Chemical and strain driven morphotropic phase boundaries in bismuth ferrite

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**CHEMICAL AND STRAIN DRIVEN
MORPHOTROPIC PHASE BOUNDARIES IN
BISMUTH FERRITE**

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School of Materials Science & Engineering

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ABSTRACT

Morphotropic phase boundary (MPB), a highly sought-after concept in piezoelectric materials, is the key factor for large electromechanical response. Unfortunately, mainstream piezoelectric materials all contain lead, a toxic element that is incompatible to the ever-growing demands for global environmental and ecological conservation. In the new wave of searching for lead-free replacements, BiFeO_3 (BFO) rises as a promising candidate due to the existence of both chemical- and strain-driven MPBs. In the chemical-driven MPB, the role of “chemical pressure” remains debated. To gain more insight into this issue, La-doped BFO films were systematically investigated in terms of structural, ferroelectric, dielectric and piezoelectric properties. It is found that under the weak chemical pressure induced by La, BFO still undergoes the ferroelectric – paraelectric phase transition with an intermediate metastable antipolar state that produces double hysteresis behavior. However, there is no enhancement in the piezoelectric measurement close to the MPB region, probably because the increase of the relative permittivity is small compared to those of BFO doped with rare-earth elements with smaller ionic radii. Furthermore, the chemical substitution is introduced into the highly-strained BFO films to combine the chemical- and strain-driven MPBs in this unique system, aiming to create multiple phase boundaries with ultrahigh piezoelectric response. Universal polarization rotation behavior is observed in rare-earth-element doped tetragonal-like BFO, analogous to those found in rhombohedral-like phase. However, a global polar instability is absent at high doping concentration before the tetragonal-like BFO lattice collapses due to epitaxial breakdown. The preliminary results of La-doped tetragonal-like BFO films show some degree of enhancement in the piezoelectric response, which requires further experimental validation.

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Table of Contents

ABSTRACT	i
ACKNOWLEDGEMENTS	ii
Table of Contents	iii
LIST OF FIGURES	vi
LIST OF TABLES	xv
Chapter 1 Introduction.....	1
1.1 Basic Concepts.....	1
1.1.1 Ferroelectricity and Piezoelectricity.....	1
1.1.2 Morphotropic Phase Boundary (MPB)	5
1.1.3 Strain Engineering in Ferroelectrics.....	7
1.2 Literature Review on Multiferroic BiFeO ₃	9
1.2.1 Characteristics of BiFeO ₃	9
1.2.2 Strain-induced MPB in BiFeO ₃	11
1.2.3 Rare-earth Substituted BiFeO ₃	15
Chapter 2 Motivation and Scope	20
2.1 Motivation of this research	20
2.2 Scope of this research	23
2.3 Organization of the Thesis	23
Chapter 3 Equipment and Methods.....	25
3.1 Film Growth.....	25
3.2 Composition Analysis	27
3.3 X-ray Diffraction.....	28
3.4 Atomic Force Microscope and Piezoelectric Force Microscopy	30
3.5 Transmission Electron Microscopy.....	34

3.6 Ferroelectric measurements	35
Chapter 4 Optimization of Pulsed Laser Deposition of Rare-earth-substituted BFO	
Thin Films.....	36
4.1 Introduction.....	36
4.2 Optimization of BSFO film growth on STO.....	40
4.3 Optimization of BSFO film growth on STO.....	43
4.4 Film composition analysis using EMPA.....	44
4.4 Conclusions.....	45
Chapter 5 Chemical-driven MPB in R-like BFO.....	46
5.1 Introduction.....	46
5.2 Single-domain BLFO thin films grown on miscut STO	46
5.3 Morphological and structural characterizations of BLFO films	50
5.4 Ferroelectric and dielectric properties of single-domain BLFO films	52
5.5 Domain structure and piezoelectric responses of single-domain BLFO films.....	57
5.6 Discussion	61
5.7 Conclusions.....	66
Chapter 6 Chemical-alloying effect in Strain-driven MPB in BFO	67
6.1 Introduction.....	67
6.2 Morphology and Structure Analysis	69
6.2.1 Rare Earth Substitution in Highly Strained Mc Phase BFO	69
6.2.2 Rare Earth Substitution in Strain-induced MPB in BFO	76
6.3 Ferroelectric Properties Analysis	86
6.3.1 Domain Structure	86
6.3.2 In-plane Polarization Hysteresis Loops.....	91
6.3.3 In-plane Domain Switching	96
6.4 Anomalous Stabilization of T-like phase in Yb-doped BFO	97
6.5 Discussion	103
6.6 Conclusions.....	109
Chapter 7 Conclusions and Future Work	110
7.1 Conclusions.....	110
7.2 Future Work	113

References	114
List of Publications	120

LIST OF FIGURES

Figure 1.1 Schematic drawing of a primitive cell for ABO_3 perovskite oxide.....	2
Figure 1.2 Typical polarization versus electric field loops under ferroelectric, antiferroelectric and paraelectric states. Figure adapted from ref. 3	3
Figure 1.3 Schematic illustration of direct and converse piezoelectric effect.	4
Figure 1.4 Versatile applications of ferroelectric materials.....	5
Figure 1.5 Phase diagram of PZT, which is a solid solution between PbZrO_3 and PbTiO_3 . Figure adapted from ref. 8.	6
Figure 1.6 Illustration of film under a compressive epitaxial strain. Figure adapted from ref. 22.....	8
Figure 1.7 (a) Polarization hysteresis loops of BTO films grown on GdScO_3 , DyScO_3 and BTO single crystals. Figures adapted from ref. 25 and 26.	9
Figure 1.8 (a)-(c) Crystal structure of BiFeO_3 viewing from different direction. (d) The G-type antiferromagnetic magnetic structure of BiFeO_3 . Figures adapted from ref. 38.....	11
Figure 1.9 (a) XRD patterns around (002) peaks of BFO films deposited on STO, LAO and YAO single crystal substrates; (b) and (c) HRTEM images of the coexistence of T-like and R-like phase in the BFO film, with insets showing schematic illustrations of unit cells; (d) The evolution of volume and area fraction of R phase with the increase of film thickness. Figure adapted from ref. 17.	13
Figure 1.10 Topography images (a,c) and XRD patterns (b, d) of highly strained BFO films grown on LSAO substrates with different film thickness: (a, b) 10 nm-thick, (c, d) 80 nm-thick. Figure adapted from ref. 53.	14

Figure 1.11 Polarization hysteresis loops of 200-nm thick BFO, $\text{Bi}_{0.86}\text{Sm}_{0.14}\text{FeO}_3$ and $\text{Bi}_{0.86}\text{Sm}_{0.16}\text{FeO}_3$ thin films. Figure adapted from ref. 62.	16
Figure 1.12 (a) Piezoelectric coefficients d_{33} versus electric field curves of $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{FeO}_3$ and $\text{Bi}_{0.86}\text{Sm}_{0.14}\text{FeO}_3$ thin films; (b) d_{33} coefficients as a function of Sm concentration of BSFO thin films. Figures adapted from ref. 62.	17
Figure 1.13 Universal phase diagram of rare earth substituted BFO with the black line indicating the MPB between the rhomboderal and the orthorhombic phase. Figure adapted from ref. 60.	18
Figure 1.14 Illustration of the polarization rotation from [111] direction towards [001] direction with the increase of Sm substitution. Figure adapted from ref. 68.	18
Figure 2.1 A hypothesis MPB region by combining polarization rotation (Polar – Polar) and polarization extension (Polar – Nonpolar) effects. Figure adapted from ref. 79.	22
Figure 3.1 Schematic drawing of a typical Pulsed Laser Deposition system.	26
Figure 3.2 Schematic diagram of EPMA.	28
Figure 3.3 Illustration of a four-circle X-ray diffractometer.	29
Figure 3.4 Schematic drawing of the basic AFM head components.	30
Figure 3.5 Schematic drawing of the vertical (a) and lateral (b) tip deformation and corresponding signal in photodiode detector.	31
Figure 3.6 Schematic of the piezoresponse force microscope (PFM) system.	32
Figure 3.7 Schematic drawing of the film deformation under applied electric field: (a) in phase, (b) out of phase; (c) phase different between the out-put signal and reference AC input.	33
Figure 3.8 Schematic drawing of TEM.	34

Figure 4.1 (a) Linear relationship between the laser fluency and the defocused distance at a constant pulsed laser energy of 40 mJ. The laser fluency slowly decays with time. (b) The evolution of Bi/Bi+Fe ratio of the target surface with increasing ablated pulses at different laser fluencies.....	38
Figure 4.2 SEI images and corresponding EDS maps of BFO target surface before and after laser ablation for 300 pulses at 40 mJ with different laser fluencies.	39
Figure 4.3 (a) Temperature – O ₂ pressure phase diagram of BFO and related impurity phases. Adapted from 110. (b) Bi ₂ O ₃ -Fe ₂ O ₃ binary phase diagram. The red dot indicates the central compositional point for producing phase-pure BFO. Adapted from 111.	40
Figure 4.4 XRD patterns of BSFO thin films grown on STO with constant pressure (a) and constant temperature (b).	41
Figure 4.5 AFM morphological images of BSFO thin films grown on STO with constant pressure (a)-(d) and constant temperature (e)-(h).	42
Figure 4.6 AFM morphological images of BSFO thin films grown on LAO with constant pressure (a)-(d) and constant temperature (e)-(h).	43
Figure 4.7 XRD patterns of BSFO thin films grown on STO with constant pressure (a) and constant temperature (b).	44
Figure 5.1 Schematics showing domain-variant selections of BFO epitaxial thin films grown on (a) exact STO, (b) STO with miscut along [100] and (c) STO with miscut along [110]. (d) Shear strain induced by miscut steps in addition to biaxial strain. Adapted from 126.....	48
Figure 5.2 Domain growth control through substrate vicinality: miscut towards [100] or [110] directions eventually leads to (110)- or (111)-oriented STO with two or one domain variant, respectively.	49

Figure 5.3 Film morphologies of BFO films with different La doping concentrations. The scale bars represent 1 μm . The arrows indicate the miscut downhill direction.	50
Figure 5.4 (a) XRD patterns of BLFO films grown on miscut STO substrates. (b) Variations of out-of-plane lattice constant with respect to La doping.	51
Figure 5.5 (a)-(e) Polarization – Electric Field (P – E) hysteresis loops of BLFO single-domain films with different La concentrations. (f) A compilation of all P – E curves.	53
Figure 5.6 (a) Field-dependent remanent polarization (P_r) of different La-doped BFO films measured using PUND method. (b) Evolutions of remanent polarization and coercive field with regard to the La doping amount.	54
Figure 5.7 Frequency-dependent (a) relative permittivity and (b) loss tangent of different La-doped BFO films. (c) Field-sweeping hysteresis loops of relative permittivity of different La-doped BFO films. (d) Evolution of relative permittivity with La doping concentration.	55
Figure 5.8 Temperature-dependent P – E loops of (a) pure BFO, (b) 20%-La-doped BFO and (c) 30%-La-doped BFO films. (d) Extrapolation of the coercive field to high temperature for different films.....	56
Figure 5.9 Upper panel: The morphological images of La-doped BFO films. Lower Panel: The corresponding OP-PFM images. The scale bars are 1 μm in all images. The OP-PFM image of a bare STO substrate is shown in the inset of 40% La-doped BFO film for comparison. White arrows indicate miscut directions.	58
Figure 5.10 Upper panel: The morphological images of La-doped BFO films, with arrows indicate the miscut directions. Middle panel: corresponding OP-PFM images of 0%, 10% and 20% La-doped BFO films with box-in-box switching patterns. Lower panel: Corresponding IP-PFM images with arrows indicating IP polarization vectors.	59

Figure 5.11 (a) Effective d_{33} of La-doped BFO films measured by PFM-based technique. (b) Evolution of effective d_{33} with different La doping.	60
Figure 5.12 (a) Proposed temperature – composition phase diagram of La-doped R-like BFO films. (b) Reported temperature – pressure phase diagram of BFO for comparison. Adapted from 145.....	64
Figure 5.13 Comparisons of (a) Dielectric hysteresis loops, (b) polarization hysteresis loops, (c) PUND remanent polarization curves and (d) piezoelectric hysteresis loops of pure BFO, 20% La-doped BFO and 10% Sm-doped BFO films.....	66
Figure 6.1 Surface morphology of 20 nm-thick BLFO thin films doped with (a) no La, (b) 5% La, (c) 10% La and (d) 15% La. Scale bars represents 1 μm . (e) XRD curves around (002) peak of 20 nm-thick BLFO films on LAO with La concentration ranging from 0 to 15%; (f) calculated c lattice parameters of BLFO films.	70
Figure 6.2 AFM topography images of 20 nm-thick BSFO films on LAO substrates with Sm substitution concentration ranging from 0 to 30%. The scan size is 3 μm	71
Figure 6.3 XRD curves around (002) peak of 20 nm-thick BSFO films on LAO with Sm concentration ranging from 0 to 30%; (b) c lattice parameters of BSFO films.	71
Figure 6.4 HR-XRD RSMs near (002) (a) and (103) (b) of 30 nm-thick pure BFO film; near (002) (c) and (103) (d) of the 32 nm-thick $\text{Bi}_{0.9}\text{Sm}_{0.1}\text{FeO}_3$ film.	73
Figure 6.5 (a) TEM cross section image of the BSFO/LAO interface. (b) HRTEM image showing the sharp interface between BSFO and LAO. (c) a phase boundary between R-like and T-like BSFO phases.	75
Figure 6.6 SAED patterns of BSFO and LAO (a), and BSFO film only (b).	76
Figure 6.7 Evolution of surface morphology of pure BFO and BL5FO films with the increase of film thickness: (a, d) 20 nm, (b, e) 40 nm and (c, f) 60 nm. Scale bars represent 1 μm	77

Figure 6.8 Surface topographies of 40 nm-thick BLFO thin films doped with (a) no La, (b) 5% La, (c) 10% La and (d) 15% La. Scale bars represent 1 μm .	78
Figure 6.9 Evolutions of mixed-phase fraction of BLFO films with different thickness; (b) critical thickness of mixed-phase formation and (c) threshold thickness of epitaxial breakdown for BLFO with different La concentration.	79
Figure 6.10 XRD curves around (002) peak of 20 nm-thick BLFO films on LAO with 5% La doping; (b) calculated c lattice parameters of BLFO films with different La doping concentration and film thickness.	80
Figure 6.11 Evolution of surface morphology with the increase of film thickness of BSFO films with 10% Sm doping: (a) 20 nm, (b) 30 nm, (c) 40 nm and (d) 60 nm. Scale bars represent 1 μm .	80
Figure 6.12 Surface morphology of stripes on BS10FO film (a) and zoom-in topography image showing details of stripes (b).	81
Figure 6.13 XRD curves around (002) peak of BS10FO films on LAO with different thickness; (b) calculated c lattice parameters of BLFO films.	82
Figure 6.14 HR-XRD RSMs near (002) (a) and (103) (b) of pure 60 nm-thick BFO film; near (002) (c) and (103) (d) of the 63 nm-thick $\text{Bi}_{0.9}\text{Sm}_{0.1}\text{FeO}_3$ film.	83
Figure 6.15 HR-XRD RSMs of HK-plane at $L=1.81$ and $L=1.62$ of the 73 nm-thick BFO film; $L=1.83$ (c) and $L=1.62$ (d) of the 70-nm thick BSFO film.	85
Figure 6.16 Surface morphologies (a-d) and out-of-plane domain structures of 30 nm-thick BLFO films with different La doping concentrations: (e-h) as grown state, (i-l) domain structures after “writing” with DC bias. Scan size is 1 μm^2 for all images.	87
Figure 6.17 In-plane domain structures (a-d) and corresponding FFT images (e-h) of 30 nm-thick BLFO films with different La doping concentrations.	88

Figure 6.18 Evolution of in-plane domain structure of pure BFO films with different thickness: (a) 38 nm, (b) 57 nm and (c) 114 nm.	89
Figure 6.19 Evolution of in-plane domain structure of BLFO films with different La concentration and film thickness: (a) 40 nm and (b) 68 nm thick BL5FO films, (c) 30 nm and (d) 36 nm thick BL10FO films. (e) Domain width versus film thickness of BLFO films with different La concentration.	89
Figure 6.20 Surface morphology (a, d), in-plane (b, e) and out-of-plane (c, f) domain structure of BSFO film at different thickness.	90
Figure 6.21 Illustration for the device structures of conventional vertical "sandwich" capacitor (a) and quasi-planar capacitor used in this study (b). Schematic illustration of the top-view of quasi-planar electrodes patterned on BFO and BSFO films (c). In this study, in-plane electric field was applied along the $\langle 100 \rangle$ and $\langle 110 \rangle$ directions of the underlying LAO substrates.	92
Figure 6.22 IP electric field distribution on the cross section of a 3.8 μm quasi-planar BSFO capacitor, simulated by finite element modeling. The relative dielectric constants used in the simulation for BSFO and LAO are 350 and 23, respectively.	93
Figure 6.23 (a) Schematic drawing of PUND; (b) Example of switched, un-switched and remanent polarization hysteresis loops of the quasi-planar BFO capacitor.	93
Figure 6.24 IP polarization hysteresis loops of BFO films with different thickness; (b) saturated polarization versus film thickness for pure BFO and BL5FO films.	94
Figure 6.25 (a) IP polarization hysteresis loops of 20 nm-thick BLFO films with different La concentration; (b) saturated polarization and coercive field versus film thickness for BLFO films.	94

