo-cubic or tetragonal magnetostrictive phase under bias will result in anisotropic response. In order to capture this effect, the changes in piezoelectric coefficient as a function of averaged Fe/Nb ratio were measured. The deviation from the linear rate of decrease in the piezoelectric coefficient has some correspondence with the anisotropy of the island – matrix microstructure. A proper model for the composite will thus be a function of all these variables, namely $\Delta V = f(H_{bias}, \Delta x_{composite}, \theta_{NZF}, R_{NZF})$, where θ represents the NZF distribution or homogeneity factor and R represents the size of islands. Using the results from this figure the BM laminates can be designed to exhibit various varying shapes for ME hysteresis as exemplified in Figure 4-11.

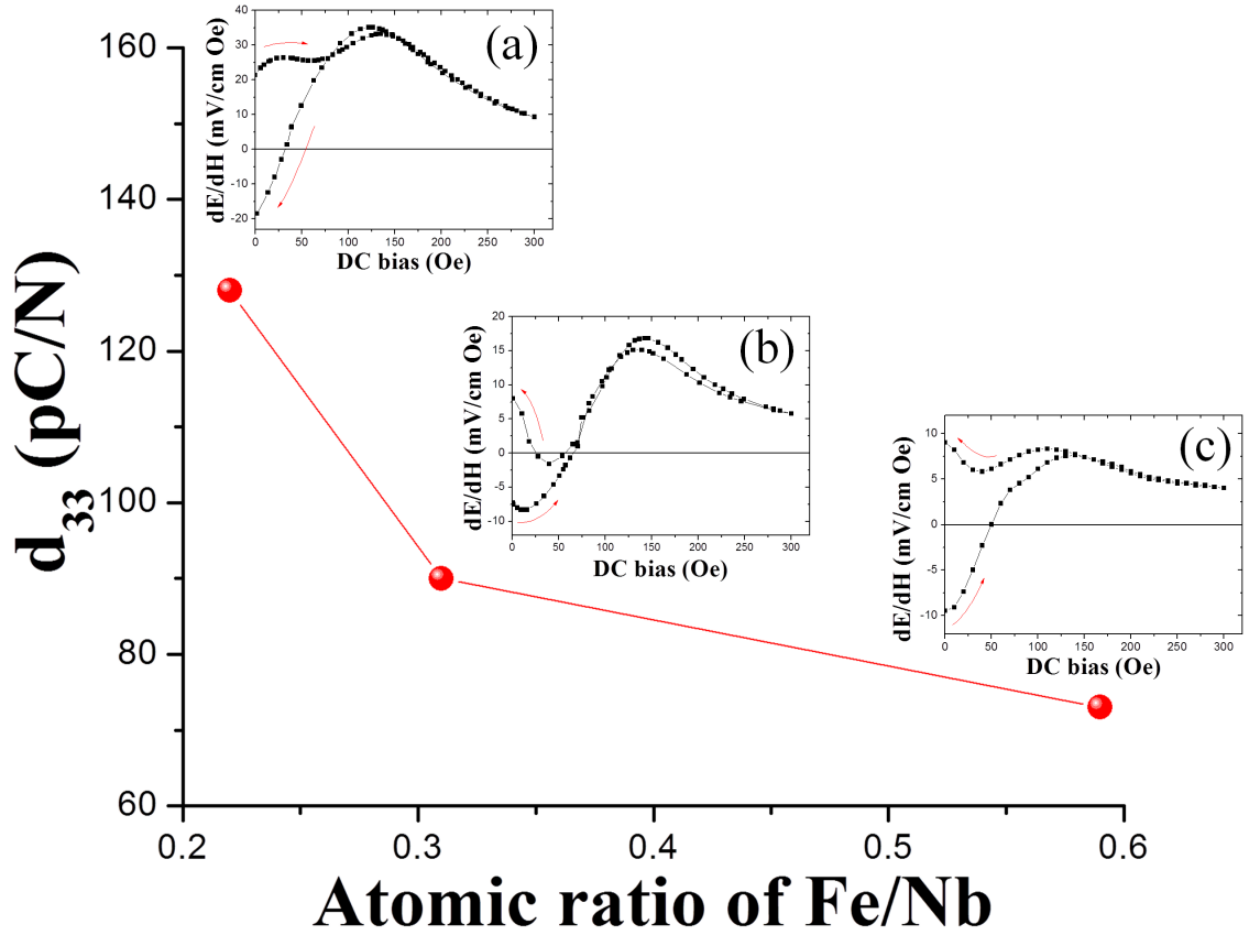


Figure 4-11. Longitudinal piezoelectric strain coefficient for $(1 - x)$ KNNLS – x NZF composites as a function of atomic ratio of Fe/Nb. Insets are ME hysteresis for $(1 - x)$ KNNLS – x NZF / Ni / $(1 - x)$ KNNLS – x NZF bending mode laminates: (a) $x = 0.1$, (b) $x = 0.2$ and (c) $x = 0.3$.

4.3 Direct and converse magnetoelectric effect

The configuration of three-phase ME composite laminates and the DME and CME measurement setup were described in Figure 4-12. First, 0.8 [0.948 ($\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$) – 0.052 (LiSbO_3)] – 0.2 [$\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$] (KNNLS-NZF) ME particulate composite disks with diameter of 10 mm and thickness of 0.5 mm were fabricated. The disks were bonded to the nickel foil in 2-2 laminate configuration and electrical connections were made to operate the sample in bending mode configuration.

Figure 4-13(a) and (b) show the change in α_{DME} and α_{CME} coefficients in three-phase ME laminate as a function of H_{bias} at off-resonance frequency of 1 kHz. The α_{DME} shows a clear hysteretic behavior during H_{bias} sweep with remanent α_{DME} value of $\sim \pm 30$ mV/cmOe at $H_{\text{bias}} = 0$ as shown in Figure 4-13(a). The shape of α_{DME} can be controlled by adjusting the concentration of NZF (i.e. effect of built-in bias) or by modifying the structure of laminate.^{9,10} The laminate used in this work was optimized to show the peak α_{DME} value at $H_{\text{bias}} = 0$ for clear observation of self-biased effect. The trend of α_{DME} with respect to the sweep directions (arrowed curves [1] and [2]) was the same. As seen in Figure 4-13(b), the laminate showed CME effect with trend similar to that of DME effect. Remanent α_{CME} of $\sim \pm 2.6 \times 10^{-6}$ mGauss·cm/V under $H_{\text{bias}} = 0$ Oe was observed with hysteresis shape similar to α_{DME} case clearly demonstrating that self-biased effect in this system is present not only for DME but also for CME effect. Note that even without pre-cycling of H_{bias} the self-biased DME and CME effects (initial remanent α_{DME} and α_{CME} values in the absence of H_{bias}) can be obtained by only applying AC magnetic and AC electric fields respectively. Similar tendency in hysteretic behavior between α_{DME} and α_{CME} reflects that the effect of λ and/or q of ferromagnetics on H_{bias} dependence of ME effect is basically identical for both DME and CME cases. Considering the relation $\alpha \propto q = d\lambda/dH_{\text{bias}}$, the effective λ behavior

can be estimated by integrating α with respect to the H_{bias} as shown in Figure 4-13(c). Arrowed curves [1] and [1'] of Figure 4-13(c) correspond to the same H_{bias} sweep directions with [1] and [1'] in Figure 4-13(a) and (b), respectively. Note that Figure 4-13(c) shows only the qualitative nature of effective λ behavior of the laminate and not quantitative values. Homogeneous ferromagnetic systems (individual NZF and Ni) usually show a symmetrical biquadratic λ behavior with respect to H_{bias} with $q = 0$ at $H_{\text{bias}} = 0$ as shown in Figure 4-13(d). However, in the heterogeneous ferromagnetic system (NZF + Ni), the position of $q = 0$ was shifted from $H_{\text{bias}} = 0$ to point (i) in Figure 4-13(c) and the tendency of λ was not symmetric any more. In DME case, at the point (i) in Figure 4-13(c), there is no change in λ under small variation of magnetic field (δH_{ac}) implying that in this state magnetic domain rotation and domain wall migration becomes difficult. Therefore, no effective mechanical strain or stress can be delivered to ferroelectric phase resulting in zero-crossing α_{DME} point (i) in Figure 4-13(a). Analogously, in CME case, since the generation of mechanical strain was restricted by domain pinning at point (i') in Figure 4-13(c), quasi-piezomagnetic effect was minimized showing zero-crossing α_{CME} point (i') in Figure 4-13(b). However, at zero-bias points (ii) and (ii') in Figure 4-13(c), the slope of effective λ has a finite value (the maximum value in the system). This large slope in λ reflects easy domain rotation under δH_{ac} or δT_{ac} , (T_{ac} : stress) resulting in strain generation and magnetization. Therefore, both DME and CME effect can be maximized under $H_{\text{bias}} = 0$ at points (ii) and (ii') in Figure 4-13(a) and (b) respectively. Different magnetic properties of NZF and Ni, including different λ behavior in Figure 4-13(d), and resultant interaction between built-in bias and H_{bias} are at the origin of the shifted and non-symmetrical shape of effective λ in Figure 4-13(c) resulting in self-biased effect. Based on this hypothesis, the λ generated on the surface of KNN-NZF disk of the laminate during H_{bias} sweep was measured. As seen in Figure 4-13(d), the

measured λ of the laminate clearly revealed the shift in curve with similar trend as obtained by integration value of α in Figure 4-13(c). Although this measured λ value may not reflect the exact magnitude of total λ of the laminate, the shifted and unsymmetrical shape well explains the cause of self-biased ME phenomena.

Results from the studies conducted on metal-bonded ferrite composites further help in explaining the results of Figure 4-13. Chen et al. have shown that CoFe_2O_4 bonded with Ag and Ni exhibits higher slope of magnetostriction $(\partial\lambda/\partial H)_\sigma$ at low applied fields (1.3×10^{-9} m/A) which is comparable to that of polycrystalline Terfenol. It was pointed out that this high magnitude of piezomagnetic coefficient was due to easier reversible motion of 90° domain walls between the pinning sites. However, if the pinning sites release the domain wall under higher effective field of stress than a hysteretic change in the magnetic response is obtained. This hysteretic response is amplified by the changes in the sign of magnetostriction coefficient and local variation of magnetic properties both of which are possible in the particulate sintered composites bonded to nickel foil.

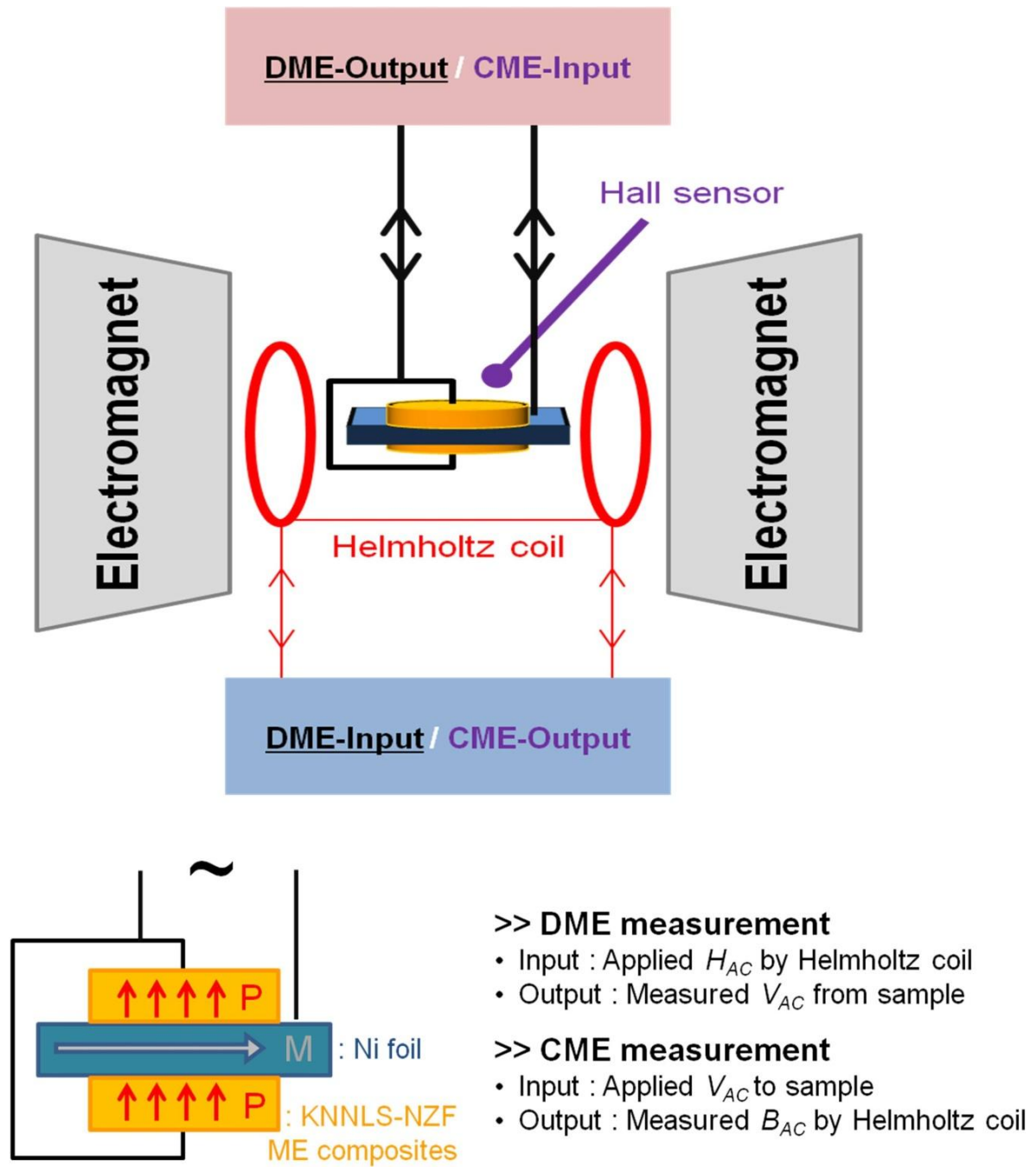


Figure 4-12. Configuration of bending-mode for three-phase laminate of KNNLS-NZF / Ni / KNNLS-NZF and schematic diagrams for DME and CME measurements.

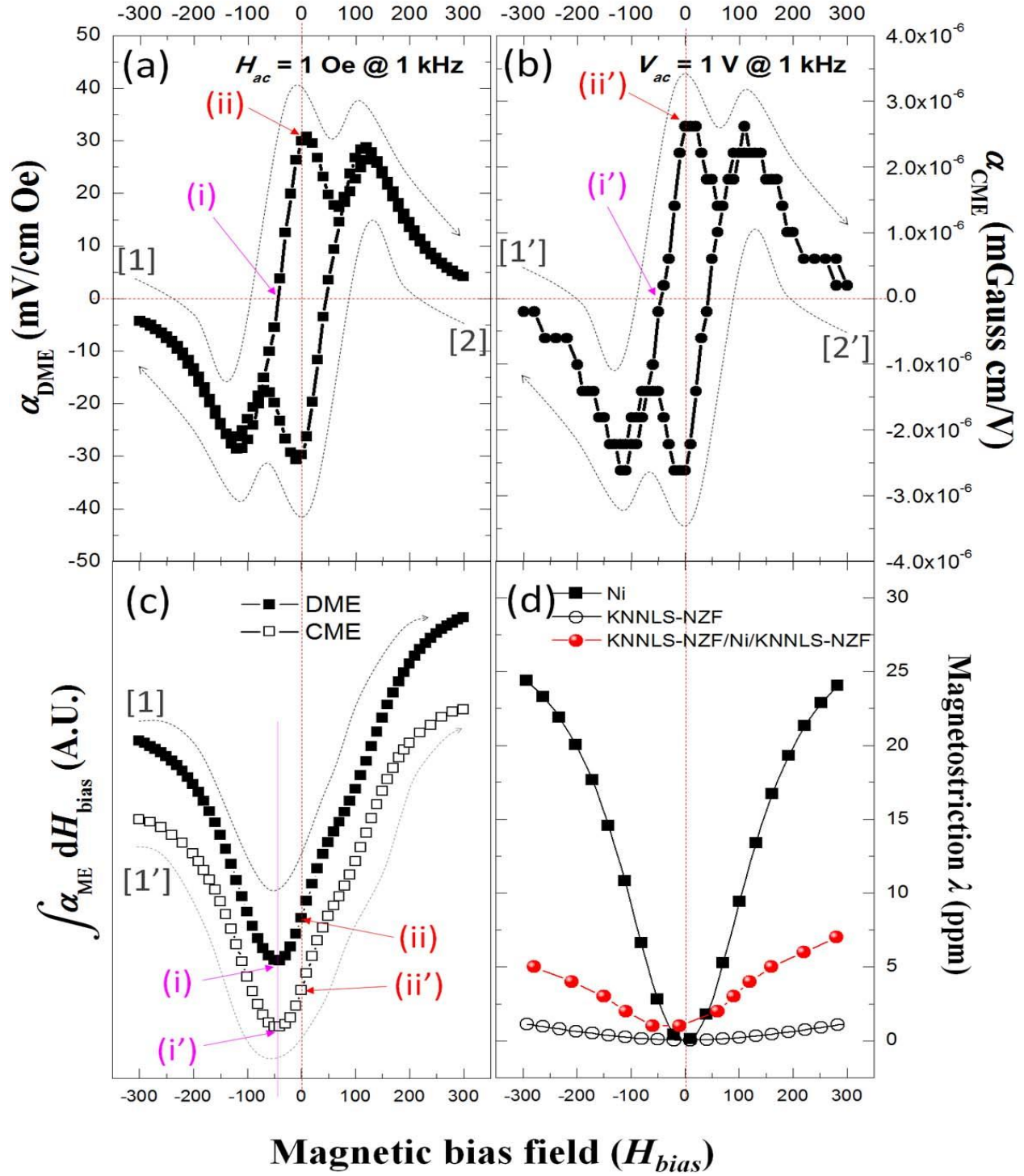


Figure 4-13. (a) α_{DME} and (b) α_{CME} coefficients as a function of H_{bias} , (c) Integral values of α_{DME} and α_{CME} with respect to the H_{bias} , and (d) Magnetostriction of Ni, KNNLS-NZF, and bending mode KNNLS-NZF / Ni / KNNLS-NZF as a function of H_{bias} .

It is well-known that ME response of composites is enhanced at electromechanical resonance of piezoelectric phase. Therefore, the frequency dependence of DME and CME response in three-phase laminate was investigated. Figure 4-14(a) shows the impedance spectrum of the laminate. The first resonance peak for mechanical bending mode due to the electrical connection with 180° current phase difference between top and bottom KNNs (B1 mode) was found at 47 kHz. However, another small resonance peak was observed at 21 kHz which is not the B1 mode resonance. This additional bending vibration mode (B2 mode) is possibly due to the slight asymmetry of top and bottom KNN disks. Note that if the laminate had perfect structural and compositional symmetry, the voltage generation would be completely zero under longitudinal magnetic field due to the 180° voltage phase difference between top and bottom KNNs.⁸ Figure 4-14(b) and (c) illustrate the DME and CME response of the laminate in the same frequency range under applied $H_{bias} = 0$ and 100 Oe. Under zero H_{bias} condition, both α_{DME} and α_{CME} values exhibited maximum enhancement at 21 kHz and much weaker response at 47 kHz. However, under $H_{bias} = 100$ Oe, the maximum response was observed at 47 kHz while smaller value was observed at 21 kHz for both DME and CME cases. This opposite trend between $H_{bias} = 0$ and 100 Oe cases indicates that (i) the bending motion from built-in bias (self-biased effect) corresponds to the B2 mode and does not include B1 mode vibration, and (ii) under high H_{bias} , the built-in bias contribution for the laminate is reduced and overall vibration mode is dominated by the B1 bending mode. It should be noted that the laminate system used in this work does not have effective net magnetic gradient because of NZF/Ni/NZF symmetry (zero net built-in bias). Moreover, when no bending motion is incorporated into this structure, no self-biased effect is observed.⁹ These facts imply that initial bending strain is required to activate interaction between built-in bias and δH_{ac} or δT_{ac} in this system. The initial bending strain is created by B2 mode

vibration which is from the structural and compositional asymmetry of KNNs. From this result, two important points can be noticed: (i) the frequency dependence of CME effect shows tendency similar to that of DME effect in both magnetic zero-biased and biased conditions, and (ii) even though there is no initial magnetic gradient in the system, self-biased effect can be achieved by applying external bending strain.

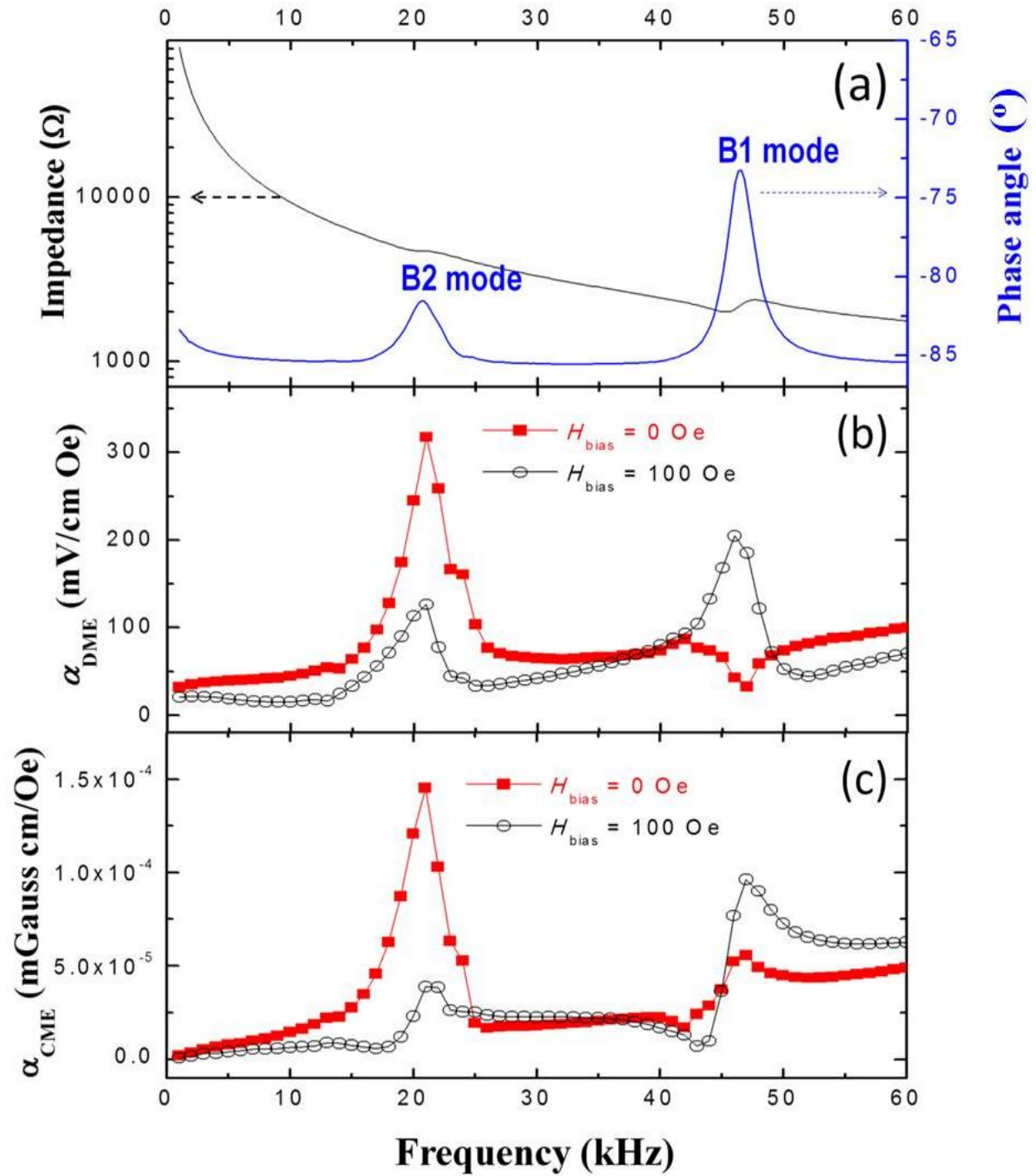


Figure 4-14. (a) Impedance and phase spectra for three-phase laminate under applied AC electric field, (b) α_{DME} and (c) α_{CME} as a function of frequency under applied H_{bias} of 0 and 100 Oe.

The CME effect of the ME composites is of technological importance for the potential applications such as core-free magnetic flux control devices and electrically controlled magnetic memory devices. However, all the previous investigations on the CME effect have revealed that additional H_{bias} is necessary for the maximum CME response alike the DME case. By eliminating additional H_{bias} , significant technical improvement of CME devices can be realized, e.g., the size reduction of devices and the exclusion of interference effect by electromagnet or permanent magnet. Figure 4-15 shows the magnetic flux density of the laminate generated by periodically applying AC voltage (V_{ac}) of 1 V at 21 kHz under $H_{bias} = 0$ Oe. The result clearly shows generation of magnetic flux density of 0.012 mGauss with reliable repeatability in the absence of external H_{bias} . Furthermore, linear increase in magnetic flux was observed with increasing applied voltage as shown in the inset of Figure 4-15 indicating promising application feasibility for tunable magnetic field generator.

In this chapter, the self-biased ME effects were discovered in the three-phase laminates consisting built-in bias under bending configuration. Further, experimental confirmation for self-biased ME effect were successfully conducted and various hysterical ME responses could be controlled by variation of material composition in the $(1 - x)$ KNNLS – x NZF / Ni / $(1 - x)$ KNNLS – x NZF system. Finally, self-biased DME and CME effects were observed in bending mode laminates consisting of heterogeneous ferromagnetic. The hysteretic behavior of ME response with remanent α values and zero-crossing characteristics of α were explained by the shift of magnetostriction curve of ferromagnetics caused by interaction between built-in bias and external magnetic bias. The result of this chapter predicts that self-biased ME effect may arise even in homogeneous ferromagnetic system when the external bending strain activates built-in bias.

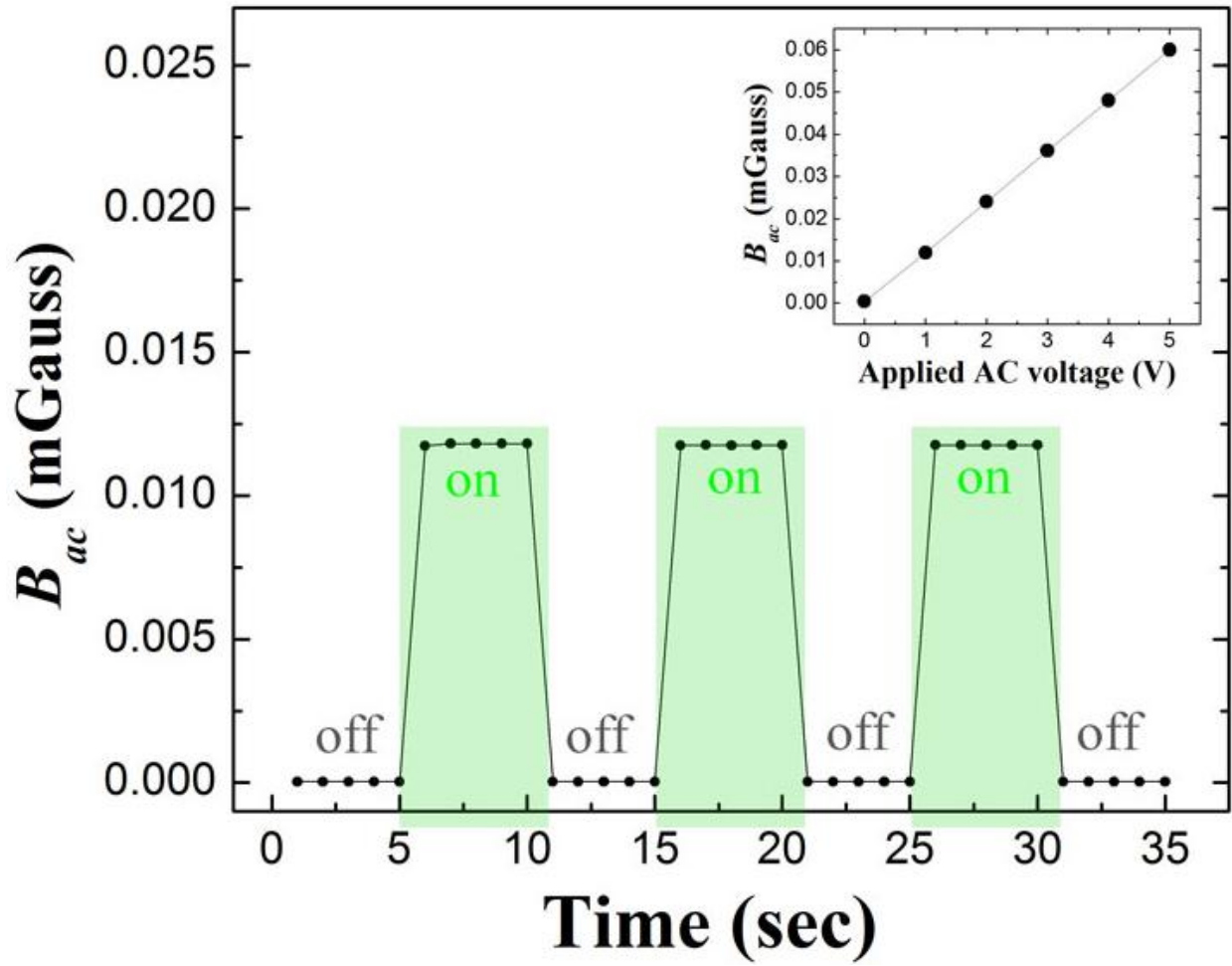


Figure 4-15. Magnetic flux density under $H_{bias} = 0$ Oe measured by periodically applying AC voltage of 1 V at 21 kHz. Inset shows the change in magnetic flux density with increasing AC voltage and sample configuration.

CHAPTER 5

LEAD-FREE TWO-PHASE MAGNETOELECTRIC COMPOSITES

5. 1 Optimization of sintered KNNLS-NZF particulate composites

0.948 $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3 - 0.052 \text{LiSbO}_3$ (KNNLS) and $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ (NZF) ceramics were synthesized by mixed oxide sintering method. Powders of K_2CO_3 (99 %), Na_2CO_3 (99.5 %), Li_2CO_3 (99 %), Nb_2O_5 (99.5 %), and Sb_2O_5 (99.998 %) (all from Alfa Aesar, Ward Hill, USA) corresponding to KNNLS phase were mixed for 24h in a polypropylene jar with zirconia milling balls and ethanol (99.5%, Sigma-Aldrich, USA). Mixed powders were dried and then calcined at 880 °C for 2h. NZF was separately synthesized by mixing NiO (99.99 %), ZnO (99 %), and Fe_2O_3 (99.945 %) (all from Alfa Aesar, Ward Hill, USA) powder in a polypropylene jar with zirconia milling balls and ethanol (99.5%, Sigma-Aldrich, USA), drying, and calcining at 1000 °C for 2h. SEM images and X-ray diffraction patterns for KNNLS and NZF powders were measured after calcination step conducted at 880 °C and 1000 °C respectively. The KNNLS powders were found to have the grain size < 1 μm and exhibited perovskite structure as shown in Figure 5-1 (a) and (b). The NZF powders had grain size range of < 300 nm with spinel structure as shown in Figure 5-1(c) and (d). Calcined NZF powders were milled in a polypropylene jar with zirconia milling balls and ethanol (99.5%, Sigma-Aldrich, USA) for 24h, dried, pressed into disks under pressure of 100 kgf/cm^2 and then sintered at 1240 °C. Sintered NZF specimens (island) were next crushed to particle size of < 25 μm by using mortar and pestle followed by sieving. Crushed NZF powders (islands with size distribution of 2 ~ 25 μm) were mixed with calcined KNNLS powders (matrix) having NZF mole fractions of 0.1, 0.2, 0.3, and 0.4. Mixed

powders were pressed into disks with diameter of 13 mm under pressure of 100 kgf/cm² and sintered at temperatures of 1040, 1050, 1060, and 1070 °C for 2h. All samples used for measurements had diameter of 10 mm and thickness of 1mm. Samples were poled in silicone oil at room temperature by applying DC field of 3.5 kV/mm for 30 min. After poling, samples were aged at room temperature for 24h. ME voltage coefficients for the laminates were measured by applying DC bias magnetic field with $H_{AC} = 1$ Oe at 1 kHz.

Figure 5-2(a) – (d) shows the X-ray diffraction (XRD) patterns for (1 - x) KNNLS – x NZF ($x = 0.1, 0.2, 0.3$, and 0.4) composites sintered at varying temperatures (1040, 1050, 1060, and 1070 °C). The patterns clearly reflect that both phases of KNNLS and NZF stabilized respectively in perovskite and spinel structures without any trace of secondary phase in the composites. As the mole fraction of NZF was increased the intensity of spinel peaks increased while the intensity of perovskite peaks decreased. Figure 5-3 shows that the peak intensity ratio of (311)/(101) increases with increasing concentration of NZF in KNNLS matrix regardless of sintering temperatures. There is significant increase in the peak intensity ratio for $x = 0.4$, which could be related to the changes in connectivity of the NZF phase.