Figure 6.26 Polarization hysteresis loops of 30 nm-thick BFO and $\text{Bi}_{0.9}\text{Sm}_{0.1}\text{FeO}_3$ films grown on LAO substrates.	95
Figure 6.27 (a) and (b) are the IP PFM image and the illustration of polarization vectors after applying +60V at the left electrode respectively. (c) and (d) are the IP PFM image and the illustration of polarization vectors after applying -60V. Insets in (a) and (c) are the illustrations of the IP domain arrangement with red arrows indicating IP polarization directions. “E” denotes the applied electric field.	97
Figure 6.28 Schematic showing the reduction of atomic radius with increasing atomic number in lanthanide group. Figure adapted from 153.	97
Figure 6.29 XRD patterns around (001) peak of pure BFO, BL15FO and BY10FO films grown on LAO with their c lattice constants denoted.	98
Figure 6.30 XRD patterns and corresponding AFM morphologic images of (a) pure BFO and (b) 10 %-Yb-doped BFO films with increasing thickness.	99
Figure 6.31 Topography, as-grown IP and OP domain structures of a pure BFO (a, b, c), BL15FO (d, e, f) and BY10FO) films grown on LAO. Scale bars represent 500 nm.	100
Figure 6.32 In-plane ferroelectric domain images of (a) BY10FO and (b) BL15FO before and after in-plane electrical switching. (c) Corresponding in-plane P – E loops of pure, 15%-La-doped and 10%-Yb-doped BFO films.	101
Figure 6.33 Topography, IP and OP domain structures after electrical writing of a pure BFO (a, b, c), BL15FO (d, e, f) and BY10FO) films grown on LAO. Scale bars represent 500 nm.	102
Figure 6.34 Schematic drawings showing the lattice distortion of BFO thin films grown on LAO substrate at (a) small thickness with purely T-like phase and (b) large thickness with relaxed T-R mixed phases.	103

Figure 6.35 (a) Zoom-in surface morphology of a thick BL5FO film. The inset shows the height profile of the mixed-phase stripes denoted by blue dotted line. (b) Linear relationship between the average depth of “stripes” region and the film thickness of BLFO thin films.	105
Figure 6.36 Schematic drawing showing the in-plane polar instability in BLFO induced by RE doping, leading to true tetragonal structure.	107
Figure 6.37 Evolution of the free energy profile for the in-plane ferroelectric order in BLFO thin films grown on LAO with the increase of La doping concentration.	108
Figure 6.38 Proposed phase diagram for La-doped highly-strain BFO.	109

LIST OF TABLES

Table 3.1 Deposition parameters for the deposition of ReBFO films in this study.....	27
Table 4.1 Melting point, boiling point and vapor pressure of related elements in the target materials. Data adapted from 106	37
Table 4.2 Physical properties of STO and LAO single crystal substrates.	40
Table 4.3 Composition analysis of BSFO films grown on STO substrates with different Sm concentration using EPMA technique.	45
Table 6.1 Effective ionic radii of relevant elements in this study. Data adapted from 141	106

Chapter 1 Introduction

1.1 Basic Concepts

1.1.1 Ferroelectricity and Piezoelectricity

A crystal is called ferroelectric if it possesses a spontaneous polarization that is switchable under electric field.¹ Ferroelectric materials lose their ferroelectricity when heated up to a critical temperature named the Curie temperature (T_c) at which the ferroelectric-to-paraelectric phase transition occurs.

Based on symmetry elements, crystals are classified into 32 groups, belonging to different point groups. Among all groups, 21 of them are non-centrosymmetric, which is an essential precondition for piezoelectricity, and 20 of them are piezoelectric. Group 432 is the only exception which is non-centrosymmetric but the presence of polarity is destroyed by a combination of other symmetry operations. 10 out of the 20 piezoelectric groups have specific polarizable axis. Piezoelectric material can be called pyroelectric if they exhibit a spontaneous polarization above a certain temperature. Pyroelectric is called ferroelectric if the polarization direction can be externally switching by applying an electric field which is larger than its coercive field.

Among all the ferroelectrics, perovskite ferroelectrics are the most studied and commercially-used one. Examples include the well-known single phase barium titanate (BaTiO_3) and lead titanate (PbTiO_3), as well as lead-zirconate-titanate ($\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ or PZT), which is a solid solution between antiferroelectric PbZrO_3 and ferroelectric PbTiO_3 . Perovskite structure has a general formula, ABO_3 , in which A and B are both cations with their valence sum to be +6.² The A-site cations with larger radius locate at eight corners while the small B-site

smaller cations are locating at the center of the unit cells (Figure 1.1). O^{2-} anions occupy the face centers. In the non-centrosymmetric ferroelectric phase, a net dipole moment is produced by the relative displacement between the positively-charged A-site framework and the negatively-charged oxygen octahedron.

Figure 1.1 Schematic drawing of a primitive cell for ABO_3 perovskite oxide.

The hallmark of a ferroelectric is the hysteresis loop showing how the spontaneous polarization (P) changes with an external electric field (E), as shown in Figure 1.2. In contrast, antiferroelectric material is characterized by antiparallel alignment of the dipoles, showing a double hysteresis loop. Across the Curie temperature, ferroelectric – paraelectric transition takes place. The dipoles become disordered due to large thermal fluctuation, accompanied by the disappearance of hysteresis behavior in the $P - E$ loop.

Figure 1.2 Typical polarization versus electric field loops under ferroelectric, antiferroelectric and paraelectric states. Figure adapted from ref. 3

All ferroelectrics are piezoelectric. Piezoelectricity refers to the interplay between the electric polarization and the mechanical pressure of a material. The direct effect is defined as the polarization change generated by an external mechanical stress. In contrast, the converse effect is referring to mechanical strain as a result of an external bias voltage (Figure 1.3).

Direct and converse piezoelectric effect can be described by the following two equations:

$$D = dE + \epsilon^T E$$

$$S = s^E T + dE$$

In the equations, D and E are the dielectric displacement and the electric field, respectively. Similarly S and T refer to the mechanical strain and the material compliance. d and ϵ is called piezoelectric coefficient and dielectric constant respectively. The superscripts indicate a quantity held constant or zero. The coefficient d_{33} which indicates both the deformation and the electric field is along “3” direction (usually defined as the vertical direction perpendicular to the film surface) is usually called “the piezoelectric coefficient” as it is the most used one for industry application and research studies:

$$D_3 = d_{33} T_3$$

$$S_3 = d_{33} E_3$$

(a) Direct piezoelectric effect

(b) Converse piezoelectric effect

Figure 1.3 Schematic illustration of direct and converse piezoelectric effect.

Ferroelectric materials are widely used in many different areas according to their properties as summarized in Figure 1.4. The fact that ferroelectrics possesses two or more stable polarization states makes it a promising candidate as nonvolatile Ferroelectric Random Access Memories (FeRAM).⁴ The two stable polarized states in the hysteresis loop correspond to the two binary states “0” and “1”. The polarization state can be externally switched by applying an electric field larger than a threshold value, which is the coercive field E_c . The high permittivity of the perovskite ferroelectrics can be used to make high-k Dynamic Random Access Memory (DRAM)⁴. The pyroelectric effect of ferroelectrics, which refers to the change of spontaneous polarization resulted from the change of ambient temperature, enables their application as infrared radiation sensors. The change of refractive index of a ferroelectric crystal in response to an applied voltage may find its application as an electro-optic switch. The large piezoelectric coefficient and low loss render ferroelectrics a good candidate for actuator elements in Micro-Electro-Mechanical-Systems (MEMS).

Figure 1.4 Versatile applications of ferroelectric materials.

1.1.2 Morphotropic Phase Boundary (MPB)

Among the piezoelectric materials discovered so far, materials with their composition near a so-called morphotropic phase boundaries (MPBs) stand out due to their enhanced

electromechanical and dielectric properties.⁵ MPB refers to a compositional boundary at which two or more adjacent phases have proximate Gibbs free energies.⁶ A good example is the renowned $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) binary system. The MPB of PZT locates at the boundary separating tetragonal Ti-rich phase and the rhombohedral Zr-rich phase, as shown in the phase diagram of PZT (Figure 1.5).^{7,8}

Figure 1.5 Phase diagram of PZT, which is a solid solution between PbZrO_3 and PbTiO_3 .

Figure adapted from ref. 8.

The exact origin of the enhancement in electromechanical and dielectric properties of PZT at the MPB composition can be briefly understood by the minimizing the energy gaps between a rhombohedral (R) phase and a tetragonal (T) phase, consequently easing the polarization rotation under electric-field excitation. However, the detailed phase evolution around the MPB region is still under debate, especially over the question whether an intermediate monoclinic emerges. Possible mechanisms are listed below:

- 1) As the free energy of these two ferroelectric phases at MPB is very close , there are 14 possible polarization directions, which promote the reorientation of domains to the external electric field and thus lead to an enhancement in piezoresponse.⁸
- 2) A monoclinic intermediate phase was observed in PZT films with composition near its MPB.⁷ First principles calculations⁹ and phenomenological theory¹⁰ also supported the stability of this phase. Noheda et al suggested that the intrinsic monoclinic deformation of the unit cell as a result of the rotation of the polarization in this monoclinic plane, leads to a large piezoelectric response.^{7, 8, 11-13}
- 3) By comparing the domain images PZT across the MPB composition, Kristin et al suggested that nanodomain with high domain wall mobility is the origin of large piezoresponse.¹⁴ They also claimed that the monoclinic diffraction pattern can directly be interpreted as the average tetragonal and rhombohedral nanodomain structure.^{14,15}

Although the origin of high electromechanical properties of MPB is still not conclusive, MPBs have been widely used in devices and industry.

1.1.3 Strain Engineering in Ferroelectrics

When searching for new MPBs, researchers demonstrated that, chemical substitution⁶, hydrostatic strain¹⁶ and epitaxial strain^{17, 18} can facilitate the formation of MPBs. When a thin film is deposited on to a single crystal substrate with a lattice constant different from that of the film, the film will be subjected to a misfit strain, which is defined as:

$$\varepsilon_s = \frac{a_{//} - a_0}{a_0}$$

in which a_0 is the bulk lattice parameter while $a_{//}$ is the in-plane lattice parameter of the epitaxial film.¹⁹ As shown in Figure 1.6, when the film is sufficiently thin and coherently strained, it will adapt the in-plane lattice parameters of the crystal substrate. With the increase of film thickness above a so-called “critical thickness”, the misfit strain is slowly relaxed by the appearance of dislocations at the interface or the appearance of ferroelastic domains.²⁰ It has been proved both experimentally and theoretically that a larger misfit strain leads to a smaller critical thickness.²¹

Figure 1.6 Illustration of film under a compressive epitaxial strain. Figure adapted from ref. 22.

Through the inherent coupling between strain and polarization, misfit strain offers a powerful tool to modify the ferroelectric properties of thin films. Some predictions of strain effect in epitaxial ferroelectric thin films by various theoretical approaches have been confirmed by experimental observations.^{11, 16, 20, 23, 24} The introduction of epitaxial strain to BaTiO₃ and PbTiO₃ films can also effectively increase their paraelectric-to-ferroelectric transition

temperature (T_c). Highly strained BaTiO_3 thin films on ReScO_3 substrates also show a dramatic enhancement in the saturated polarization (Figure 1.8a).²⁵ An even more pronounced example is SrTiO_3 , which is normally paraelectric at any temperature but changes into a room-temperature ferroelectric with a tensile strain of 1%.²⁶

Besides polarization and T_c , other ferroelectric properties, such as the ferroelectric domain structure, piezoelectric coefficients and dielectric constants of certain ferroelectric thin films can be altered with the application of epitaxial strain.^{17, 20, 22, 23}

Figure 1.7 (a) Polarization hysteresis loops of BTO films grown on GdScO₃, DyScO₃ and BTO single crystals. Figures adapted from ref. 25 and 26.

1.2 Literature Review on Multiferroic BiFeO_3

1.2.1 Characteristics of BiFeO_3

Most ferroelectric and piezoelectric materials used in electrical devices or ceramic capacitors contain lead, such as PbTiO_3 , PZT, and $\text{Pb}(\text{Mg,Nb})\text{O}_3\text{-PbTiO}_3$ (PMN-PT).^{27, 28} With the increasing concern of lead toxicity and environmental pollution, the exploration of new lead-

free ferroelectric/piezoelectric materials has attracted tremendous amount of attention.²⁹ Among the possible candidates, BiFeO₃ (BFO) stands out. Compared with other ferroelectrics, BFO possesses following advantages:

- 1) BFO possesses a large spontaneous polarization (around 60 $\mu\text{C}/\text{cm}^2$ and 100 $\mu\text{C}/\text{cm}^2$ for (001) and (111) orientated films, respectively).³⁰
- 2) BFO has a high Curie temperature ($T_c \sim 1100\text{K}$)³¹, which facilitates possible high-temperature applications;
- 3) BFO, being a room-temperature multiferroic with both ferroelectricity and antiferromagnetism, is highly promising for realizing the sought-after concept of electric control of magnetism for next-generation memory.³²⁻³⁴

Structure of bulk BFO can be presented by two highly distorted rhombohedral perovskite units whose body diagonals are connected along pseudo-cubic $\langle 111 \rangle_{\text{pc}}$ directions,³⁵ as shown in Figure 1.8. The lone pair electrons of Bi³⁺ 6s² generate a relative displacement between negative-charged FeO₆ octahedron and positive-charged Bi³⁺. Such displacement leads to a large spontaneous polarization in BFO along $\langle 111 \rangle$ directions.³⁶ Considering the polarity along body diagonal, BFO possesses four structural variants and a total of eight possible polarization directions. Meanwhile, magnetic moments of Fe is found to couple ferromagnetically within (111)_{pc} plane, but antiferromagnetically between adjacent planes, forming a G-type antiferromagnetic ordering (Figure 1.6d).³⁷

Figure 1.8 (a)-(c) Crystal structure of BiFeO₃ viewing from different direction. (d) The G-type antiferromagnetic magnetic structure of BiFeO₃. Figures adapted from ref. 38.

Multiferroics refers to materials which possess two or more ferroic orders.^{32, 39} The coexistence of ferroelectricity and antiferromagnetism in BFO enables the possibility of controlling magnetism with an electric field, or controlling polarization with a magnetic field.^{32, 38, 40, 41}

However, BFO films also have several disadvantages, as listed below:

- 1) BFO thin films have a large coercive field of up to 300 kV/cm^2 ;³⁴
- 2) BFO has a lower piezoelectric coefficient of around 60 pm/V as compared with around 200 pm/V for PZT films at the MPB composition;³⁰
- 3) BFO has a small dielectric constant with its reported value varying from 30 to 100.^{42, 43}
- 4) With a small band gap of $\sim 2.8 \text{ eV}$, BFO films usually suffer from a high leakage current.⁴⁴

These drawbacks hinder BFO's possible application in industry.

1.2.2 Strain-induced MPB in BiFeO₃

Epitaxial strain, which has been proven to be an effective tool to obtain desired physical properties of ferroelectric materials through structure modification²², has been utilized to enhance the desired properties of bismuth ferrite films, like polarization rotation⁴⁵, Curie temperature tuning⁴⁶ or even magnetic structures.⁴⁷

The perovskite structure of bulk BFO is rhombohedrally-distorted (R) with symmetry space group $R3c$ at room temperature.⁴⁸ Under compressive/tensile strain, the symmetry of the lattice is reduced to monoclinic (M_A or M_B depending on compressive or tensile strain). Within the moderate strain range, the lattice structure is still a distorted rhombohedral cell following conventional elastic distortion, namely the so-called R-like phase. However, it was recently found that when the compressive strain exceeded certain threshold, a tetragonal-like (T-like) phase with a c/a ratio up to 1.24 can be achieved in thin epitaxial BFO films grown on single crystal substrates with a large lattice match, including LaAlO_3 (LAO), LaSrAlO_4 or YAlO_3 (YAO) (Figure 1.9).^{17,49}

Early first-principle calculations suggested a tetragonal $P4mm$ symmetry for that phase, with a giant polarization of up to $150 \mu\text{C}/\text{cm}^2$ along $[001]_{\text{pc}}$ direction.²³ However, recent study of highly-strained BFO films deposited on LAO and LSAO substrates revealed a monoclinic Mc phase whose polarization vector lying not along the $[001]$ direction but in the (100) plane instead.^{50,51} Based on polarization measurements of BFO films with mixed T-like and R-like phases, a spontaneous polarization of $\sim 150 \mu\text{C}/\text{cm}^2$ was further deduced for the T-like phase.⁵²

Figure 1.9 (a) XRD patterns around (002) peaks of BFO films deposited on STO, LAO and YAO single crystal substrates; (b) and (c) HRTEM images of the coexistence of T-like and R-like phase in the BFO film, with insets showing schematic illustrations of unit cells; (d) The evolution of volume and area fraction of R phase with the increase of film thickness. Figure adapted from ref. 17.

Figure 1.10 Topography images (a,c) and XRD patterns (b, d) of highly strained BFO films grown on LSAO substrates with different film thickness: (a, b) 10 nm-thick, (c, d) 80 nm-thick. Figure adapted from ref. 53.