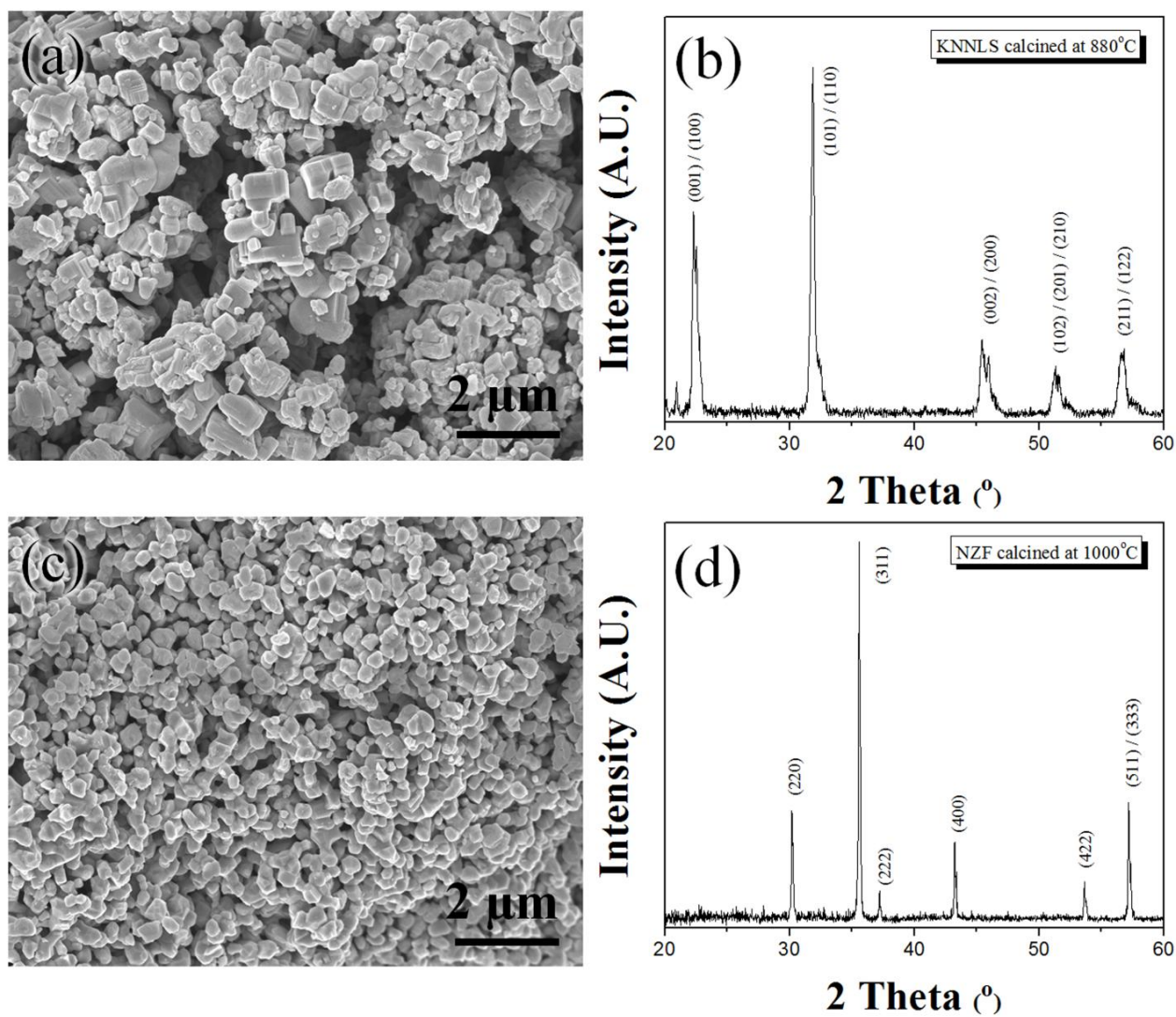


Figure 5-1. (a) SEM image and (b) XRD patterns of KNNLS calcined at 880°C. (c) SEM image and (d) XRD patterns of NZF calcined at 1000°C.

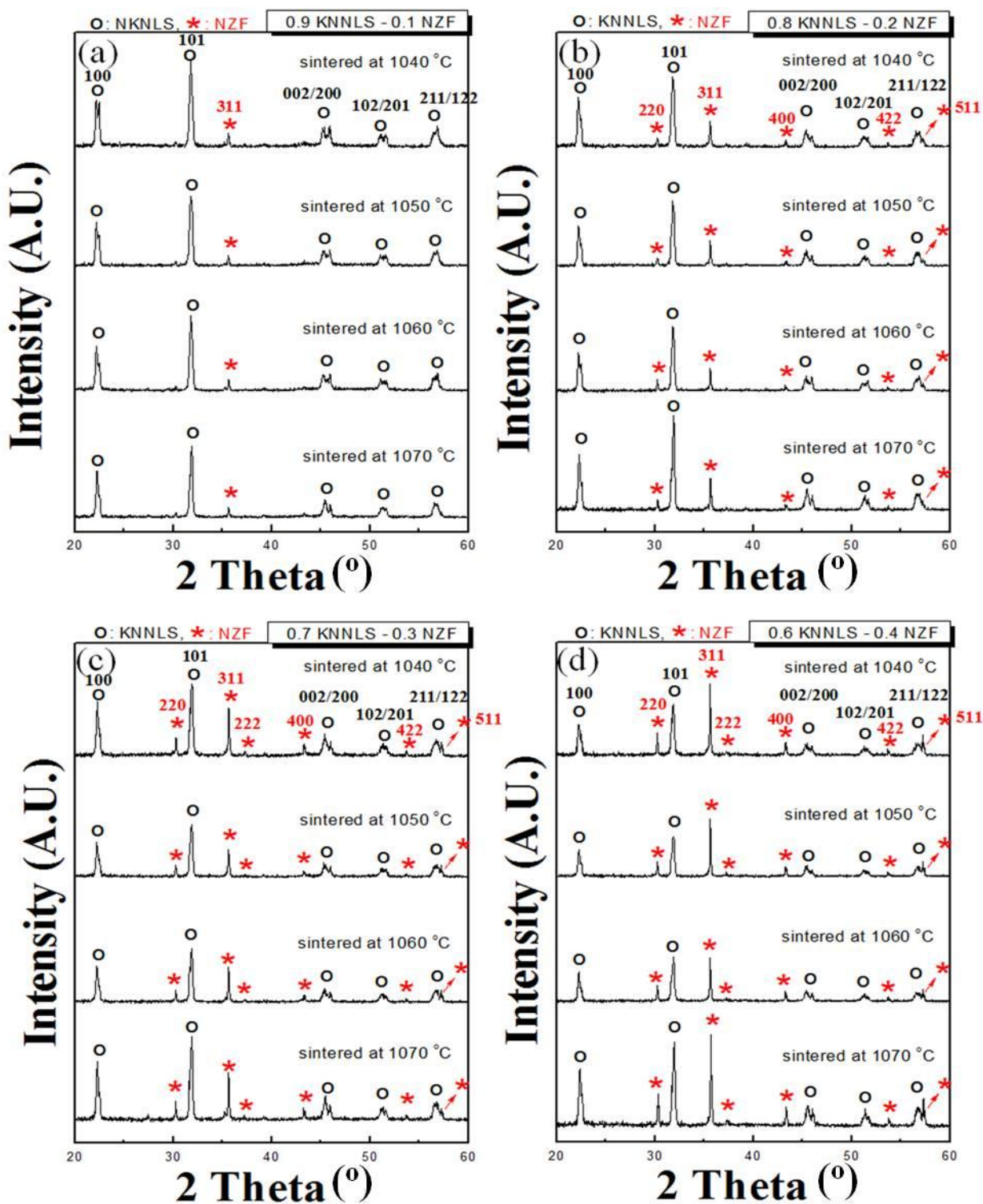


Figure 5-2. XRD patterns for $(1-x)$ KNNLS - x NZF composites. (a) $x = 0.1$, (b) $x = 0.2$, (c) $x = 0.3$ and (d) $x = 0.4$.

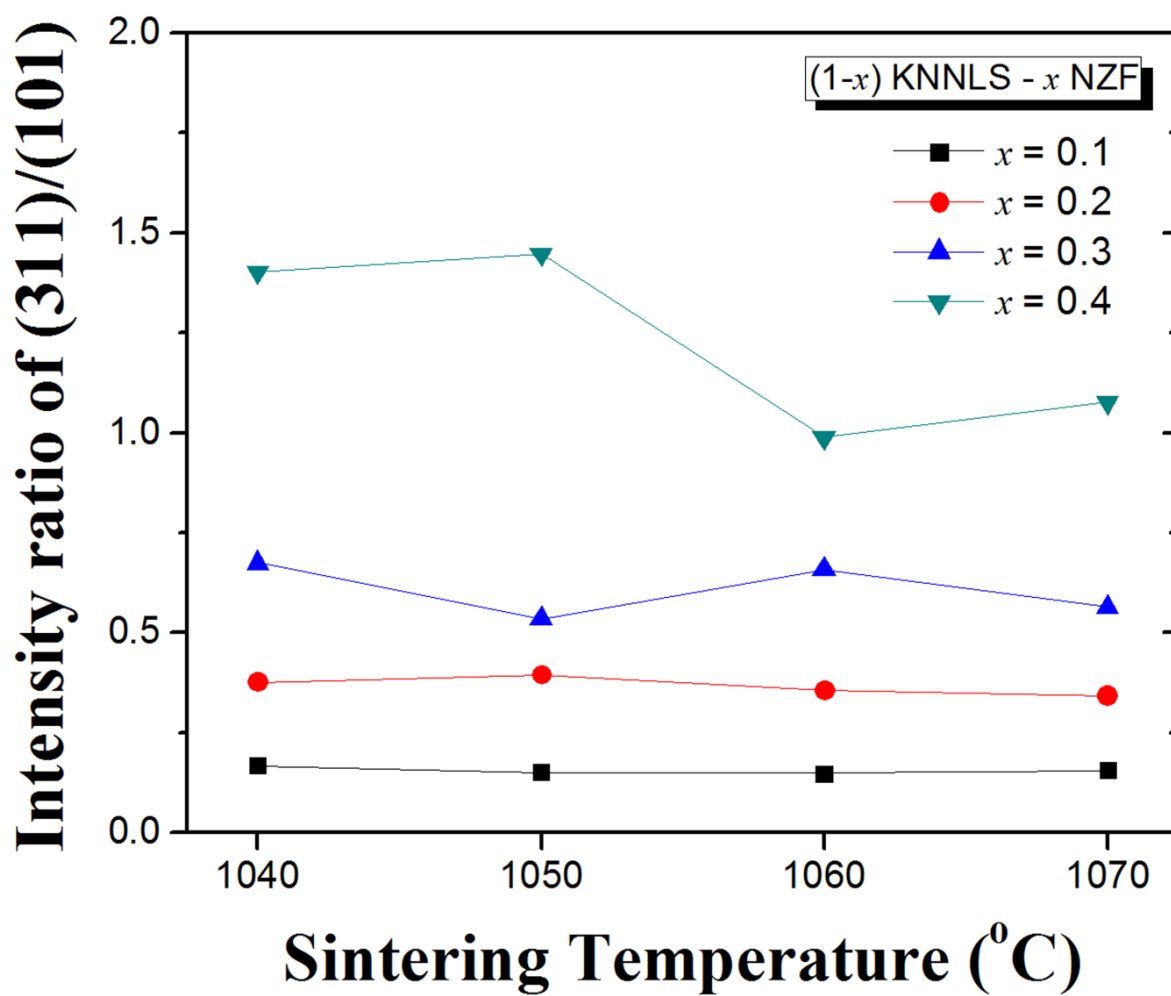


Figure 5-3. Intensity ratio of (311)/(101) for (1 - x) KNNLS – x NZF composites as a function of sintering temperature.

Variations of longitudinal piezoelectric strain constant (d_{33}) and radial mode electromechanical coupling factor (k_p) with composition for all composites are shown in Figure 5-4(a) and (b). The magnitude of both d_{33} and k_p decreased with increasing NZF concentration, and was found to maximize at the sintering temperatures of both 1050 °C and 1060 °C regardless of x values. It can be noticed that there is critical sintering temperature of 1070 °C above which the electromechanical properties decreased. Clearly 0.9 KNNLS – 0.1 NZF composites exhibit variation of piezoelectric properties with sintering temperature. The changes occurring in other KNNLS-NZF composites are relatively small and this could be associated to varying factors including poling percentage, grain size, resistivity, and space charge. Figure 5-4(c) and (d) show that the magnitude of dielectric constant (ϵ_r/ϵ_0) decreased with increasing NZF concentration and the magnitude of loss factor ($\tan \delta$) was found to minimize at the sintering temperature of 1050 °C and 1060 °C. The low $\tan \delta$ at the optimum sintering points resulted from the composite structures possessing high relative density of > 95 %. As the composites were sintered at 1040 °C and 1070 °C, the relative density was found to decrease below 95 % reflecting high porosity. Further, it is found in Figure 5-4 that the composites with high NZF concentration of $x = 0.4$ is still below the percolation threshold as the dielectric and piezoelectric properties did not exhibit any significant drop.

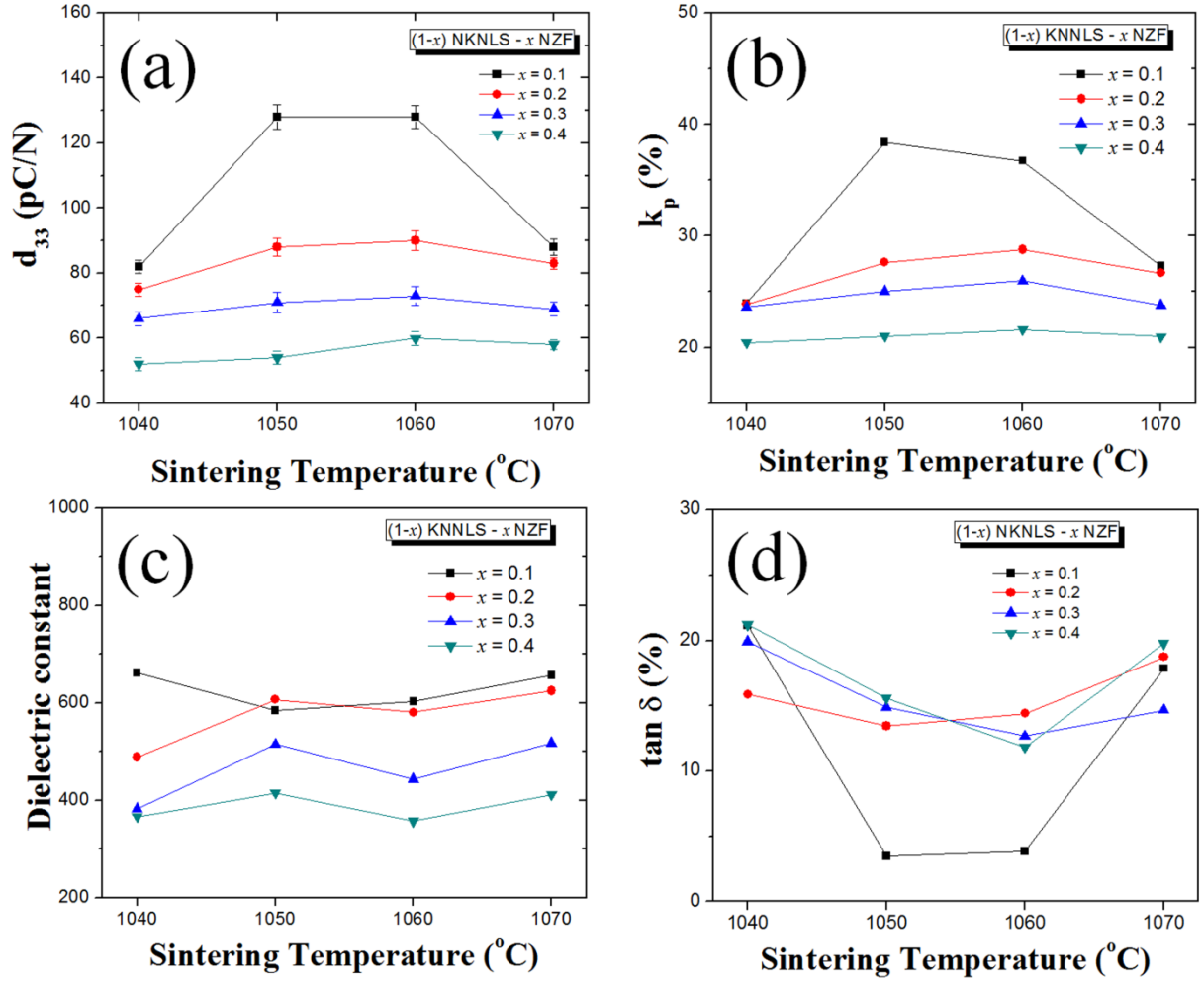


Figure 5-4. Piezoelectric and dielectric properties for $(1 - x)$ KNNLS – x NZF composites, (a) longitudinal piezoelectric constant, (b) radial mode coupling factor, (c) dielectric constant, and (d) tangent loss factor.

Figure 5-5(a) – (d) shows the magnetic hysteresis loops for the NZF particles and $(1 - x)$ KNNLS – x NZF ($x = 0.1, 0.2, 0.3$, and 0.4) composites measured by VSM at room temperature. The crushed NZF particles were found to exhibit saturation magnetization (M_s) of 63.90emu/g as shown in Figure 5-5(a) and (b), which decreased for the sintered KNNLS-NZF composites. The magnitude of M_s for the composites was found to increase from 6.58 to 23.48 emu/g with increasing NZF concentration as shown in Figure 5-5(c) and (d). The remanent magnetization (M_r) for NZF particles was found to be 0.29 emu/g and the magnitude of M_r for the composites increased from 0.13 to 0.77 emu/g with increasing NZF concentration. The magnitude of coercive field (H_c) for KNNLS-NZF composites was found to be constant regardless of the change in composition.

In order to verify the coupling between magnetic polarization and mechanical strain for the $(1 - x)$ KNNLS – x NZF ($x = 0.1, 0.2, 0.3$, and 0.4) composites, magnetostriction (λ) and piezomagnetic coefficients (q) were determined in the range of 0 – 1000 Oe as shown in Figure 5-6(a) – (d). The parameters λ_{11} and λ_{12} correspond to in-plane parallel magnetostriction and in-plane perpendicular magnetostriction to applied magnetic field (H). With increasing NZF concentration, the magnitude of λ_{11} and λ_{12} was found to increase. The magnitude of λ_{11} and λ_{12} for composition $x = 0.4$ was found to be -8ppm and 3 ppm. The in-plane piezomagnetic coefficients q_{11} and q_{12} were calculated by differentiating λ_{11} and λ_{12} with respect to magnetic field. As NZF concentration increases, the magnitude of q_{11} and q_{12} was found to increase and the peak shifted to low H . The position of peak in piezo-magnetic constant is an important characteristic in design of high sensitivity magnetic field sensors as it corresponds with the peak observed in magnetoelectric coefficient.

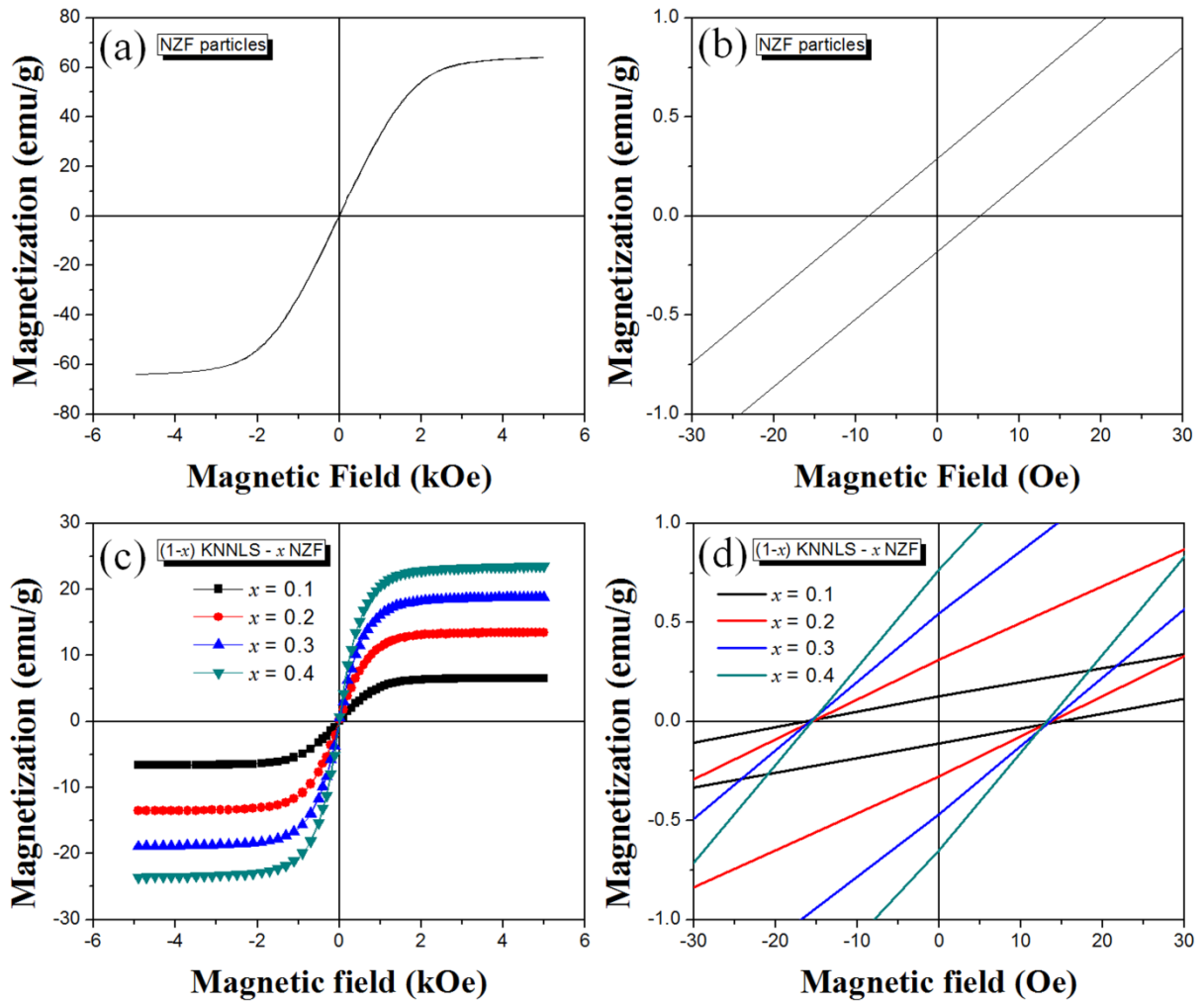


Figure 5-5. M – H curves for NZF particles and (1 - x) KNNLS – x NZF composites. (a) magnetization as a function of magnetic field for NZF particles, (b) amplified curve in the low magnetic field region shown in (a), (c) magnetization as a function of magnetic field for (1 - x) KNNLS – x NZF composites, and (d) amplified curve in the low magnetic field region shown in (c).

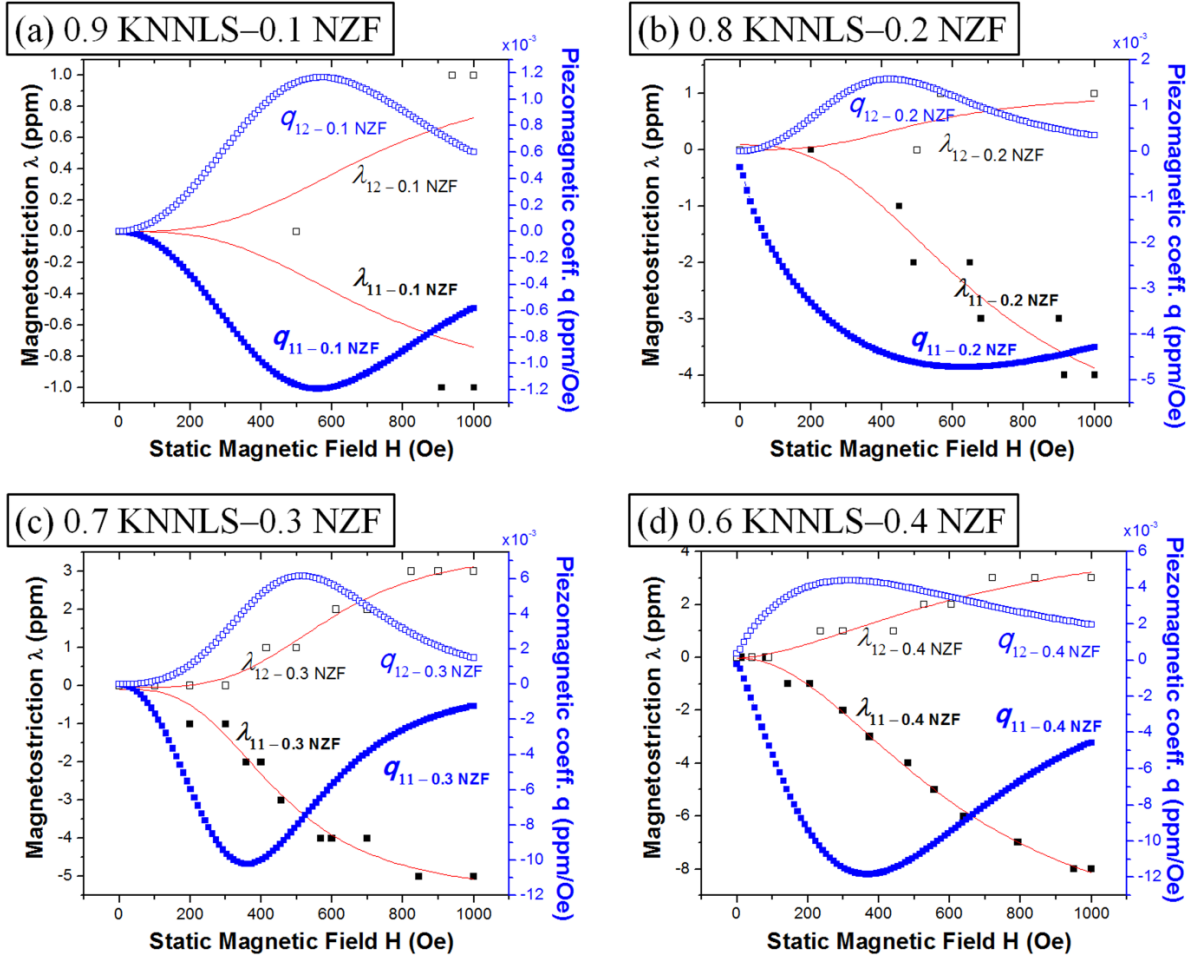


Figure 5-6. Magnetostrictions and piezomagnetic coefficients for $(1-x)$ KNNLS - x NZF composites. (a) $x = 0.1$, (b) $x = 0.2$, (c) $x = 0.3$ and (d) $x = 0.4$.

Figure 5-7(a) and (b) show the variation of ME coefficient (α_E) and optimum DC bias (H_{bias}) for the $(1 - x)$ KNNLS – x NZF ($x = 0.1, 0.2, 0.3, \text{ and } 0.4$) composites with sintering temperatures, measured at 1 kHz under $H_{ac} = 1$ Oe. With increasing NZF concentration, the magnitude of α_E was found to increase to 20.14 mV/cm·Oe under $H_{bias} = 380$ Oe at $x = 0.3$ and then slightly drop to 18.17 mV/cm·Oe under $H_{bias} = 330$ Oe at $x = 0.4$. For all the compositions, the composites sintered at 1050 and 1060 °C were found to exhibit maximum α_E due to their optimized piezoelectric and dielectric values as shown in Figure 5-4. The magnitude of optimum H_{bias} decreased from 545 to 326 Oe with increasing NZF concentration. The reason for shift in H_{bias} is related to the difference in magnetic susceptibilities of the composites and variation in peak piezo-magnetic coefficient as shown in Figure 5-6.

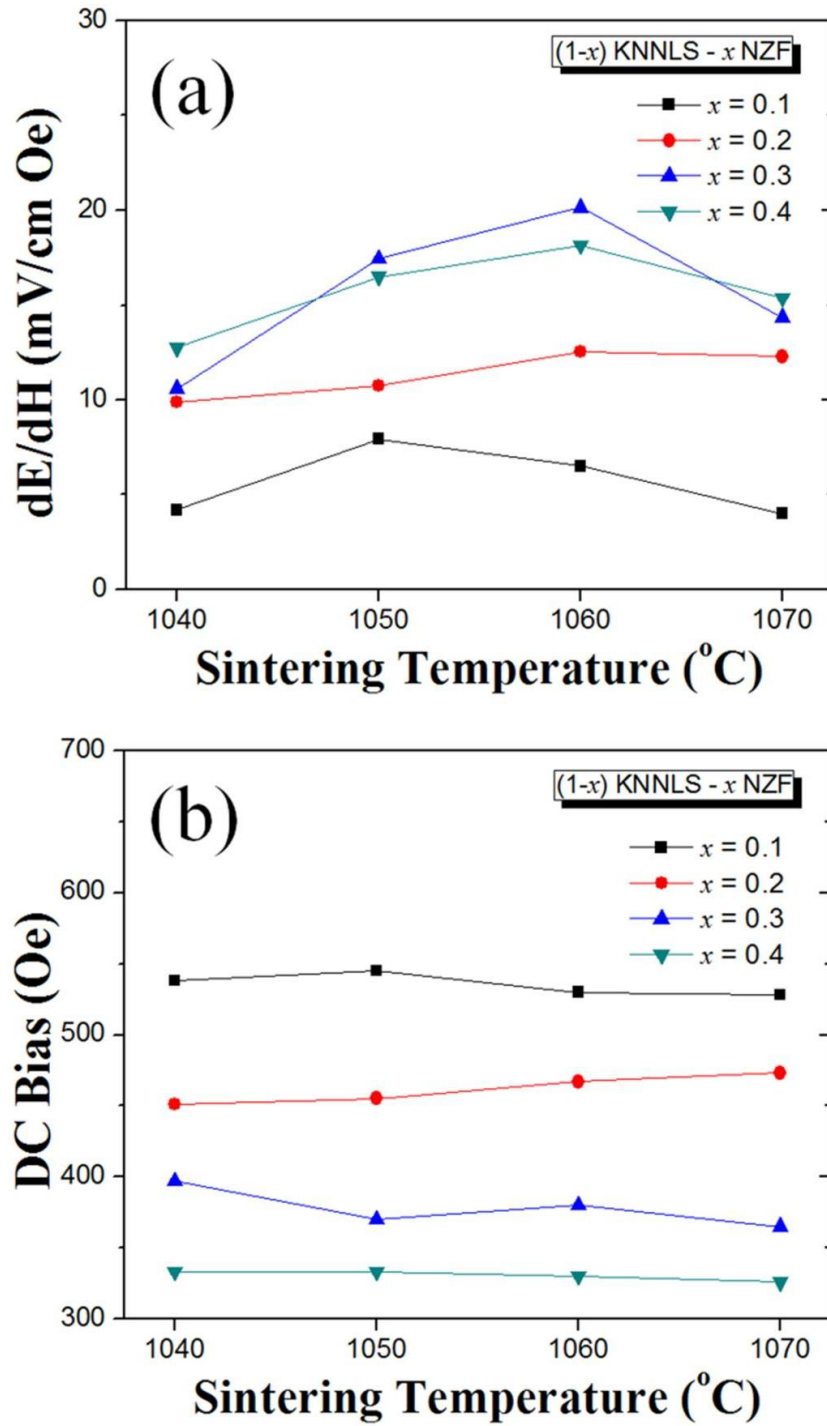


Figure 5-7. Variation of (a) ME coefficient and (b) H_{bias} for $(1-x)$ KNNLS - x NZF composites with $x = 0.1, 0.2, 0.3$ and 0.4 as a function of sintering temperature.

For particulate ME composites with 3-0 connectivity in off-resonance condition, Boomgaard et al. have described α_E by the following expression:

$$\alpha_E = (dE/dH)_{\text{comp}} = (dS/dH)_{\text{comp}} (dE/dS)_{\text{comp}} = m_v (dS/dH)_{\text{ferrite}} (1 - m_v) (dE/dS)_{\text{piezoelectric}} \quad (5-1)$$

where m_v is the volume fraction of ferrite, (dE/dS) is the resulting electric field, and (dS/dH) is the change in strain per unit change in magnetic field. Since $dE = g.dX$ and $dS = dX/C$, where X is the stress, S is strain, g is piezoelectric voltage constant, and C is the stiffness, Eq.(7) can be written as:

$$\alpha_E = m_v (dS/dH)_{\text{ferrite}} (1-m_v) (g_{ij}C_{ij})_{\text{piezoelectric}} \quad (5-2)$$

Assuming the deformation is occurring along the thickness direction and electric field is measured along the same direction, Eq. (8) can be approximated as:

$$\alpha_E = m_v (dS/dH)_{\text{ferrite}} (1-m_v) (g_{33}C_{33})_{\text{piezoelectric}} \quad (5-3)$$

Vlasko-Vlasov et al. have shown that magnetization and magnetostriction are correlated by the expression:

$$\varphi \sim \frac{3\lambda\sigma}{(K + 2\pi M^2)} \quad (5-4)$$

where φ is the angle of magnetic moments, λ and K are the magnetostriction and anisotropy constant, σ is the stress and M is the magnetization. Using this expression, it can be shown that M^2 is proportional to magnetostriction (λ). Recently, Park and Priya have shown that differential of M^2 with magnetic field exhibits similar variation as that observed for magnetoelectric coefficient with H_{bias} . Thus, optimization in magnitude of M_s can lead to optimum magnitude of magnetostriction. The composites with $x = 0.3$ were found to exhibit the optimum values of $g_{33} = 19 \times 10^{-3} \text{ V} \cdot \text{m/N}$ and $M_s = 19 \text{ emu/g}$ which explains the result shown in Figure 5-7.

In order to form the island-matrix composite, following considerations were taken into account: (i) matrix had smaller particle size than that of island to achieve control of the surface area, and (ii) sintering temperature of matrix and island was quite different to eliminate the elemental diffusion. Bordia et al. have described the sintering phenomenon with rigid inclusions in terms of transient stresses and strain rates.¹⁶¹ The analysis shows that volume fraction of the inclusion is an important parameter in determining the sintering of the composite. The KNNLS matrix normally has residual porosity due to the cubical shape of grains but the KNNLS-NZF composites were found to exhibit high relative density of > 95%. This high density can be associated with NZF which provides an interface for nucleation and growth. The densification rate of the composite is expressed as:

$$\frac{1}{\rho_m} \frac{d\rho_m}{dt} = \frac{1}{\rho_c} \frac{d\rho_c}{dt} \left(\frac{\rho_{co}}{\rho_{co} - v_{io}\rho_c} \right) \quad (5-5)$$

where ρ_c and ρ_m are the relative densities of composite and the matrix, and ρ_{co} and v_{io} are initial values for density and volume fraction of inclusion. Three stages of sintering were identified in these systems. The first stage corresponds to re-arrangement of random shape particle to form stack of plate type particles. The second stage is characterized by rapid grain growth promoted by liquid phase. The liquid phase formation was found to be related to Na₂O volatilization. In the final stage of sintering, densification slows and microstructural coarsening becomes the dominant process. The fraction control of liquid phase was an important factor to obtain a dense and uniform microstructure. Muffling was used to reduce the loss of the alkali ions during high temperature sintering, and sintering temperature and time was used to control the volume fraction of the liquid phase.