With the increase of film thickness, a strain-relaxation-mediated MPB between T-like matrix phase and T-R phase mixture emerges in BFO films on LAO or LSAO to release the strain energy. Detailed synchrotron structure analysis revealed that, besides the T-like phase, a rhombohedral-like (R-like) phase and two triclinic phases were present in the MPB.⁵³ With the increase of film thickness, film topography evolves from a homogeneous surface with unit-cell steps for pure T-like phase BFO film to a relatively-rough surface with a series of

topological stripes consisting of alternating T – R phases for mixed-phase BFO film, as shown in Figure 1.10.^{17, 53, 54}

A dramatic enhancement of electromechanical response was also observed in mixed-phase region when an external electric field was applied.⁵⁵ This enhancement was attributed to the phase transition between the T-like and R-like phases bridged by the two coexisting triclinic phases under external electrical stimuli.^{53, 54}

1.2.3 Rare-earth Substituted BiFeO₃

In addition to epitaxial strain, chemical substitution is another important tool to modify the structure and properties of BFO.^{56, 57} Among a variety of dopants, rare earth (RE) elements, e.g., RE = Sm, Gd and Dy, were reported to introduce a MPB in BFO thin films.⁵⁸ The solid solutions made from the substitution of Bi by RE in BFO, denoted here as RE-doped BFO, exhibit a compositionally-induced rhombohedral-to-orthorhombic phase transition, which is accompanied by enhanced electromechanical response and dielectric constant at the phase boundary.^{59, 60}

The study of RE-doped BFO started since the report of the large polarization in BiFeO₃ thin films in 2003.³⁰ Several groups synthesized Bi_{1-x}Sm_xFeO₃ (BSFO) bulk samples by solid-state reaction or liquid phase sintering.^{58, 61} With the increase of Sm concentration, a phase transition from a rhombohedral to an orthorhombic phase with a triclinic bridging phase was observed at a composition of Bi_{0.8}Sm_{0.2}FeO₃.⁶¹ In 2008, Takeuchi et al reported the discovery of a MPB with enhanced piezoelectric and dielectric properties in BSFO thin film prepared by a combinatorial method.⁶² As shown in Figure 1.11, It was firstly proposed that the boundary, located at Bi_{0.86}Sm_{0.14}FeO₃, is a boundary between a ferroelectric rhomboderal

phase and an antiferroelectric pseudo-orthorhombic phase.^{62, 63} As compared with pure BFO films, the coercive field of $\text{Bi}_{0.86}\text{Sm}_{0.14}\text{FeO}_3$ is effectively reduced while the saturated polarization value remains unchanged (Figure 1.11).⁶² The piezoelectric coefficient d_{33} increases to a maximum value of 110 pm/V, which is comparable to that of PZT thin films with the MPB composition (Figure 1.12).⁶²

Figure 1.11 Polarization hysteresis loops of 200-nm thick BFO, $\text{Bi}_{0.86}\text{Sm}_{0.14}\text{FeO}_3$ and $\text{Bi}_{0.86}\text{Sm}_{0.16}\text{FeO}_3$ thin films. Figure adapted from ref. 62.

The phase transition was firstly described as a “ferroelectric to anti-ferroelectric” transition, because of the presence of “double polarization hysteresis loops” observed. But theoretical calculations by First principles give another explanation, saying that the double hysteresis loop is actually originated from an electric-field-induced phase transition between a orthorhombic phase (paraelectric) to a rhombohedral phase (ferroelectric).⁶⁰ Detailed structure analysis by both high-resolution XRD and TEM also revealed the coexistence of multi-phases in BSFO films at the MPB composition.⁶³⁻⁶⁵

Figure 1.12 (a) Piezoelectric coefficients d_{33} versus electric field curves of $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{FeO}_3$ and $\text{Bi}_{0.86}\text{Sm}_{0.14}\text{FeO}_3$ thin films; (b) d_{33} coefficients as a function of Sm concentration of BSFO thin films. Figures adapted from ref. 62.

The formation of MPB in RE-doped BFO was attributed to a chemical pressure originating from the ionic radii mismatch between RE and Bi.⁶⁰ It is further confirmed that such rhombohedral-to-orthorhombic phase transition is an universal behavior of rare earth doping by controlling the average ionic radius of the A-site cation.^{60, 66, 67} Not only Sm, other rare

earth elements substitution, including Gd and Dy, can also induce the formation of MPB in BFO.⁶⁰ A universal phase diagram of RE-doped BFO is shown in Figure 1.13.⁶⁰

Figure 1.13 Universal phase diagram of rare earth substituted BFO with the black line indicating the MPB between the rhombohedral and the orthorhombic phase. Figure adapted from ref. 60.

Figure 1.14 Illustration of the polarization rotation from [111] direction towards [001] direction with the increase of Sm substitution. Figure adapted from ref. 68.

Furthermore, it was recently reported that the polarization vector is rotating continuously within the (110) plane in Sm-substituted BFO (BSFO) systems.⁶⁸ As shown in Figure 1.14, the polarization rotation leads to an out-of-plane polarization, which remains almost unchanged with the RE substitution .⁶⁸

Chapter 2 Motivation and Scope

2.1 Motivation of this research

Pb-based piezoelectric materials, such as PZT and PMN-PT, remain indispensable in transducers, actuators and sensors. However, with the ever-increasing concern of Pb pollution and environmental issues, the quest for lead-free materials with comparable performances has since started.⁶⁹⁻⁷¹ BiFeO₃, a perovskite oxide which possesses both ferroelectricity and antiferromagnetism at room temperature, has been a “blossomed” candidate for the past ten years.³⁴ BFO possess a large polarization of 100 $\mu\text{C}/\text{cm}^2$ along the $[111]_{\text{pc}}$ direction.³⁰ A large polarization as such is an ideal starting point for searching MPBs with enhanced electromechanical response, just like PbTiO₃. MPB, by definition, is the boundary connecting two structurally-different ferroelectric phases. Thus, conventional route to create MPBs is via forming solid solutions between different ferroelectric end members. For example, PZT is the solid solution of ferroelectric PbTiO₃ (PTO) and antiferroelectric PbZrO₃ with its MPB near $x = 0.52$ between tetragonal and rhombohedral ferroelectric phases. Following the same principle, a flurry of studies tried to pair rhombohedral BFO with another tetragonal ferroelectric material, e.g. BaTiO₃ (BTO) or PTO to produce a MPB.⁷²⁻⁷⁸ However, owing to the aliovalent chemical substitution (Bi^{3+} and Fe^{3+} versus Ba^{2+} or Pb^{2+} and Ti^{4+}), point defects (cation or oxygen vacancies) may prevail to compensate for the charge imbalance, thus deteriorating the material performances. On the other hand, rare-earth (RE) lanthanides exhibit prevalent 3+ valence and comparable ionic radii to Bi^{3+} . Unfortunately, the other end member of the solid solution, namely, REFeO₃ is a paraelectric. As a consequence, the possible phase transition within the compositional phase diagram would be ferroelectric – paraelectric (FE-PE) instead of ferroelectric – ferroelectric (FE-FE)

as observed in conventional MPBs with enhanced electromechanical response. Nevertheless, as pointed out by Damjanovic,⁷⁹ while conventional MPBs rely on the polarization rotation between energetically-proximate ferroelectric phases with different symmetries, a FE-PE phase transition also flattens the free energy profile, and may lead to great enhancement of properties owing to polarization extension. A prominent example was demonstrated by Liu and Ren,⁸⁰ who reported exceptionally large piezoresponse at an FE-FE-PE tricritical point, where both polarization rotation and polarization extension play a role. As for RE-doped BFO, among the enormous studies reported, a series of systematic work done by Takeuchi's group is highly notable and well-established.^{68, 81-84} Overall, they found a universal phase transition behavior in RE-doped BFO films: with more RE doping, BFO films were driven from a rhombohedral-like ferroelectric phase towards an orthorhombic paraelectric phase. In between, antiferroelectric-like double hysteresis loops were observed due to electric-field induced FE-PE transition. Significant increase of the piezoelectric effect was measured at the proximity of the FE-PE transition.

In their study, because no significant double hysteresis loop as well as enhancement of the piezoelectric response was observed in BFO film doped with La, which has a similar ionic radius as Bi^{3+} , chemical pressure was believed to be at the heart of the phase transition. The onset of the FE-PE phase transition was correlated with the reduction of the effective ionic radii upon RE doping. However, La-doping-induced polar – antipolar transition was widely reported in bulk ceramics,⁸⁵⁻⁸⁸ which casts doubts over the indispensable role of “chemical pressure”. Moreover, first-principle simulations also supported an antipolar pattern in moderate La dopant concentration.⁸⁹

In addition, strain-driven MPB in BFO opens up another unique platform for exploring giant electromechanical response. An unprecedented strain of 14% can be achieved in

2.2 Scope of this research

Aiming to resolve aforementioned problems, namely, (1) figure out the role of chemical pressure in the MPB of RE-doped BFO; (2) whether it is possible to create a multiple-phase boundary by combining chemical- and strain-driven MPBs in BFO, we embark our study by looking into the La-doped BFO with R-like structure, since La barely induces chemical pressure. Furthermore, the chemical-substitution effect in highly-strained T-like phase or T – R mixed phases will be investigated, as both the chemical and strain effects are involved. In particular, the work flow of this thesis is listed as follows:

- (i) Optimize the deposition conditions of RE-doped BFO films.
- (ii) Study La-doping effect on R-like BFO, and compare the results with other RE doping like Sm with considerable chemical pressure effect.
- (iii) Explore the RE-doping effect on T-like BFO as well as the strain-driven MPB.

2.3 Organization of the Thesis

The organization of this thesis is listed as following:

Chapter 1 introduces the basic concepts and literature reviews related to this study. Chapter 2 outlines the motivation and the scope of this work. Chapter 3 details the equipments and methods employed for the deposition and characterization of RE-doped BFO thin films. The optimization process of deposition conditions for epitaxial RE-doped BFO thin films is described in Chapter 4. In Chapter 5, the evolution of the structure and ferroelectric properties of La-doped R-like BFO is systematically investigated and the effect of chemical pressure is clarified. Chapter 6 focuses on the RE-doping effect on T-like BFO and strain-

driven T – R MPB. Chapter 7 presents the overall findings of this project and the suggestions for future work.

Chapter 3 Equipment and Methods

In this chapter, the equipments and methods used for the fabrication and characterizations of RE-doped BFO thin films will be briefly introduced. Specifically, thin films were deposited using pulsed laser deposition. Composition of the film was characterized by scanning electron microscopy (SEM)-based techniques like energy-dispersive spectroscopy (EDS) or Electron Probe Micro-Analyzer (EPMA). The phase purity and structure of the film were analyzed using both X-ray diffraction (XRD) and high resolution transmission electron microscopy (TEM). Detailed structure information was further obtained by reciprocal space mapping (RSM) with high-resolution synchrotron XRD. Film morphology and ferroelectric domain imaging and manipulation were carried out using piezoelectric force microscopy based on an atomic force microscope (AFM). Measurements of electric properties were performed on a probe station equipped with various meters.

3.1 Film Growth

Figure 3.1 shows the schematic drawings of a typical PLD. During the deposition process, a laser beam with modulated pulse width and energy is focused onto the target in a high vacuum environment. Under such high energy density, target materials will be evaporated, forming a plasma plume. Then, the plume was directed to the surface of a single crystal substrate, which is usually heated and recrystallizes into the desired phase.^{90, 91}

Figure 3.1 Schematic drawing of a typical Pulsed Laser Deposition system.

Typical oxide deposition by PLD is carried out according to the following steps:

- (1) Substrate cleaning and target preparation.

Before deposition, the substrate is ultrasonically cleaned in acetone and ethanol successively. The target surface is carefully polished to remove the laser burned layer formed during previous deposition.

- (2) Setting up, pre-pump chamber, oxygen pressure adjustment, substrate heating.

The chamber is pumped to a high vacuum of $<10^{-5}$ Torr after placing the target and substrates inside. The oxygen flow rate is adjusted to maintain a desired dynamic pressure (typically 10~100mTorr). Then the substrate is heated up to 675 ~ 750 °C at a rate of 20°C/min.

- (3) Laser energy calibration and deposition.

Before the deposition, laser energy and frequency are adjusted to the desired values. The energy of the KrF excimer laser with 248nm wavelength was maintained at around 1 J/cm².

The target-substrate distance is fixed at around 6 cm. Ceramic BSFO targets with La, Sm and Yb with different concentrations were used. Details of the primary deposition parameters of films are listed in Table 3.1.

Table 3.1 Deposition parameters for the deposition of ReBFO films in this study.

	Substrate temperature	Oxygen partial pressure	Energy density	Laser frequency
ReBFO	700 °C	100 mTorr	$\sim 1 \text{ J/cm}^2$	5 Hz

(4) Post-deposition annealing.

Right after deposition, ambient pressure oxygen is introduced into the chamber. Finally the sample is gradually cooled down to 200°C with a step of 5°C/min, after which, the heater is turned off.

3.2 Composition Analysis

EPMA is a microbeam instrument with the capability of precise chemical analysis for solid-state material. EMPA is essentially a combination of SEM and wavelength-dispersive spectroscopy (WDS). The electron beam, which is generated from a W-filament cathode, is accelerated and focused by a series of electromagnetic lenses before hitting the sample surface. After the bombardment, electrons and x-rays emitted from the sample surface were collected and analyzed by a variety of detectors, among which WDS selected and counted specific X-ray wavelengths. After a comparison of the intensities of characteristic X-rays from the sample and that from the standard materials, the precise chemical composition of the sample is determined. With the capability of quantitative composition analysis non-destructively at high sensitivity, EPMA also has some disadvantages, such as its low

sensitivity of elements with low atomic weight. In some tests, EDS was employed instead, which has a similar working principle as EPMA.

Figure 3.2 Schematic diagram of EPMA.

3.3 X-ray Diffraction

As a non-destructive method, XRD has been widely used to obtain detailed phase and structural information of bulk and thin film samples.⁹² The basis of XRD lies in the Bragg's law which states $n\lambda = 2d \sin\theta$; where λ is the wavelength of the x-ray, d is the spacing of crystal planes, and θ is the incident angle of the x-ray beam. Figure 3.2 shows the schematic illustration of a conventional θ - 2θ scan, during which the X-ray tube is fixed while sample

and detector rotates with an angular speed of θ and 2θ respectively. Based on the position of diffraction peaks, the out-of-plane lattice parameters can be calculated using the Bragg's Law.

Figure 3.3 Illustration of a four-circle X-ray diffractometer.

To further explore the structural parameters and to determine the epitaxial relationships between film and substrate, reciprocal space maps (RSMs) were performed using high-resolution synchrotron X-ray. RSM is consisted of a series of θ - 2θ scans while varying the ω angles around specific symmetrical and asymmetrical reflections. The conversion of the angular space into the reciprocal space is done using the following equations:

$$Q = \frac{4\pi}{\lambda} \sin\theta \sin(\omega - \theta)$$

$$Q_{\perp} = \frac{4\pi}{\lambda} \sin\theta \cos(\omega - \theta)$$

In this thesis, the XRD system used for routine θ - 2θ scan is a Rigaku four-circle X-ray diffractometer equipped with a Cu K_{α} x-ray tube. The wavelength of X-ray is 1.5406 Å. High-resolution RSMs were performed at Singapore Synchrotron Light Source with the same wavelength.

3.4 Atomic Force Microscope and Piezoelectric Force Microscopy

Atomic Force Microscope (AFM) is a unique method for morphology and properties mapping at nanoscale by monitoring the interaction between a sharp probe and sample surface. An AFM is composed of a head, X, Y and Z scanning piezos and a controlling system. Basic AFM head components are shown in Figure 3.3. The laser beam emitted from the light source is carefully aligned and focused on the back of the cantilever. The interactions between the tip and the sample surface change the deflection of the cantilever. The reflected laser beam is directed by an adjustable mirror towards the four-segmented photodiode detector.

Figure 3.4 Schematic drawing of the basic AFM head components.

Both the lateral and vertical angular displacement of the cantilever results in two segments of the photodiode collecting more light than the other two (Figure 3.4).

Figure 3.5 Schematic drawing of the vertical (a) and lateral (b) tip deformation and corresponding signal in photodiode detector.

There are three primary operation modes for AFM: contact mode, tapping mode (or AC mode), and non-contact mode.

In contact mode, AFM tip is brought in to continuous contact with sample surface while scanning through the sample line by line. The controller monitors the deflection change in the photodiode detector. A feedback loop maintains a constant deflection, which implies a constant force which is applied to the probe, by changing the vertical “z” value of the scanner at each lateral (x, y) point. The changes of z form the topography image of the sample.

In the tapping mode, the AFM probe scans through the sample with its cantilever oscillating near its resonant frequency. The tip gently hits sample surface for a short period when it reaches the bottom of its oscillation circle. Based on the feedback loop, AFM controller will

adjust the vertical position of scanner to maintain an user-defined tapping amplitude of the cantilever.

Non-contact mode usually refers to Electrostatic Force Microscopy (EFM) or Kelvin Probe Force Microscopy (KPFM), in which the cantilever lifted up from sample surface for a certain distance while oscillating at a frequency near its resonance frequency. An static or AC voltage is applied to the cantilever to detect the Vander Waals forces between the tip and the sample by monitoring the change of resonant frequency.

PFM works in contact mode. It measures the eletcromechnical response of a piezoelectric/ferroelectric material when an AC modulation signal is applied between a conductive probe and the sample.⁹³⁻⁹⁵ Then the deformation of a ferroelectric sample underneath the tip induced by the ac voltage is detected by the photodiode detector and extracting piezoresponse phase and amplitude signal using a lock-in amplifier (Figure 3.5).

Figure 3.6 Schematic of the piezoresponse force microscope (PFM) system.

The equation between modulation electric field and resulting sample deformation can be simplified as the converse piezoelectric effect. The electric field on the tip is:

$$V_{tip} = V_{dc} + V_{ac} \cos(\omega t)$$

resulting the strain in the sample:

$$\Delta Z = d_{33}V_{dc} + d_{33}V_{ac} \cos(\omega t + \varphi)$$

which is detected as the cantilever displacement. The d_{33} is the piezoresponse coefficient of the sample while the “phase” output φ indicates the ferroelectric domain orientation (Figure 3.6).

Figure 3.7 Schematic drawing of the film deformation under applied electric field: (a) in phase, (b) out of phase; (c) phase different between the out-put signal and reference AC input.

The vertical component of the tip deformation indicates the out-of-plane displacement of the sample, while the lateral components corresponding to the in-plane domain structure, which is called lateral PFM.