Figure 5-8(a) – (d) shows the SEM micrographs for KNNLS-NZF composites with island-matrix microstructure sintered at 1060 °C. All the compositions exhibited dense microstructure with high density which illustrates that growth occurred at the NZF interface leading to bridging of the residual porosity. The NZF islands were randomly dispersed in KNNLS matrix which is highly beneficial for the poling of piezoelectric matrix. Two different grain structures can be noticed in the microstructure, cubical large grains corresponding to matrix and random-shaped small grains corresponding to island. There was no significant change observed in the size of the islands during sintering. From this microstructure, the connectivity of composites can be considered to be 3-0.

The EDS elemental mapping images shown in Figure 5-9 (a) – (h) further confirm this conclusion. In this Figure, the element Nb (white color in Figure 5-9 (a) – (d)) represents the KNNLS matrix and Fe (white color in 5-9 (e) ~ (h)) represents the NZF island. It can be seen that the NZF islands were isolated from each other for the composition $x = 0.1 \sim 0.3$ but the connectivity pattern changes at high mole fraction of $x = 0.4$.

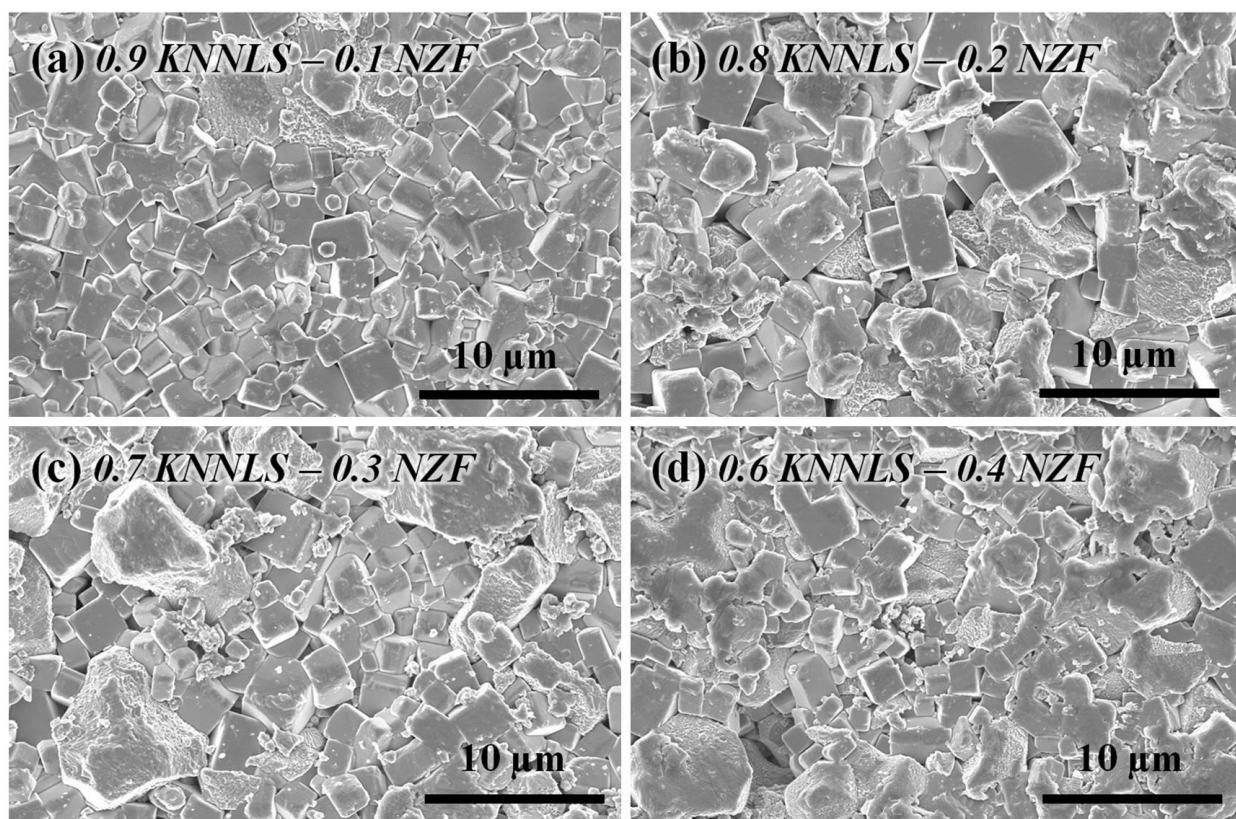


Figure 5-8. SEM micrographs for $(1 - x)$ KNNLS – x NZF composites sintered at 1060 °C. (a) $x = 0.1$, (b) $x = 0.2$, (c) $x = 0.3$ and (d) $x = 0.4$.

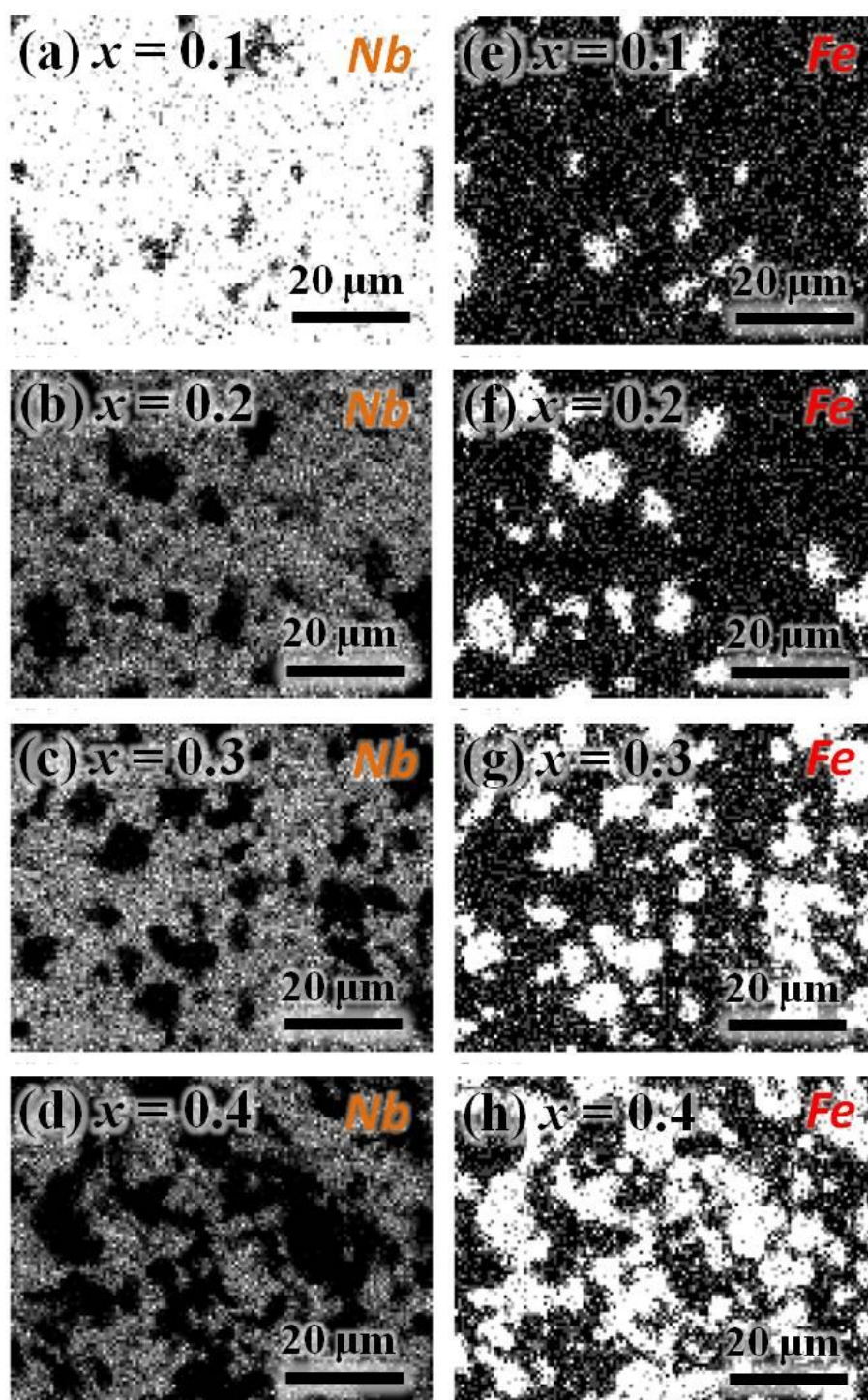


Figure 5-9. EDS elemental mapping images for $(1 - x)$ KNNLS – x NZF composites sintered at 1060 °C. (a) – (d) SEM images for $x = 0.1 - 0.4$, (e) – (h) Nb mapping for $x = 0.1 - 0.4$, and (i) – (l) Fe mapping for $x = 0.1 - 0.4$.

5. 2 Magnetoelectric effect of KNNLS-NZF / Ni laminates

Figure 5-10 shows the schematic diagram for $(1 - x)$ KNNLS - x NZF / Ni / $(1 - x)$ KNNLS - x NZF ($x = 0.1 \sim 0.3$) laminates fabricated by embedding the Ni plate between KNNLS-NZF disks with same poling direction. The impedance and phase spectra for bimorph laminates were measured under a small applied AC electric field as shown in Figure 5-11. It was found that the radial mode laminates exhibited only resonance peaks over 200 kHz. Variation of α_E for the laminates was measured by applying H_{bias} with $H_{ac} = 1$ Oe at 1 kHz as shown in Figure 5-12(a). The laminates were found to exhibit typical ME behaviors with peak in ME coefficient and no-remanent α_E at zero DC bias. The magnitude of α_E for the laminates was found to increase from 161.5 to 261.3 mV/cm·Oe with decreasing NZF concentration. It can be shown that ME response in the laminates dominantly depends on piezoelectric properties. Figure 5-12 (b) – (d) show the variation of ME output voltage for the laminates measured by applying $H_{ac} = 1$ Oe with a step-change in DC magnetic field. At 1 kHz frequency, all laminates were able to measure step change of 1 μ T DC magnetic field. The sensitivity data corresponds well with the ME coefficient graph as the slope of the curve in Figure 5-12 (a) decreases with increasing NZF concentration. Low field sensitivity is mainly governed by the magnitude of this slope and variation in piezomagnetic coefficient. The change in output voltage (V) with applied magnetic field (H) in off-resonance condition can be expressed as: $dV/dH = (dX/dH) \cdot g \cdot t$, where X is generated stress, g is piezoelectric voltage constant and t is the thickness of the composite layer. The coefficient dX/dH can be shown to be proportional to q/s , where s is the elastic compliance of the NZF islands. Thus, the sensitivity will be dependent upon the mechanical impedance matching of the NZF phase with the KNNLS matrix and the composite layer with that of nickel.

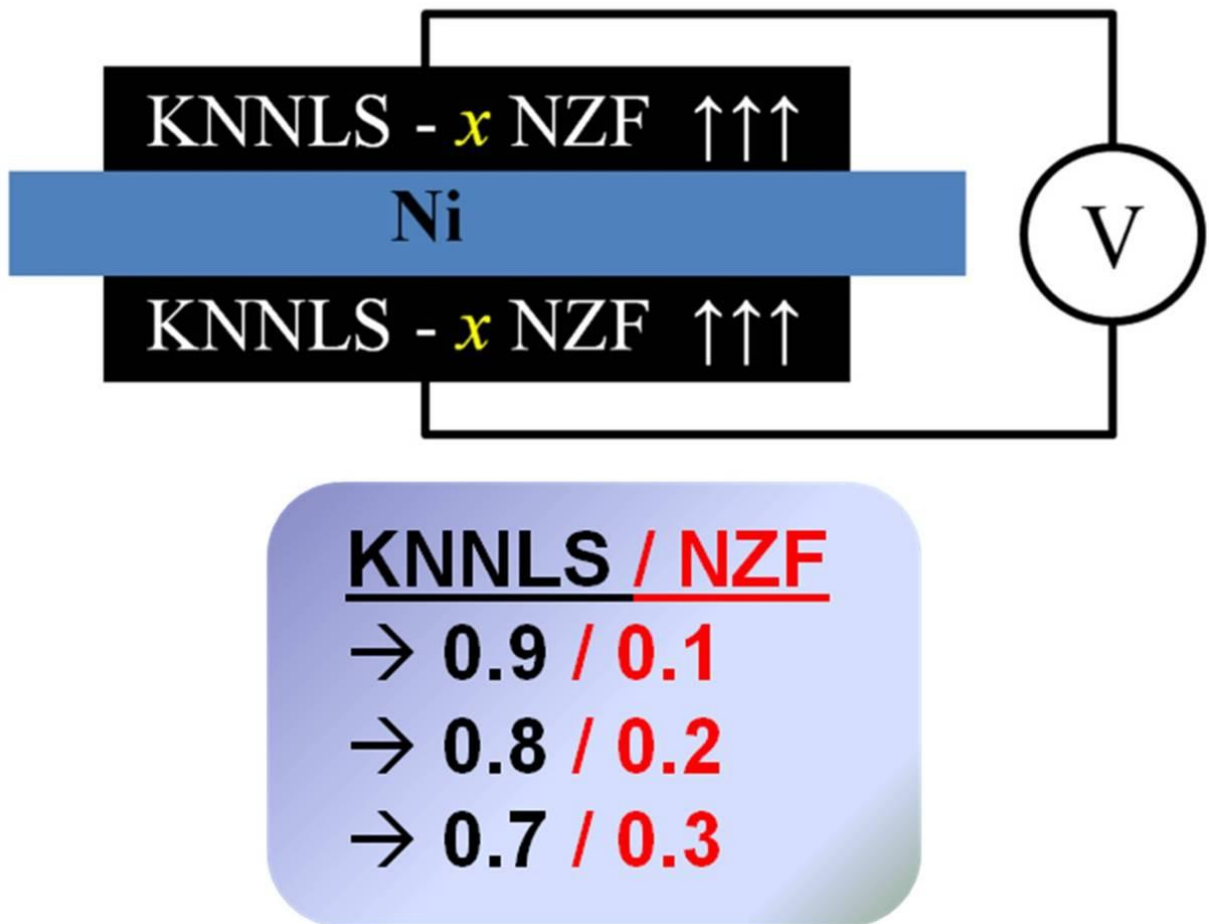


Figure 5-10. Schematic diagram for 2-2 ME laminate composites with variation of materials composition. $(1 - x)$ KNNLS – x NZF / Ni / $(1 - x)$ KNNLS – x NZF with $x = 0.1, 0.2$ and 0.3 .

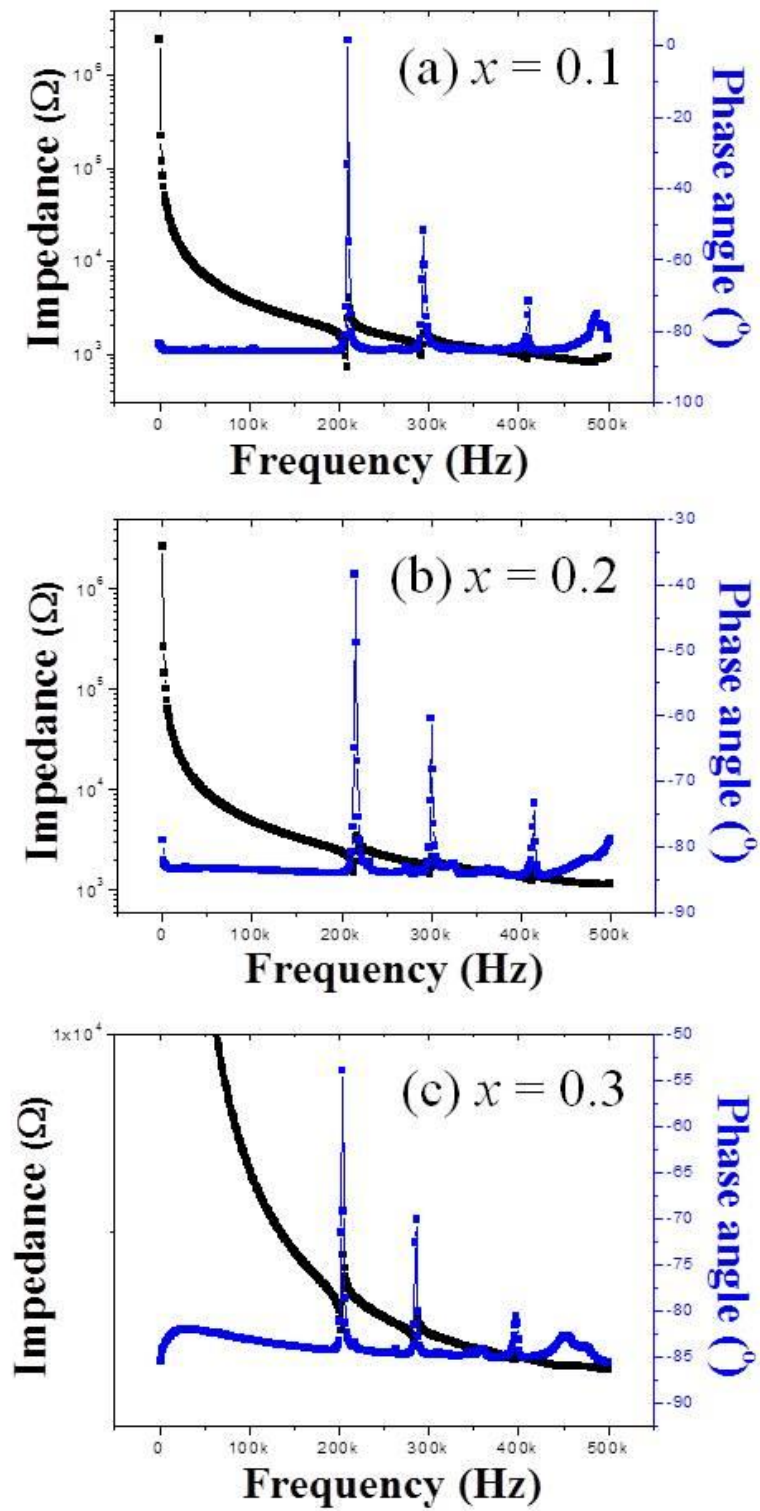


Figure 5-11. Impedance and phase spectra for radial mode configuration trilayer laminates with $x = 0.1, 0.2$ and 0.3 under AC electric field.

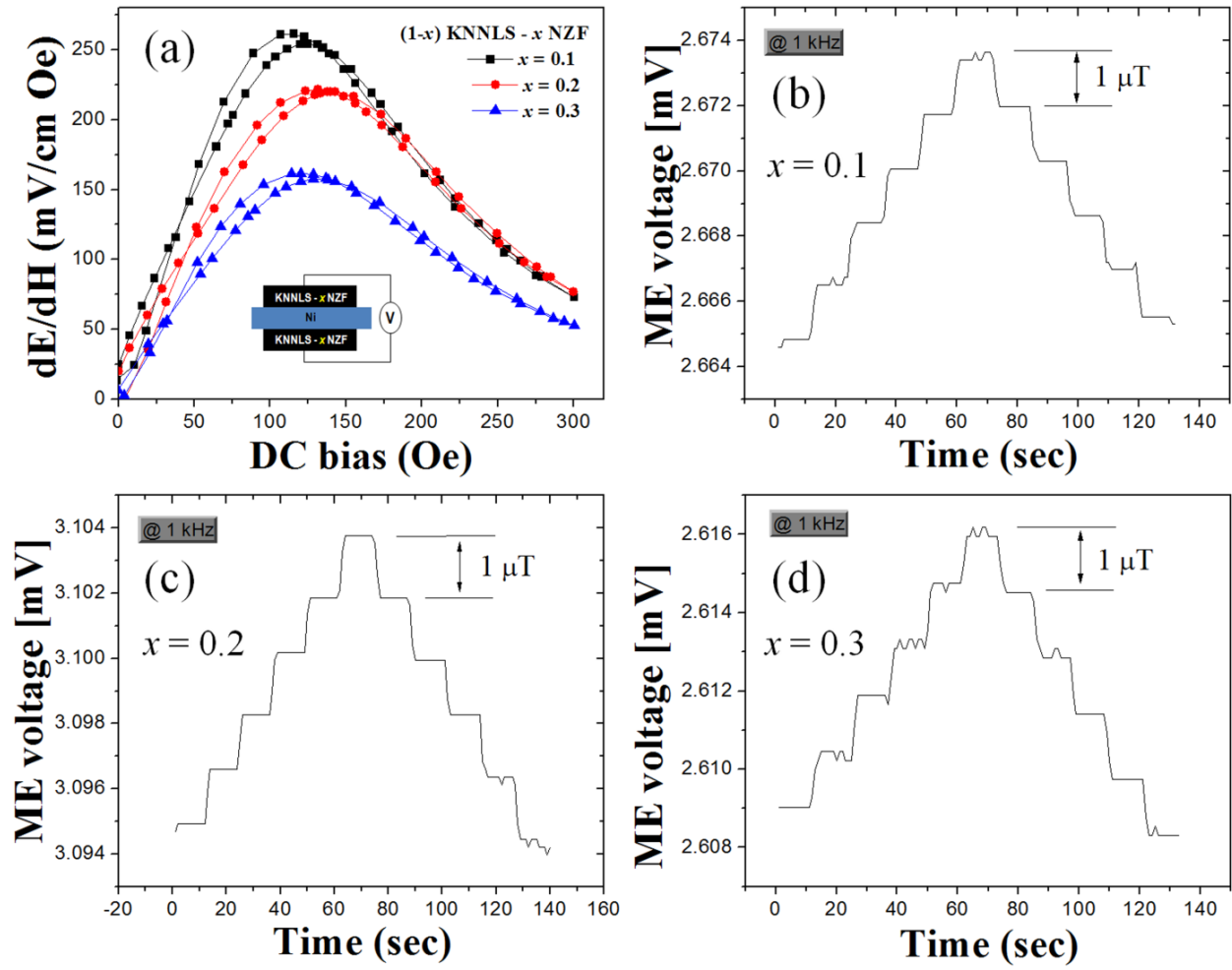


Figure 5-12. (a) ME coefficient and sensitivity limit of dc magnetic field for radial mode laminates. (b) $x = 0.1$, (c) $x = 0.2$ and (d) $x = 0.3$.

In this chapter, the lead-free $(1 - x)$ KNNLS – x NZF ME composites with island-matrix microstructure were developed. In order to form the island-matrix composite, following considerations were taken into account: (i) matrix had smaller particle size than that of island to achieve control of the surface area, and (ii) sintering temperature of matrix and island was quite different to eliminate the elemental diffusion. The island-matrix structure of KNNLS-NZF composites were found to exhibit high relative density of $> 95\%$ even though KNNLS matrix normally has residual porosity. Finally, the $(1 - x)$ KNNLS – x NZF ME composites were optimized via sintering at $1060\text{ }^{\circ}\text{C}$ and maximum ME coefficient $\alpha_{E,max}$ of $20.14\text{ mV/cm}\cdot\text{Oe}$ was observed in the $0.7\text{ KNNLS} - 0.3\text{ NZF}$ composition under applied $H_{bias} = 467\text{ Oe}$ with $H_{ac} = 1\text{ Oe}$ at $f = 1\text{ kHz}$. Further, the result clearly shows that the optimum H_{bias} can be controlled from 326 to 545 Oe with change in piezomagnetic coefficient by variation of NZF concentration.

CHAPTER 6

LEAD-FREE SINGLE-PHASE MAGNETOELECTRIC MATERIALS

6. 1 Magnetolectric phase diagram for BT-BFO solid-solutions

Solid solution of lead-free $(1 - x)$ $\text{BaTiO}_3 - x$ BiFeO_3 (BT- x BFO, $x = 0.025 - 1.0$) were synthesized for determining the high magnetolectric (ME) coupling composition. Figure 6-1(a) shows the room-temperature XRD patterns for BT- x BFO ($x = 0.025 - 1.0$) ceramics. The XRD patterns illustrate that the BT- x BFO exhibits tetragonal ($x = 0.025$), psudo-cubic ($x = 0.1 - 0.7$), and rhombodedral ($x = 0.8 - 1.0$) phases across the whole range of composition. The emphasis was laid on the crystal structures of compositions corresponding to BT- x BFO ($x = 0.710 - 0.775$) shown in Figure 6-1(b), where optimum ME coupling was found. The XRD pattern for pure BFO ($x = 1.0$) exhibited rhombohedral phase with splitting in the peaks of (110), (111), (210), and (211). On modification with BT, the splitting gradually disappeared as BFO mole fraction decreased from $x = 1.0$ to $x = 0.725$ as shown in Figure 6-1 (c). With further decrease in BFO mole fraction to $x = 0.71$, the peaks showed negligibe splitting. The peaks shifted to lower 2 theta values with BT modification in BFO ceramics due to the substitution of large ionic radii Ba^{2+} ($1.35 \text{ \AA}$) ion on A-site and Ti^{4+} ($0.68 \text{ \AA}$) ion on B-site as compared to the Bi^{3+} ($1.08 \text{ \AA}$) and Fe^{3+} ($0.64 \text{ \AA}$) ion respectively. Figure 6-2 (a) and (b) show the lattice parameter (a), rhombohedral distortion angle (α), and volume of unit cell for the BT- x BFO ($x = 0.71 - 0.775$ and 1.0). With decreasing BFO mole fraction, the lattice parameter a increased from $3.956 \text{ \AA}$ ($x = 1.0$) to $3.986 \text{ \AA}$ ($x = 0.71$) and the distortion angle α increased and peaked at 89.99° ($x = 0.725$). The volume

of unit cell increased from $61.90 \text{ \AA}^3$ ($x = 1.0$) to $63.31 \text{ \AA}^3$ ($x = 0.725$) with decreasing BFO mole fraction.

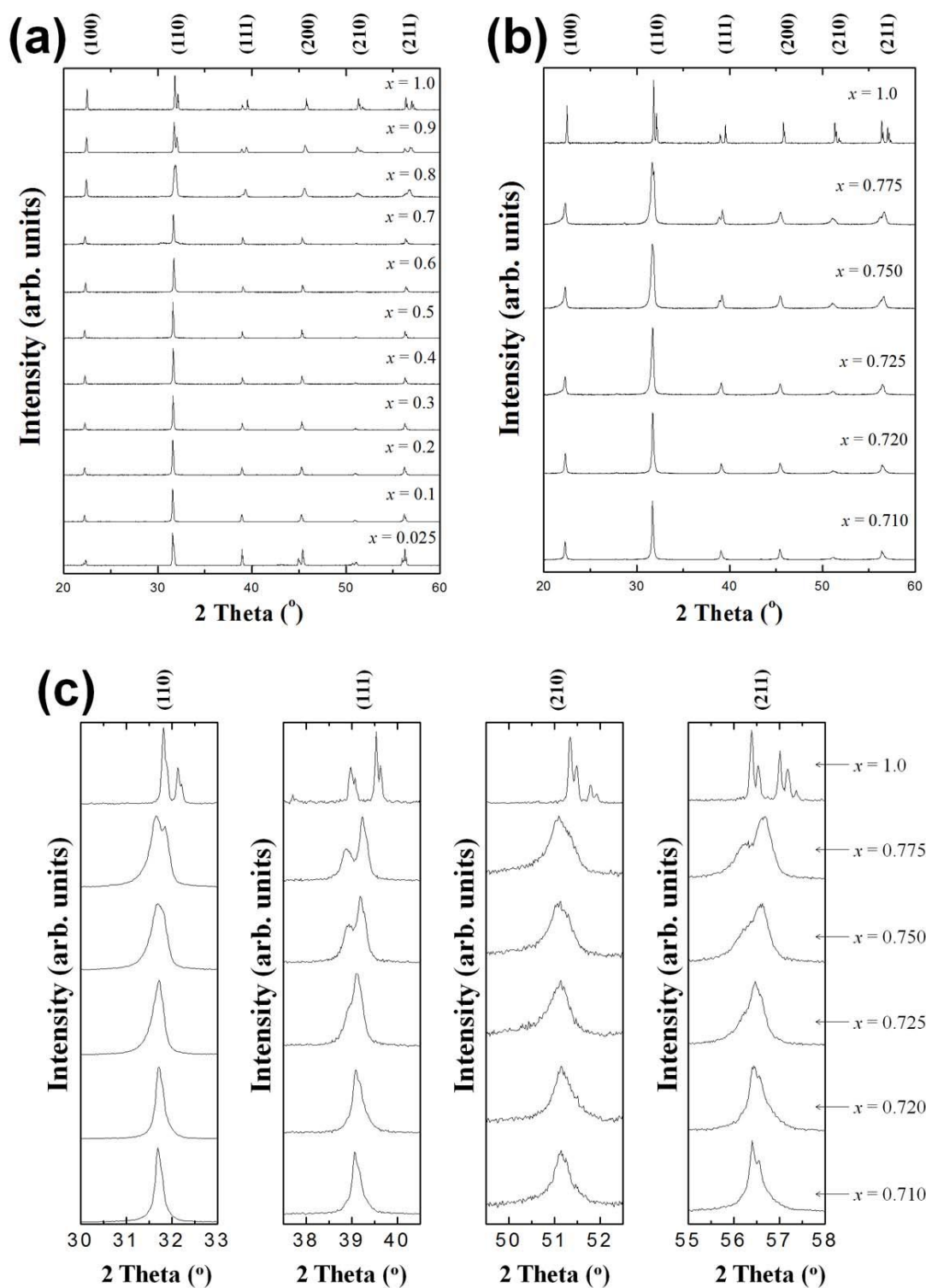


Figure 6-1. XRD patterns for BT-xBFO ceramics (a) with $x = 0.025 - 1.0$ and (b) with $x = 0.710 - 0.775$ and 1.0 , and (c) extended peak values for (110), (111), (210) and (211).

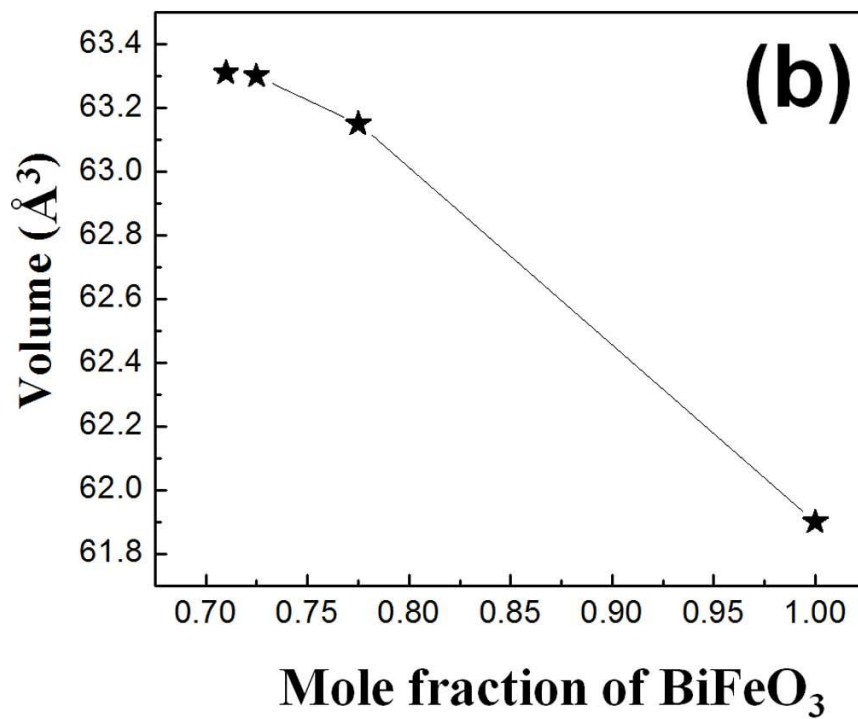
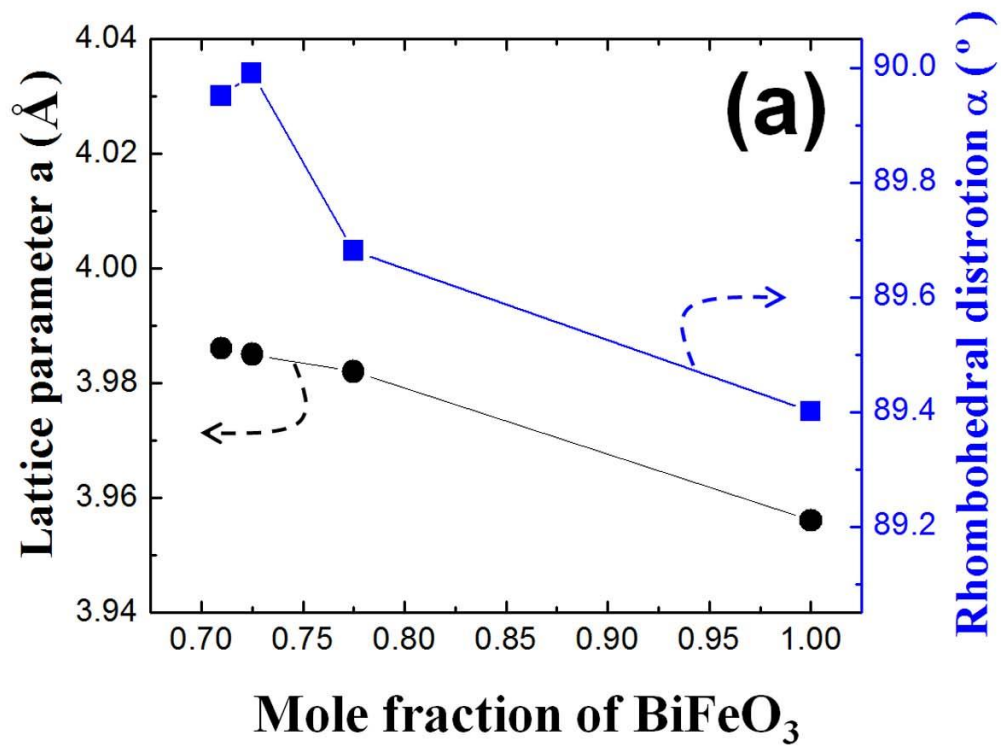


Figure 6-2. (a) Lattice parameter and rhombohedral distortion angle and (b) volume of unit cell for BT- x BFO ceramics with $x = 0.710 - 0.775$ and 1.0.

Figure 6-3 (a) – (h) show the composition dependence of magnetoelectric, piezoelectric, and dielectric properties of BT- x BFO ceramics at room temperature. From Figure 6-3 (a) and (b), it can be noted that the DME effect was enhanced with proportional change of α_{DME} phase angle in the limited range of BT- x BFO compositions ($x = 0.71 - 0.8$) and the maximum α_{DME} (0.87 mV/cmOe) was observed at the optimum composition of BT- x BFO ($x = 0.725$). As shown in Figure 6-3 (c), the poling percent ($100 \times (P^0/180^\circ)$), which is determined from the change of phase angle ($P^0 = P_f^0 - P_i^0$), illustrates that the poling was only achieved in the compositions BT- x BFO ($x = 0.025$ and $0.710 - 0.8$) exhibiting tetragonal and rhombohedral phases. Thus, the piezoelectric and dielectric properties can be achieved in the limited range of compositions of BT- x BFO. At the optimum composition of BT- x BFO ($x = 0.725$), piezoelectric charge constant (d_{33}), electromechanical coupling factor (k_p) and dielectric constant ($\varepsilon = \varepsilon^T/\varepsilon^0$) were maximized ($d_{33} = 124$ pC/N, $k_p = 29.1\%$, $\varepsilon = 760$) and the loss factor ($\tan \delta$) at 1 kHz was minimized ($\tan \delta = 7.8\%$) as shown in Figure 6-3 (e) – (h). The piezoelectric voltage coefficient ($g_{33} = d_{33}/\varepsilon^T$) shown in Figure 6-3 (d), which is one of the main parameters for achieving high ME coupling was found to be maximized ($g_{33} = 18.5$ mV·m/N) for the composition BT- x BFO ($x = 0.725$). The measured maximum d_{33} (124 pC/N) of pure BT-0.725BFO for the samples is quite promising compared with the reported d_{33} (116 pC/N) for Mn-doped BT-0.75BFO.¹³⁸ The measured d_{33} (54 pC/N) of pure BT-0.75BFO is also comparable with the reported d_{33} (47 pC/N) of pure BT-0.75BFO.¹³⁸ Systematic measurement of d_{33} with composition led to the identification of BT-0.725BFO composition that provides best performance. There was no ME response in the BT-0.025BFO due to its small magnetic properties given by low content of Fe ions even though it exhibited good piezoelectric values ($g_{33} = 10.5 \times 10$ mV·m/N and $d_{33} = 78$ pC/N).

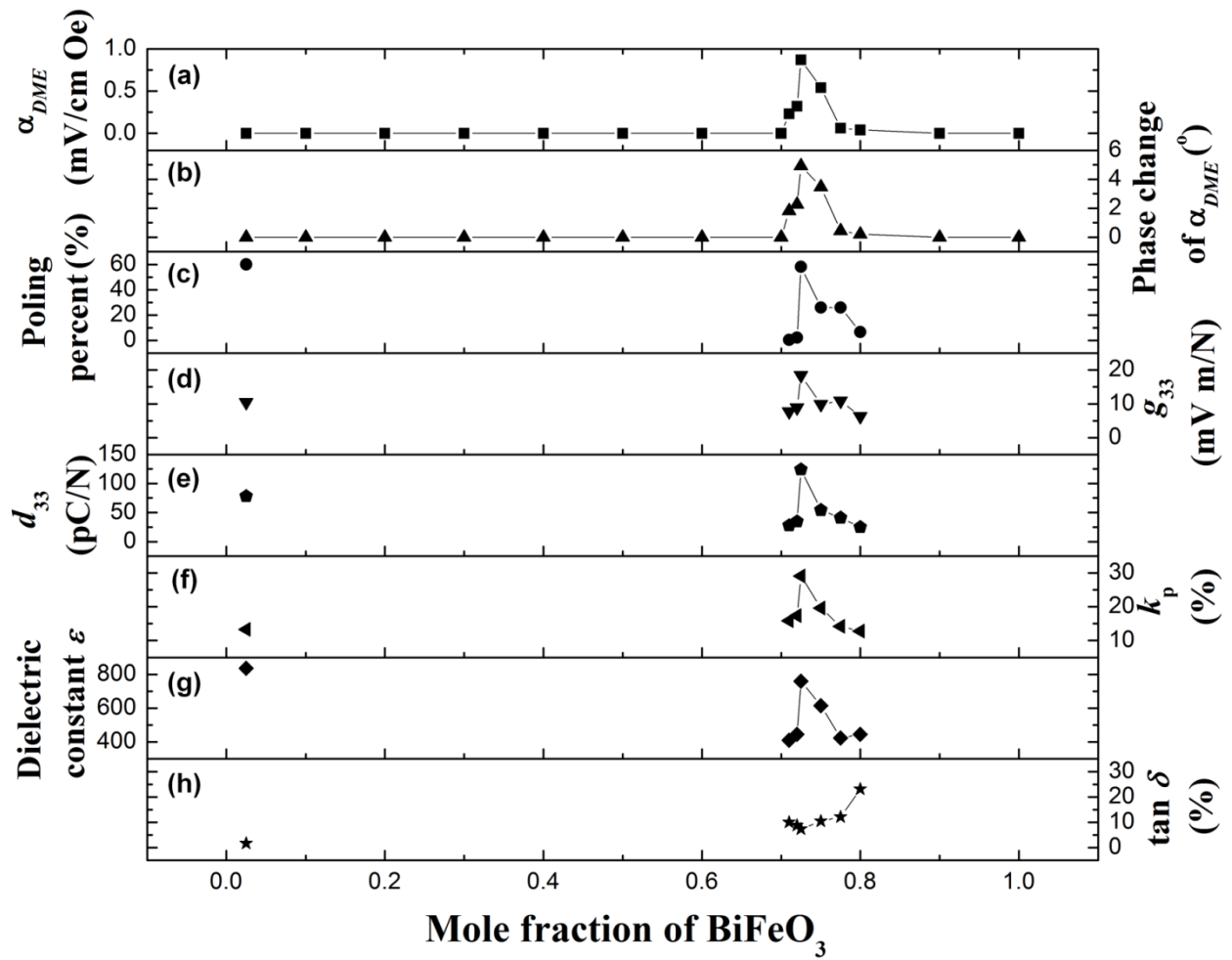


Figure 6-3. Variation of magnetoelectric, piezoelectric, and dielectric properties as a function of BFO mole fraction for BT-xBFO ceramics with $x = 0.025 - 1.0$; (a) DME coefficient, (b) phase change of α_{DME} , (c) poling percent, (d) piezoelectric voltage constant, (e) piezoelectric charge constant, (f) radial mode electromechanical coupling factor, (g) dielectric constant and (h) tangent loss factor.

To understand the relationship between improved ME performance and the local structure, the BT- x BFO compositions ($x = 0.710 - 0.775$) were further investigated through Raman spectroscopy. Figure 6-4(a) shows the Raman activity indicating the polar state of the BT- x BFO systems ($x = 0.71, 0.725, 0.775$ and 1.0). The characteristic modes for pure BFO ($x = 1.0$) occur at 74 (s), 130(vs), 167(m), 217(m), 273(m), 294(vw), 343(vw), 406(vw), 470(vw) and 553(vw) cm^{-1} , where, s, vs, m and vw, are abbreviated for strong, very strong, medium and, very weak intensity, respectively. The modes caused by the internal vibration of FeO_6 octahedra are mainly located above 200 cm^{-1} , while the modes related to various sites occupied by bismuth are found below 200 cm^{-1} .¹⁶² The rhombohedral R3c primitive cell contains two formula units and exhibits total 20 ($5A_1 + 5A_2 + 10E$) r-point phonon modes. Among these, $5A_2$ modes are silent. Further, two ($A_1 + E$) modes are acoustic, and therefore only 13 ($4A_1 + 9E$) modes are Raman active. Peaks at 130, 167, 217 and 470 cm^{-1} correspond to $4A_1$ modes and at 74, 273, 294, 343, 406, 553 can be ascribed to 6E modes. Additional 3E modes appear nearly 130, 343 and 553 cm^{-1} and therefore, are masked with the other modes at similar position.¹⁶³⁻¹⁶⁵ With incorporation of BT in BFO, two noticeable changes were observed in Raman spectra (i) drastic enhancement and disappearance of intensity of Raman modes at 74 and 130 cm^{-1} and (ii) broadening and blue shift/appearance of new modes. The change in the intensity and shift in O-Fe-O modes is too high to be caused by change in lattice size of rhombohedral phase, since there is not enough difference in ionic radii of B-site ($\text{Fe}^{3+} = 0.64 \text{ \AA}$ and $\text{Ti}^{4+} = 0.68 \text{ \AA}$) ions. Therefore, this maybe related to the structural changes from rhombohedral (R3c) to pseudo-tetragonal (P4mm) phase in short range for the certain compositions of BT- x BFO.¹⁶⁶ Moreover, the primitive cell of the tetragonal (P4mm) phase contains one formula unit and reveals 10 ($4A_1 + B_1 + 5E$) r-point phonon modes. Among these, eight ($3A_1 + 4E + B_1$) modes are Raman active and two ($A_1 + E$)

are acoustic. Raman modes in nearly tetragonal BiFeO₃ thin films have been noticed approximately at 146, 220, 227, 242, 266, 273, 321, 368, 587 and 691 cm⁻¹.¹⁶⁷ Though many of modes are common some additional modes appear giving indication of possible monoclinic distortion.^{166,167} Monoclinic BFO exhibits 30(15A' + 15A'') r-point phonon modes, among these, 27(14A' + 13A'') modes are Raman active (three A' + 2A'' acoustic modes). Further, increase in BT content causes a slight red shift and enhancement in intensity, followed by subsequent blue shift and reduction in intensity on addition of BT. The addition of BT in BFO causes the monoclinic distortion and the highest monoclinic distortion can be noticed at the composition of BT-xBFO (x = 0.725).

To understand the local structure atomic pair distribution function (PDF) analysis was performed. Figure 6-4 (b) shows the PDFs for BT-xBFO (x = 0.725) and BFO (x = 1.0). Experimental XRD patterns were taken with Ag radiation ($\lambda = 0.56 \text{ \AA}$) and converted into atomic PDFs. The PDFs for pure BFO (x = 1.0) very well fit with a structure model featuring a rhombohedral structure (S.G. R3c) with lattice parameters in hexagonal setting (a = 5.583 Å, c = 13.835 Å and gamma = 120°). The PDFs for BT-xBFO (x = 0.725) better fit at lower r values with a structure model featuring a monoclinic structure (S.G. Cm) with parameters (a = 5.499 Å, b = 5.631 Å, c = 3.974 Å and beta = 91°). At higher r values (see the encircled area), a rhombohedral model (S.G. R3c) (a = 5.558 Å and c = 13.834 Å and gamma = 120°) seems to get somewhat better. Thus this material may be featured as rhombohedral on average but with local monoclinic distortions/symmetry.

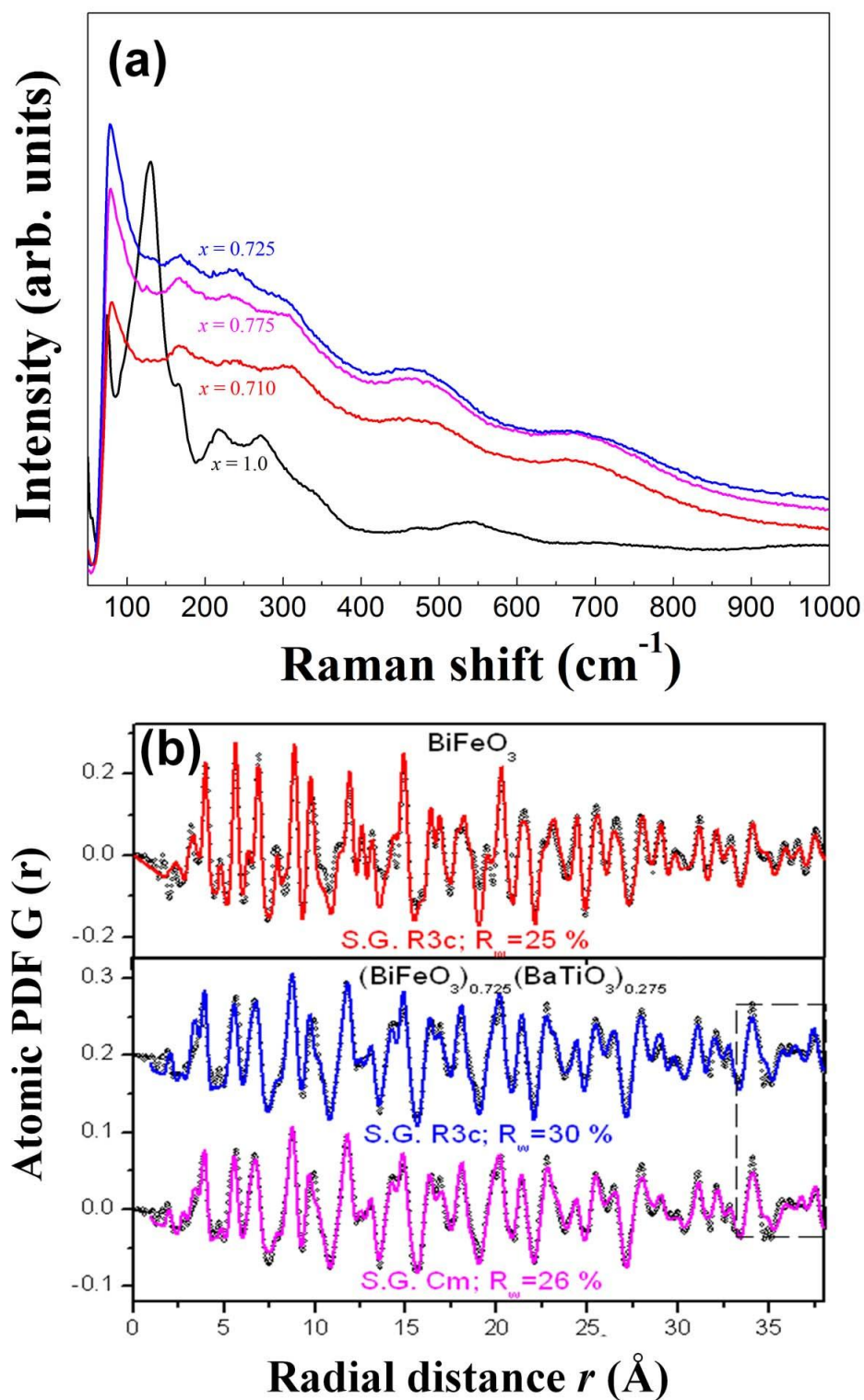


Figure 6-4. (a) Raman spectra and (b) PDFs analysis for BT-xBFO ceramics.

Figure 6-5 (a) shows the polarization-electric field ($P - E$) hysteresis for BT- x BFO ceramics ($x = 0.710 - 0.775$). With increasing BFO mole fraction, the coercive electric field (E_c) was increased up to 36.4 kV cm^{-1} ($x = 0.775$) and the remanent polarization (P_r) was also enhanced with high magnitudes of 12.5 ($x = 0.725$), 13.8 ($x = 0.750$) and $10.9 \text{ } \mu\text{C cm}^{-2}$ ($x = 0.775$). The composition of BT- x BFO ($x = 0.725$) was found to exhibit saturated hysteretic curve. Figure 6-5 (b) shows the magnetization-magnetic field ($M - H$) curves for BT- x BFO ceramics ($x = 0.710 - 0.775$) which were measured under a magnetic field of -7 kOe to $+7 \text{ kOe}$ at room temperature. The $M - H$ curves exhibited linear behavior and no saturation with low magnetic susceptibility (χ) representing insufficient cycloidal spiral in the BT- x BFO solid solutions. With increasing BFO mole fraction from 0.710 to 0.750 , the magnetic permeability (μ) was improved and the magnitude of magnetization was increased up to 0.03 emu/g at 7 kOe for the composition BT- x BFO ($x = 0.750$). The improved magnetic properties may be due to the increased amount of Fe ions in the BT- x BFO system. On the other hand, the enhanced magnetic properties with decreasing BFO mole fraction from 0.775 to 0.750 could be attributed to active spin modulation of ordered Fe-O-Fe. It is illustrated that the substitution of large ions of Ba^{2+} and Ti^{4+} on the A- and B- sites respectively may enlarge the distortion of bond angle of Fe-O-Fe to release the spiral magnetic modulation.

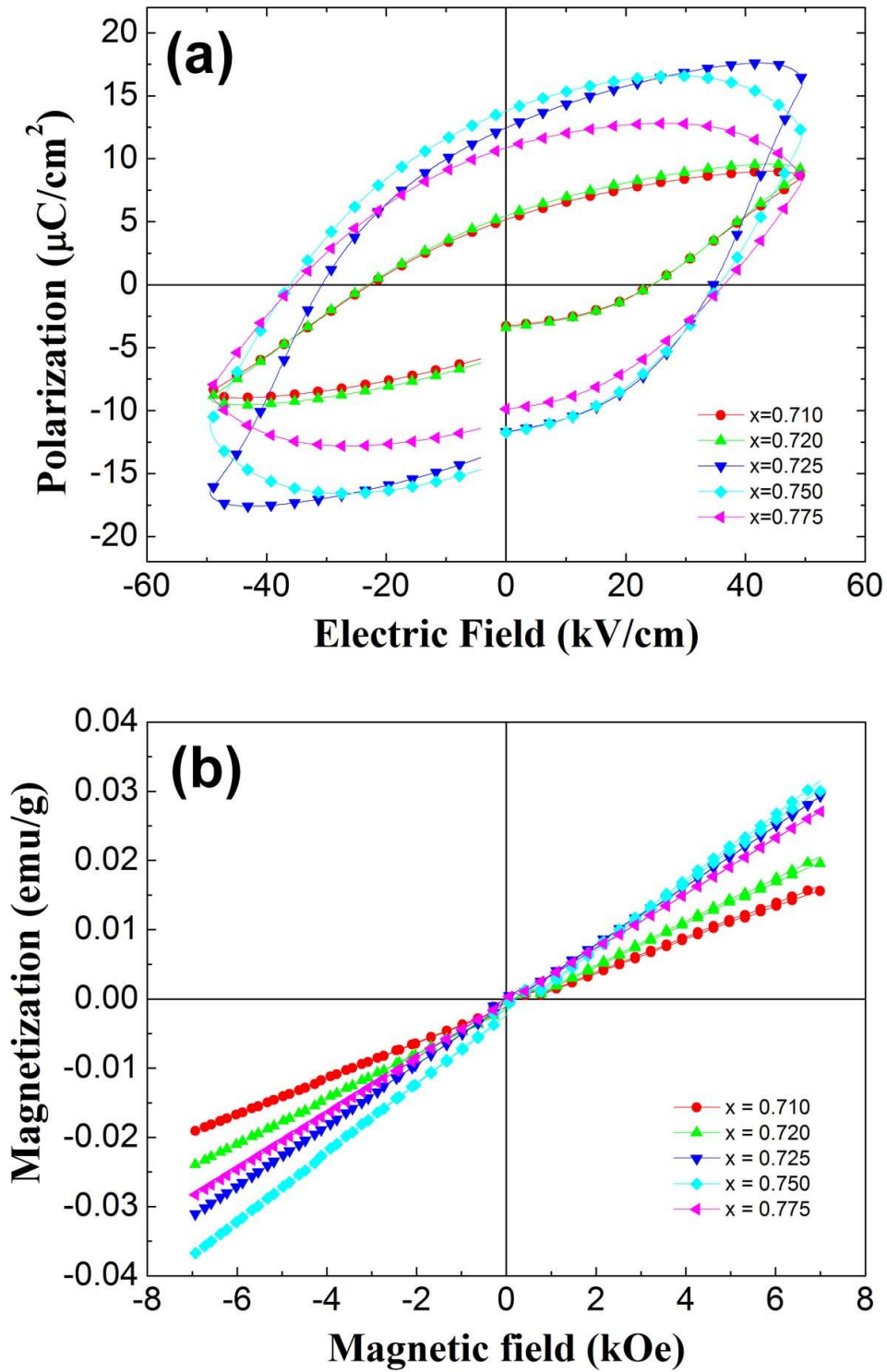


Figure 6-5. (a) Room-temperature $P - E$ curves and (b) Room-temperature $M - H$ curves as a function of BFO mole fraction.

6. 2 Magnetoelectric effect of BT-BFO / Ni laminates

BT-0.725BFO / nickel (BT-BFO / Ni) bilayer laminates were fabricated with longitudinally poled and transversely magnetized configuration to understand the tunability of DME and CME effect. Figure 6-6 (a) and (b) show the DME and CME responses for BT-BFO/Ni laminate. For DME measurement, H_{AC} of 1 Oe at 1 kHz was applied through the Helmholtz coil to the laminate and the induced voltage was measured. Figure 6-6 (a) shows that the α_{DME} exhibits maximum magnitude of 75.4 mV/cm·Oe at H_{bias} of 100 Oe with remanent α_{DME} of 13.6 mV/cm·Oe at zero H_{bias} during H_{bias} sweeps. The presence of remanent α_{DME} was realized with exactly the same magnitude by only turning on H_{AC} in the absence of H_{bias} sweep. The result definitely illustrates that the remanent α_{DME} is not a hysteretic characteristic but a spontaneous effect. For CME measurement, V_{AC} of 1 V with 1 kHz was applied directly on the sample and then the induced magnetic flux density was measured by using Helmholtz coil. In the CME response shown in Figure 6-6 (b), the hysteretic behavior was same with respect to H_{bias} sweep; the maximum α_{CME} was observed with magnitudes of 2.41×10^{-6} mG·cm/V at $H_{bias} = 100$ Oe and the remanant α_{CME} was obtained with magnitude of 4.02×10^{-7} mG·cm/V at $H_{bias} = 0$ Oe under applied $V_{AC} = 1$ Oe. The self-biased ME effects in BT-BFO / Ni laminates can open possibility for developing magnetically or electrically tunable nano-devices.

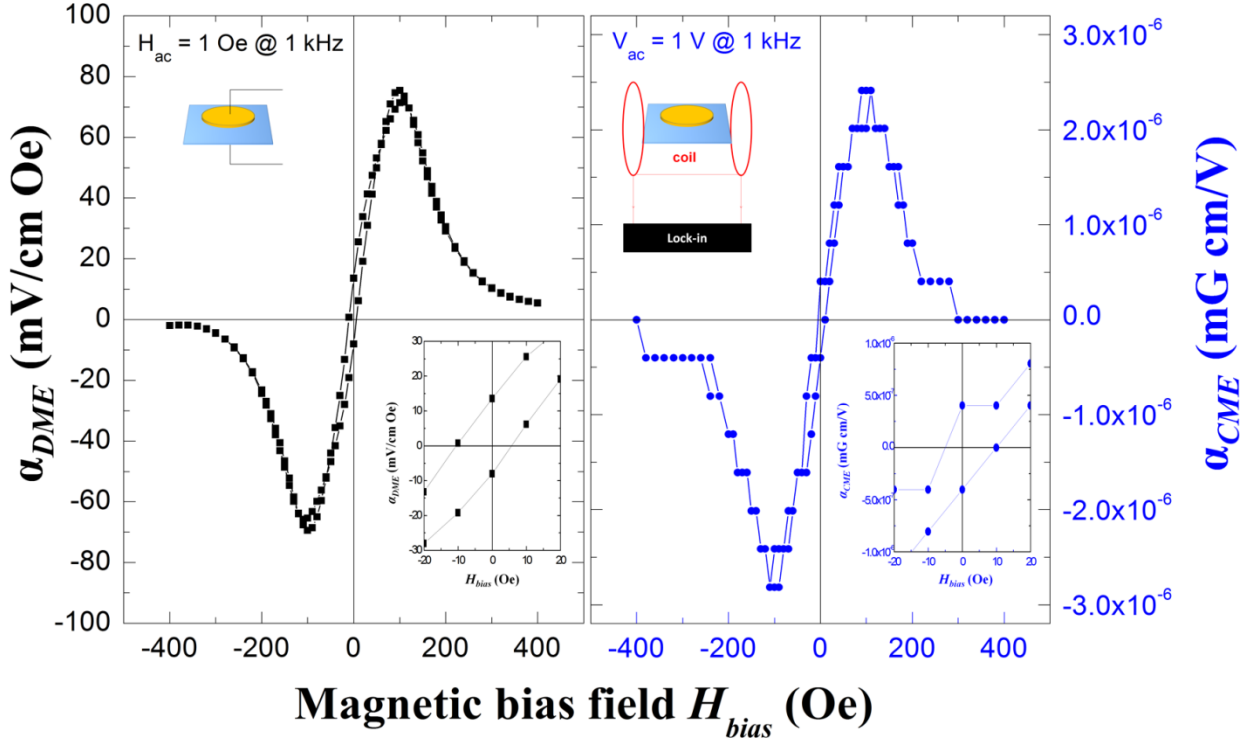


Figure 6-6. (a) DME coefficient and (b) CME coefficient for BT-0.725BFO/Ni laminates as a function of H_{bias} . Insets are schematic diagrams of DME and CME samples and expanded views of α_{ME} - H_{bias} hysteresis to show the remnant α_{DME} and α_{CME} at zero H_{bias} .

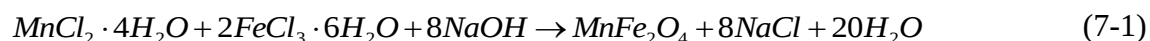
In this chapter, solid solutions of lead-free $(1 - x) \text{BaTiO}_3 - x \text{BiFeO}_3$ (BT- x BFO, $x = 0.025 - 1.0$) were synthesized for high magnetoelectric (ME) coupling determined by compositional structure transformations in single-phase multiferroics. The BT- x BFO multiferroic ceramics exhibited structural changes as a function of BFO mole fraction; tetragonal ($x = 0.025$) – pseudo-cubic ($x = 0.1 - 0.7$) – rhombohedral ($x = 0.8 - 1.0$). In the limited compositions of BT- x BFO ($x = 0.71 - 0.8$), the room-temperature ME responses were observed due to their sufficient piezoelectric and magnetic properties. Particularly, the maximum ME coupling coefficient (0.87 mV/cmOe) was achieved in the optimized composition of BT- x BFO ($x = 0.725$) exhibiting high piezoelectric properties ($g_{33} = 18.5 \times 10 \text{ mV} \cdot \text{m/N}$ and $d_{33} = 124 \text{ pC/N}$). From the detail structural analysis of Raman and atomic pair distribution functions (PDFs), it was revealed that the enhanced piezoelectric characteristics were related to local monoclinic distortions in rhombohedral phase of the BT- x BFO ($x = 0.725$). Finally, the BT-0.725BFO/Ni bilayer laminates were fabricated and its direct magnetoelectric (DME) and converse magnetoelectric (CME) effects were investigated at room temperature. Especially, the self-biased ME effects with zero magnetic bias (H_{bias}) reflects a feasibility of magnetically or electrically tunable nano-devices.

CHAPTER 7

CORE-SHELL FERROMAGNETIC-METAL NANOPARTICLES

7. 1 High performance MFO nanoparticles

In this chapter, the focus was on the synthesis of ceramic-metal core-shell particles via an aqueous method as schematically illustrated in Figure 7-1. First, MnFe_2O_4 core particles exhibiting high magnetization were synthesized by a solvothermal method. Chemical reaction during the synthesis of MnFe_2O_4 nanoparticles is described as:



Through the solvothermal synthesis, the magnetic nanoparticles can be formed with precise control of size, shape and crystallinity. Especially, the primary particle size is a critical factor towards determining the magnetic properties.¹⁵⁹ Therefore, the synthetic conditions for high magnetization were optimized by variations of molecular weight of polymer, stirring rpm, synthetic temperature and time. In order to well encapsulate nickel onto the core magnetic particles, aqueous electroless coating method was conducted using ionic interactions between Ni^+ ions and negatively charged MnFe_2O_4 particles. The surface charges of magnetic particles were changed as a function of pH value of colloidal solutions. Under base condition (pH 10 – 12), the magnetic particles exhibited negative surface charges which can be interacted with positive Ni ions. Moreover, the metal encapsulation via the ionic interaction would be adjustable in Ni coating with thickness range of 1 to 5nm on MnFe_2O_4 nanoparticles. Finally, the entire EMS effect in metal-coated ferromagnetic nanoparticles would be electrically controllable.

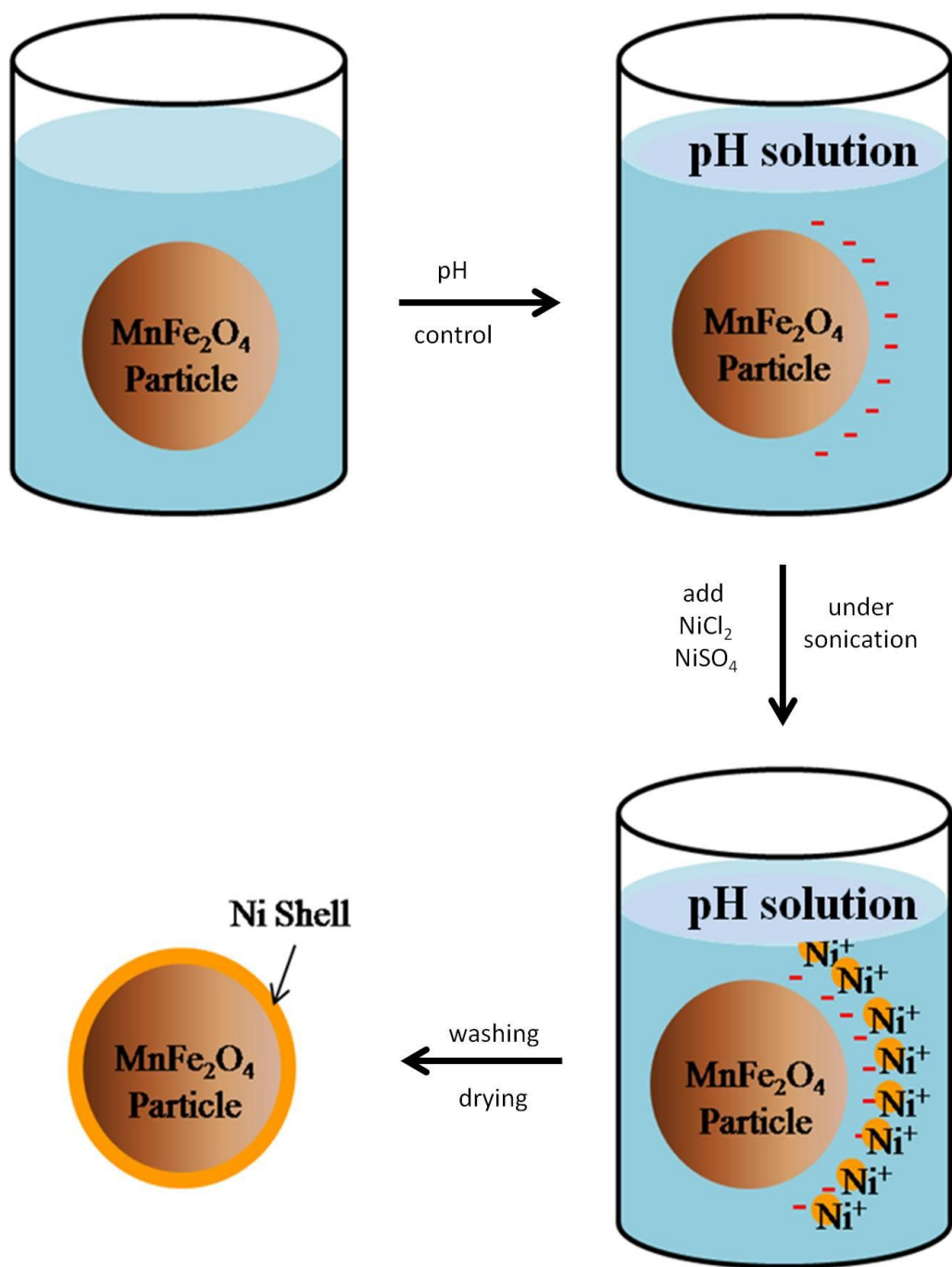


Figure 7-1. Schematic diagram of experimental procedure for the synthesis of core-shell MnFe_2O_4 -Ni nanoparticles.

Nanoparticles of MnFe_2O_4 were synthesized by coprecipitation of Mn^{II} and Fe^{III} ($\text{Mn}^{2+}/\text{Fe}^{3+} = 0.5$) in ethylene glycol. Starting materials of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.50 g, 2.5 mmol) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.35g, 5mmol) were dissolved in ethylene glycol (40ml) after which 3.6g of NaAc and 1.0g of polyethylene glycol was added to the solution. The mixture was stirred vigorously for 30min and then sealed in an autoclave. The autoclave was heated to 200°C for 24h and slowly cooled to room temperature resulting in the formation of MnFe_2O_4 particles. These particles were retrieved, washed several times with ethanol and dried at 60°C for 6h. To characterize the magnetic response of individual particles through magnetic force microscopy (MFM), MnFe_2O_4 particles were spread on a glass substrate by repeated dipping. For this purpose, 0.1mg of MnFe_2O_4 was added into 15ml ethanol and the colloidal solution was sonicated for 10min. After which a glass substrate was vertically dipped five times in this colloidal ethanol solution and subsequently dried at room temperature. MnFe_2O_4 -Ni composite core-shell particles were synthesized by an aqueous method as illustrated in Figure 7-1. One mg of MnFe_2O_4 was added into 15ml of aqueous solution with $\text{pH} = 10$: where the pH magnitude was adjusted by adding HNO_3 or TEAOH (tetraethylammonium hydroxide). Particles of MnFe_2O_4 suspended in the aqueous solution ($\text{pH} = 10$) possessed a negative surface potential of -40mV , as shown the Figure 7-2(a). The raw materials of 0.08g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.23g of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ were added to the solution and the mixture was then sonicated for 10 min, resulting in the formation of MnFe_2O_4 -Ni core-shell particles. During this step, the Ni^+ ions dissociated in the aqueous solutions, and subsequently were coated onto the negatively-charged MnFe_2O_4 particles. The MnFe_2O_4 -Ni core-shell particles were washed several times with distilled water and methanol, and then dried at room temperature.

Figure 7-2(b) shows the morphology of the MnFe_2O_4 particles synthesized by the solvothermal method. The particles had a high density with a mean size of about 200nm. These MnFe_2O_4 particles were formed by agglomeration of primary nanoparticles with a mean diameter of 15nm. Phase formation of MnFe_2O_4 was confirmed by XRD, as shown in Figure 7-2(c). No measureable trace of any secondary phase was found in the XRD pattern. At room temperature, the M-H curves for these MnFe_2O_4 particles exhibited a saturation magnetization of 74 emu/g and a coercivity of 89 Oe, as shown in Figure 7-2(d). Figure 7-3 further confirms that synthesized individual MnFe_2O_4 particles were magnetic, which shows MFM images obtained from monolayer, spread onto a glass substrate.