3.5 Transmission Electron Microscopy

TEM was used to confirm the epitaxial quality and to acquire detailed structure information of RE-doped BFO thin films.

Figure 3.8 Schematic drawing of TEM.

In this thesis, TEM system is a JEOL JEM2100F, operating at 200 kV. High-resolution images of the interface between film and substrate were obtained on cross-section TEM specimens.

3.6 Ferroelectric measurements

The ferroelectric properties, including the polarization hysteresis loops, remnant polarizations (PUND) were measured on a ferroelectric tester (Precision LC, Radiant Technologies).

Dielectric properties were characterized by a commercial LCR meter (Agilent E4980A). Temperature-dependent measurements were performed on a probe station integrated with a hot chuck.

Pt electrodes were patterned using a standard photolithography method and served as top electrodes for both vertical and quasi-planar capacitors. Detailed information of quasi-planar capacitors is given in Chapter 6.

Chapter 4 Optimization of Pulsed Laser Deposition of Rare-earth-substituted BFO Thin Films

4.1 Introduction

Pulsed laser deposition (PLD) is initially advocated as a cheap and efficient physical deposition method with instantaneous and stoichiometric material transfer.⁹⁶ However, even though the kinetic energy scale of the ablated plasma species in PLD is orders of magnitude higher compared with other physical deposition methods like sputtering or thermal evaporation, the congruent material transfer cannot be guaranteed.^{91, 97} Besides, the physics and film growth dynamics behind PLD is strongly non-equilibrium and much more complicated than commonly thought. Early experimental studies by Dam et al⁹⁸ and Ohnishi et al^{99, 100}, and more recently by Martin's group¹⁰¹⁻¹⁰⁵ on complex oxides have shown that the material transfer in PLD can be highly incongruent and depends sensitively on the laser fluence and the material itself. The conclusion is understandable as the laser fluence affects firstly the melting and vaporization temperature of the target material and subsequently the kinetic energies of the ablated species on the substrate surface. The former process determines the ablation yields of different elements in the target depending on their respective melting points and vapor pressures, while the latter one decides the atom incorporation and re-evaporation rate at the substrate side. Owing to these convoluted factors, the elementary characteristics of the studied materials need to be carefully reviewed first.

Table 4.1 Melting point, boiling point and vapor pressure of related elements in the target materials. Data adapted from 106.

Element	Melting point (°C)	Boiling point (°C)	Temperature required to reach vapor pressure @10 ⁵ Pa (°C)
Bi	271	1450	1562
Fe	1535	3000	2859
La	920	3464	3453
Sm	1072	1900	1788
Yb	824	1196	1192

The related physical properties of the individual elements involved in the study are listed in Table 4.1. For pure BFO, as can be seen, the temperature necessary for Bi to produce a vapor pressure of 10⁵ Pa is much lower than Fe, which correlates with the volatile nature of Bi. As a consequence, when a laser pulse is shined on the BFO target and vaporizes it, more Bi is expected to come out compared to Fe. To verify this assumption, scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS) was employed to examine the surface composition of the target before and after laser ablation. Since the compositional yields may depend on the laser fluence, a series of laser fluences were tested by varying the distance between the focusing lens and the target at fixed laser energy. The laser fluence thus scaled linearly with the defocused distance (Fig. 4.1a). Three laser fluences were chosen, namely 1.75, 1.3 and 0.85 J/cm². As shown in Figure 4.1b, the Bi/Bi+Fe decreased steeply from the pristine 0.5 to ~0.23 for the first 100 pulses, and remained almost steady afterwards. A more straightforward picture can be visualized in the EDS mapping (Fig. 4.2).

Figure 4.1 (a) Linear relationship between the laser fluency and the defocused distance at a constant pulsed laser energy of 40 mJ. The laser fluency slowly decays with time. (b) The evolution of Bi/Bi+Fe ratio of the target surface with increasing ablated pulses at different laser fluencies.

After long-term ablation (300 pulses), the ablated surface exhibited strong Bi deficiency and slight Fe excess than the pristine target surface, irrespective of the laser fluence used. According to the discussion above, this behavior can be attributed to the dramatic difference between the volatility of Bi and Fe elements. Although minor compositional variation can be perceived for different laser fluences, the effect of Bi volatility is so overwhelming that the ablation yield of Bi much higher than Fe. Another implication from Figure 4.1b is that the Bi/Bi+Fe ratio will converge to an almost constant value after sufficient ablation. This can be understood from the balance between the surface Bi/Bi+Fe ratio (decrease) and the ablation yields (Bi higher than Fe). A few conclusions can be drawn from above results: (1) the laser ablation yield of Bi is much higher than Fe; (2) the laser fluence doesn't affect Bi and Fe yields too much and (3) the surface composition and thus the ablation yields will become stable after sufficient pre-ablation. Based on the conclusions, a standard deposition protocol can be set up for the following film growth: (1) a moderate laser fluence of $\sim 1.3 \text{ J}/\text{cm}^2$ is

chosen and (2) the target surface is pre-ablated for sufficient time before actual deposition starts.

Figure 4.2 SEI images and corresponding EDS maps of BFO target surface before and after laser ablation for 300 pulses at 40 mJ with different laser fluencies.

In addition to the parameters of laser input, substrate temperature and background gas pressure are the other two critical factors in PLD as they determine the thermodynamic condition of film growth. BFO is notorious for its narrow growth window in terms of temperature and O_2 pressure. This is caused by the small Gibbs energy difference between BFO and other impurity phases (Bi-rich phase: Bi_2O_3 , $Bi_{25}FeO_{40}$; or Fe-rich phase: $Bi_2Fe_4O_9$ or Fe_2O_3).¹⁰⁷ In other words, BFO is thermodynamically metastable at the growth temperature. Typically, the films grown at high temperature and low O_2 pressure end up with iron-rich impurities or even decomposition of BFO, whereas the opposite condition leads to Bi excess, as depicted in Figure 4.3a.¹⁰⁸⁻¹¹⁰ Besides, insight can be gained from the single-crystal BFO growth using flux method. As shown in Figure 4.3b, a molar ratio of Bi_2O_3 : $Fe_2O_3 \sim 3:1$ is required to obtain pure BFO phase.¹¹¹ This value is surprisingly consistent

with our EDS results of an ablated target surface, suggesting that extra Bi flux is necessary for stabilizing BFO at high temperature. The mapping of growth window of pure BFO was previously studied both in the literature and in our lab.^{108, 112} In the following section, we performed similar practices for rare-earth(RE)-doped BFO films on both STO and LAO substrates (Table 4.2) by varying growth temperature and oxygen pressure.

Figure 4.3 (a) Temperature – O₂ pressure phase diagram of BFO and related impurity phases. Adapted from 110. (b) Bi₂O₃-Fe₂O₃ binary phase diagram. The red dot indicates the central compositional point for producing phase-pure BFO. Adapted from 111.

Table 4.2 Physical properties of STO and LAO single crystal substrates.

Substrate	Structure	Lattice Parameters (Å)	Thermal Expansion Coefficient (10 ⁻⁶ K ⁻¹)
LaAlO ₃	Rhombohedral	3.789	10
SrTiO ₃	Cubic	3.905	10.4

4.2 Optimization of BSFO film growth on STO

Bi_{0.9}Sm_{0.1}FeO₃ thin film was selected as a typical example to demonstrate the optimization process of PLD parameters. Other RE-doped films showed very similar behavior. For the two

variables in deposition parameters, namely temperature and oxygen pressure, we chose a simple methodology to tune them by fixing one while varying the other. Specifically, the temperature was changed within 650-725 °C with oxygen pressure fixed at 50 mTorr, whereas oxygen pressure was varied from 25 to 100 mTorr with constant temperature at 700 °C. The XRD patterns and AFM images of the resulting films were shown in Figure 4.4 and 4.5. In accordance with the trend seen in pure BFO, when the pressure is maintained at 50 mTorr, low temperature resulted in films with Bi-rich impurities, while high temperature caused the disappearance of the BSFO peak and the emergence of Fe-rich phase (Figure 4.4a). On the other hand, the change of oxygen pressure seemed to affect little on the XRD results when the films were deposited at 700 °C.

Figure 4.4 XRD patterns of BSFO thin films grown on STO with constant pressure (a) and constant temperature (b).

Figure 4.5 AFM morphological images of BSFO thin films grown on STO with constant pressure (a)-(d) and constant temperature (e)-(h).

The topography images and RSM of BSFO films deposited at a fixed temperature of 700 °C but with a varying oxygen pressure are shown in Figure 4.5 and Figure 4.6 respectively. The BSFO film deposited with an oxygen pressure of 500 mTorr shows atomic-smooth surface and a smallest roughness.

XRD patterns of all four BSFO films show a pure phase BSFO without any impurity. Based on AFM and XRD data, the oxygen partial pressure for BSFO deposition was fixed at 50 mTorr.

4.3 Optimization of BSFO film growth on STO

$\text{Bi}_{0.9}\text{Sm}_{0.1}\text{FeO}_3$ thin films were deposited on LAO substrates by PLD at different substrate temperatures and oxygen partial pressures. Figures 4.6a-d show the AFM topography images of BSFO films deposited with the substrate temperature ranging from 675°C to 750°C. The film deposited at 700 °C shows smooth and homogeneous surface with clear steps, indicating a “step-flow” growth mode. A decrease in temperature to 675 °C leads to step-bunching growth mode while an increase in temperature to 725 °C results in the appearance of large particles. The film deposited at 750 °C shows a rough surface with the disappearance of unit-cell steps.

Figure 4.6 AFM morphological images of BSFO thin films grown on LAO with constant pressure (a)-(d) and constant temperature (e)-(h).

XRD patterns of BSFO films are shown in Figure 4.7a. Films deposited at 675°C, 700 °C and 725 °C show a highly-strained phase with a large c lattice constant of around 4.62 Å, in contrast with the film grown at 750°C which shows a relaxed bulk-like phase with c lattice around 4.01 Å.

Figure 4.7 XRD patterns of BSFO thin films grown on STO with constant pressure (a) and constant temperature (b).

Combined the results of AFM topography and XRD patterns, 700 °C is chosen as the substrate temperature for BSFO films deposition.

Similar optimization was carried out for the oxygen partial pressure. The topography images and RSM of BSFO films deposited at a fixed temperature of 700 °C but with a varying oxygen pressure are shown in Figure 4.6e-h and Figure 4.7b respectively. The BSFO film deposited with an oxygen pressure of 100 mTorr shows atomic-smooth surface and a smallest roughness. XRD patterns of all four BSFO films show a highly-strained phase without any impurity.

Based on AFM and XRD data, the oxygen partial pressure for BSFO deposition was fixed at 100 mTorr.

4.4 Film composition analysis using EMPA

The high volatility of bismuth may leads to the deviation of stoichiometry between thin films and ceramic targets. To confirm the stoichiometry in the BSFO films, we analyzed the

element composition using EMPA technique. BSFO films with Sm concentration ranging from 0 to 30% grown on STO were coated with a thin layer of conductive carbon for the EPMA test. The results are shown in Table 4.3.

Table 4.3 Composition analysis of BSFO films grown on STO substrates with different Sm concentration using EPMA technique.

Nominal Composition		BiFeO₃	Bi_{0.9}Sm_{0.1}FeO₃	Bi_{0.8}Sm_{0.2}FeO₃	Bi_{0.7}Sm_{0.3}FeO₃
Weight Percent (%)	Bi	68.57	62.52	59.38	52.71
	Sm	0.00	5.33	10.60	14.69
	Fe	18.30	18.75	16.82	18.82
	O	13.12	13.40	13.20	13.79
Atomic Percent (%)	Bi	22.23	19.84	19.04	16.29
	Sm	0.00	2.35	4.63	6.31
	Fe	22.21	22.26	20.42	21.76
	O	55.56	55.55	55.92	55.65
Sm Concentration (%)		0.00	10.59	19.56	27.93

The results show a good agreement in the stoichiometry between the ceramic targets and the BSFO films.

4.5 Conclusions

In this chapter, we systematically optimized the growth conditions of BSFO films on STO and LAO substrates. The substrate temperature and oxygen partial pressure used for film deposition is 700 °C and 100 mTorr respectively.

EPMA composition analysis confirms that the stoichiometry of BSFO films on STO is in good accordance with the ceramic targets.

Chapter 5 Chemically-Driven MPB in R-like BFO

5.1 Introduction

Ever since the rediscovery of huge ferroelectric polarization in BFO, considerable efforts have been devoted into the search for MPBs in BFO with enhanced piezoelectric performance. To date, the RE-doped BFO has been the most studied system with potentially promising properties. It has been widely reported that chemical pressure plays a crucial role in the FE – PE phase transition. However, La-doped BFO ceramics with very weak chemical pressure were also reported to exhibit similar phase evolution behavior. In order to resolve these disputes and shed some light into the phase transitions in RE-doped BFO system, single-domain $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ (BLFO) epitaxial thin films were fabricated and their ferroelectric properties were systematically investigated. The advantage of single-domain samples is that extrinsic contributions originating from ferroelastic domain wall motions can be excluded in electrical measurements.¹¹³⁻¹¹⁸ Thus, intrinsic effect of La doping on the ferroelectricity can be assessed.

5.2 Single-domain BLFO thin films grown on miscut STO

To achieve single-domain BLFO thin films, degeneracy between energetically-equivalent ferroelastic domain variants must be lifted through the symmetry breaking of the substrate template in epitaxial film growth. Practically, commonly-used methods include vicinal (miscut) substrates^{116, 119} or anisotropic (low-symmetry) substrates, such as orthorhombic REScO_3 .¹²⁰⁻¹²² In this study, (001)-oriented STO with 4°-miscut along [110] direction was employed according to those reported in literature.^{123, 124} Due to the rhombohedral symmetry of the BFO unit-cell, there are totally four ferroelastic (in-plane) domain variants if grown on

exact (001)-oriented STO as shown in Figure 5.1a. However, if the (001)-oriented STO is miscut along $[100]$ direction, only two domain variants are energetically favorable, because the miscut step edges impose additional strain that couples to the in-plane biaxial strain, resulting in a “shear” effect, which eventually stabilizes BFO domain variants with consistent lattice distortions (Figure 5.1d).

Figure 5.1 Schematics showing domain-variant selections of BFO epitaxial thin films grown on (a) exact STO, (b) STO with miscut along $[100]$ and (c) STO with miscut along $[110]$. (d) Shear strain induced by miscut steps in addition to biaxial strain. Adapted from 126.

Likewise, a miscut along $[110]$ direction will favor a single-domain state, as the in-plane distortion of the BFO lattice is along $[110]$, as depicted in Figure 1c. In terms of the two possible ferroelectric variants (out-of-plane), only upward polarization direction is preferred as a result of the interfacial uncompensated charges between STO/LSMO and BFO.¹²⁵

Figure 5.2 Domain growth control through substrate vicinality: miscut towards $[100]$ or $[110]$ directions eventually leads to (110)- or (111)-oriented STO with two or one domain variant, respectively.

Typical ferroelectric domain evolutions with increasing miscut angles are schematically shown in Figure 5.2. It should be noted that (110)- or (111)-oriented STO can be deemed as two extreme cases of the (001)-oriented STO miscut along $[100]$ by 45° or along $[110]$ by 60° , respectively. From the trend, we can conclude that when the miscut angles exceed

certain thresholds along these two directions, 2-variant or single-domain BFO thin film can be achieved.

5.3 Morphological and structural characterizations of BLFO films

Figure 5.3 Film morphologies of BFO films with different La doping concentrations. The scale bars represent 1 μm . The arrows indicate the miscut downhill direction.

The film morphologies of the BLFO thin films are presented in Figure 5.3. All films exhibit distinct zig-zag ledges that were consistent with the miscut directions denoted by the arrows. However, the step-bunching of the pure BFO appeared much stronger compared to the La-doped ones, leading to exceptionally large surface roughness. We conjectured it could be caused by the large surface energy of polar BFO since the deposition temperature ($\sim 700^\circ\text{C}$) was way below its ferroelectric Curie temperature ($\sim 830^\circ\text{C}$). La doping, on the one hand, reduced the Curie temperature, rendering BLFO a non-polar state during film growth. On the

other hand, the chemical inhomogeneity caused by La doping would decrease the atom mobility on the surface, suppressing the step-bunching growth.

Figure 5.4 (a) XRD patterns of BLFO films grown on miscut STO substrates. (b) Variations of out-of-plane lattice constant with respect to La doping.

Basic structural characterization was performed by symmetric theta-2theta XRD scans (Figure 5.4a). Except for some minor Bi-rich impurity phase in pure BFO film, all BLFO films were phase-pure, exhibiting only (00L) peaks from both the films and substrates. Noticing that vicinal substrate might induce significant crystallographic tilt, all the XRD scans were intentionally carried out along the orthogonal axis with regard to the miscut direction.^{127, 128} However, the calculated c lattice parameter of the BLFO films showed an unexpected behavior upon La doping: it first increased, peaked at 20 % La concentration, and started to drop at higher doping ratio. The deviation from a monotonic relationship can be understood if structural relaxation was taken into account. The film thickness in this study is around 130 nm, at which BLFO films should be partially relaxed, not to mention the substrate miscut should accelerate the relaxation process. The degree of relaxation is closely

related to the film morphology. Specifically, large roughness, namely, more pronounced 3D growth would facilitate the strain relaxation due to weakened substrate constraint. On the contrary, smooth surface with 2D growth help to retain the substrate biaxial strain. Therefore, the observed *c* lattice evolution was a consequence of cooperative effect from both the structural relaxation and La doping. Since the roughness of the BLFO films decreased with more La being added, the lattice became more strained accordingly, leading to the increased out-of-plane lattice constant. However, the drop beyond 20 % La doping could be due to intrinsic lattice shrinkage. Fortunately, the ferroelectric polarization of BFO is weakly coupled to the epitaxial strain.^{45, 129, 130} Hence, despite the different strain state of the BLFO films, it won't affect the subsequent electrical measurements.