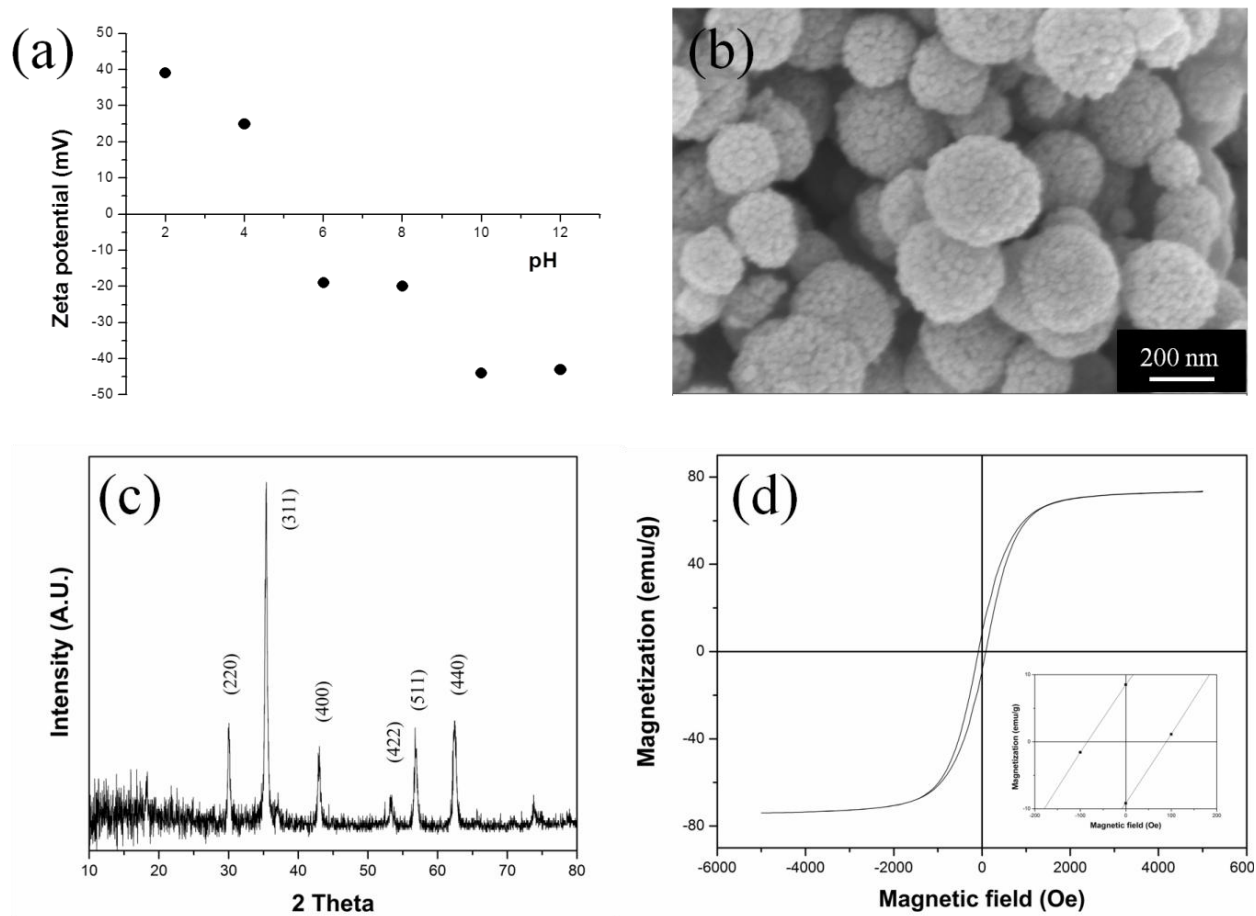


Figure 7-2. (a) Zeta-potentials of MnFe₂O₄ particles for $2 \leq \text{pH} \leq 12$, (b) SEM image of MnFe₂O₄ particles, (c) XRD pattern of MnFe₂O₄ particles, and (d) M-H curve of MnFe₂O₄ particles.

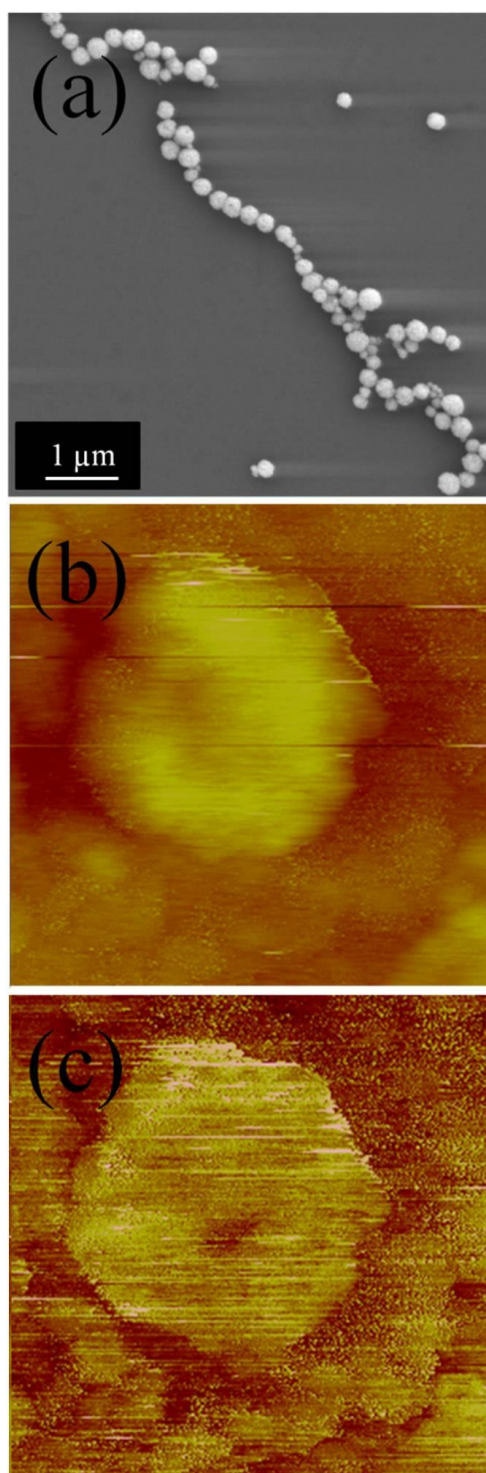


Figure 7-3. (a) SEM image, (b) AFM image, and (c) MFM image of MnFe_2O_4 particles onto a glass substrate.

7.2 Ni encapsulation onto MFO nanoparticles

The zeta-potentials for the MnFe_2O_4 particles were found to be in the range of + 40 mV to - 40 mV for $2 \leq \text{pH} \leq 12$ (see Figure 7-2(b)). Higher negative surface charges, such as the particles for $\text{pH} > 10$, were used as a driving force to coat Ni onto the MnFe_2O_4 particles. In the alkaline conditions, Ni^{+} ions dissociating from NiCl_2 and NiSO_4 interact with the negatively-charged MnFe_2O_4 particles. Figure 7-4(a) shows SEM images of Ni-coated MnFe_2O_4 particles that were synthesized in the pH range of 2 to 12. The Ni content in the MnFe_2O_4 -Ni composite particles increased from a total weight percentage of 0.6 wt% to 6.3 wt% for $8 \leq \text{pH} \leq 11$, as shown in Figure 7-4(b). The results of Figure 7-4 were utilized to identify the optimum solution process conditions, and indicate how the metal-shell thickness ratio can be controlled by varying the pH. The adhesion between the metal and ceramic was found to be quite good as further processing did not indicate any changes in the morphology.

Figure 7-5 shows the magnetic properties of MnFe_2O_4 -Ni core-shell particles. At room temperature, the saturation magnetization and remanent magnetization of core-shell particles decreased to 43 % and 50 % of that of the core particles, respectively. The core-shell particles exhibited a coercivity of 100 Oe which was similar to that of core particles. Figure 7-6(a) and (b) show TEM images of the MnFe_2O_4 particles before and after Ni coating. The core-shell particles in Figure 7-6(b) were synthesized under a $\text{pH} = 11$. Figure 7-6(c) shows a high resolution TEM image for a MnFe_2O_4 -Ni core-shell particle. This image reveals that Ni shells uniformly coat onto MnFe_2O_4 particles with a thickness of 1nm. EDS analysis conducted at point 2 (marked in Figure 7-6(c)) revealed a higher Ni concentration as compared to Fe, than that at point 1. This confirms that the Ni coating was limited to the surface of the MnFe_2O_4 particles with almost no inter-diffusion. Figure 7-7 shows selected area electron diffraction patterns for (a) MnFe_2O_4

particles and (b) MnFe_2O_4 -Ni core-shell particles. Additional rings from Ni can be seen in the diffraction pattern of core-shell particles. Rings from (111) and (200) of Ni were indexed for the Ni-coated MnFe_2O_4 particles. Thus, by combining the results, the uniform coating onto the MnFe_2O_4 particles was confirmed.

In this chapter, MnFe_2O_4 -Ni core-shell nanoparticles were synthesized to be used as an electromagnetostrictive material for electrically controllable single devices. The ferromagnetic nanoparticles of MnFe_2O_4 were synthesized in the range of 200 nm by solvothermal method and exhibited high saturation magnetization of 74 emu/g with coercivity of 89 Oe. The Ni encapsulations on MnFe_2O_4 nanoparticles were conducted by adjusting ionic interactions in different pH MnFe_2O_4 solutions. Finally, Ni shells were coated with a uniform thickness of 1 nm on MnFe_2O_4 nanoparticles and the Ni encapsulation was confirmed by TEM, EDS, and SAED characterizations. The core-shell ceramic-metal nanoparticles have being used in the application for memristor as an electrically controlled device.

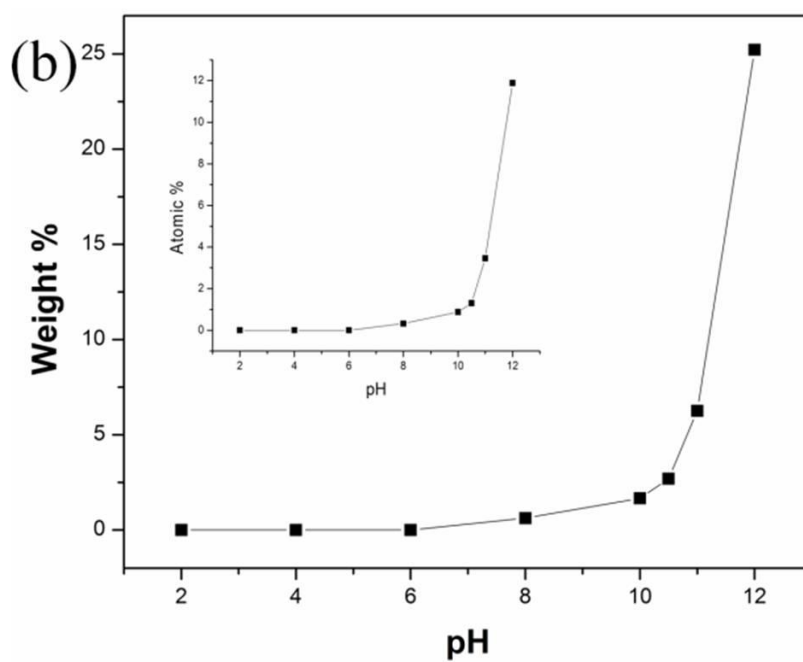
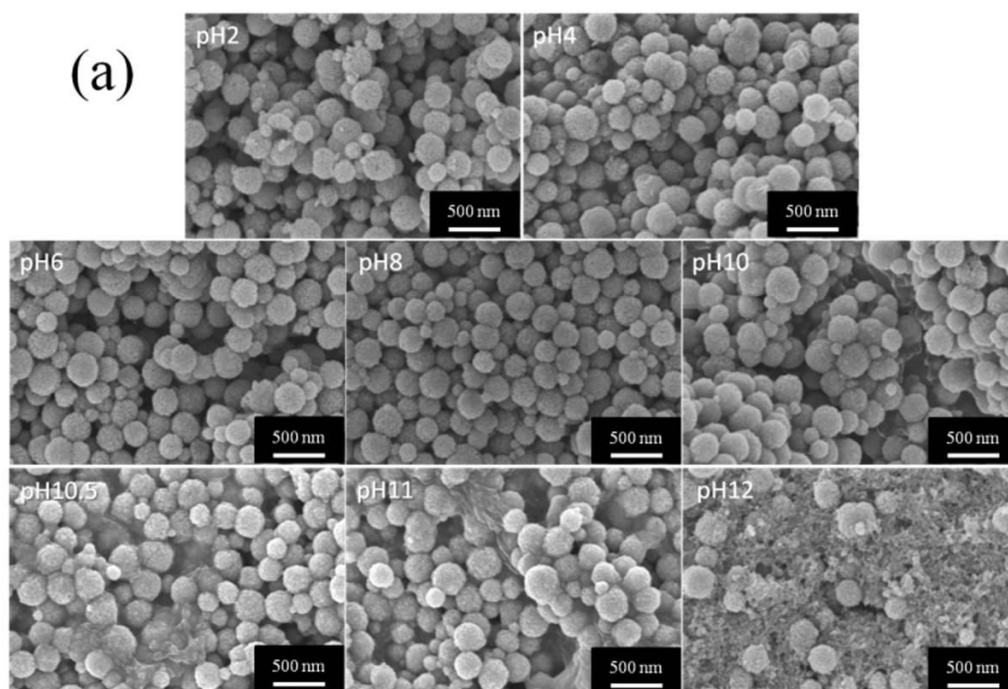


Figure 7-4. (a) SEM images and (b) Ni concentration of MnFe₂O₄-Ni core-shell particles synthesized for $2 \leq \text{pH} \leq 12$.

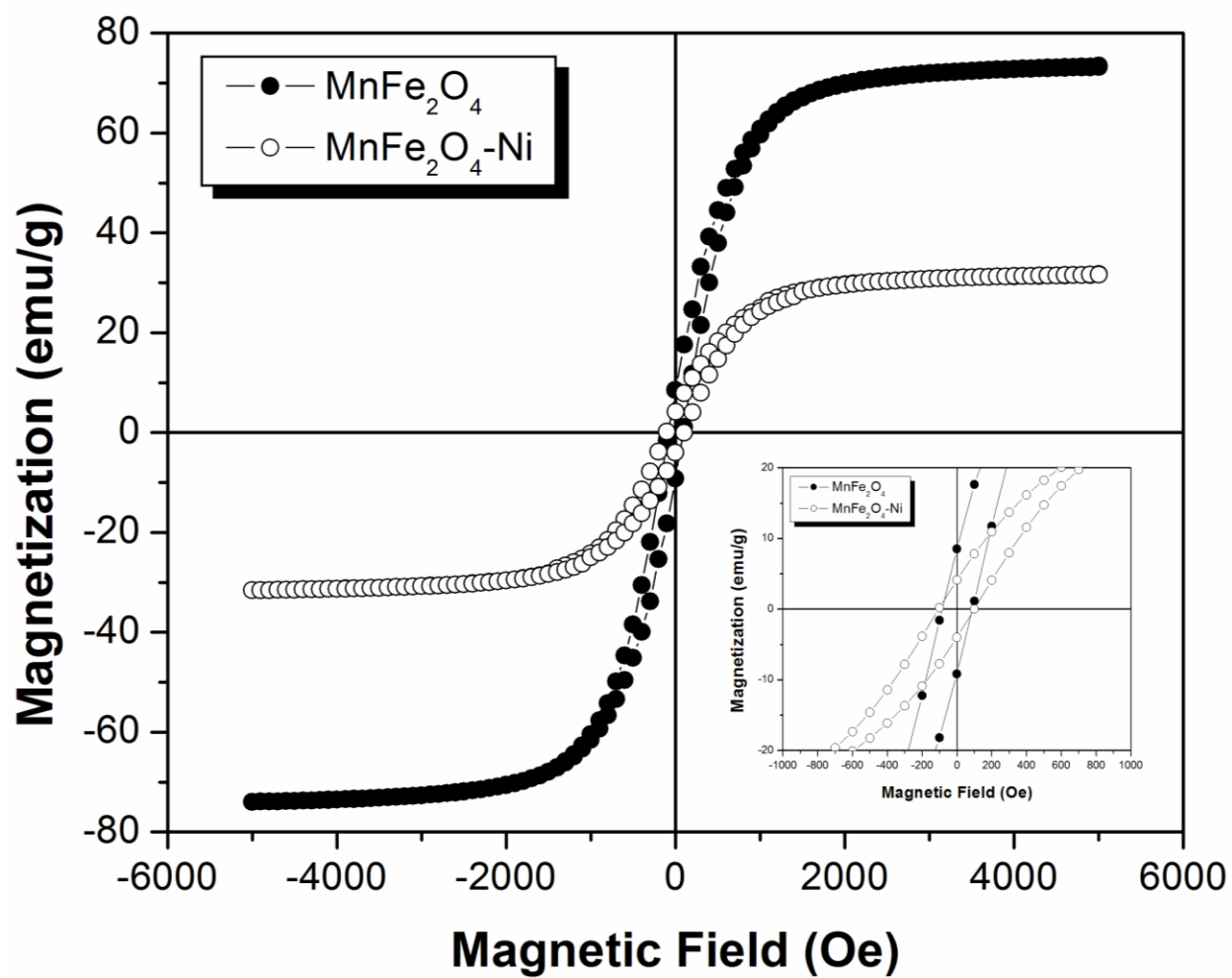


Figure 7-5. M – H curves for MnFe_2O_4 and Ni-coated MnFe_2O_4 nanoparticles.

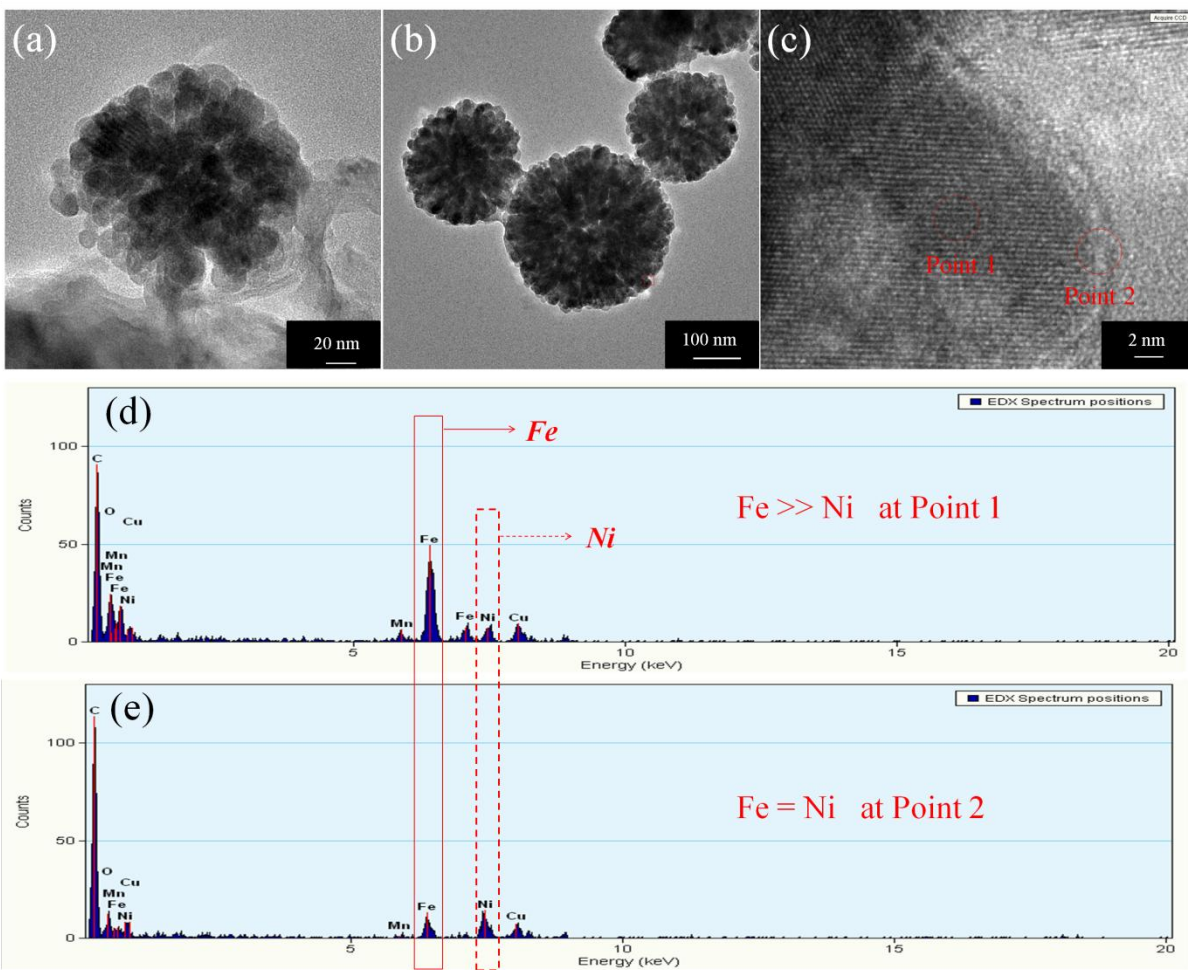


Figure 7-6. TEM images of (a) MnFe₂O₄ particles and (b) MnFe₂O₄-Ni core-shell particles, (c) HR-TEM image of MnFe₂O₄-Ni core-shell particles, (d) EDS at Point 1 of MnFe₂O₄-Ni core-shell particles, and (e) EDS at Point 2 of MnFe₂O₄-Ni core-shell particles.

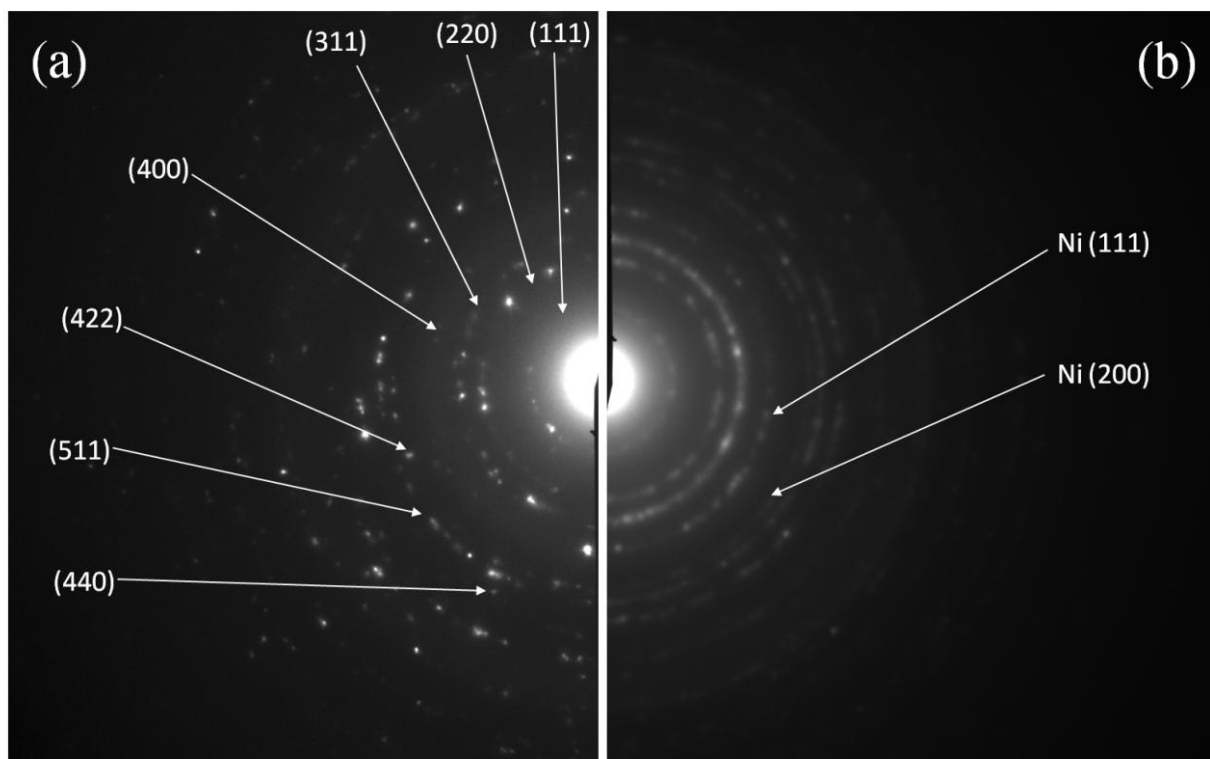


Figure 7-7. Selected area electron diffraction patterns of (a) MnFe_2O_4 particles and (b) MnFe_2O_4 -Ni core-shell particles.

CHAPTER 8

VERTICALLY ALIGNED PIEZOELECTRIC NANORODS

8. 1 Synthesis of PZT nanorods via template transfer method

In this chapter, vertically aligned PZT nanorod arrays were synthesized on a platinized silicon substrate via transfer method using well ordered porous templates. Figure 8-1 illustrates the experimental procedure. The synthesis processes proposed here consists of: (i) two-step aluminum anodizing (Figure 8-1 (b)) to fabricate well-ordered and straight cylindrical pores, (ii) complete aluminum anodizing (Figure 8-1 (c)) to completely remove anodic aluminum oxide (AAO) templates during final step, (iii) vacuum infiltration of PZT precursor solution (Figure 8-1 (d)) to make dense nanostructures, (iv) transfer of infiltrated-PZT AAO (PZT-AAO) films on a Pt-Si substrate (Figure 8-1 (f)) using adhesive PZT layer to improve contact adhesion, and (v) selective AAO etching (Figure 8-1 (g)) to expose the PZT nanostructures on Pt-Si substrate.

High purity aluminum (Al) foils with a thickness of 0.32 mm (99.999%, Goodfellow Inc.) were used as a raw material for fabricating well-ordered porous template. Prior to anodizing, the Al foil was cleaned in acetone. Subsequently, the two-step aluminum anodizing was conducted on top-surface of Al foils using 0.3 M oxalic acid electrolyte. The 1st anodized AAO layers on Al foil were prepared by 5 min anodizing at 25 °C under applied voltage of 50 V and then removed by etching for 4 hr at 70 °C under a mixed solution consisting 6 wt% H₃PO₄ and 1.8 wt% H₂CrO₄. The 2nd anodized AAO layers on Al foil were prepared by 30s anodizing at 25 °C under applied voltage of 50 V and then AAO pore opening was conducted for 37 min at 30 °C under 6

wt% H_3PO_4 solution. The pore structures of AAO template were controlled by variations of anodizing conditions (electrolytes, voltage, time and temperature) and pore opening conditions (etching solutions, time and temperature). For the transfer method in this system, the Al foils were totally anodized by complete aluminum anodizing for 24h at 25 °C under applied voltage of 50 V using 0.3 M oxalic acid electrolyte. In the cylindrical pores of AAO templates, 0.2 M PZT precursor solutions were infiltrated via vacuum and then spin coating was conducted for 45s with 3000 rpm. The PZT-AAO films were pyrolyzed for 1h at 300 °C on a hot plate and were annealed for 10 min at 650 °C in a vertical furnace. Transfer of PZT-AAO films was conducted onto a Pt-Si substrate using adhesive PZT layer with a thickness of 90 nm. After PZT thermal annealing, the selective AAO etching was performed for 12h at 25 °C under 0.1M NaOH solution. The final structure of PZT nanorods on Pt-Si substrate were obtained by water rinsing and room temperature drying for 24h.

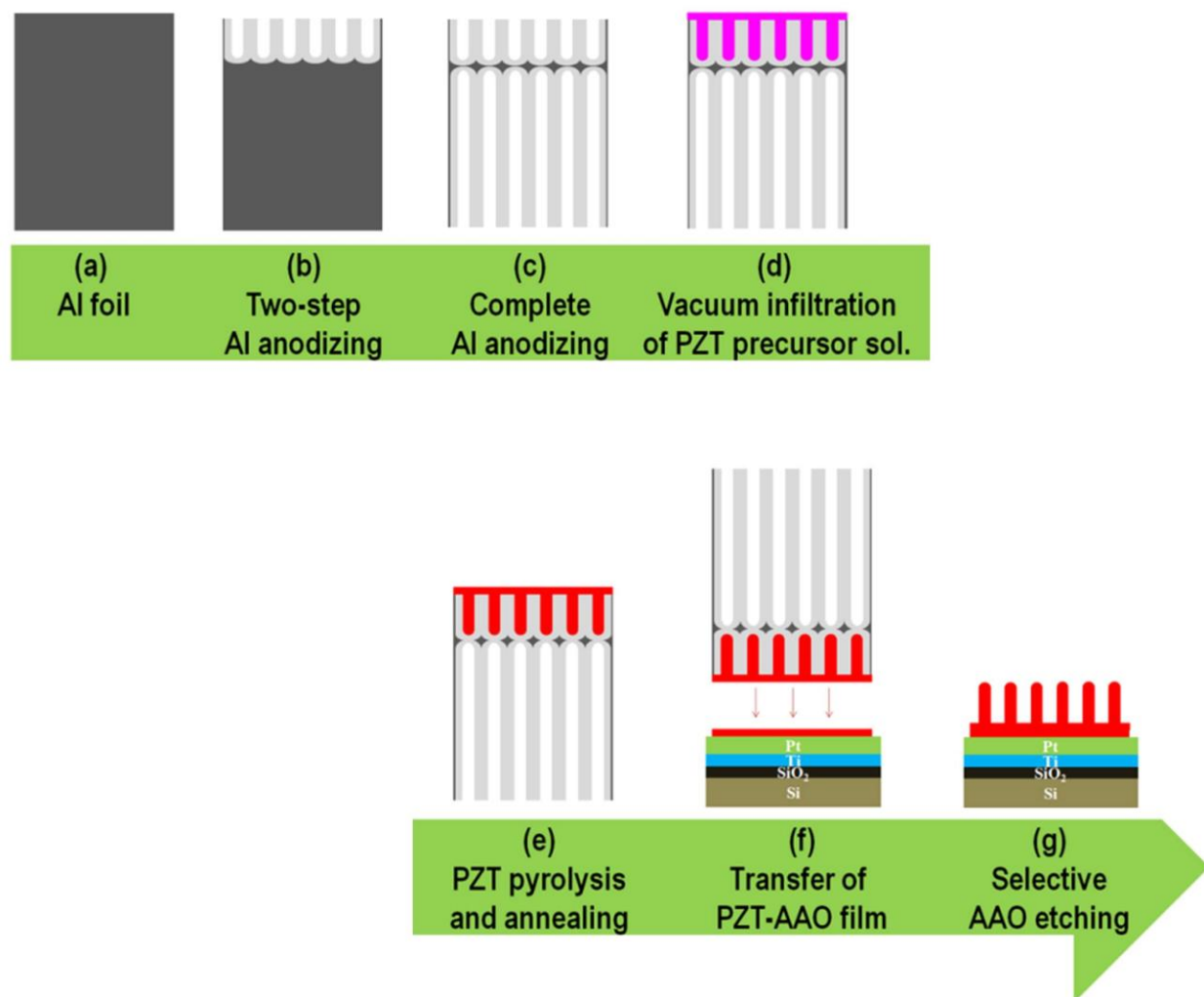


Figure 8-1. Schematic diagram of experimental procedures for vertically aligned PZT nanorod-arrays on Pt-Si substrates.

Figure 8-2 (a) - (c) are the top-view SEM images showing the surface morphologies of AAO on Al foils prepared during two-step Al anodizing. The 1st anodized AAO layers on Al foils (Figure 8-2 (a)) had rough surface and disordered pore structure. However, the ordered patterns on the surface of Al foils (Figure 8-2 (b)) were revealed by removal of 1st anodized AAO layers. With 2nd anodization on the ordered patterns of aluminum foils, ordered pore structures of AAO layers (Figure 8-2 (c)) were prepared with hexagonal patterns. The interpore distance and pore size of 2nd anodized AAO layers were 150 nm and 40 nm respectively which were controlled by varying applied voltage, reaction time and temperature. For the formation of well-ordered rod-structures, the AAO templates with pore size of 90 nm and pore length of 900 nm were prepared by AAO pore opening. The cross-sectional SEM image (Figure 8-2 (d)) describes that the AAO templates exhibited straight cylindrical and well-ordered pore structures with aspect ratio of 10. After complete anodizing on the bottom of Al foils, the cross-sectional microstructure of AAO templates (Figure 8-2 (e)) clearly illustrates the two-separated parts which will serve as a porous template (thickness of $< 1\ \mu\text{m}$) for PZT nanostructures and a supporting template (thickness of $> 300\ \mu\text{m}$) for transfer method. In order to make PZT nanorod structure, 0.2 M PZT precursor solution was infiltrated into the AAO templates via vacuum and then thermal annealing was conducted. From the top-view morphology of PZT-AAO films (Figure 8-2 (f)), it is clear that the PZT nanostructures were formed into AAO templates with thin PZT layer having a thickness of 40 nm on the top of AAO templates. The top PZT layers exhibited smooth surface formed by spin coating which is a requirement for transfer onto a flat Pt-Si substrate.

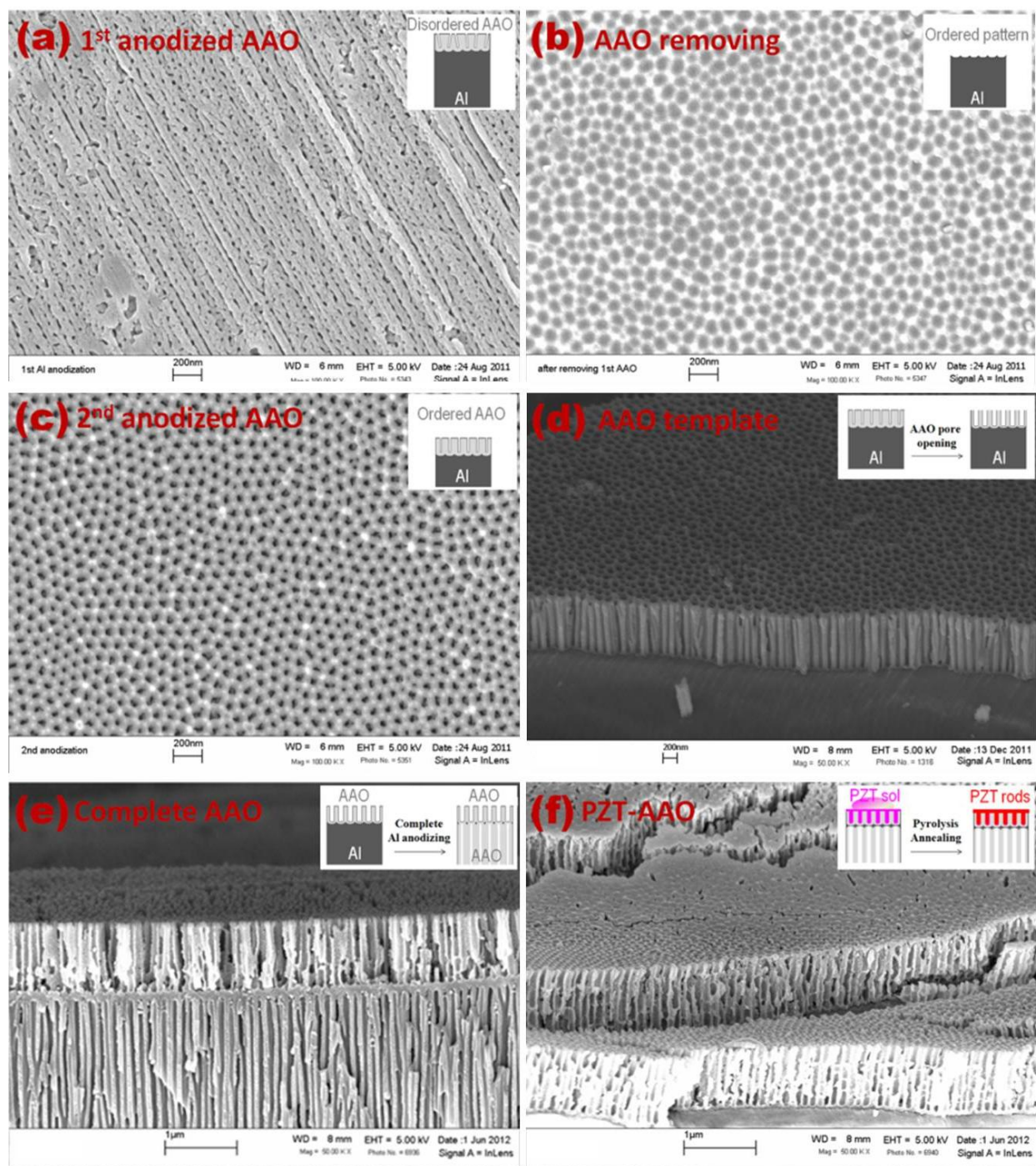


Figure 8-2. SEM images for (a) 1st anodized AAO films, (b) Al films after 1st AAO removing, (c) 2nd anodized AAO films, (d) AAO templates after pore opening, (e) complete anodized AAO templates and (f) PZT infiltrated AAO films.

Figure 8-3 (a) presents the X-ray diffraction (XRD) patterns for pure Al foils, completely anodized AAO films and annealed PZT-AAO films. The Al foils exhibited a main peak of (004) at 2θ of 45° . After complete anodizing of the Al foils, it can be seen that the peak representing Al (004) was decreased and a broad peak near 2θ of 30° appeared which can be correlated with Al_2O_3 (211).¹⁵⁵ With thermal annealing, the PZT-AAO films revealed a broad peak near 2θ of 20° that can be related to PZT (100) without any peaks for Al_2O_3 (211) and Al (004). Figure 8-3(b) shows the crystal structure of vertically aligned PZT nanorod arrays on Pt-Si substrates. The final structure of PZT nanorods (thickness of 900 nm) / PZT adhesive layer (thickness of < 150 nm) / Pt-Si substrate was prepared by PZT-AAO transfer with selective AAO etching. The PZT nanorod arrays on Pt-Si substrates exhibited XRD peaks of (100), (110) and (200) representing perovskite structure.

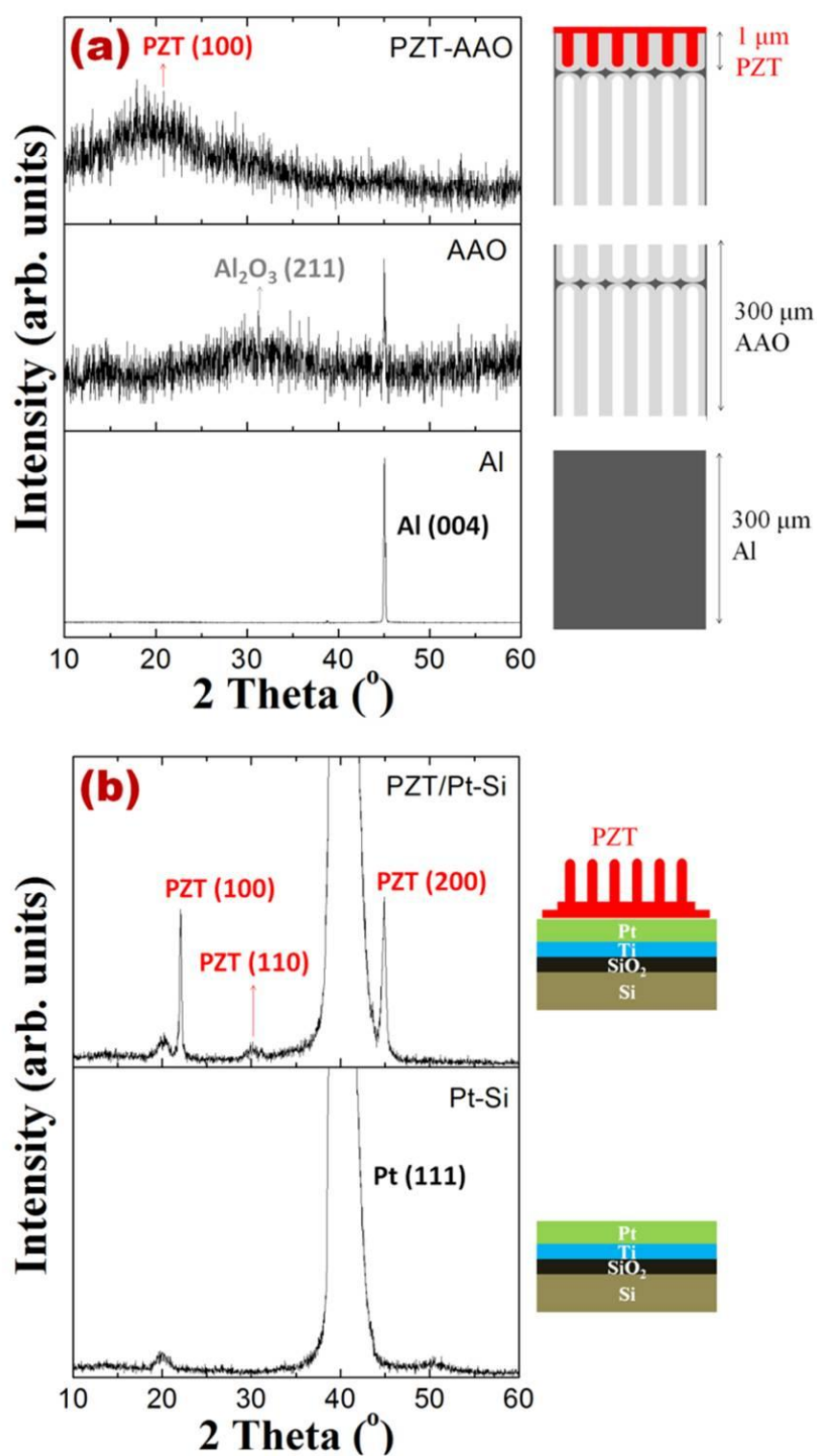


Figure 8-3. XRD patterns for (a) Al, AAO and PZT-AAO films and (b) Pt-Si substrates and PZT nanorod-arrays on Pt-Si substrates.

Figure 8-4 (a) - (c) show top-view microstructures of vertically aligned PZT nanorod-arrays on Pt-Si substrates. The PZT nanorods were found to exhibit uniform diameter with vertical ordering on the Pt-Si substrate. Further, the nanorods were obtained on large substrate area without any aggregation. The elemental composition for nanorod-arrays was investigated by EDS analysis. Figure 8-4 (d) illustrates that the rod-arrays consisted mainly of Pb, Zr and Ti elements but also small concentration of Al which could not be removed completely during selective AAO etching step. In order to confirm the geometry of PZT nanorods, the cross-sectional image of separated nanostructures from bottom PZT layer on Pt-Si substrates (Figure 8-4 (e)) was examined. The PZT nanorod-array exhibited vertical alignment with aspect ratio of 10 (average diameter of 90 nm and length of 900 nm) as expected from the AAO template. It can be noted that there was no shrinkage in the PZT nanorod with thermal annealing which further reflects that dense infiltration of PZT solution occurred in the AAO template. Recently, it has been shown that the density and aspect ratio of piezoelectric 1D nanostructure are main factors determining piezo-responses.¹⁶⁸ Thus, the dense structure of PZT nanorod (Figure 8-4 (f)) indicates that a high piezoelectric response can be obtained.

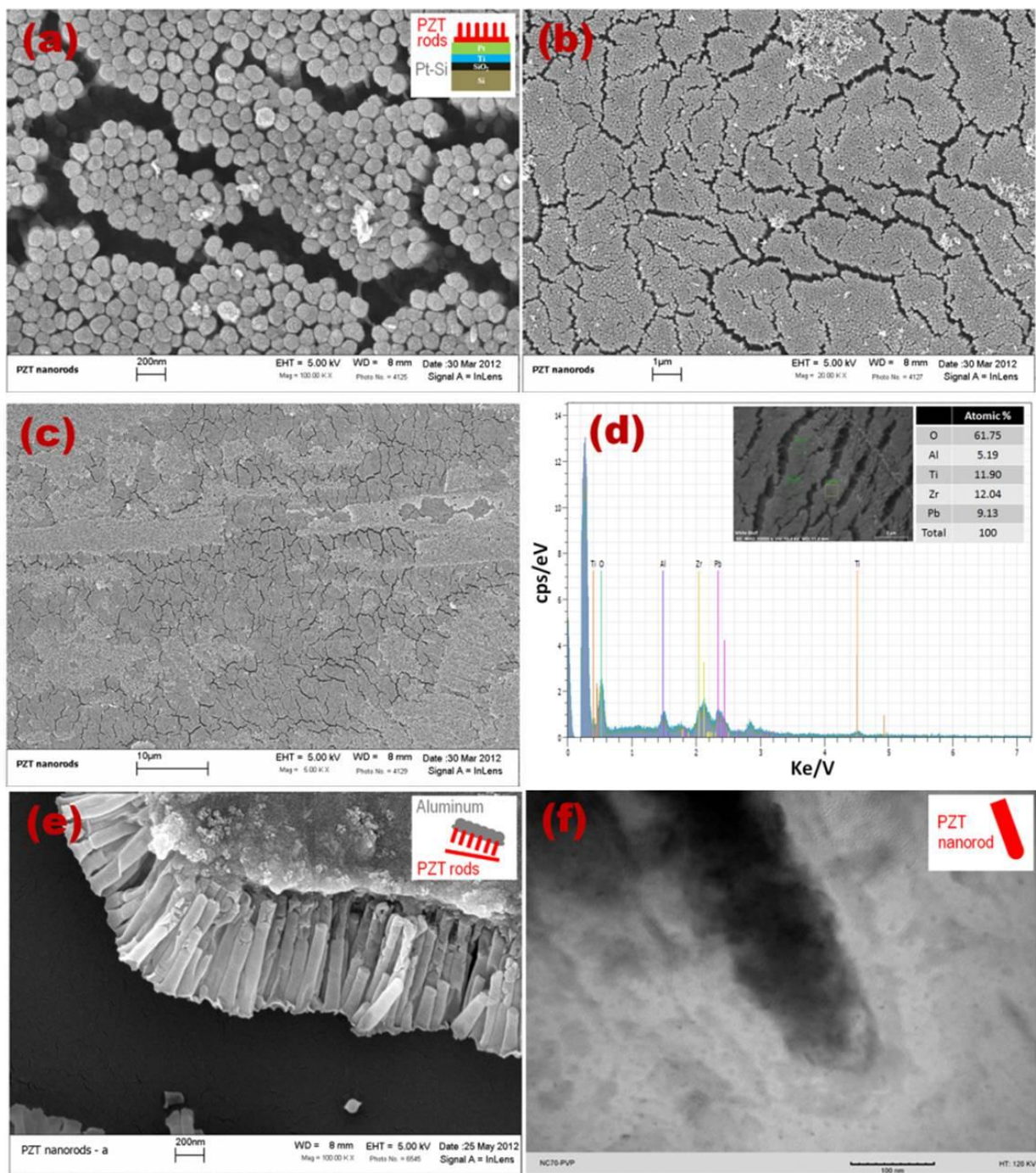


Figure 8-4. (a) - (c) Top-view SEM images for PZT nanorod-arrays on Pt-Si substrates, (d) EDS analysis for PZT nanorod arrays, (e) cross-sectional SEM image for PZT nanorod arrays and (f) TEM image of single PZT nanorod.

8.2 Piezoelectric responses of PZT nanorods

Figure 8-5 shows the piezoelectric responses for PZT nanorods measured by PFM with contact and ramp modes. To investigate the direct piezo-responses from single structure of PZT nanorod, the individual 1D nanostructure without any aggregation was selected and then characterized. From the surface topology, it can be seen that the PZT nanorods can be isolated which allowed single nanostructure measurement. The contrasts in the amplitude and phase images represent vertical direction piezo-responses for PZT nanorods on a Pt-Si substrate. The direct piezo-responses from single nanostructure were measured at the marked PZT nanorod shown on topology image by applying DC bias of $\pm 8\text{V}$. The isolated PZT nanorod was found to exhibit good hysteretic curves of piezoresponse given by the butterfly behavior of PFM amplitude and clear phase angle change with saturations as shown in Figure 8-5 (d) - (f).

In addition, the piezo-responses of PZT thin films as an adhesive layer with a thickness of 120 nm on Pt-Si substrates were measured in the contact and ramp modes to investigate distinct piezo-responses between nanorod and film. Figure 8-6 (a) describes smooth surface of PZT films on a Pt-Si substrate. Figure 8-6 (b) and (c) show clear contrasts in vertical direction piezo-response amplitudes and phase signals. At the marked point shown on topology image, the piezo-responses were investigated by applying DC bias of $\pm 8\text{V}$. The piezo-responses for PZT films were found to be asymmetric butterfly shape of piezo-responses with decreased magnitude and large shift of phase angles as compared with those for single structure of PZT nanorod. Therefore, the PZT films exhibit no hysteretic behaviors in piezoresponse – DC bias curve as shown in Figure 8-6 (f). It can be hypothesized that the asymmetric piezo-responses with low amplitude and large phase shift were related to clamping effect of Pt-Si substrates.^{147,168}

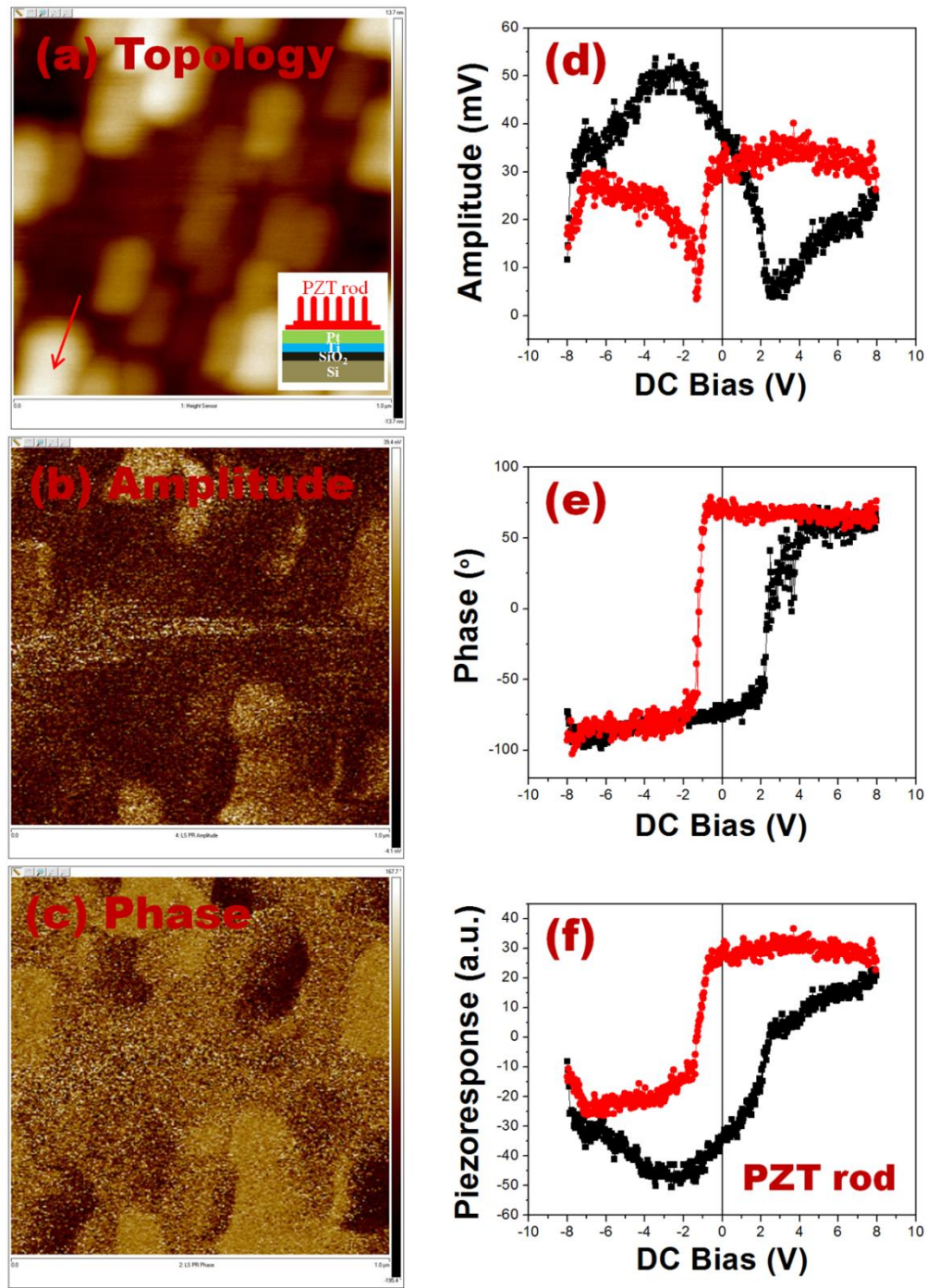


Figure 8-5. Piezo-responses for PZT nanorods with a length of 900 nm on a Pt-Si substrate; (a) topology image, (b) amplitude image, (c) phase image, (d) ramp-mode amplitudes and (e) ramp-mode phase angles and (f) ramp-mode piezoelectric responses as a function of DC bias voltage.

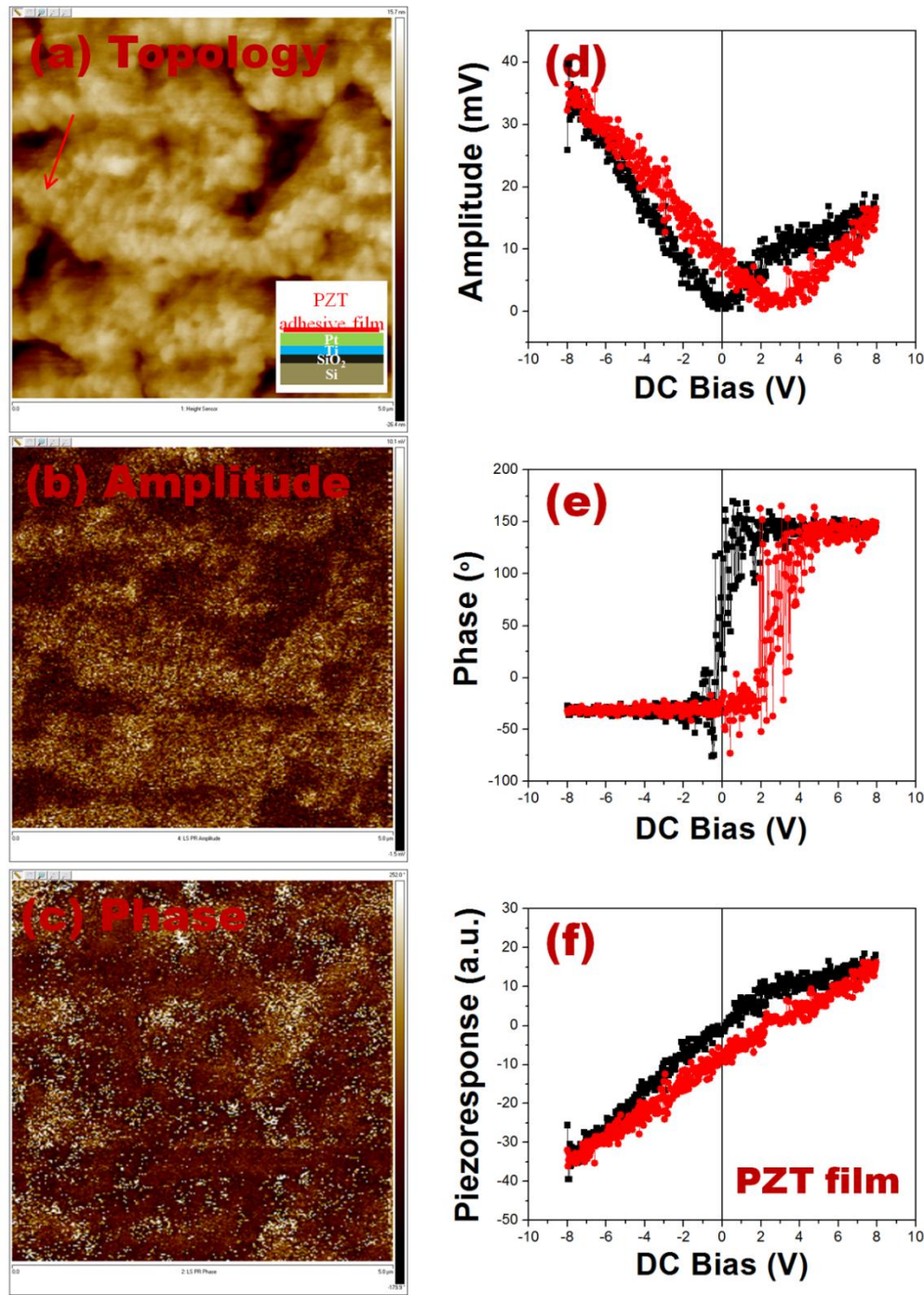


Figure 8-6. Piezo-responses for PZT thin films with a thickness of 120 nm on a Pt-Si substrate; (a) topology image, (b) amplitude image, (c) phase image, (d) ramp-mode amplitudes and (e) ramp-mode phase angles and (f) ramp-mode piezoelectric responses as a function of DC bias voltage.

Figure 8-7 (a) and (b) shows the effective piezoelectric coefficients (d_{33}) for PZT nanorod and PZT thin films calculated by conversion of piezoelectric amplitudes in Figure 8-5 (d) and Figure 8-6 (d), respectively. The deflection sensitivity of amplitude is 47 nm/V and the drive amplitudes is 4V during DC bias sweep. With the conversion for effective d_{33} , the single structure of PZT nanorod exhibited hysteretic curve of piezoelectric responses with maximum d_{33} of 52 pm/V as shown in Figure 8-7 (a). On the other hand, the PZT thin films showed asymmetric hysteresis and poor piezoelectric responses with maximum d_{33} of 28 pm/V as shown in Figure 8-7 (b). It can be noted that the PZT nanorod has less clamping effect of Pt-Si substrate due to its high aspect ratio of 10 and thus it provided better performances.^{147,169-171} This result demonstrates a good ferroelectric switching behavior and promising electromechanical properties in single structure of PZT nanorod on Pt-Si substrate.

In summary, the 1D structures of PZT nanorod arrays on Pt-Si substrates were formed with very uniform in diameter of 90 nm and length of 900 nm, well-ordered, straightly vertical with respect to the Pt-Si substrate. The direct piezo-response obtained for single PZT nanorod confirmed its good electromechanical properties due to the reduced clamping effect from the Pt-Si substrates. The 1D nano-structures with promising piezoelectric characteristics will find potential application in sensors and energy harvesters.

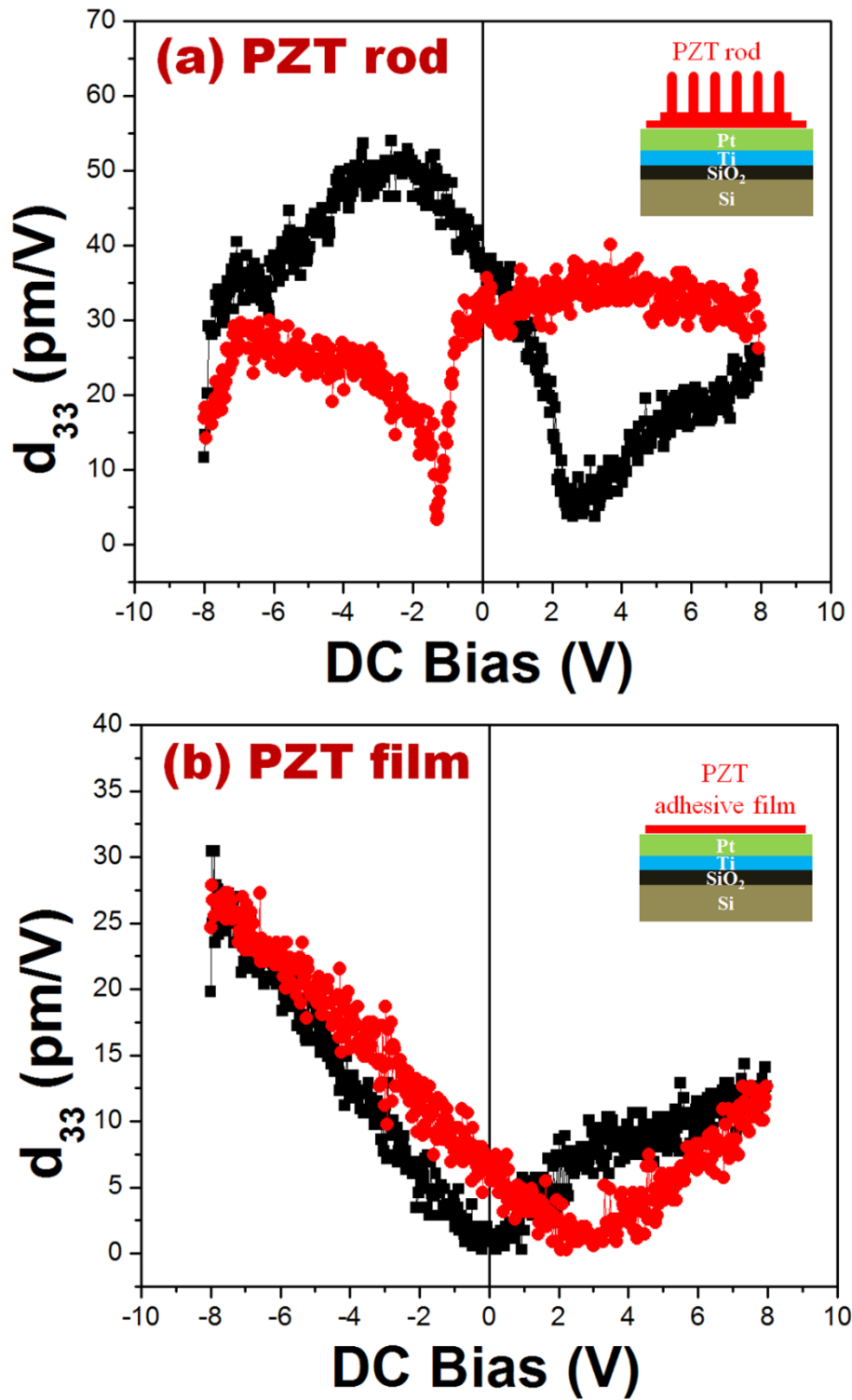


Figure 8-7. Effective piezoelectric coefficients (d_{33}) as a function of bias voltage; (a) PZT single-rod with length of 900 nm and (b) PZT thin films with a thickness of 120 nm on Pt-Si substrates.

8.3 Synthesis of PZT nanorods via reactive ion etching

Figure 8-8 shows the schematic diagram for synthesis of vertically aligned PZT nanorods on Pt-Si substrate via direct ion etching of PZT films. The advantages of this method are replication of good ferroelectric characteristics of PZT film on Pt-Si substrate into nanorod and no wet etching process prevents aggregation of nanorods. In this process, first PZT films were deposited by sol-gel coating, and then pyrolysis and annealing was performed. Next, aluminum film was deposited on PZT film to be used as an electrode for poling and also as a porous membrane for Pt-mask patterns. The porous AAO membranes were prepared by two-step aluminum anodization and then platinum patterns were deposited on PZT film by Pt evaporation and AAO etching. Then PZT nanorods can be obtained via dry ion etching of PZT film using patterned Pt masks.

Figure 8-9 shows surface morphology and cross-sectional image of PZT film prepared by sol-gel method. In the sol-gel PZT deposition on Pt-Si substrate, 0.4 M PZT precursor solutions were spin-coated, pyrolyzed at 350 °C and annealed for 10 min at 650 °C. After thermal treatment, the crack-free PZT thin films were obtained with a thickness of 570 nm. Ferroelectric characteristics of PZT thin films were characterized after platinum deposition on the PZT film as shown in Figure 8-10 (a) – (d). From the P – E curve, it can be shown that the PZT films exhibited good ferroelectric hysteresis at 100 and 1000 Hz. The C – F curve shows high dielectric constant of 1131 and low loss of 4.22 % at 1 kHz. Further, the C – V curves indicate good ferroelectric behavior.

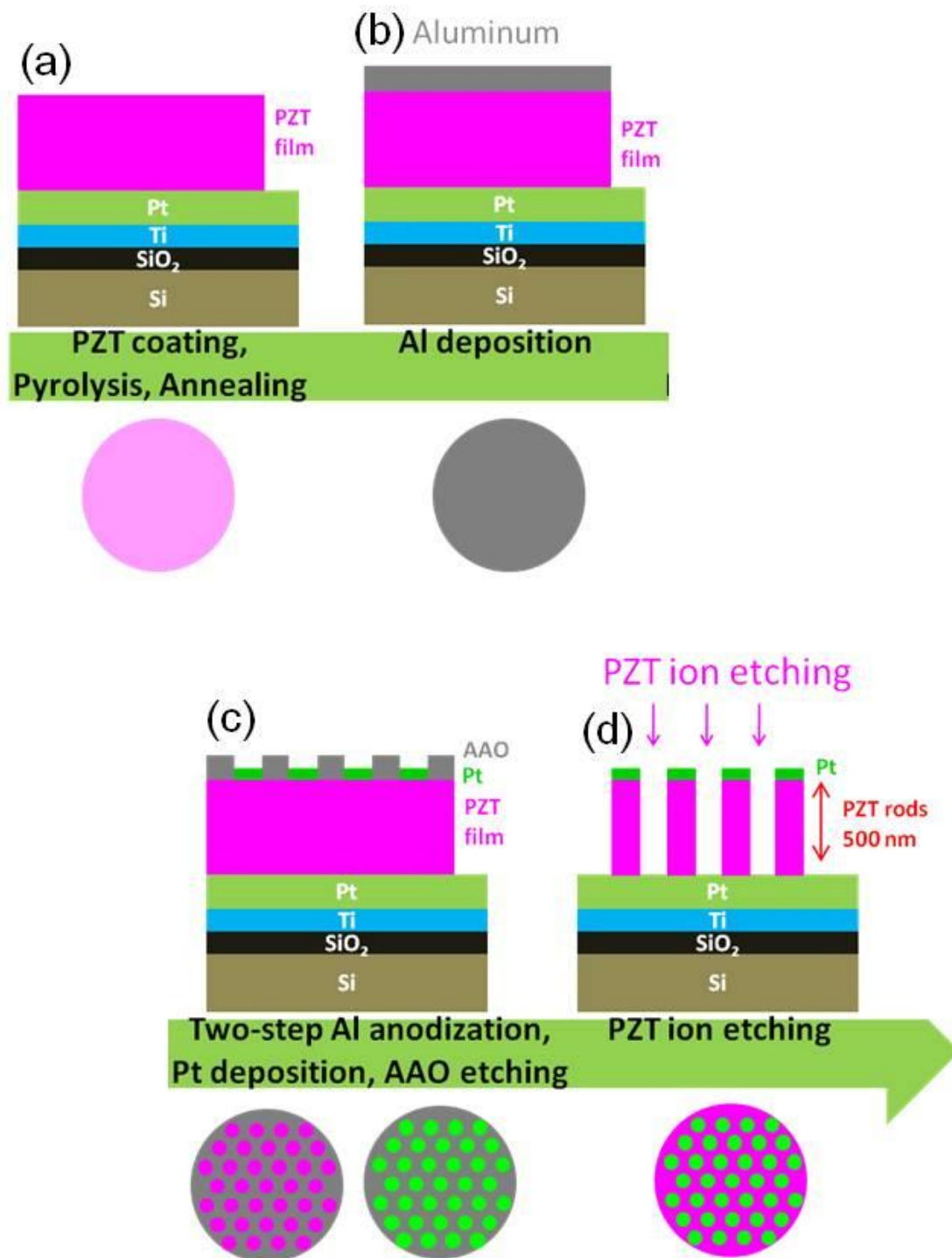


Figure 8-8. Schematic diagram of experimental procedure for synthesis of vertically aligned PZT nanorods via direct PZT ion etching.