5.4 Ferroelectric and dielectric properties of single-domain BLFO films

Next, we move on to the central question in this study: how does La-doping affect the ferroelectric order of BFO film? In order to measure the electrical properties, $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ was first coated on STO as bottom electrode. After the deposition of BLFO films, $20 \times 20 \mu\text{m}^2$ Pt was fabricated by photolithography as the top contact. The samples were thus tested under vertical sandwiched configuration. Typical polarization – electric field (*P* – *E*) hysteresis loops were acquired for all BLFO films, as summarized in Figure 5.5. At a glance, it could be seen that BLFO films remained robust ferroelectric phase with La content up to 20 %. At 30 % La level, a clear double-hysteresis loop appeared. Finally, for 40 % La-doped sample, strongly canted and slim loop was observed. At this point, we could say that BFO lost its ferroelectric stability at around 30% La doping.

Figure 5.5 (a)-(e) Polarization – Electric Field (P – E) hysteresis loops of BLFO single-domain films with different La concentrations. (f) A compilation of all P – E curves.

Positive-up-negative-down (PUND) pulse measurement was applied to determine the magnitude of polarization more accurately, and the results were plotted in Figure 5.6. The remanent polarization was barely affected by La doping up to 20 %, but suddenly dropped to zero from 30 % La content onwards. This behavior signified a global polar instability triggered by La substitution. The coercive field (E_c), in contrast, exhibited an opposite trend. Increasing La dopants resulted in enhanced E_c , implying that it became more and more difficult to switch the polarization in BLFO films.

Figure 5.6 (a) Field-dependent remanent polarization (Pr) of different La-doped BFO films measured using PUND method. (b) Evolutions of remanent polarization and coercive field with regard to the La doping amount.

Dielectric characteristics of different BLFO films were also measured and compiled in Figure 5.7. From the frequency-dependent curves, a monotonic increase of relative permittivity can be observed with higher La content. However, a sharp jump from 20% to 30 % La-doped films suggested a phase transition (Figure 5.7d), in agreement with the results of P – E measurements. The field-sweeping dielectric constants showed hysteresis loops consistent with the differential of the corresponding P – E curves (Figure 5.7c). The double peaks in 30% La-doped film correlated with the polarization double hysteresis loop. Moreover, the tunability of 30% and 40% La-doped films were very large, with high-field value close to the films with less La dopants. Correlating with this behavior was the distinct up-turn of the dielectric loss in heavily-doped films when entering MHz range (Figure 5.7b), which implied that dipole reorientation could be main origin of the huge dielectric susceptibility at low field.

Figure 5.7 Frequency-dependent (a) relative permittivity and (b) loss tangent of different La-doped BFO films. (c) Field-sweeping hysteresis loops of relative permittivity of different La-doped BFO films. (d) Evolution of relative permittivity with La doping concentration.

To determine possible high-temperature phase transitions and construct the temperature – composition phase diagram, temperature-dependent electric properties were measured from room temperature to ~ 200 °C, above which the samples became too leaky to be tested.

Figure 5.8 Temperature-dependent P – E loops of (a) pure BFO, (b) 20%-La-doped BFO and (c) 30%-La-doped BFO films. (d) Extrapolation of the coercive field to high temperature for different films.

Apart from the leakage contribution in the P – E loops, ferroelectric polarization of pure BFO, 20 % and 30% La-doped BFO barely changed up to 200 °C, probably because it is still far away from the transition temperatures. On the other hand, the coercive fields of all three samples showed systematic decrease upon heating, indicating the switching barriers were gradually lowered due to thermal excitation. Therefore, it is possible for us to determine the possible phase transition temperature by extrapolating the coercive field to zero, where the energy barrier for polarization switching diminished. The extrapolation for pure BFO yielded a transition temperature around 850 °C, generally in good agreement with the reported Curie

temperature of 830 °C, and it justified the feasibility of this method. The deduced Curie temperature of 20% La-doped film was around 430 °C, much lower than the undoped one. As for 30% La-doped film, the obtained characteristic temperature (~470 °C) should correspond to the transition towards a complete paraelectric phase without metastable states in the energy profile. In addition, temperature-dependent dielectric constants of different films were also measured. However, as the phase transitions were probably first-order, the extrapolation using the Curie – Weiss law should overestimate the transition temperatures.¹³¹

5.5 Domain structure and piezoelectric responses of single-domain BLFO films

Above findings were all macroscopic measurements, which reflected an average characteristic of the whole film. To gain deeper insight into the evolution of the ferroelectric order due to La doping, microscopic domain structures needed to be investigated, which was performed using piezoelectric force microscopy (PFM) on a commercial AFM. The morphological and corresponding out-of-plane PFM (OP-PFM) images of BLFO films were shown in Figure 5.9. As mentioned, the out-of-plane polarization direction of BFO was determined by the charge discontinuity at the bottom interface. Both STO and LSMO were B-site terminated, giving rise to $\text{TiO}_2^0\text{-BiO}^{+1}$ and $\text{MnO}_2^{-0.7}\text{-BiO}^{+1}$ configuration with positive valence mismatch. Therefore, upward polarization was stabilized. Since La^{3+} substituting Bi^{3+} was isovalent, the upward polarization state was preserved in 10 % and 20 % La-doped films. The latter, however, displayed inhomogeneous piezoelectric response. Both 30 % and 40 % samples showed almost no detectable signal in the PFM images, comparable to that of a bare STO substrate, and consistent with the zero remanent polarization as found in the P – E loops.

Figure 5.9 Upper panel: The morphological images of La-doped BFO films. Lower Panel: The corresponding OP-PFM images. The scale bars are 1 μm in all images. The OP-PFM image of a bare STO substrate is shown in the inset of 40% La-doped BFO film for comparison. White arrows indicate miscut directions.

The obvious inconsistency between PFM images and previous $P - E$ results was discerned in 20 % La-doped film. The PFM signal of 20 % La-doped sample was not homogeneous as those found in 0 % and 10 % ones. However, all their $P - E$ loops showed similar remanent polarization values. To resolve this discrepancy, local polarization switching was performed by applying a DC bias to the AFM probe while doing scans. Box-in-box patterns were created for all three samples as shown Figure 5.10. The polarization in the outer box was first switched downward, and then switched back to the original upward state. The amplitudes of the piezoresponse were almost the same for upward and downward polarization directions, whereas their phase difference was 180° (not shown). Particularly, it can be seen that 20 % La-doped film can be fully switched into a uniformly-polarized state, just as the 0 % and 10 % ones.

Figure 5.10 Upper panel: The morphological images of La-doped BFO films, with arrows indicate the miscut directions. Middle panel: corresponding OP-PFM images of 0%, 10% and 20% La-doped BFO films with box-in-box switching patterns. Lower panel: Corresponding IP-PFM images with arrows indicating IP polarization vectors.

This finding verified the similar remanent polarization values in the $P - E$ tests. The pristine inhomogeneous PFM signal could probably imply a coexistence of metastable phases. In terms of in-plane PFM (IP-PFM) images, as-grown BFO exhibited a uniform color tone (area outside the box), consistent with a single-domain state. After switching, the contrast reversed,

suggesting the 180° switching of the polarization vector in both in-plane and out-of-plane axes. The film with 10 % La contained minor other domain variants (some brown-color area). The contrast of the switched boxes was greatly weakened compared to pure BFO film, from which we could infer a reduction of the in-plane polarization component. Finally, at 20 % La content, though there was still a trace of piezoelectric signal, the box-in-box pattern almost vanished, pointing to the loss of in-plane polarization.

Figure 5.11 (a) Effective d_{33} of La-doped BFO films measured by PFM-based technique. (b) Evolution of effective d_{33} with different La doping.

Last but not least, piezoelectric responses of BLFO films were measured using PFM-based technique. Calibration was done using X-cut quartz, and the results were also verified by a laser-scanning vibrometer.¹³² As shown in Figure 5.11, the shapes of the butterfly d_{33} loops basically followed those of the $P - E$ loops. For La composition from 0 to 20 %, the hysteresis loops were square with the remanent d_{33} values around 20 to 25 pm/V, in agreement with the value reported for single-domain BFO film.¹¹⁶ At 30 % La concentration, the d_{33} loop coincided with double-hysteresis-loop behavior with almost no remanent

piezoresponse. These findings were in complete accordance with the OP-PFM images of the films.

5.6 Discussion

Aiming to understand the evolutions of the properties upon La doping, the interplay between the atomic structure and the ferroelectric order of parent BFO phase must be clarified first. It is widely accepted that the ferroelectricity of BFO originates from the stereochemically active $6s^2$ lone pair of Bi^{3+} .¹³³⁻¹³⁵ Due to the hybridization mainly between Bi 6s and O 2p orbitals, the charge density of the $6s^2$ lone pair adopts an asymmetric lobe-shape, which, in turn, leads to the large relative displacement of Bi and O ions along the body diagonal ($[111]_{\text{pc}}$) of the pseudocubic perovskite unit cell. Structure-wise, the relatively small Goldschmidt tolerance factor¹³⁶ (~ 0.88) of BFO results in strong buckling of the O-Fe-O bonds, thus rotations of oxygen octahedra. The pattern of the octahedral tilt is $\bar{c}\bar{c}\bar{c}$ under Glazer's notation,¹³⁷ in accordance with the $R3c$ symmetry. In particular, the two neighboring oxygen octahedra along $[111]_{\text{pc}}$ axis are rotating along the same axis out of phase by ~ 11 - 14° .¹³⁸⁻¹⁴⁰

What happens if the Bi atoms are gradually replaced by La? Because the ionic radius (under eightfold coordination) of La^{3+} is $1.16 \text{ \AA}$, almost the same as $1.17 \text{ \AA}$ of Bi^{3+} , very weak chemical pressure is induced.¹⁴¹ However, the lack of electron lone pair in La^{3+} would probably tend to switch off the large polarization in BFO. With increasing La concentration, instability of the ferroelectric order should be expected. Besides, LaFeO_3 belongs to the orthoferrites with orthorhombic $Pbnm$ symmetry and an O_6 rotation pattern of $a^-a^+b^+$.¹⁴² As a result, La substitution will also cause structural instability of BFO lattice.

Based on these facts, we now try to understand the property evolution of La-doped BFO films. First, we do observe the destabilization of the polar order when La dopant concentration is above 20 % according to the P – E measurements. The double-hysteresis behavior at 30 % La doping can be interpreted as either an antiferroelectric state or an electric-field-induced PE – FE transition. The exact ground state around this composition range remains controversial. While several studies on bulk ceramics of BLFO solid solution suggested the emergence of PbZrO₃-like antipolar phase at around 20 % La doping concentration,⁸⁵⁻⁸⁸ the work on epitaxial thin films asserted a non-polar ground state, and the double-hysteresis loop was the manifestation of non-polar – polar transition triggered by external field.⁸³ However, more direct evidence from TEM with atomic-scale resolution confirmed the existence of anti-polar phase when entering MPB region.¹⁴³ Accordingly, a transition sequence from polar – antipolar – nonpolar can be envisioned in the phase diagram. The experimentally determined transition point lies around 30 % La doping, which is consistent with the first-principle calculations.^{77, 89} From the inhomogeneous response of the OP-PFM of 20 % La-doped sample, we can infer that the coexistence of polar and antipolar phase starts to appear. However, the antipolar phase is metastable, as it can be fully transformed into polar phase under electrical poling, which is further verified by the conservation of the remanent polarization in the P – E measurements. On the other hand, the IP-PFM signal gradually vanishes with increasing La dopants, suggesting a continuous rotation of the polarization vector towards [001]_{pc} direction. Similar behavior has been reported for Sm-doped BFO films, which points to a universal behavior of BFO upon RE-element doping.⁶⁸ The enhancement of coercive field for La doping up to 20 % supports this assumption. As it is reported, the direct 180° polarization switching in single-domain BFO can be circumvented by an intermediate 71° switching with greatly reduced energy barrier.¹²³

However, with the polarization vector pointing more towards out-of-plane direction, the switching angle would be closer to 180° , thus increasing the potential barrier and consequently the coercive field. The polarization rotation induced by chemical substitution echoes those observed due to biaxial strain.^{45, 46} Accompanying the polar rotation is the structural instability associated with the oxygen octahedral tilt. As the rhombohedral octahedral tilt is destabilized by the strain, the polar stability is accordingly weakened, since they are intimately coupled. This results in the decrease of Curie temperature with increasing strain. Likewise, the La-doping also leads to the polar rotation and competes with the ground state of rhombohedral-like octahedral tilt. Hence, similar reduction of Curie temperature has been derived with increasing La doping, which is also supported by recent study on ceramic BLFO.¹⁴⁴ Built on the above findings, a simple temperature – composition phase diagram is proposed as shown in Figure 5.12a. La doping from 0 to 20 % doesn't change ground state of the rhombohedral-like polar phase, but it causes the polarization to rotate towards $[001]_{pc}$ direction. At around 20 % La concentration, antipolar phase starts to emerge, which, however, remains metastable and can be converted into polar phase by external field. With La doping up to 30 %, the antipolar phase becomes more energetically favorable, but around this composition range competing phases may coexist, due to proximity of the energy landscape. Beyond 40 % La, paraelectric nonpolar phase becomes the ground state with still trace of the polar or antipolar residues. The phase transition behavior reminds us that of BFO under hydrostatic pressure (Figure 5.12b), where a large amount of competing phase variants have been found between rhombohedral and orthorhombic ground states.

Figure 5.12 (a) Proposed temperature – composition phase diagram of La-doped R-like BFO films. (b) Reported temperature – pressure phase diagram of BFO for comparison. Adapted from 145.

Lastly, we will discuss the La-doping effect on the piezoelectric response, and the influence of the so-called “chemical pressure” induced by RE-elements with smaller ionic radii. For La-doped BFO, we neither observed an enhancement of the effective d_{33} around the phase boundary, nor a strong decrease as reported in literature.⁸² The piezoelectric coefficient d_{33} can be expressed as follows:^{146, 147}

$$d_{33} = 2\varepsilon_0\varepsilon_{\text{int}}Q_{33}P(E)$$

where ε_0 is the permittivity of free space, ε_{int} is the intrinsic relative permittivity, Q_{33} is the electrostrictive coefficient and $P(E)$ is the polarization under the electric field. According to the equation, the d_{33} should be linearly proportional to ε_{int} and $P(E)$. Since the polarization of BLFO remains almost constant from pure BFO towards the phase-transition region and the ε_{int} is only slightly increased, we didn't see a prominent rise in the piezoelectric response. However, when the system enters the antipolar region, due to the loss of the remanent polarization, the remanent d_{33} reduces to almost zero. However, at high field, the d_{33} value is comparable to polar BLFO films, as the polarization is restored by the field.

Next, we compare the properties of 20 % La-doped and 10 % Sm-doped films, both of which are in close proximity to the phase transition boundary. As shown in Figure 5.13, though the remanent polarization of Sm-doped sample slightly decreases compared with the pure or La-doped BFO, its d_{33} shows some enhancement under large field. This probably originates from its giant dielectric constant compared to the La-doped one. It should be noted that this great enhancement in dielectric constant is distinctively different with those observed in 30 % and 40 % La-doped films, which exhibit large tunability at high field. Therefore, it is an intrinsic characteristic of the Sm-doped BFO film, arising probably from the softening of the lattice instead of the contribution from dipole reorientations. However, the improvement of the d_{33} is not so prominent as those reported in the literature.^{81, 83} We suspect extrinsic effects like multidomain structures may account for the large enhancement. More detailed study is required to fully clarify the discrepancy.

In the end, we would like to address the effect of “chemical pressure” on the phase transitions in RE-doped BFO. Our results unambiguously suggest the polar – antipolar transition also occurs in La-doped BFO films, similar to those doped with small RE-elements. This finding indicates that chemical pressure is probably not a prerequisite to induce the global polar instability. Instead, the substitution of Bi ion is at the core of all the property evolutions. Nonetheless, we cannot deny the role of chemical pressure in boosting the polar instability of BFO via lattice shrinking just as that induced by hydrostatic pressure. Therefore, a much narrower region of competing phases is expected in the phase diagram compared to the La one. Besides, the doping of Sm does show to soften the lattice and improve the electromechanical response to some degree. Such enhancement can be attributed to the “polarization extension” in comparison to the “polarization rotation” in FE – FE type MPB. However, the magnitude of the enhancement seems much weaker.

Figure 5.13 Comparisons of (a) Dielectric hysteresis loops, (b) polarization hysteresis loops, (c) PUND remanent polarization curves and (d) piezoelectric hysteresis loops of pure BFO, 20% La-doped BFO and 10% Sm-doped BFO films.

5.7 Conclusions

In this chapter, the effect of La-doping on the property evolutions of BLFO single-domain films were systematically investigated and analyzed. To summarize, La substitution induces polar instability just as those reported for small RE-elements, suggesting a universal behavior of RE doping. The absence of chemical pressure in La case probably leads to a broad region of phase coexistence among polar, antipolar and nonpolar phases. Besides, La doping also causes polarization rotation associated with the competing instability of oxygen octahedral

tilt as well as a reduction of the transition temperature. Lastly, the longitude piezoelectric response depends insensitively on the La doping, probably because La-doping fails to soften the lattice as implied from the relative permittivity results. In contrast, Sm-doped films exhibit some degree of enhancement of the piezoelectric coefficient, highlighting the role of chemical pressure in softening the lattice.

Chapter 6 Chemical-Alloying Effect in Strain-Driven MPB in BFO

6.1 Introduction

Ferroelectric/piezoelectric materials have been widely used in commercialized devices, including sensors, actuators, MEMS, etc. Currently the most commonly used materials are still toxic Pb-based oxide solutions, such as $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT) with composition near its morphotropical phase boundary (MPB). Among possible candidates for lead-free piezoelectric materials, BiFeO_3 (BFO) stands out due to its large polarization at room temperature. BFO also has disadvantages such as a low piezoelectric coefficient as compared with PZT. Recent study has reported a lead-free MPB in Sm substituted BFO with enhanced dielectric and piezoelectric properties. Our study in the previous chapter also revealed that polarization instability and polarization rotation is a universal behavior in rare earth (Re) substituted BFO while the enhancement in piezoelectric property is only observed in Sm, which has a smaller atomic radius than Bi.

Besides chemical substitution, another route to create MPB is the introduction of epitaxial strain resulting from the lattice mismatch between oxide film and single crystal substrates. A lead-free MPB was also observed in BFO thin film grown on LAO or LSAO substrates which results in a lattice mismatch exceeding 4%. A T-like Mc phase with a large c/a ratio was stabilized by the large compressive strain as LAO or LSAO has a much smaller lattice constant than BFO. With the gradual increase of film thickness, MPB was formed with the emerging of tetragonal-rhombohedral (T-R) phase coexistence and two new monoclinic

phases with lower symmetry, to relieve the epitaxial strain. Giant large electromechanical response has been reported for the mixed-phase film, arising from the phase transitions among these co-existing phases under the stimuli of external electric field.

So far, the combination of both chemical substitution and epitaxial strain in one material system and their effect in the structure and properties of MPBs has been an open question.

In this chapter, epitaxial BReFO films with different doping elements were deposited on LAO substrates. Firstly, the effect of Re substitution in the morphology, crystal structure, and ferroelectric properties of fully strained Mc BFO films with a small thickness is systematically studied. Then, with the increase of film thickness, the effect of Re substitution in strain-induced MPB in BFO is investigated.

6.2 Morphology and Structure Analysis

6.2.1 Rare Earth Substitution in Highly Strained Mc Phase BFO

BFO films with Rare earth element substitution (La, Sm and Yb) with different doping concentrations were deposited on to LAO substrates using PLD method described in Chapter 4. Film thickness is controlled by the deposition duration.

Topography images of around 20 nm-thick BLFO films with various La doping concentrations are shown in Figure 6.1 (a-d). All films show homogenous and atomic smooth surface with clear terrace structure, indicating a high quality epitaxial growth mode. XRD curves for all BLFO films are shown in Figure 6.1(e). Besides the (00 l) peaks of LAO substrates, only (002)_{pc} peaks from BSFO films were present, indicating that films are of epitaxial growth without any impurity and second phases. The c lattice parameters are calculated, as shown in Figure 6.1(f). With the doping of La, the c lattice of BLFO keeps decreasing: 4.649 Å for pure BFO, 4.640 Å for BL10FO and 4.628 Å for BL15FO film. The

reason is that La^{3+} has a relatively smaller cation radius of 1.27 Å as compared with 1.28 Å of Bi^{3+} . The large c lattice of BLFO with La doping level up to 15% indicates all these films are of T-like Mc phase.

Figure 6.1 Surface morphology of 20 nm-thick BLFO thin films doped with (a) no La, (b) 5% La, (c) 10% La and (d) 15% La. Scale bars represents 1 μm. (e) XRD curves around (002) peak of 20 nm-thick BLFO films on LAO with La concentration ranging from 0 to 15%; (f) calculated c lattice parameters of BLFO films.

Meanwhile, surface morphology of 20 nm-thick BSFO films is shown in Figure 6.2. All BSFO thin films have homogeneous and smooth surface, as similar to that of pure BFO and BLFO films. XRD patterns around (002)pc of these films and corresponding c lattice parameters are shown in Figure 6.3 (a) and (b) respectively.

Figure 6.2 AFM topography images of 20 nm-thick BSFO films on LAO substrates with Sm substitution concentration ranging from 0 to 30%. The scan size is 3 μm .

Figure 6.3 XRD curves around (002) peak of 20 nm-thick BSFO films on LAO with Sm concentration ranging from 0 to 30%; (b) c lattice parameters of BSFO films.

Pure BFO film has the largest c lattice of 4.648 Å. The c lattice also decreases continuously with the increase of Sm substitution level to 4.642 Å for BS10FO and finally reaches 4.627 Å for BS30FO. The decrease of c lattice of highly-strained BSFO films is mainly due to Sm^{3+}

has a smaller ionic radius than Bi^{3+} . The ionic radius for Sm^{3+} and Bi^{3+} with eight coordinations is 1.28 Å and 1.36 Å respectively.¹⁴⁸

As a result of the large compressive strain up to -4% induced by the lattice mismatch between BSFO film and LAO substrate, only T-like phase with c lattice larger than 4.62 Å is present. This indicates that the phase transition from a rhombohedral phase to a orthorhombic phase in bulk-like BSFO films disappeared. The Sm substitution induced MPB located at $\text{Bi}_{0.86}\text{Sm}_{0.14}\text{FeO}_3$ in bulk BSFO is also absent with the introduction of the large compressive strain.⁶²

However, even though Sm has a smaller atomic radius than La, the c lattice constants of BSFO film is larger than that of BLFO film with the same doping concentration. For films with 10% substitution, c lattice parameter for BL10FO and BS10FO is 4.640 Å and 4.642 Å, respectively. Two possible reasons for this discrepancy are discussed below:

- 1) The actual composition of BSFO may be deviated from ceramic targets. As shown in Table 4.1, the boiling point for Sm (1900 °C) is significantly lower than that of La (3464 °C). Thus it is possible that actual doping concentration in BSFO films is smaller than BLFO with the same nominal doping level.
- 2) With the decrease of cation radius of doping elements, it is possible that some Sm^{3+} will substitute B site Fe^{3+} instead of A site Bi^{3+} . As the cation radius of Sm^{3+} is smaller than that of Bi^{3+} but larger than that of Fe^{3+} , the doping of Sm^{3+} in to B site will compensate the decrease of lattice constant due to A site substitution, and thus results in a smaller decrease in lattice constant.

Detailed structure characterization was carried out with by high resolution synchrotron X-ray Diffraction Reciprocal Space Mappings (RSMs) and Transmission electron microscopy

(TEM) on a 30-nm thick pure BFO and a 32-nm thick $\text{Bi}_{0.9}\text{Sm}_{0.1}\text{FeO}_3$ (BSFO) film was grown on LAO substrates. Both BFO and BSFO films show a homogeneous surface with a roughness of 0.37 nm without any topographical stripes, indicating that both films consist of pure T-like phase.

Figure 6.4 HR-XRD RSMs near (002) (a) and (103) (b) of 30 nm-thick pure BFO film; near (002) (c) and (103) (d) of the 32 nm-thick $\text{Bi}_{0.9}\text{Sm}_{0.1}\text{FeO}_3$ film.

This is further confirmed by high resolution synchrotron RSMs. The RSM around (002) shows of both BFO and BSFO films only diffraction spots from the LAO substrate and the T-like phase (Figure 6.4a and c). Peak splitting is observed for the T-like phase in (103) RSM.

Besides the central peak, two satellite peaks appear with one peak is shifted upwards while another is shifted downwards (Figure 6.4b and d). This peak splitting confirms that this T-like phase is of monoclinic Mc symmetry.

The structural parameters of BSFO are determined to be: $a_m=3.782\pm0.004$ Å and $b_m=3.764\pm0.004$ Å for the in-plane lattice parameters, $c_m=4.653\pm0.005$ Å for the out-of-plane lattice parameter, and the monoclinic angle β is equal to $89.4\pm0.1^\circ$.¹⁴⁹ In comparison, the Mc phase of pure BFO grown on LAO, the corresponding parameters are $a_m=3.811$ Å, $b_m=3.734$ Å, $c_m=4.670$ Å, and $\beta=88.2^\circ$.⁵⁴ In other words, the average in-plane lattice parameter is basically identical between BFO and BSFO grown on LAO, but the Sm substitution leads to a decrease in the anisotropy of the in-plane lattice parameters. Similarly, the monoclinic distortion is much smaller in BSFO than in BFO, as evidenced by the increase of the monoclinic angle towards 90° after the Sm substitution.

TEM was also used to analyze the epitaxial quality and structure of the BSFO film, in collaboration with Dr. Qi Yajun. As shown in Figure 6.5a, the cross-sectional TEM image shows a clear interface between the BSFO film and the LAO substrate, indicating that the film has good epitaxial quality. The High-Resolution TEM (HRTEM) image further confirms the epitaxial quality. As shown in Figure 6.5b.

The selected area electron diffraction (SAED) patterns taken along the $[010]$ zone axis focused at the BSFO and LAO interface as well as at BSFO film only is shown in Figure 6.6a and Figure 6.6b respectively. Both SAED patterns are indexed according to the pseudo-cubic unit cell. Only spots corresponding to $[001]$ and $[100]$ variants were observed in the SAED pattern of BSFO film. The SAED for the interface is basically the superimposition of $[010]$

BFO and [010] LAO with the orientation relationship determined as (001) BSFO // (001) LAO and [010] BSFO // [010] LAO.

Figure 6.5 (a) TEM cross section image of the BSFO/LAO interface. (b) HRTEM image showing the sharp interface between BSFO and LAO. (c) a phase boundary between R-like and T-like BSFO phases.

The lattice parameters of the T-like phase calculated from the SAED pattern is 3.79 Å and 4.58 Å for in-plane and out-of-plane respectively. The lattice parameters calculated from TEM is different from those from RSMs, which is a result of strain relaxation due to the change of mechanical boundary conditions.¹⁵⁰

Figure 6.6 SAED patterns of BSFO and LAO (a), and BSFO film only (b).

6.2.2 Rare Earth Substitution in Strain-induced MPB in BFO

For thin film BFO grown on LAO/LSAO, pure Mc BFO was stabilized by the large epitaxial strain. However, with the increase of film thickness, strain energy in film also increases. To relieve the epitaxial strain, MPB was formed with the emerging of tetragonal-rhombohedral (T-R) phase coexistence and two new monoclinic phases with lower symmetry. To explore the chemical substitution effect on this strain-induced MPB in BFO, a series of epitaxial ReBFO thin films with different thicknesses were deposited on LAO substrates. The morphology and crystal structure of ReBFO with MPB were characterized.

Figure 6.7 Evolution of surface morphology of pure BFO and BL5FO films with the increase of film thickness: (a, d) 20 nm, (b, e) 40 nm and (c, f) 60 nm. Scale bars represent 1 μm .

The evolution of film morphology of pure BFO and BL5FO films with the increase of film thickness is shown in Figure 6.7. For both BFO and BL5FO, 20 nm-thick films with pure Mc phase show homogeneous surface with clear terrace. With the increase of film thickness to a “critical thickness”, topographic stripes start to appear. The smooth area with terrace corresponds to pure Mc phase area, while the stripes are signatures of mixed-phase area where multiple phases with lower symmetry coexist. For both films, the fraction of striped area on surface increases with the further increase of film thickness. However, for films with the same thickness, BL5FO film has more stripes than pure BFO.

To further verify this phenomenon, BLFO films with different La concentration but same thickness are deposited and characterized, as shown in Figure 6. 8. For BL15FO film with 15%

La doping, as shown in Figure 6.8d, a rough surface showing epitaxial breakdown is observed. This suggests that the epitaxial strain in BL15FO is so large that it can't be fully released by the formation of mixed-phase. Instead, bulk-like rhombohedral phase is formed.

Figure 6.8 Surface topographies of 40 nm-thick BLFO thin films doped with (a) no La, (b) 5% La, (c) 10% La and (d) 15% La. Scale bars represent 1 μm .

For a quantitative analysis, the fraction of mixed-phase area is extracted from topographic images for BLFO with different La concentration at different thickness, as shown in Figure 6.9 (a). The critical thickness at which mixed-phase stripes appears and the thickness at which BLFO film shows epitaxial breakdown are calculated and plotted against La doping level, as shown in Figure 6.9 (b and c). It is clear that the introduction of La effectively decrease the critical thickness at which stripes appear in Mc phase BFO film. For films with same thickness, the fraction of striped area increases with more La doping. Meanwhile, the critical thickness at which stripes appear in film surface decreases with more La doping.

Figure 6.9 Evolutions of mixed-phase fraction of BLFO films with different thickness; (b) critical thickness of mixed-phase formation and (c) threshold thickness of epitaxial breakdown for BLFO with different La concentration.

XRD curves around (002)_{pc} peaks and calculated *c* lattice parameters of BL5FO films with various thickness are shown in Figure 6.10. Only (002) peaks from BLFO film and LAO substrates are observed, without any other peaks from impurity phases. With the increase of film thickness, a shift of (002) peak of BLFO films towards lower diffraction angles, indicating *c* lattice constant of BLFO films keeps increasing. This phenomenon is consistent with previously reported experimental data of pure BFO films. According to first principles calculation, *Mc* BFO has an in-plane lattice parameter of 3.67 Å, which is smaller than the lattice constant of LAO (3.79 Å). Thus *Mc* BFO is under tensile strain when it is epitaxially grown on LAO, resulting in a smaller *c* lattice constant. With the increase of film thickness, the film will relax gradually which leads to a recovery of *c* lattice.

Figure 6.10 XRD curves around (002) peak of 20 nm-thick BLFO films on LAO with 5% La doping; (b) calculated c lattice parameters of BLFO films with different La doping concentration and film thickness.

Figure 6.11 Evolution of surface morphology with the increase of film thickness of BSFO films with 10% Sm doping: (a) 20 nm, (b) 30 nm, (c) 40 nm and (d) 60 nm. Scale bars represent 1 μm.

The evolution of surface morphology and structure of Sm substituted BFO is similar to BLFO. Figure 6.11 shows the topographic evolution of BSFO films with the increase of film thickness. For BSFO films thinner than 30nm, atomically smooth surface with clear terrace structure are observed. Stripes are observed in BSFO films with thickness ranging from 40

nm to 70 nm. However, with a further increase in the thickness to above 80 nm, BSFO films show epitaxial breakdown.

Figure 6.12 Surface morphology of stripes on BS10FO film (a) and zoom-in topography image showing details of stripes (b).

Thus, we focus on the topographical stripes in thinner BSFO films. These lines with a depth of around 1.5 nm and a length ranging from 0.5 μm to 10 μm, are indications of the existence of mixed-phases. As shown in Figure 6.12, even smaller stripes consisting of parallel lines with a depth of smaller than 1 nm and a length of around 150 nm are observed in zoom-in topographical images. These small lines are closely packed with a density of over 20 lines within 1 μm (Figure 6.12). The shape of these stripes in BSFO films is quite similar to those in BLFO films but different from shorter and bolder stripes observed in pure BFO films (Figure 6.7)

Figure 6.13 XRD curves around (002) peak of BS10FO films on LAO with different thickness; (b) calculated c lattice parameters of BLFO films.

Figure 6.13 shows XRD patterns and c lattice constants of BS10FO thin films with different thickness grown on LAO substrates. It is clear that peaks corresponding to the R-like phase emerged and increases its intensity with the increase of film thickness. Coexistence of multi-phases was observed. An increase in c lattice is observed with the increase of film thickness, reflecting a gradual relaxation of the tensile strain in the film.

Detailed structure analysis was carried out using RSMs with synchrotron XRD. Figure 6.14(a, c) shows the two-dimensional reciprocal space mapping near the (002) diffraction of a 60 nm-thick pure BFO and a 63 nm-thick BS10FO film deposited on LaAlO_3 .

Figure 6.14 HR-XRD RSMs near (002) (a) and (103) (b) of pure 60 nm-thick BFO film; near (002) (c) and (103) (d) of the 63 nm-thick $\text{Bi}_{0.9}\text{Sm}_{0.1}\text{FeO}_3$ film.

Firstly, compared with 20 nm-thick films, both BFO and BSFO thicker films show an additional diffraction peak with its L value located between the (002) diffraction peaks of the LAO substrate and the T-like phase. This diffraction, which was also detected in the conventional Theta-2theta scan, corresponds to the R-like phase with a c lattice parameter of 3.977 Å for BFO and 3.970 Å for BSFO (Figure 6.3 a and c). The low intensity of this diffraction peak indicates the small amount of R-like phase in the mixed-phase film.

Secondly, the H values of diffraction peak corresponding to the T-like and R-like phase are the same with that of the LAO substrate, suggesting that the (001) plane of the two phases aligned perfectly with the LAO one without any tilting for both BFO and BSFO films.

Thirdly, the (002) diffraction of the T-like phase in both BFO and BSFO films is broadened horizontally, as compared with the (002) diffraction of thin film with pure Mc phase. The “tail” of the diffraction indicates the existence of other phases, which is further confirmed by the RSM near the (103) diffraction (Figure 6.9b and d).

The (103) peak of the T-like phase splits into three adjacent peaks, confirms it remains a monoclinic Mc phase. This T-like phase is similar to the one observed in thin BSFO film but with slightly different lattice parameters. The disappearance of diffraction originated from the R-like phase again confirms the small volume fraction of the R-like phase.

Furthermore, two satellite peaks are observed located on either side of the (002) diffraction of the T-like phase. Another diffused diffraction peak with H value ranged between 2.75 and 2.85 was also detected. According to the phases, all three diffraction peaks are originated from two triclinic phases. The former two peaks correspond to a phase named “*Tri-1*” while the later one peak corresponds to a phase named “*Tri-2*”.