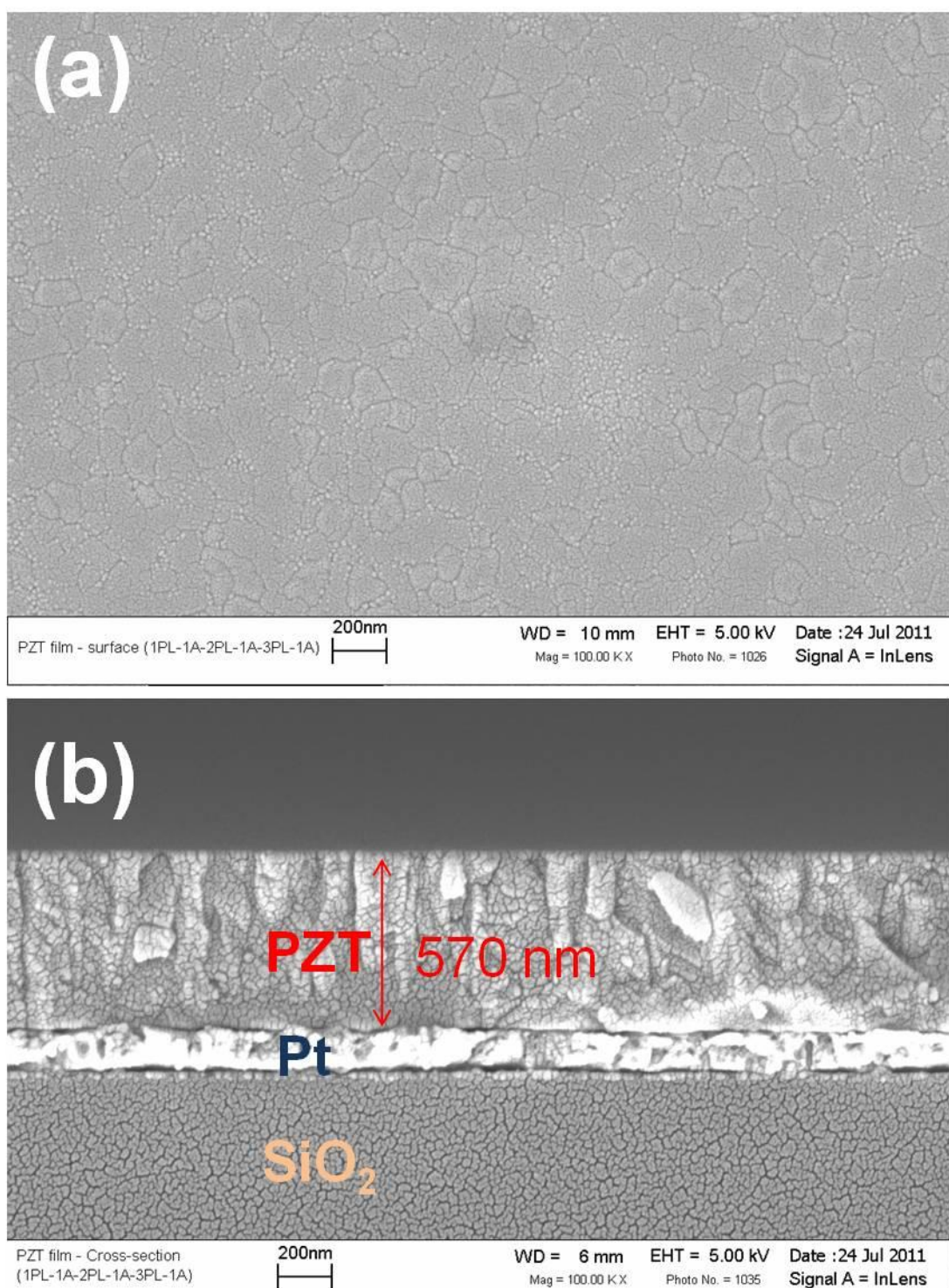


Figure 8-9. SEM images for PZT film on platinumized silicon substrate: (a) top-view and (b) cross-sectional view.

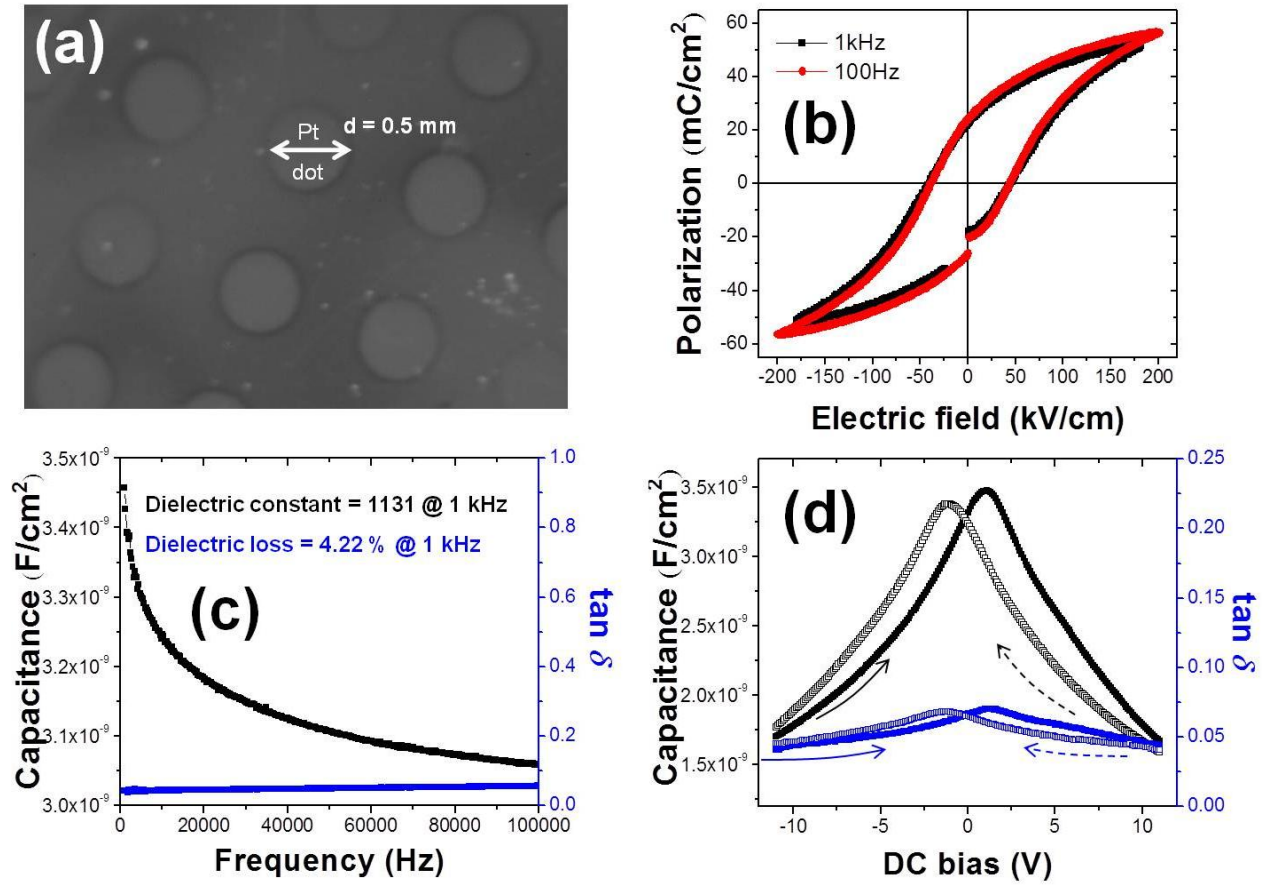


Figure 8-10. Ferroelectric characteristics for PZT thin films: (a) Pt-dot patterned PZT film, (b) P – E hysteresis, (c) C – F curves, and (d) C – V curves.

Reactive ion etching (RIE) was conducted for 60 sec using BCl_3 gas with gas flow of 40 sccm under pressure of 5 mTorr, source power of 500 W, and bias power of 150 W. Figure 8-11 (a) – (c) shows SEM images for Pt-patterned PZT film after the ion etching. The reactive ion etching was performed with PZT etching rate of 100 nm / min under BCl_3 gas. For patterning using RIE, aluminum films will be deposited on the ferroelectric PZT films by physical evaporation. Next, well-ordered porous patterns will be prepared by two-step anodizing of deposited aluminum layer for Pt-mask patterns. Finally, vertically aligned PZT nanorods can be obtained on platinized silicon substrate by dry ion etching with optimized RIE conditions.

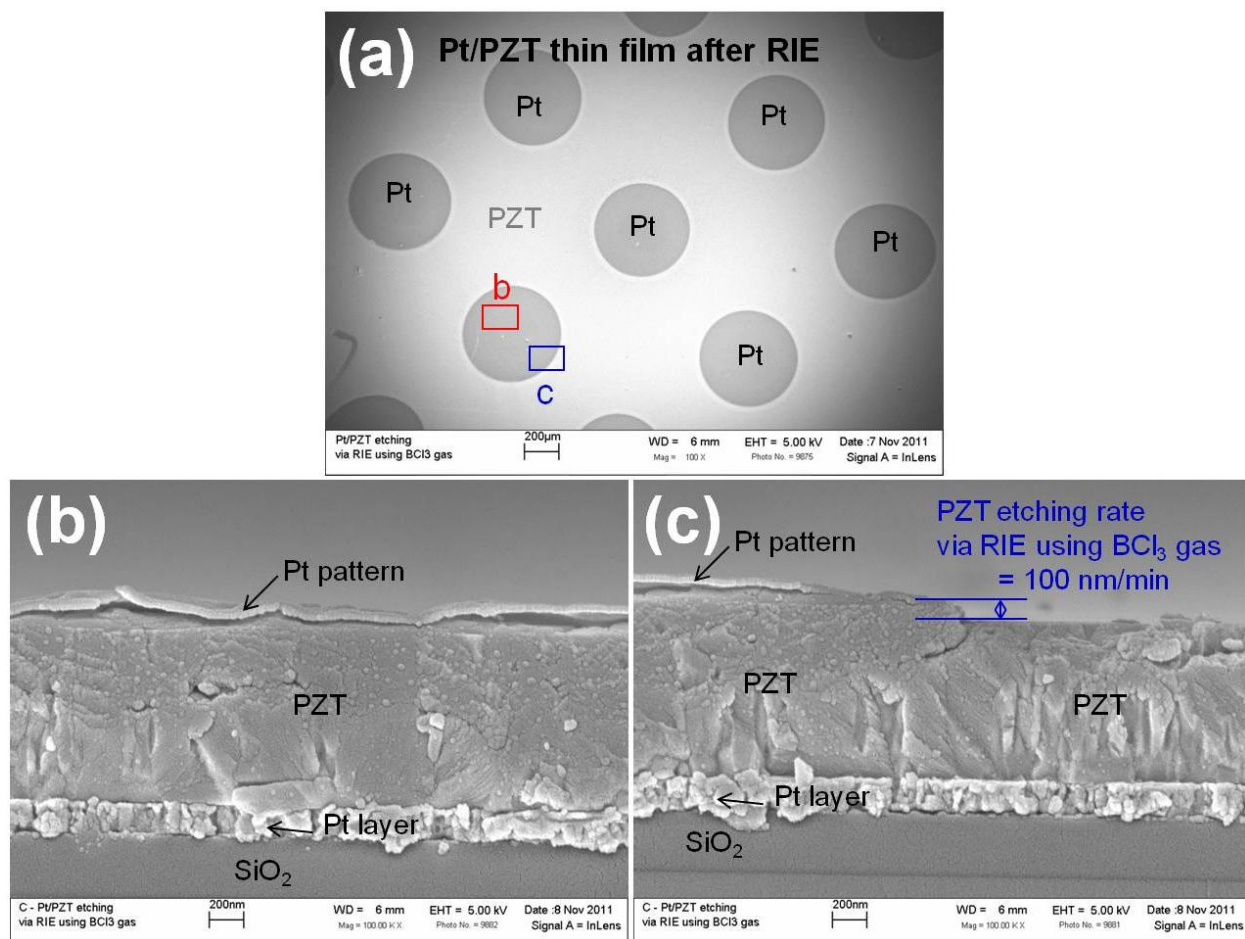


Figure 8-11. SEM images for Pt-patterned PZT film after reactive ion etching: (a) surface image, (b) cross-sectional image on center of Pt-patterned PZT film, and (c) cross-sectional image on edge of Pt-patterned PZT film.

CHAPTER 9

ELECTROACTIVE POLYMER ACTUATORS WITH INHERENT MAGNETIC FIELD SENSING CAPABILITY

The goal of this chapter for was to conduct preliminary investigations towards developing flexible actuators with inherent magnetic field sensing capability. The functioning of the composite actuators was envisioned in the following manner: (i) the actuation occurs by inducing redox reaction in the conducting polymer layers, and (ii) the sensing occurs by inducing strain in the magnetostrictive nanoparticles resulting in deformation of the PVDF layer that generates voltage. The focus in this study was on optimizing the performance of sandwich structure PPy/PVDF/PPy.

9. 1 Optimization of PVDF interlayer films

50 μm thick tapes were placed around the edges of slide glass to produce the uniform thickness of PVDF films. The PDVF solutions were prepared from PVDF powder (Kynar Corp.) with variation of dimethylacetamide (DMAc) and acetone in different ratio (wt % in mixed solution). After screen printing the PVDF solutions on slide glass, the samples were dried for 24h at either 25°C and 80°C on a hot plate in air. Thin layers of gold were coated on both sides of the PVDF films by sputtering. PPy was electrochemically deposited on the PVDF-Au films by the cyclic voltammetry method in a three electrode setup. The actuator was selected as the working electrode, platinum foil in the same dimensions as the counter electrode, and an

Ag/AgCl as the reference electrode. A pyrrole monomer-containing aqueous solution of 0.25 M Pyrrole, 0.10 M TBAP and 0.5 M KCl was used. Deposition parameters were -1.3 – 1.5V at a scan rate of 100 mV per second. 50 total sweep segments were generated over a period of 24 min.

The PVDF films were synthesized using a solution with PVDF powers with 5, 10, 25, and 50 wt % in mixed solutions of DMAc and acetone solvents with ratio of 0/100, 25/75, 50/50, 75/25 and 100/0. The optimum PVDF films were obtained using 25 wt % PVDF in 50/50 DMAc and acetone solvents. Figure 9-1 shows surface morphologies of gold-coated PVDF films dried for 24h at 25 °C and 80 °C, respectively. The films exhibit smooth surfaces with uniform morphology on a large area.

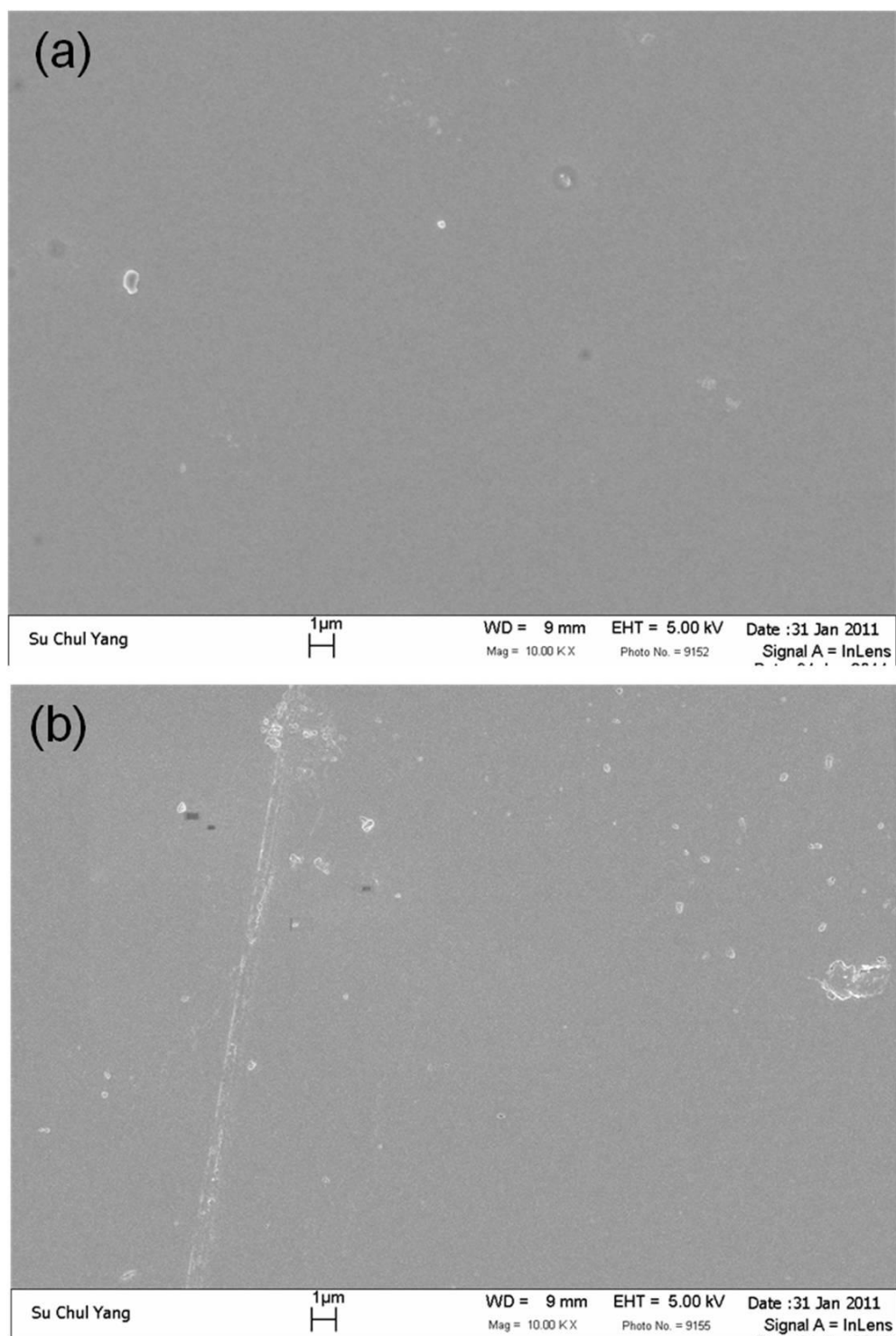


Figure 9-1. Surface morphologies of gold-coated PVDF films dried for 24h at (a) 25 °C and (b) 80 °C.

Figure 9-2 shows cyclic voltammograms for 50 growth cycles where each cycle represents a PPy deposition step on both sides of gold-coated PVDF films. The number of cycles was varied in the range of 10 – 50 and, for each cycle, three equally sized samples were synthesized. From the cyclic voltammograms, it was found that the PPy layers were well deposited on gold-coated PVDF films during electrochemical polymerization.

Figure 9-3 shows the surface morphologies of polymer actuators after PPy polymerization. The deposited PPy films on gold coated-PVDF films dried at 25 °C and 80 °C respectively exhibit similar morphology with dense and rough surface. Figure 9-4 shows cross-sectional morphologies of the actuators using PVDF films dried at 25 °C and 80 °C, respectively. The data is shown for the PVDF interlayer films have different thickness 12 μm and 17 μm with different drying temperatures of 25 °C and 80 °C respectively. The thickness was a critical factor in actuation properties due to different porous channels for proper ion movement.

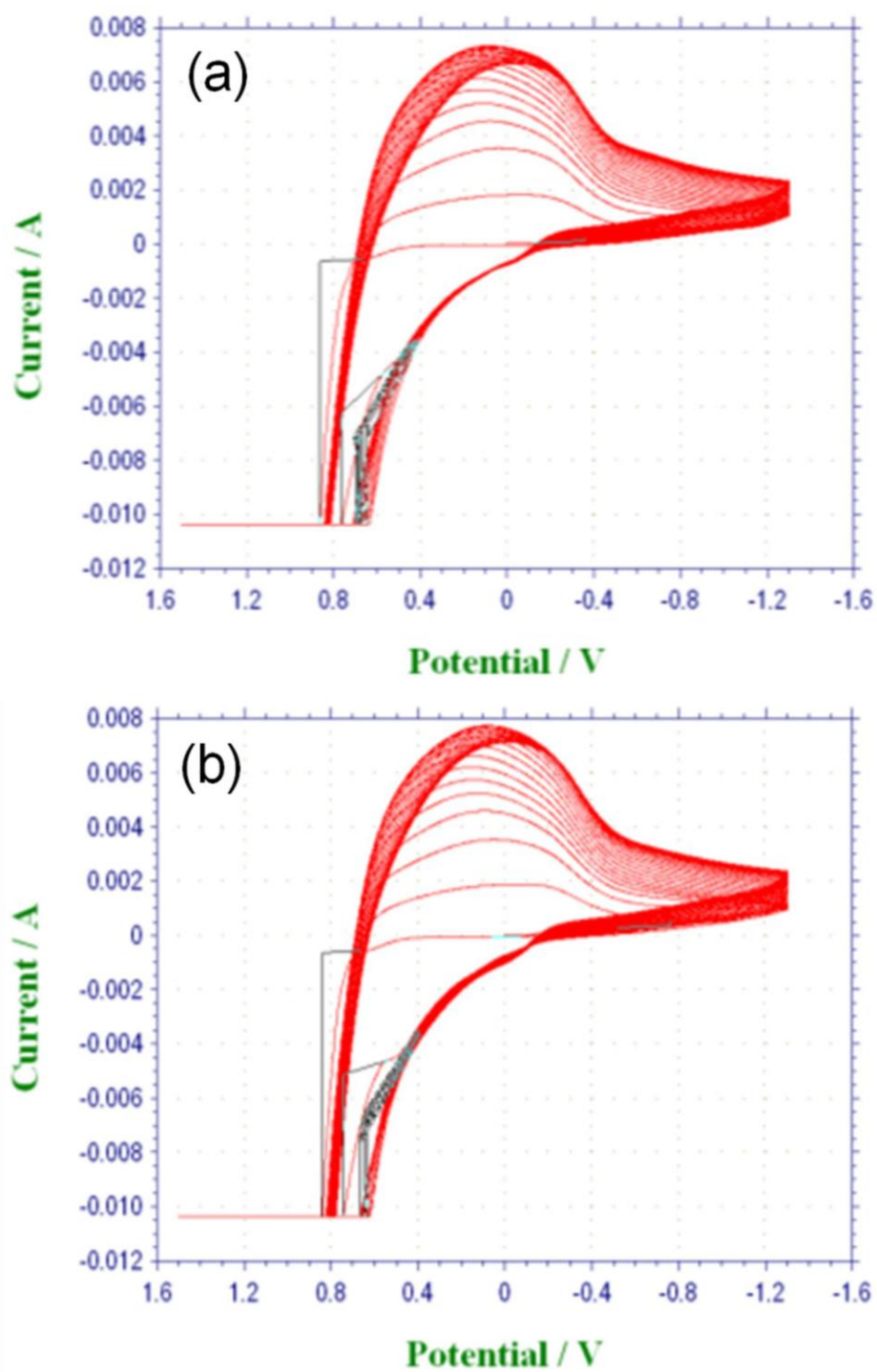


Figure 9-2. Cyclic voltammety curves for 50 layers of PPy coating on (a) 25°C and (b) 80°C dried PVDF-Au films.

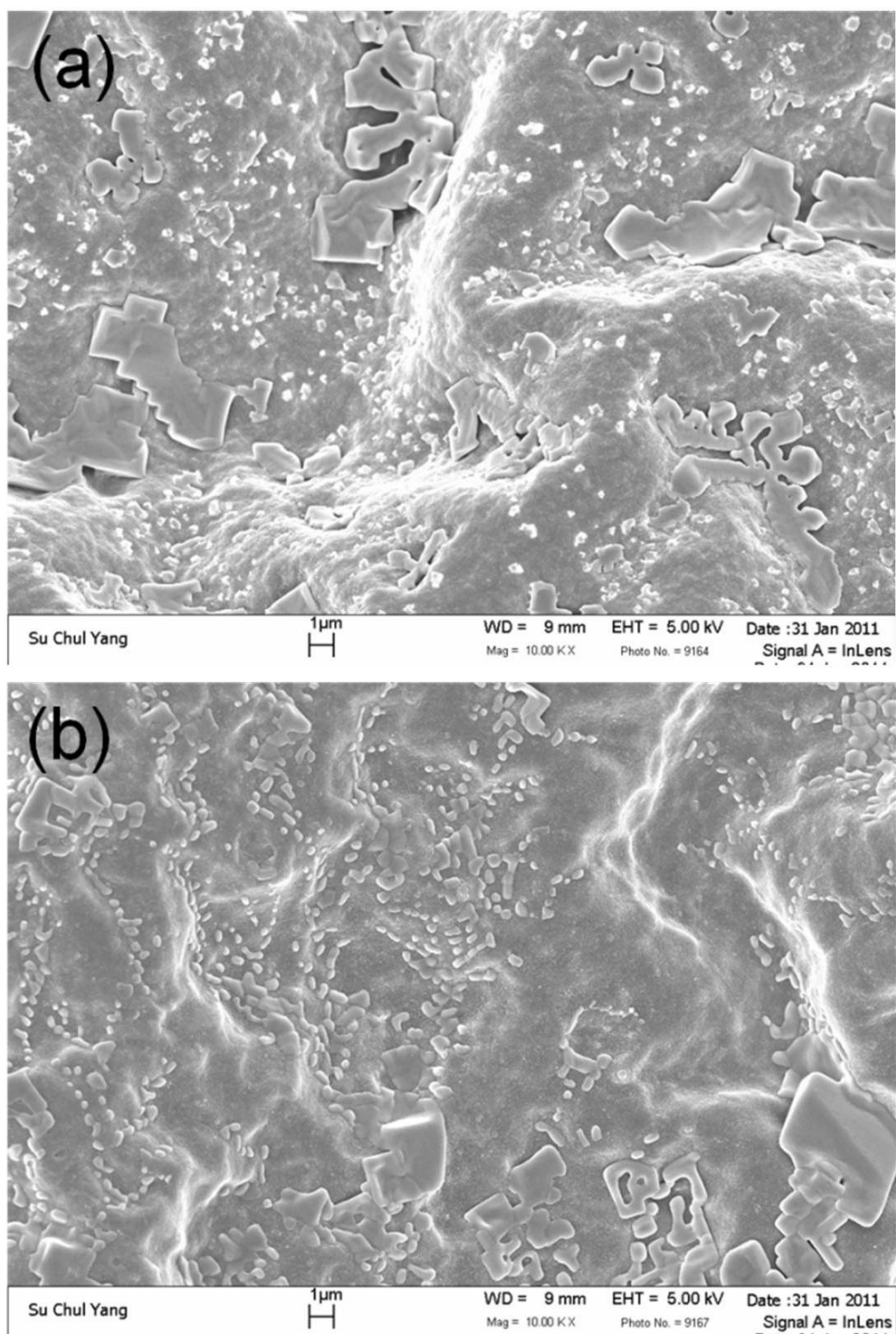


Figure 9-3. Surface morphologies of (a) PPy / Au / PVDF dried 25°C / Au / PPy films and (b) PPy / Au / PVDF dried 80°C / Au / PPy films.

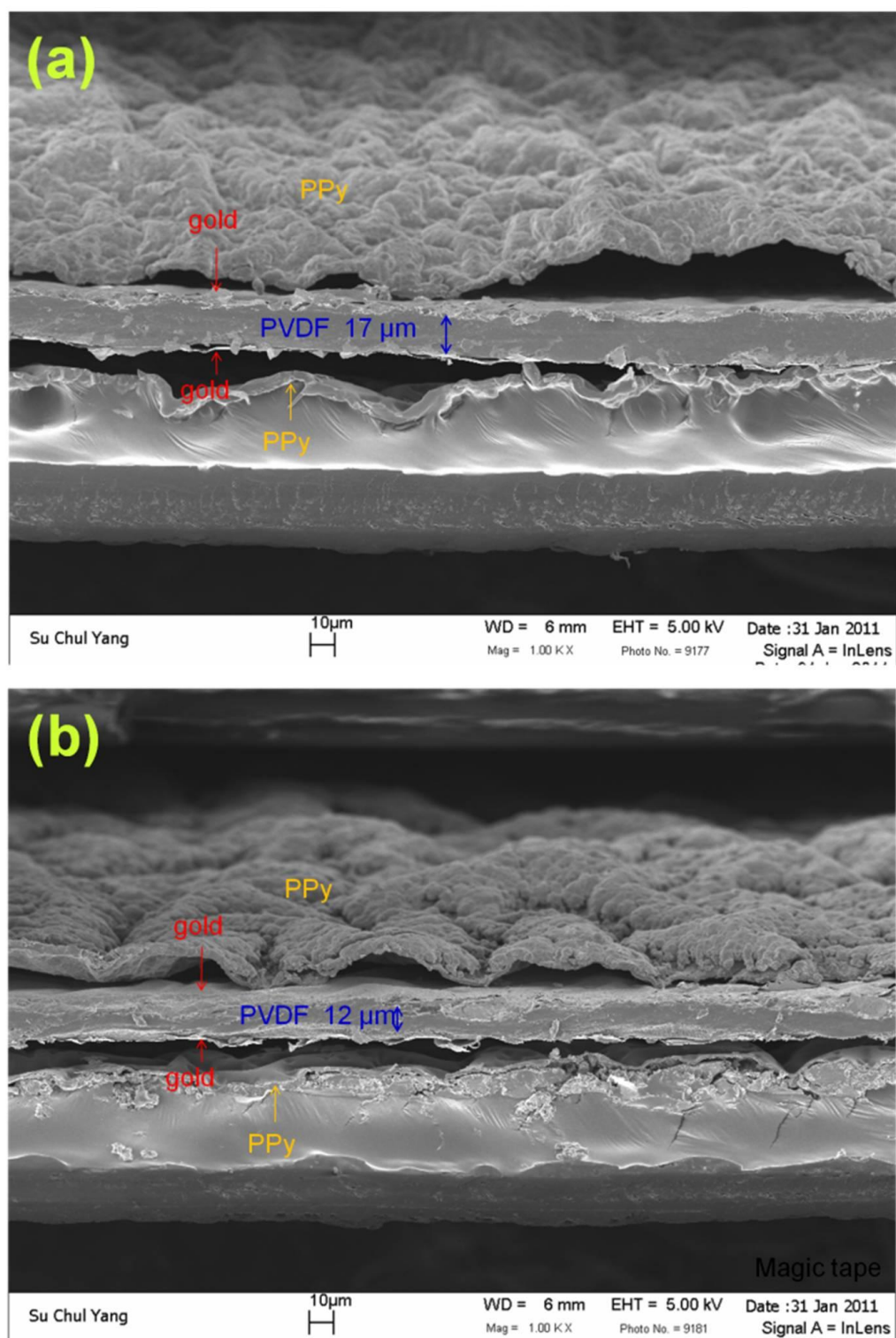


Figure 9-4. Cross-sectional images of (a) PPy / Au / PVDF dried at 25°C / Au / PPy films and (b) PPy / Au / PVDF dried at 80°C / Au / PPy films.

9.2 Electroactive performance of PPy-PVDF actuators

After electrochemical polymerization, the actuators were stored in either 3 M or 0.5 M KCl solution overnight until testing could be performed. Samples were actuated in air at 0 – 6 V_{dc} by placing the 5 mm gold section of the actuator between two copper electrodes. Figure 9-5 was taken during the initial motion and used to determine the strain properties. Strain was taken linearly as the percentage of the total actuator length to the tip moved. The deformation over time was recorded in 15 fps video and run through a MATLAB program to extract change in position as shown in Figure 9-6. Composite video screenshots are shown with the initial and final states superimposed on top of each other.

The maximum strain achieved was 33% of original actuator length. Voltage was applied to the actuator for 30s, and the ions within the PVDF membrane and the conducting polymer layer were allowed to diffuse. Figure 9-7 shows the resulting motion of the actuator over time. One interesting aspect to note is that the actuator shows initial motion opposite to the desired direction. This is due to the differing diffusion time constants between cation and anion. Since the anion is much larger than the cation, it produces the eventual large deflection in the desired direction. However, since the cation is smaller it has a much faster diffusion rate. This means that we can see the initial movement in the opposite direction because the cations are causing a larger volumetric change at the outset of actuation. That initial deflection accounts for a movement of 4.5% of the actuator length.

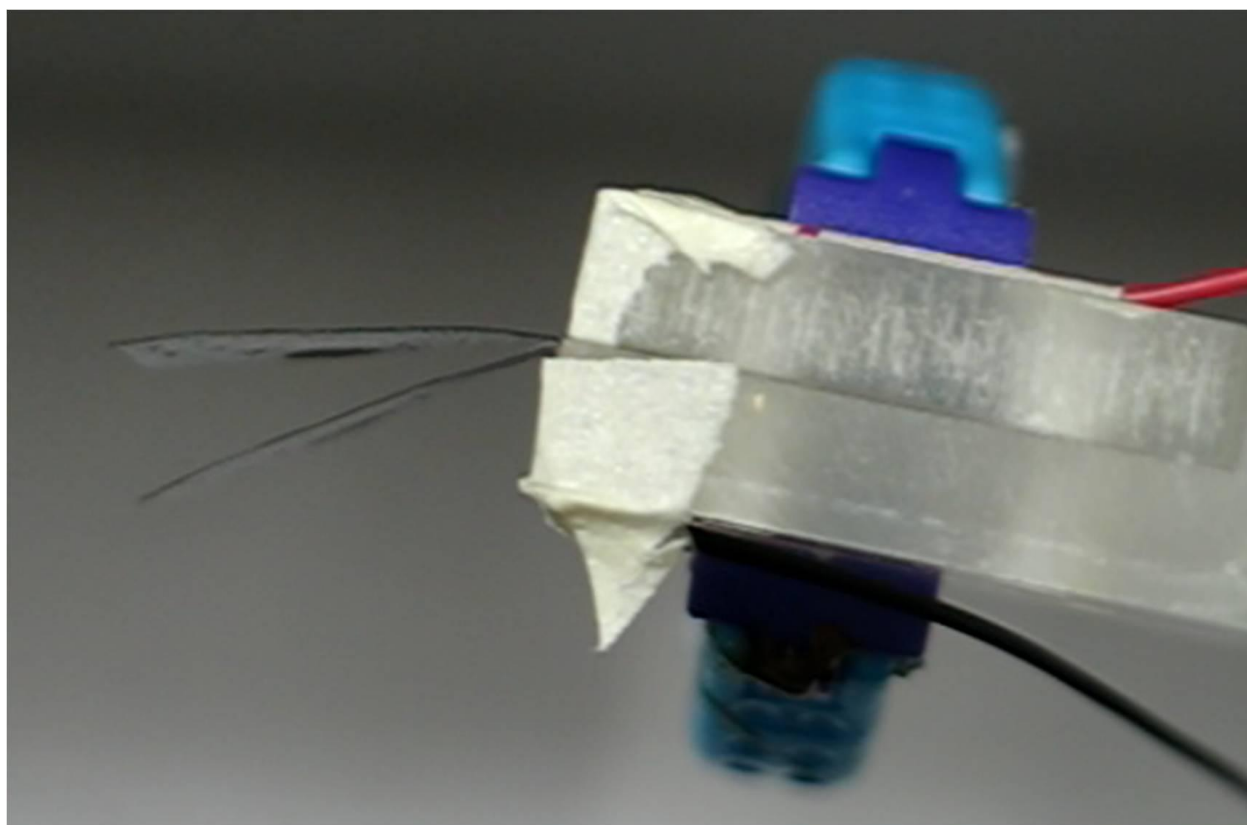


Figure 9-5. Overlay of the initial and final states of a 6 x 20 mm PPy / Au / PVDF / Au / PPy actuator stored in 3M KCl solution actuated at 6 V_{dc} potential.