More structural information of these two tilted phases were revealed by HK mappings around (002) diffraction with L values set at the peaks of these two phases (Figure 6.10). Both RSMs show eight diffraction peaks that are paired into four sets surrounding a center peak. Two sets with the same H values but opposite K values are distributed vertically while the other two sets with opposite H values and same K values are distributed horizontally. Based on the RSMs, the *Tri-1* phase is tilted away $\pm 0.4^\circ$ along $[100]$ and $\pm 1.5^\circ$ away along $[010]$. The *Tri-2* phase also tilts away along $[100]$ and $[010]$ with an angle of $\pm 0.4^\circ$ and $\pm 1.4^\circ$ respectively.

Figure 6.15 HR-XRD RSMs of HK-plane at $L=1.81$ and $L=1.62$ of the 73 nm-thick BFO film; $L=1.83$ (c) and $L=1.62$ (d) of the 70-nm thick BSFO film.

Although these four sets of diffraction peaks are almost symmetric, the intensities are quite different, suggesting that both *Tri-1* and *Tri-2* phases have preferred tilting orientations. For the *Tri-1* phase, two tilting orientations are preferred: 0.4° along $[100]$ with 1.5° along $[010]$, and 1.4° along $[100]$ with 0.4° along $[010]$. For the *Tri-2* phase, the strong peaks correspond

to tilting -0.4° along [100] with -1.5° along [010], and -1.4° along [100] with -0.4° along [010].

For pure BFO film, Tri-1 phase has an out-of-plane lattice constant of $4.178(1) \text{ \AA}$ with a tilt angle of $\pm 2.7^\circ$ along [100] and $\pm 0.5^\circ$ along [010], while lattice constant of Tri-2 phase is $4.682(2) \text{ \AA}$ with $\pm 1.5^\circ$ along [100] and $\pm 0.4^\circ$ along [010] respectively.

The average in-plane lattice parameter is basically identical between BFO and BSFO grown on LAO, but the Sm substitution leads to a decrease in the anisotropy of the in-plane lattice parameters. Similarly, the monoclinic distortion is much smaller in BSFO than in BFO, as evidenced by the increase of the monoclinic angle towards 90° after the Sm substitution.

6.3 Ferroelectric Properties Analysis

In this section, the ferroelectric properties of Re-BFO films will be characterized and discussed. Firstly, as-grown state of in-plane (IP) and out-of-plane (OP) domain structures of Re-BFO films will be characterized by piezoelectric force microscopy (PFM). The change of domain structure with Re substitution in both pure Mc phase BFO and BFO with MPBs are studied. Macroscopic polarization hysteresis loops are then obtained using quasi-planar electrodes on a probe station. During in-plane polarization switching, nano-scale domain switching behaviors of various Re-BFO films after applying external electric field are also studied by PFM at nano-scale.

6.3.1 Domain Structure

Firstly, ferroelectric domain evolution with Re substitution in Mc phase BFO films are studied. Topography and OP domain structures of 20 nm-thick BLFO films with doping level ranging from 0 to 15% are shown in Figure 6.16. Smooth and homogeneous surface with terraces suggest a pure Mc phase. A homogeneously “purple” contrast is observed in OP

PFM phase images of all films in as-grown state, indicating OP component of the polarization vector is uniformly pointing downwards (Figure 6. 16e-h). To confirm these ferroelectric domains are switchable by an external electrical field, a “box in box” pattern was written on all BLFO films by applying DC bias with opposite polarity between film and the conductive probe. As shown in Figure 6.16(i-l), these patterns are stable after writing, indicating that the switchable OP polarization persists in Mc phase BLFO with La doping level up to 15%.

Figure 6.16 Surface morphologies (a-d) and out-of-plane domain structures of 30 nm-thick BLFO films with different La doping concentrations: (e-h) as grown state, (i-l) domain structures after “writing” with DC bias. Scan size is $1 \mu\text{m}^2$ for all images.

On the other hand, IP domain structures are more complicated for BLFO films. As shown in Figure 6. 17a, pure BFO film has regular stripe domains with domain wall along $[110]_{pc}$

direction. Two contrasts are observed, yellow and brown, suggesting two domain variants. Such stripe domain structure is consistent with previous report.

With 5% La doping, the BL5FO film still shows stripe domain structure but with some crosstalk from topographical terraces. The domain width of BL10FO is smaller than that of pure BFO. With La doping level increasing to 10%, regular stripes are barely seen while more topography crosstalk emerges in IP PFM, suggesting a decrease in IP ferroelectricity. For BL15FO film with 15% La doping, regular stripes vanishes completely with almost no noticeable domain contrast in IP PFM. Fast Fourier transformation (FFT) was carried out for these IP PFM images, as shown in Figure 6.17 (e-h). A decrease in regularity is observed, from highly regular stripes in pure BFO to almost no noticeable patterns in BL15FO.

Figure 6.17 In-plane domain structures (a-d) and corresponding FFT images (e-h) of 30 nm-thick BLFO films with different La doping concentrations.

As introduced in previous section, topographical stripes appear in pure BFO film with the increase of film thickness. IP domain structure of pure BFO and BLFO (with 5% and 10% La doping) films with different thickness are shown in Figure 6. 18 and Figure 6.19, respectively.

Figure 6.18 Evolution of in-plane domain structure of pure BFO films with different thickness: (a) 38 nm, (b) 57 nm and (c) 114 nm.

Figure 6.19 Evolution of in-plane domain structure of BLFO films with different La concentration and film thickness: (a) 40 nm and (b) 68 nm thick BL5FO films, (c) 30 nm and (d) 36 nm thick BL10FO films. (e) Domain width versus film thickness of BLFO films with different La concentration.

Even though mixed-phase stripes appear in these BLFO films, the flat T-like phase matrix still show regular in-plane domain structure while IP PFM contrast in mixed-phase stripes

mimics the topography patterns. With the increase of La doping up to 10%, striped IP domain contrast is still visible but with its domain width gradually narrow down. The evolutions of IP domain width of BFO, BL5FO and BL10FO with film thickness are plotted in Figure 6.19e. It is clear that IP domain width decrease with the increase of film thickness as well as the increase of La doping level.

Figure 6.20 Surface morphology (a, d), in-plane (b, e) and out-of-plane (c, f) domain structure of BSFO film at different thickness.

IP and OP PFM images of the mixed-phase BSFO film are shown in Figure 6.8. The OP PFM image shows uniform purple color, indicating that the OP component of the polarization is pointing downward. The IP PFM shows three contrasts: yellow, brown and purple, suggesting the existence of multi-domains.

For Sm substituted BFO, the scenario of domain evolution is similar to that of La substituted BFO. Topography, IP and OP PFM images of BS10FO films with 10% Sm doping are shown

in Figure 6.20. The 15 nm-thick BS10FO film is of pure Mc phase while the thicker 45 nm-thick film show some stripes with mixed-phase. OP PFM of both films show uniform purple color, indicating that the OP component of the polarization vector is pointing downwards. Regular stripe IP domains are also observed in both BSFO films.

6.3.2 In-plane Polarization Hysteresis Loops

Quasi-planar electrodes were patterned to measure the remnant polarization hysteresis loop. The device structures of a conventional vertical capacitor and a quasi-planar capacitor are shown in Figure 6.21. The advantage of a planar capacitor is the ability to measure the polarization of films even with a small thickness.

We modeled the electric field distribution across the quasi-planar capacitor by using Finite Element Analysis (Figure 6.22). The dielectric constant for LaAlO_3 is 23. The dielectric constant for the Mc phase of BSFO is unknown. Here we use that of the R-like BSFO which is 350. Despite the highly non-uniform field close to the electrode edges, almost uniform distribution of in-plane electric field is observed for sample films sitting between two planar electrodes. It is expected that the actual electric field will be which is slightly smaller than the nominal value which is calculated by dividing the voltage by the channel width.

Figure 6.21 Illustration for the device structures of conventional vertical "sandwich" capacitor (a) and quasi-planar capacitor used in this study (b). Schematic illustration of the top-view of quasi-planar electrodes patterned on BFO and BSFO films (c). In this study, in-plane electric field was applied along the $\langle 100 \rangle$ and $\langle 110 \rangle$ directions of the underlying LAO substrates.

Compared to traditional "sandwich" capacitors, the quasi-planar capacitor has a greatly reduced capacitor area ($\sim 3.2 \mu\text{m}^2$) and a large thickness ($3.8 \mu\text{m}$). During the polarization hysteresis loop measurements, the linear capacitance resulting from both the connection wires and stray field in air and LAO substrate dominates the ferroelectric polarization (Figure 6.22). Fortunately, these parasitic elements are non-remanent and can be removed by subtracting the unswitched polarization hysteresis loop from the switched one (Figure 6.23). Using this method, square hysteresis loops are obtained with well-defined coercive field and remanent polarization values.

Figure 6.22 IP electric field distribution on the cross section of a 3.8 μm quasi-planar BSFO capacitor, simulated by finite element modeling. The relative dielectric constants used in the simulation for BSFO and LAO are 350 and 23, respectively.

Figure 6.23 (a) Schematic drawing of PUND; (b) Example of switched, un-switched and remanent polarization hysteresis loops of the quasi-planar BFO capacitor.

Quasi-planar electrodes were patterned on to pure BFO, BLFO and BSFO films to measure the remnant polarization hysteresis loops. The polarization hysteresis loops of pure BFO films with different thickness are shown in Figure 6.24. With the increase of thickness, well-defined square hysteresis loops persists with a slightly increase in coercive field E_c while saturated polarization P_s of BFO films shows a drop.

Figure 6.24 IP polarization hysteresis loops of BFO films with different thickness; (b) saturated polarization versus film thickness for pure BFO and BL5FO films.

Figure 6.25 (a) IP polarization hysteresis loops of 20 nm-thick BLFO films with different La concentration; (b) saturated polarization and coercive field versus film thickness for BLFO films.

Polarization hysteresis loops of 20 nm-thick BLFO films with different La concentration and calculated P_s and E_c are shown in Figure 6.25a. Saturated polarization and coercive field versus film thickness for BLFO films are plotted in Figure 6.25b.

These P-E loops demonstrate that the polarization vector in the T-like phase BFO and BSFO is tilted away from the [001] OP direction with a non-negligible IP polarization component. This result is consistent with previous reports of the observation of IP PFM domains in highly-strained BFO films grown on LSAO substrates.^{151, 152} With the increase of La doping level, the polarization hysteresis loops become “thinner”, reflecting a sharp decrease in coercive field. The shape of hysteresis loop also transform from a well-defined square for pure BFO to an antiferroelectric-like double hysteresis loop for BL10FO. For BL15FO film with 15% La doping, a tilted hysteresis loop with decreased P_s is observed. The small IP polarization value measured in BL15FO is consistent with the weak IP PFM signal for BL15FO film.

Figure 6.26 Polarization hysteresis loops of 30 nm-thick BFO and $\text{Bi}_{0.9}\text{Sm}_{0.1}\text{FeO}_3$ films grown on LAO substrates.

For comparison, IP polarization hysteresis loops of BS10FO films with 10% Sm substitution are also measured and shown in Figure 6.26. With the substitution of Bi by Sm, the coercive

field is effectively reduced, from 207 kV/cm for pure BFO to only 47.5 kV/cm for BSFO with 10% Sm. Meanwhile, saturated IP polarization is also decreased, similar to BLFO films. The reason could be that the polarization vector of BSFO rotates towards (001) direction with the Sm substitution, which is evidenced by the decrease of monoclinic angle in BSFO. Similar polarization rotation behavior is also observed in BSFO films deposited on STO substrates.⁶⁸

6.3.3 In-plane Domain Switching

The ferroelectric domain structure within the quasi-planar channel was also monitored during the polarization switching cycle. Figure 6.27 show the OP and IP domain images of BSFO film across the quasi-planar capacitor in different states: as grown, after applying +60V at the left electrode and after applying -60 V at the left electrode.

After a voltage pulse (+60V and 1 ms duration) is applied to the left electrode with electric field parallel to the [100] direction, striped brown domains align their net IP polarization along the electric field (Figure 6.27a). The yellow/brown and purple/brown stripes correspond to the combinations of P_2/P_1 and P_4/P_1 domains respectively, as shown in Figure 6.27b. When an opposite electric field is applied, brown domains with IP polarization aligned anti-parallel to the electric field (P_1) are switched by 180°, while purple and yellow domains with IP polarization perpendicular to the electric field (P_2 and P_4) remain unchanged (Figure 6.27c and 6.27d). Meanwhile, domain walls rotate 90° to avoid the formation of charged domain walls. However, OP PFM images showed no contrast change, irrespective of the polarity of the applied electric field (Figure not shown).

Figure 6.27 (a) and (b) are the IP PFM image and the illustration of polarization vectors after applying +60V at the left electrode respectively. (c) and (d) are the IP PFM image and the illustration of polarization vectors after applying -60V. Insets in (a) and (c) are the illustrations of the IP domain arrangement with red arrows indicating IP polarization directions. “E” denotes the applied electric field.

6.4 Anomalous Stabilization of T-like phase in Yb-doped BFO

Figure 6.28 Schematic showing the reduction of atomic radius with increasing atomic number in lanthanide group. Figure adapted from 153.

Following the rule based on aforementioned findings, if the ionic size of the dopant continues to shrink, the lattice mismatch between T-like BFO and LAO will increase, which should lead to the mixed-phase formation and epitaxial breakdown at even lower thickness. To testify our hypothesis, Yb, the penultimate element in the lanthanide group, was employed, as it has a much smaller atomic (ionic) radius compared to Bi/La (Figure 6.28). Surprisingly, 40-nm-thick 10 %-Yb-doped BFO (BY10FO) grown on LAO turned out to be T-like phase without structural relaxation or epitaxial breakdown. By comparing the XRD patterns with pure and La-doped BFO films, it could be found the Yb-doped film showed unexpected lattice expansion despite the small size of the dopant (Figure 6.29).

Figure 6.29 XRD patterns around (001) peak of pure BFO, BL15FO and BY10FO films grown on LAO with their *c* lattice constants denoted.

Moreover, by increasing the thickness, Yb-doped film consistently exhibited a homogeneous surface without the mixed-phase formation. The XRD results also showed no relaxation of the lattice, which was in sharp contrast with the pure BFO film, as illustrated in Figure 6.30. According to all the observations, we can infer that Yb-doping stabilized T-like phase rather than inhibiting it.

Figure 6.30 XRD patterns and corresponding AFM morphologic images of (a) pure BFO and (b) 10 %-Yb-doped BFO films with increasing thickness.

Figure 6.31 Topography, as-grown IP and OP domain structures of a pure BFO (a, b, c), BL15FO (d, e, f) and BY10FO) films grown on LAO. Scale bars represent 500 nm.

To gain more understanding into this unusual behavior, the ferroelectric domain structures of the Yb-doped BFO film was probed using PFM, and compared with those acquired for pure and La-doped BFO. As mentioned, T-like M_C phase of BFO organized into ordered stripe domains in IP-PFM image, whereas La-doping destroyed this order, resulting in vanishment

of the in-plane polarization component, as shown in Figure 6.31b&e. In contrast, the Yb-substitution mysteriously restored the stripe-domain structure as observed in pure BFO. Furthermore, the stripe domains in BY10FO film can be switched by electric field in a planar capacitor, rendering a macroscopic P – E loop similar to pure BFO. Contrarily, the domain structure of BL15FO film cannot be switched by electric field, and correspondingly no obvious loop can be seen in the P – E measurement (Figure 6.32).

Figure 6.32 In-plane ferroelectric domain images of (a) BY10FO and (b) BL15FO before and after in-plane electrical switching. (c) Corresponding in-plane P – E loops of pure, 15%-La-doped and 10%-Yb-doped BFO films.

Figure 6.33 Topography, IP and OP domain structures after electrical writing of a pure BFO (a, b, c), BL15FO (d, e, f) and BY10FO) films grown on LAO. Scale bars represent 500 nm.

Lastly, electrically-induced T – R mixed-phase formation was employed to examine the relative energy landscape between T-like and R-like phase. By biasing the AFM probe while scanning the surface, mixed-phase nanodomains can be written in pure BFO, as well as in BL15FO film (Figure 6.33). However, no pronounced amount of mixed-phase region can be created in BY10FO film, even its in-plane domain structure has been significantly modified

by the field. All the above observations pointed to the same fact that the free energy of the T-like M_C phase was reduced by Yb doping, which became the ground state of the film.

6.5 Discussion

Figure 6.34 Schematic drawings showing the lattice distortion of BFO thin films grown on LAO substrate at (a) small thickness with purely T-like phase and (b) large thickness with relaxed T-R mixed phases.

Before the discussion of RE-doping effect on the structural and morphological evolutions of the highly-strained BFO thin film grown on LAO, the characteristic of this strain-relaxation-mediated MPB needs to be clarified. Firstly, T-like BFO is subjected to tensile strain by LAO rather than compressive strain, which first seems counterintuitive. However, the large compressive strain we normally refer to is with regard to the rhombohedral bulk phase, whereas the ground-state of T-like phase possesses a smaller in-plane lattice compared with LAO, as supported by the theoretical calculations.^{129, 135, 154, 155} Experimentally, T-like BFO

phase unexceptionally shows shrinking of the in-plane lattice and expansion of the out-of-plane lattice towards constant values with increasing thickness.^{17, 156, 157} All the evidence justifies tensile strain is imposed on T-like BFO when grown on LAO, as shown in Figure 6.34a. At small thickness, BFO is fully strained to the substrate with reduced *c* lattice. As the film is getting thicker, elastic strain energy builds up and tends to release. However, instead of conventional dislocation formation to relieve strain, spinodal phase separation into T – R phase mixture takes place in T-like BFO matrix. Since R-like phase has a larger in-plane lattice, it happens to compensate the shrinkage of the in-plane lattice of T-like phase, thus maintaining an overall balance with the LAO lattice. However, the huge mismatch in the out-of-plane direction between T and R-like phases causes their crystallographic lattice to tilt away from the surface normal due to mechanical constraints. Besides, within the T – R lamellar mixture, strain relaxation only occurs along one dimension as depicted by the cross-sectional view in Figure 6.34b. The lattices of both T- and R-like phases remain fully clamped to LAO along the in-plane orthogonal direction. Fortunately, other domain variants form to relax the strain along other directions, thus resulting in eight pairs of T – R mixtures as indicated in the previous RSM results.^{53, 158} The phase mixture consists of alternating T- and R-like phases and a saw-toothed surface profile due to the tilted crystallographic plane. The average depth of the mixed-phase region with regard to the T-like matrix is due to the difference of the *c* lattice of the T-like and R-like phases, thus proportional to the film thickness (Figure 6.35). Morphologically, with increasing film thickness and strain relaxation, more and more T – R lamellar stripes form and uniformly disperse on the surface. However, if the thickness continues to increase, even the formation of T – R mixed phase is unable to sustain a coherent film, eventually leading to epitaxial breakdown.¹⁵⁷

Figure 6.35 (a) Zoom-in surface morphology of a thick BL5FO film. The inset shows the height profile of the mixed-phase stripes denoted by blue dotted line. (b) Linear relationship between the average depth of “stripes” region and the film thickness of BLFO thin films.