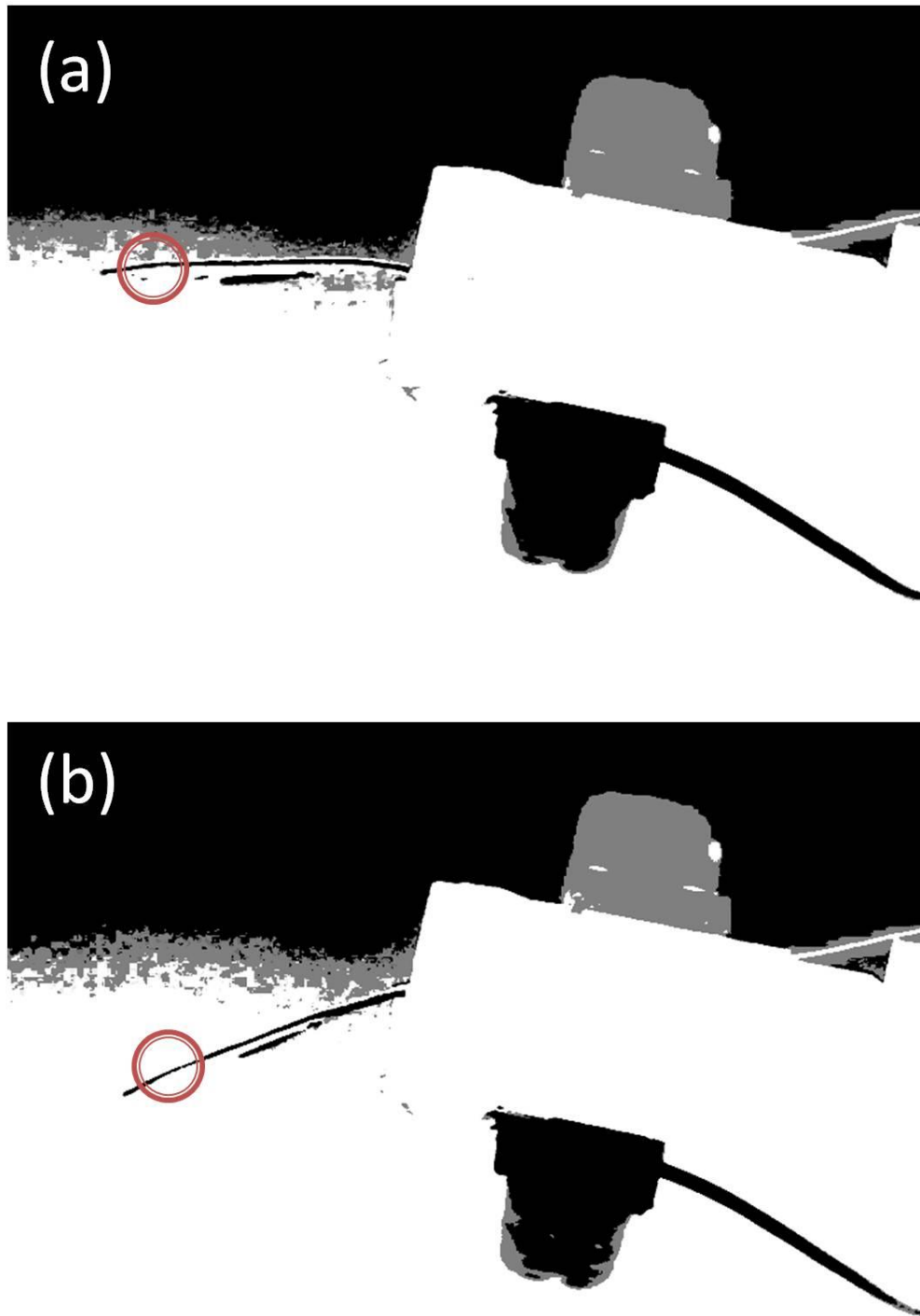


Figure 9-6. MATLAB image processing techniques were used to extract actuator tip displacement.

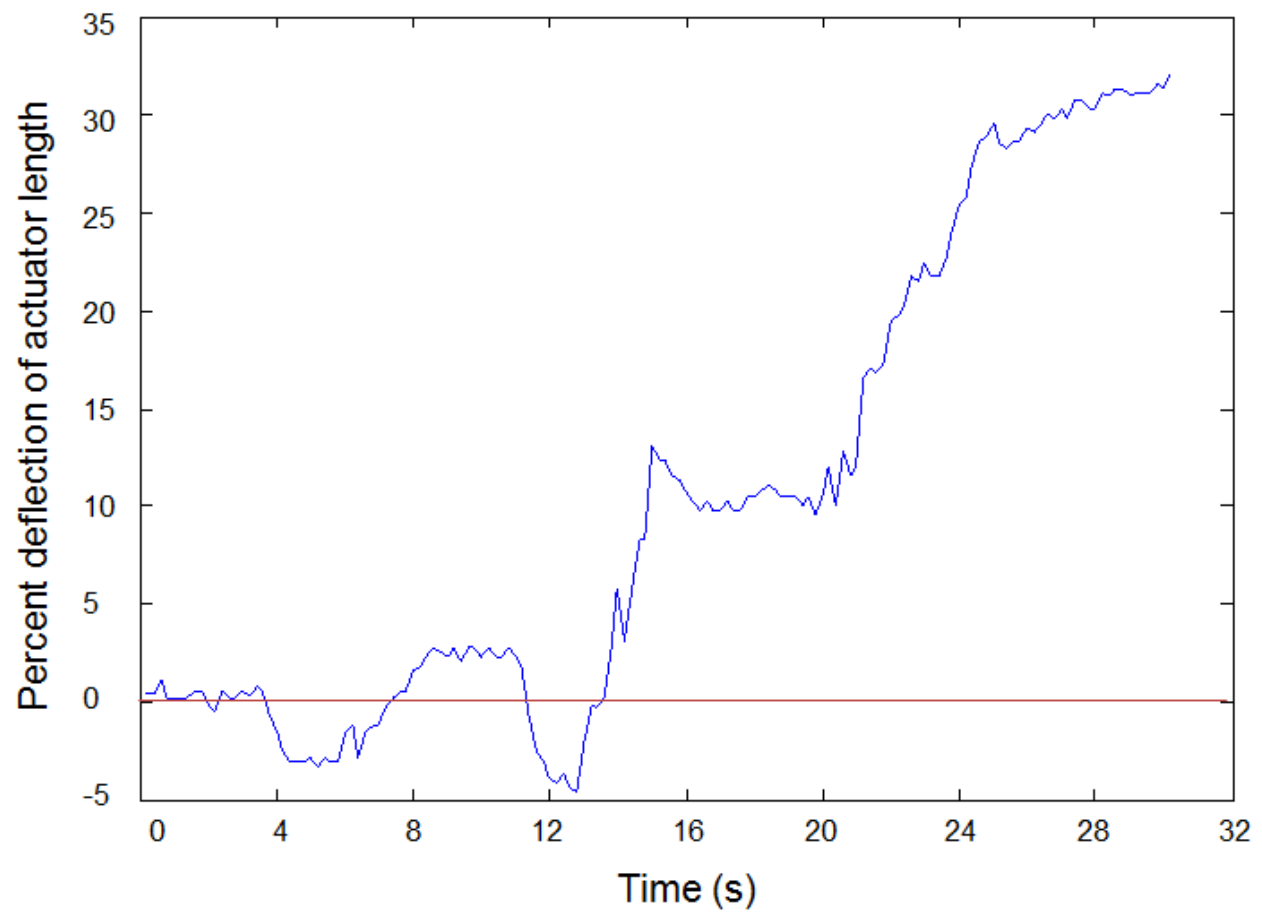


Figure 9-7. Deflection of actuator tip over time expressed as a percentage of total actuator length.

It should be noted that some burning was observed in the actuator. It is suspected that there are two reasons for this deterioration. First, the actuator was overdriven at $6 V_{dc}$. Secondly, the actuators were stored in a highly concentrated 3 M KCl solution. A close up of the burnt area is shown in Figure 9-8. Most of the burning occurs near to the copper electrodes at the base. Bubbling and delamination were the two signs that burning has occurred. In order to reduce the effect of burning, both a lower voltage and lower concentration solution was used to store the actuators. The second attempt was made with 0.5 M KCl solution. The input potential was set at 4V. Figure 9-9 revealed that the actuator produced an impressive 90% deflection. In addition, the strain rate was extremely fast, at 50% deflection per second. This strain rate was taken over the entire actuation cycle; maximum instantaneous strain rates would be slightly higher than this.

In summary in this chapter, electroactive actuators of PPy/Au/PVDF/Au/PPy were fabricated using a pyrrole monomer-containing aqueous solution of 0.25 M Pyrrole, 0.10 M TBAP and 0.5 M KCl. Strip actuators under a potential of $6 V_{dc}$ showed burning due to high potential and high concentration of storage electrolyte solution. An actuator was then produced that showed 90% strain as a function of initial actuator length, with an extremely fast strain rate of 50 % per second over the entire actuation cycle and minimized burning. This reduction in burning was due to a reduction in potential to $4 V_{dc}$, as well as a reduction in storage electrolyte concentration to 0.5 M KCl from 3 M KCl.

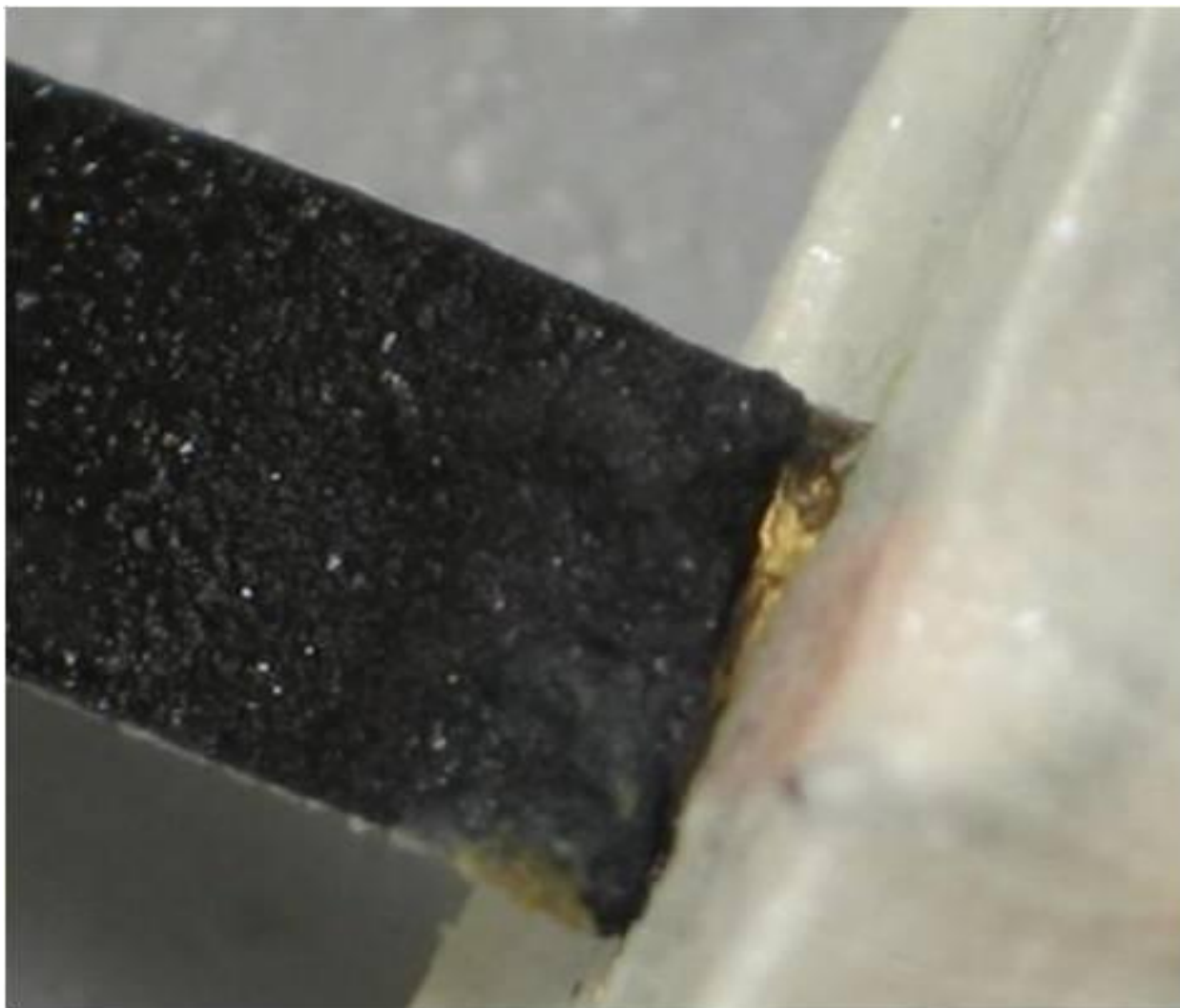


Figure 9-8. Close-up photograph of the actuator showing burning due to high voltage and storage in 3M KCl.

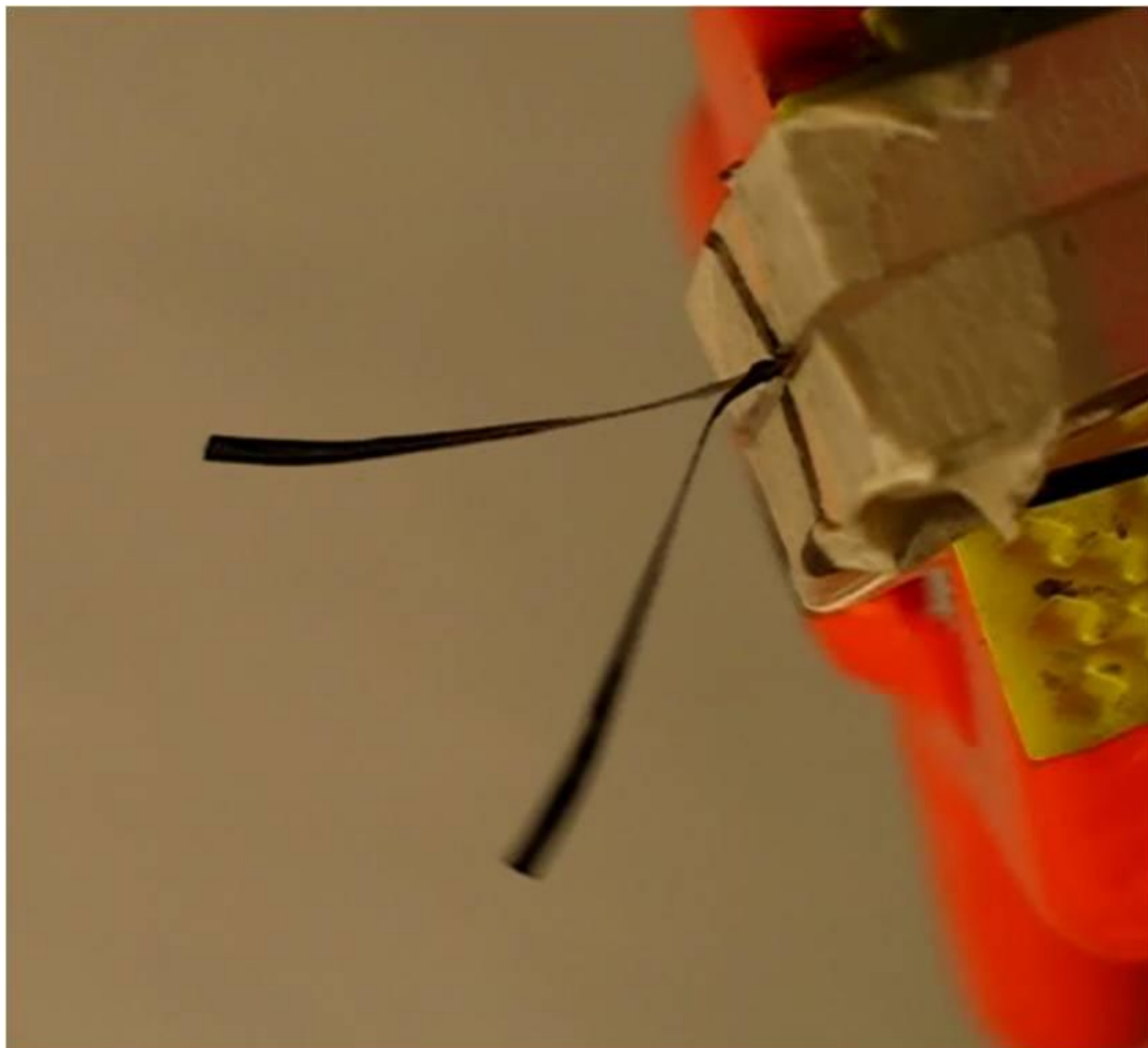


Figure 9-9. Overlay of the initial and final states of a 3.5 x 21.5 mm PPy / Au / PVDF / Au / PPy actuator stored in 0.5M KCl solution actuated at 4 V_{dc} potential.

CHAPTER 10

CONCLUSION

In this dissertation, self-biased ME effects were studied by designing lead-free three-phase laminate composites consisting of one piezoelectric and two magnetostrictive phases. The self-biased ME effects were discovered in the three-phase (KNNLS, NZF, and Ni) laminates consisting of built-in bias under bending configuration. Experimental confirmation for self-biased ME effect was successfully conducted and various hysteretic ME responses were produced by variation of material composition in the $(1 - x)$ KNNLS – x NZF / Ni / $(1 - x)$ KNNLS – x NZF system.

Self-biased DME and CME effects were also observed in bending mode laminates consisting of heterogeneous ferromagnetic phase. The hysteretic behavior of ME response were demonstrated by the shift of magnetostriction curve of ferromagnetic phase caused by interaction between built-in bias and external magnetic bias. This result opens up the opportunity for developing electrically controlled nano-devices without the need for external magnetic bias.

Lead-free $(1 - x)$ KNNLS – x NZF ME composites were developed with the island-matrix microstructure for enhancing the ME coupling effect in particulate composites. The island-matrix microstructure of KNNLS-NZF composites were found to exhibit high relative density of $> 95\%$ even though KNNLS matrix normally has residual porosity. The 0.7 KNNLS – 0.3 NZF composites exhibited maximum ME coefficient of 20.14 mV/cm·Oe and low optimum H_{bias} of 467 Oe. Further, the 0.6 KNNLS – 0.4 NZF composites still had high ME coefficient even

though there was high amount of ferrite particles. These results provide potential ME applications using KNNLS-NZF particulate composites with a requirement of low H_{bias} .

Solid solutions of lead-free $(1 - x) \text{BaTiO}_3 - x \text{BiFeO}_3$ (BT- x BFO, $x = 0.025 - 1.0$) magnetoelectric (ME) multiferroics were synthesized and characterized for designing thin film applications. In the narrow range of compositions ($x = 0.71 - 0.8$), the room-temperature ME responses were found to have significant magnitude. The maximum ME coupling coefficient of 0.87 mV/cmOe was achieved in the optimized composition of $x = 0.725$ exhibiting local monoclinic distortions in rhombohedral phase. Self-biased ME effects was observed in the laminates of nickel and BT - 0.725 BFO. This result reflects a feasibility of room-temperature magnetically or electrically tunable thin-film devices using the optimized BT-BFO multiferroics.

Core-shell MFO-Ni nanoparticles were synthesized and characterized for electro-magnetostrictive single devices. MFO nanoparticles in the range of 200 nm were synthesized with mean primary nanoparticle size of 15 nm by solvothermal method. The MFO nanoparticles exhibited high saturation magnetization of 74 emu/g and coercivity of 89 Oe. Ni encapsulation on MFO nanoparticles was performed by aqueous ionic coating method. Ni shells with uniform thickness of 1 nm were coated on MFO nanoparticles. The 0D magnetic nanostructures will be developed as a single memristor for flexible resistive random access memory.

Vertically-aligned piezoelectric nanorods were synthesized using PZT instead of lead-free KNN materials to verify a feasibility of 1D piezoelectric nanostructure. For high performance 1D piezoelectric devices with dimension of $< 1\mu\text{m}$, free standing PZT nanorod arrays were developed on Pt-Si substrates via template transfer method using AAO template. The final structure of PZT nanorods exhibited rod-like morphology with uniform diameter of 90 nm and aspect ratio of 10. The piezo-response of PZT nanorods showed good electromechanical

characteristics with low clamping effect on the Pt-Si substrates. The result opens the possibility of developing nanoscale high performance ME devices based on lead-free piezoelectric materials.

Finally, dual-functional flexible devices were designed which has the potential to exhibit magnetic field sensing and actuation ability. The electroactive actuators of Polypyrrole (PPy) / Au / Polyvinylidene fluoride (PVDF) / Au / Polypyrrole (PPy) were synthesized and optimized. Pore size and thickness of PVDF layer was adjusted by changing solvent, viscosity and drying temperature. Different types of electrolyte solutions were investigated to improve their strain and response time. The actuators exhibited high strain of 90 % deflection with fast response of 50% deflection per second. Dual-functional structure of PPy-MFO / Au / PVDF / Au / PPy-MFO was developed by PPy polymerization including MFO nanoparticles via cyclovoltammetric method.

CHAPTER 11

FUTURE APPLICATIONS

11. 1 Memristive ferromagnetic nanoparticles

Since 2008, interest in developing memristors has significantly increased due to its non volatile memory characteristics with fast responses.¹⁷²⁻¹⁷⁵ Memristance $M(q)$ appears as a slope in ϕ - q curve with two different slopes, where $W(\phi)$ is the memductance as described by Chua et al.¹⁷⁶ The memristic characteristics can be described as following:

$$M(q) = \frac{d\Phi_m}{dq} \quad (11-1)$$

Most studies on memristor have been conducted using thin film metal oxides on conductive substrate. Recent studies on memristor nanoparticles describe that ferrite oxide nanoparticle such as Fe_3O_4 , MnFe_2O_4 , CoFe_2O_4 and NiFe_2O_4 exhibit unique characteristics of resistive switching in current – voltage ($I - V$) curves.^{87,177-180} The measurement samples were prepared by deposition on conductive substrate and the electrical properties were analyzed by applying a voltage at the top electrodes. Nanoparticles based memristor have several advantages including low price (without vacuum process), compatibility with mass production and high degree of flexibility (high compliance). However, the memristor nanoparticle arrays require (i) easy patterning of top electrodes and (ii) high stability under bending for flexible devices. Figure 11-1(a) and (b) shows possible cracks in particle array samples under bending.

MFO nanoparticles in diameter of 200 nm with primary particle size of 15 nm synthesized by solvothermal method can be promising for single memristors on conductive substrates with high stability against bending. Figure 11-1(c) and (d) shows advantages of MFO nanoparticles as a single device on flexible conductive substrate. The spherical shape and dense structure of MFO particles can provide high stability against bending. Moreover, the zero dimensional (0D) nanostructures can be well ordered on conductive substrates without using any mask patterns. Therefore, the MFO nanoparticles will be easily used as a single memristor with 0D, 1D and 2D patterns on conductive substrates.

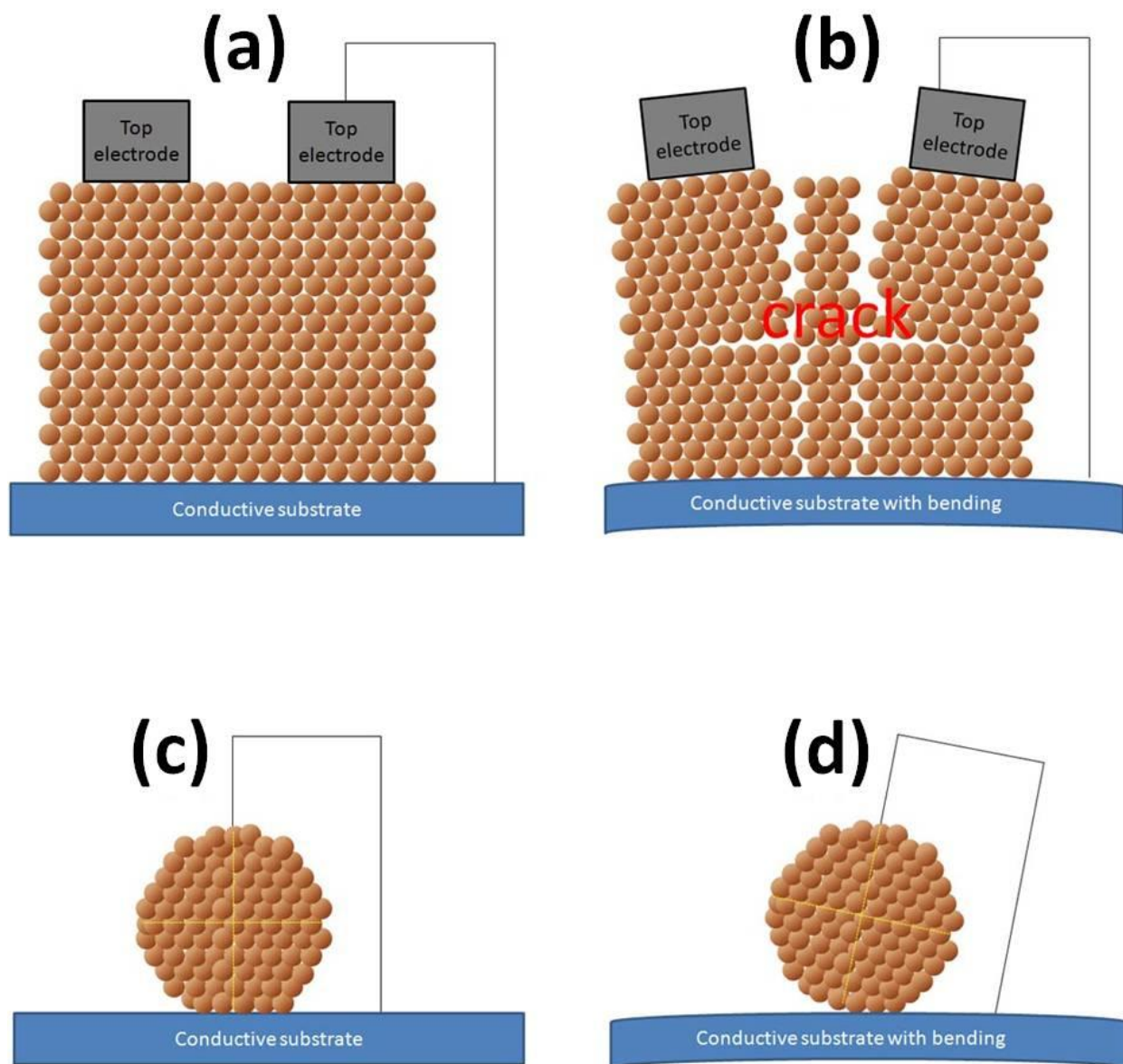


Figure 11-1. Schematic diagrams for memristive particle array (thickness of ~ 400 nm); (a) on a rigid substrate and (b) on a flexible substrate, and for single memristive particle (diameter of 200 nm); (c) on a rigid substrate and (d) on a flexible substrate.

11. 2 Lead-free magnetoelectric nanostructures

The promising piezoelectric characteristics of 1D nanostructure can be used for potential applications such as sensors, transducers, actuators and energy harvesters.^{79,80,91} The 1D nanostructures exhibit good piezoelectric coefficients by overcoming the substrate clamping effect. Further, the 1D piezoelectric nanostructures can be developed with functional polymeric materials such as conductive polymer and magnetic ferrites for developing new applications.¹⁸¹⁻

183

Lead-free magnetoelectric nanostructures can be developed using KNN and MFO as a lead-free piezoelectric and ferromagnetic phases respectively for high performance magnetic nano-sensors as shown in Figure 11-2. Free-standing KNN nanorods can be synthesized on conductive substrate and then magnetic materials can be deposited on the 1D KNN nanostructures. Especially, embedding method can be used through conductive epoxy to make good contact between piezo-nanorods and conductive substrate. The approach will provide less aggregation of 1D nanostructure with no delamination from the substrate.

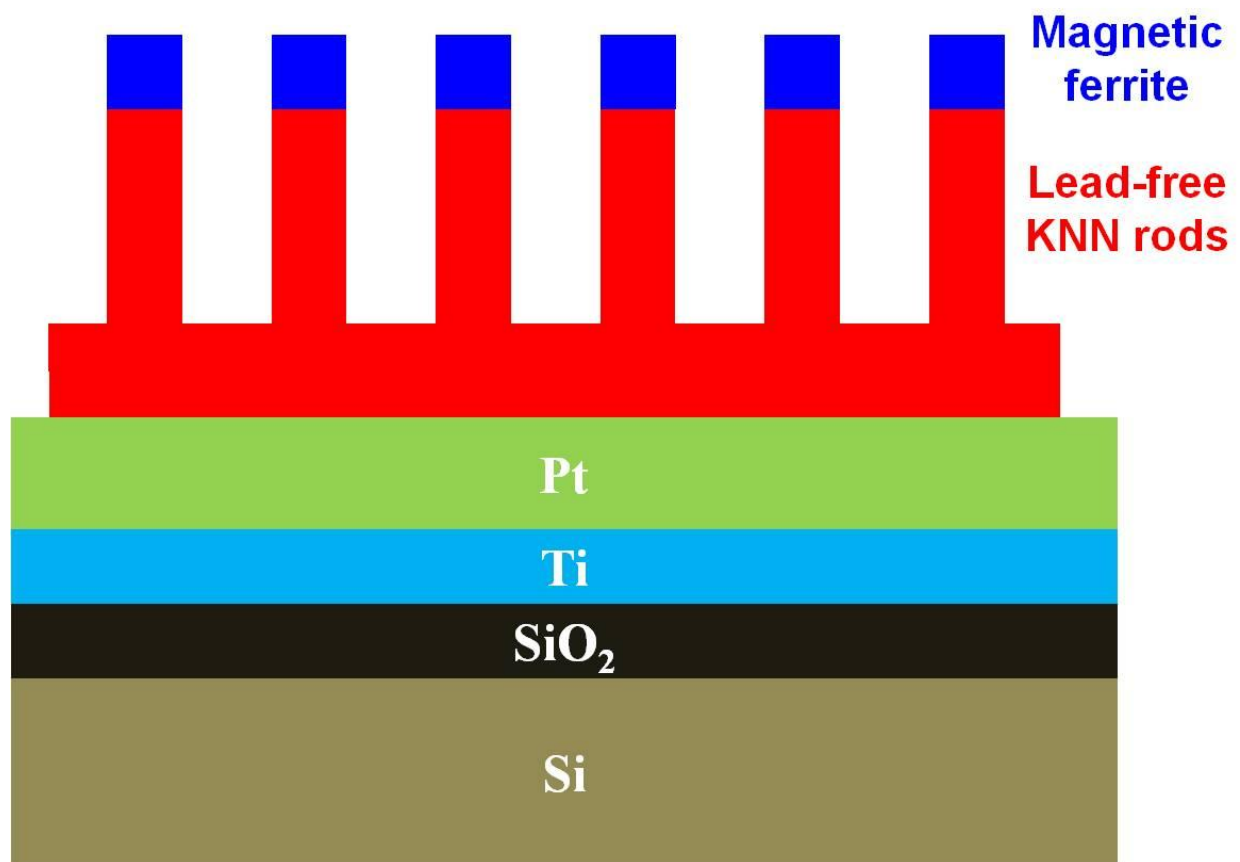


Figure 11-2. Schematic diagram for lead-free magnetoelectric nanostructures.

11. 3 Dual functional flexible devices

The electroactive polymer actuators of PPy / Au / PVDF / Au / PPy exhibit high flexibility with good actuation performances such as high strain and fast response. The PVDF polymers have attracted attention as a piezoelectric material in ME sensors due to its high flexibility.^{45,48} Zhai et al. have reported a high ME coefficient of 7.2 V/cm·Oe in the flexible ME device of PVDF / Metgals laminate.⁴⁵ For potential use of the flexible actuators, a dual-functional flexible device can be designed as shown in Figure 11-3. The schematic diagram shows a polymer actuator and magnetic sensors from device structure of PPy-MFO / Au / PVDF / Au / PPy-MFO. In order to synthesize dual functional flexible devices, PPy polymerization with MFO nanoparticles can be conducted by adjusting pH of colloidal electrolyte solutions. The final structure of dual-functional device are expected to exhibit good actuation performance by applying DC voltage as well as high magnetoelectric responses by applying magnetic bias field.

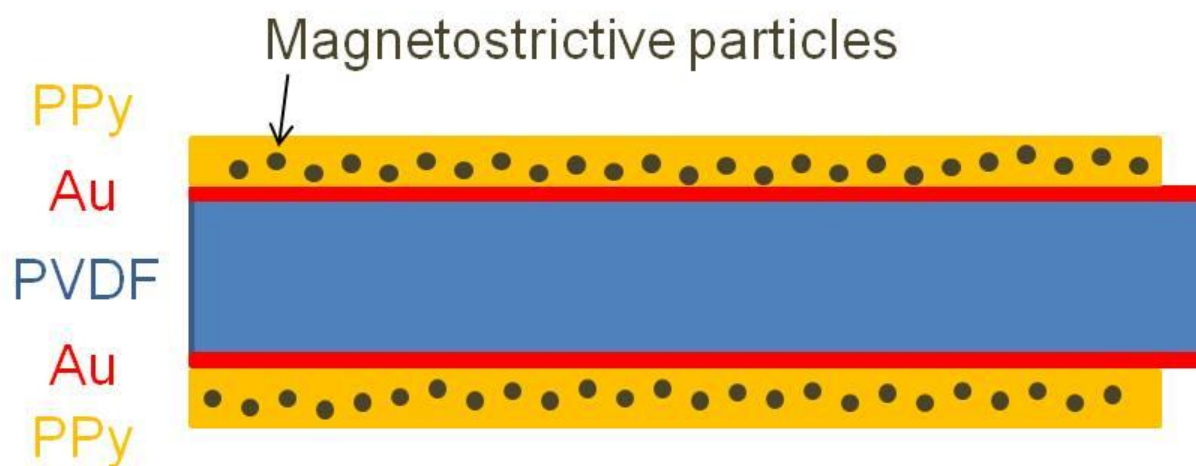


Figure 11-3. Schematic diagram for dual-functional polymer actuator and magnetic sensor.

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