Next, let's look at what happens in this strain-driven MPB system if Bi^{3+} is replaced by RE ions. The first thought is the chemical strain induced by the mismatch of the ionic radii. Table 6.1 lists the related ionic radii under eight-fold coordination for the A-site ions (because 12-CN data is not available) and six-fold coordination for the Fe^{3+} . Although the radius of La^{3+} is very close to Bi^{3+} , the La-doping still has a huge impact on the strain-relaxation-mediated mixed-phase formation, which is highly sensitive to trivial strain variations. Basically, due to the slight shrinkage of the La-doped BFO lattice, the lattice mismatch with respect to LAO becomes larger, which causes the strain relaxation, namely, mixed-phase formation to occur at lower thickness. This can be understood in analogous to the classic strain relaxation via dislocation formation, where the “critical thickness” for the dislocation to appear is inversely proportional to the lattice mismatch between film and

substrate.^{21, 159} As a consequence, the mixed-phase formation as well as the epitaxial breakdown initiates at a lower thickness in La-doped BFO films.

Table 6.1 Effective ionic radii of relevant elements in this study. Data adapted from 141.

Element	Bi (8 CN)	La (8 CN)	Sm (8 CN)	Yb (8 CN)	Fe (6 CN)
Ionic radius (Å)	1.17	1.16	1.079	0.985	0.645

Sm-doped samples adopt similar behavior. However, it is noticeable that Sm^{3+} is much smaller than Bi^{3+} or La^{3+} . Thus, an even smaller threshold thickness should be expected for the mixed-phase formation or epitaxial breakdown, which contradicts to the experimental observation. Possible explanation is that Sm is much volatile compared with La (Table 4.1), so the true dopant concentration in the film may be lower than the nominal value. Similar finding was reported for Pb-doped highly-strained BFO, in which Pb is also highly volatile.¹⁶⁰ Another evidence to support this assumption is that the out-of-plane lattice parameter of BFO films doped with Sm up to 30 % shows similar values compared with those doped with La up to 15 %. It would be unreasonable if the dopant concentration in Sm-doped film is same as the nominal one.

As for the structural evolution of the T-like M_C phase, RE-doping results in (1) the increase of the monoclinic angle towards 90° and (2) the reduction of the in-plane lattice anisotropy, both of which renders the lattice closer to a true tetragonal structure. Such behavior seems to be universal for A-site doping in highly-strained BFO films as generally reported.^{51, 161} Owing to the smaller lattice anisotropy, and consequently smaller domain wall energy, longer MPB stripes can be formed in both La and Sm doped films,¹⁶¹ which also explains the reduced stripe-domain size in T-like M_C phase. However, before the lattice becomes

completely tetragonal, the mixed-phase variant remains eight-fold degenerate as evidenced by the H-K RSM.

Figure 6.36 Schematic drawing showing the in-plane polar instability in BLFO induced by RE doping, leading to true tetragonal structure.

Correlated with the structural change, the in-plane polarization of the T-like M_C phase is destabilized by RE-doping according to both the PFM and $P - E$ measurements. In particular, the striped ferroelectric domains of the T-like BFO gradually vanish upon increasing La doping, and eventually disappear. In agreement, macroscopic in-plane $P - E$ loops reveal first the decrease of coercive field, followed by the emergence of double-hysteresis loop and lastly a slant loop signifying paraelectric-like state. These findings echoes those observed in RE-doped R-like BFO films, where the polarization first rotates towards the c axis, and finally a global polar instability takes place, leading to FE – PE transition (Figure 6.36). In T-like BFO phase, the polar instability only occurs in the film plane, which can be phenomenologically explained by the evolution of the free energy profile from a FE state to a

PE state through first-order transition, as depicted in Figure 6.37. Unfortunately, a global polar instability is absent, which rules out a possible FE – PE phase boundary for T-like BFO. In fact, considering the giant c/a ratio of T-like phase, it is implausible to be paraelectric phase at room temperature, even if the Bi^{3+} is extensively substituted, unlike the R-like BFO case. Besides, Fe^{3+} displacement also partially contributes to the huge polarization in T-like BFO.^{52, 162} Hence, the chemical-driven global polar instability becomes a missing piece in the corresponding phase diagram, as shown in Figure 6.38.

Figure 6.37 Evolution of the free energy profile for the in-plane ferroelectric order in BLFO thin films grown on LAO with the increase of La doping concentration.

Figure 6.38 Proposed phase diagram for La-doped highly-strain BFO.

Lastly, we will discuss the anomalous behavior observed in Yb-doped BFO. Although Yb is the most volatile element in the lanthanide group, the composition deviation obviously cannot explain the experimental results. Based on the strong evidence of lattice expansion instead of shrinkage, we make a wild speculation that Yb substitutes, or at least partially substitutes the B-site Fe ions. It is noted that Yb^{3+} is much larger than Fe^{3+} . However, given that one oxygen ion is not coordinated with Fe, we expect the lattice has more degree of freedom to accommodate a larger cation at the B-site. Moreover, the restoration of the monoclinically-distorted M_C phase by Yb-doping also implies that Yb is probably not replacing Bi, as the monoclinic distortion is the remanent signature of 6s lone pair of Bi^{3+} . Certainly, further experiments are warranted to validate this assumption.

6.6 Conclusions

In this chapter, we performed detailed characterizations on RE-doped highly-strained BFO on the basis of the unique strain-driven MPB. To sum up, A-site RE-doping imposes a

chemical pressure large enough to shift the strain-driven MPB in BFO. Specifically, the smaller ionic radii of RE elements cause a larger lattice mismatch between RE-doped BFO and LAO substrate, consequently reducing the “critical thickness” for mixed-phase formation as well as epitaxial breakdown. For structural and physical properties wise, rare earth doping in pure tetragonal-like BFO, average in-plane lattice parameters are unchanged but a decrease in the anisotropy of the in-plane lattice parameters is observed. Meanwhile, the monoclinic distortion is much smaller, as evidenced by the increase of the monoclinic angle towards 90° after the rare earth Sm substitution. Furthermore, significant reduction in coercive field for in-plane polarization switching is also observed.

Accompanying the shift in the strain-driven MPB is the weakening of the in-plane polar order, which is very similar to the RE-doping-induced polarization rotation in the R-like BFO as discussed in Chapter 5. However, further doping didn't lead to the global polar instability, but a collapse of the T-like lattice into R-like one. Hence, the initial goal to combine both the chemical- and strain-driven MPBs cannot be achieved due to the lack of FE – PE phase transition in T-like BFO at room temperature. These findings are valuable for understanding the physical origin of the property evolution in RE-doped BFO, and for future design of the material system for giant electromechanical response.

Chapter 7 Conclusions and Future Work

7.1 Conclusions

Major conclusions of this thesis are summarized below:

- (1) Rare earth element (Re) substituted BiFeO_3 (BFO) thin films were successfully deposited on SrTiO_3 (STO) and LaAlO_3 (LAO) substrates with high epitaxial quality. Growth conditions of epitaxial Re-BFO films were systematically optimized. This enabled the following study of the structure and physical properties of Re-BFO films under different chemical pressure and epitaxial strain.
- (2) The effect of La-doping on the property evolutions of BLFO single-domain films were systematically investigated and analyzed.
 - a. La substitution induces polar instability just as those reported for small RE-elements, suggesting a universal behavior of RE doping. The absence of chemical pressure in La case probably leads to a broad region of phase coexistence among polar, antipolar and nonpolar phases.
 - b. La doping also causes polarization rotation associated with the competing instability of oxygen octahedral tilt as well as a reduction of the transition temperature.
 - c. The longitude piezoelectric response depends insensitively on the La doping, probably because La-doping fails to soften the lattice as implied from the relative permittivity results.

- d. Sm-doped films exhibit some degree of enhancement of the piezoelectric coefficient, highlighting the role of chemical pressure in softening the lattice.
- (3) The chemical substitution is introduced into the highly-strained BFO films to combine the chemical- and strain-driven MPBs in this unique system, aiming to create multiple phase boundaries with ultrahigh piezoelectric response.
- a. A-site RE-doping imposes a chemical pressure large enough to shift the strain-driven MPB in BFO. Specifically, the smaller ionic radii of RE elements cause a larger lattice mismatch between RE-doped BFO and LAO substrate, consequently reducing the “critical thickness” for mixed-phase formation as well as epitaxial breakdown.
 - b. With rare earth doping in pure tetragonal-like BFO, average in-plane lattice parameters are unchanged but a decrease in the anisotropy of the in-plane lattice parameters is observed. Meanwhile, the monoclinic distortion is much smaller, as evidenced by the increase of the monoclinic angle towards 90° after the rare earth Sm substitution. Furthermore, significant reduction in coercive field for in-plane polarization switching is also observed.
 - c. Universal polarization rotation behavior is observed in rare-earth-element doped tetragonal-like BFO, analogous to those found in rhombohedral-like phase. However, a global polar instability is absent at high doping concentration before the tetragonal-like BFO lattice collapses due to epitaxial breakdown.
 - d. The initial goal to combine both the chemical- and strain-driven MPBs cannot be achieved due to the lack of FE – PE phase transition in T-like BFO at room

temperature. These findings are valuable for understanding the physical origin of the property evolution in RE-doped BFO, and for future design of the material system for giant electromechanical response.

7.2 Future Work

The successful deposition of high quality BFO and Re-BFO thin films paves the way for further investigations for the properties of this materials system. Further studies in the following directions could be carried out.

- (1) Our study reveals that the large polarization of around $150\mu\text{C}/\text{cm}^2$ for the highly-strained Mc phase BFO with rare earth substitution. Furthermore, a reduced coercive field is observed with La, Sm and Yb substitution. These facts suggest T-like phase Re-BFO is a better candidate for memory applications. Thus, a systematic study of detailed properties of T-like phase Re-BFO related for the memory application is required, such as the polarization relaxation behavior and the fatigue behavior, etc.

In this study, we also focused on the interplay of epitaxial strain and chemical substitution in highly-strained Re-BFO with different film thickness and rare earth element substitution concentration. It is clear that the epitaxial strain dominant the highly-strained Re-BFO films while the chemical substitution induced MPB in bulk BSFO is not observed. How about BSFO films under a smaller compressive strain or even a tensile strain? With the commercial availability of single crystal substrates of various lattice constants, further investigations can be carried out to study the structure and properties of Re-BFO films deposited on to single crystals such as LaSrAlO_3 , DyScO_3 , KTaO_3 and PrScO_3 .

References

- 1 D. Damjanovic, Rep Prog Phys **61**, 1267 (1998).
- 2 A. M. Glazer, Acta Crystallographica Section A **31**, 756 (1975).
- 3 S. T. Lagerwall, in *Ferroelectric and Antiferroelectric Liquid Crystals* (Wiley-VCH Verlag GmbH, 2007), p. 7.
- 4 J. F. Scott and C. A. P. Dearaujo, Science **246**, 1400 (1989).
- 5 S.-E. Park and T. R. Shrout, J Appl Phys **82**, 1804 (1997).
- 6 D. E. Cox, B. Noheda, G. Shirane, Y. Uesu, K. Fujishiro, and Y. Yamada, Appl Phys Lett **79**, 400 (2001).
- 7 B. Noheda, D. E. Cox, G. Shirane, J. A. Gonzalo, L. E. Cross, and S. E. Park, Appl Phys Lett **74**, 2059 (1999).
- 8 B. Noheda, J. A. Gonzalo, L. E. Cross, R. Guo, S. E. Park, D. E. Cox, and G. Shirane, Phys Rev B **61**, 8687 (2000).
- 9 L. Bellaiche, A. García, and D. Vanderbilt, Physical Review Letters **84**, 5427 (2000).
- 10 D. Vanderbilt and M. H. Cohen, Phys Rev B **63**, 094108 (2001).
- 11 D. Vanderbilt and M. H. Cohen, Phys Rev B **63**, 094108 (2001).
- 12 B. Noheda, D. E. Cox, G. Shirane, S. E. Park, L. E. Cross, and Z. Zhong, Physical Review Letters **86**, 3891 (2001).
- 13 B. Noheda, D. E. Cox, G. Shirane, J. Gao, and Z. G. Ye, Phys Rev B **66** (2002).
- 14 K. A. Schönau, M. Knapp, H. Kungl, M. J. Hoffmann, and H. Fuess, Physical Review B **76**, 144112 (2007).
- 15 J. Frantti, J Phys Chem B **112**, 6521 (2008).
- 16 A. A. Belik, H. Yusa, N. Hirao, Y. Ohishi, and E. Takayama-Muromachi, Chem Mater **21**, 3400 (2009).
- 17 R. J. Zeches, et al., Science **326**, 977 (2009).
- 18 C. W. Huang, Y. H. Chu, Z. H. Chen, J. L. Wang, T. Sritharan, Q. He, R. Ramesh, and L. Chen, Appl Phys Lett **97** (2010).
- 19 P. E. Janolin, J Mater Sci **44**, 5025 (2009).
- 20 S. Venkatesan, B. J. Kooi, J. T. M. De Hosson, A. H. G. Vlooswijk, and B. Noheda, J Appl Phys **102** (2007).
- 21 J. W. Matthews and A. E. Blakeslee, Journal of Crystal Growth **27**, 118 (1974).
- 22 D. G. Schlom, L. Q. Chen, C. B. Eom, K. M. Rabe, S. K. Streiffer, and J. M. Triscone, Annu Rev Mater Res **37**, 589 (2007).
- 23 C. Ederer and N. A. Spaldin, Phys Rev Lett **95**, 257601 (2005).
- 24 G. Xu, H. Hiraka, G. Shirane, J. Li, J. Wang, and D. Viehland, Appl Phys Lett **86**, 182905 (2005).
- 25 K. J. Choi, et al., Science **306**, 1005 (2004).
- 26 J. H. Haeni, et al., Nature **430**, 758 (2004).
- 27 A. A. Bokov and Z. G. Ye, J Mater Sci **41**, 31 (2006).
- 28 V. V. Shvartsman and A. L. Kholkin, J Appl Phys **108**, 042007 (2010).
- 29 J. X. Zhang, et al., Nat Nano **6**, 98 (2011).
- 30 J. Wang, et al., Science **299**, 1719 (2003).
- 31 J. R. Teague, R. Gerson, and W. J. James, Solid State Commun **8**, 1073 (1970).
- 32 Y.-H. Chu, L. W. Martin, M. B. Holcomb, and R. Ramesh, Materials Today **10**, 16 (2007).
- 33 R. Ramesh and N. A. Spaldin, Nature Materials **6**, 21 (2007).

- 34 G. Catalan and J. F. Scott, *Adv Mater* **21**, 2463 (2009).
- 35 F. Kubel and H. Schmid, *Acta Crystallogr. Sect. B-Struct. Commun.* **46**, 698 (1990).
- 36 J. B. Neaton, C. Ederer, U. V. Waghmare, N. A. Spaldin, and K. M. Rabe, *Physical Review B* **71** (2005).
- 37 I. Sosnowska, T. Peterlinneumaier, and E. Steichele, *Journal of Physics C-Solid State Physics* **15**, 4835 (1982).
- 38 L. W. Martin, S. P. Crane, Y. H. Chu, M. B. Holcomb, M. Gajek, M. Huijben, C. H. Yang, N. Balke, and R. Ramesh, *Journal of Physics: Condensed Matter* **20**, 434220 (2008).
- 39 N. A. Spaldin, S. W. Cheong, and R. Ramesh, *Phys Today* **63**, 38 (2010).
- 40 T. Zhao, et al., *Nature Materials* **5**, 823 (2006).
- 41 P. Ravindran, R. Vidya, A. Kjekshus, H. Fjellvag, and O. Eriksson, *Phys Rev B* **74** (2006).
- 42 S. Kamba, D. Nuzhnyy, M. Savinov, J. Šebek, J. Petzelt, J. Prokleška, R. Haumont, and J. Kreisel, *Physical Review B* **75**, 024403 (2007).
- 43 J. Lu, et al., *European Physical Journal B -- Condensed Matter* **75**, 451 (2010).
- 44 S. J. Clark and J. Robertson, *Appl Phys Lett* **90**, 132903 (2007).
- 45 H. W. Jang, et al., *Physical Review Letters* **101**, 107602 (2008).
- 46 I. C. Infante, et al., *Physical Review Letters* **105**, 057601 (2010).
- 47 D. Sando, et al., *Nat Mater* **12**, 641 (2013).
- 48 N. Spaldin, S. Cheong, and R. Ramesh, - **63** (2010).
- 49 H. Béa, et al., *Phys Rev Lett* **102**, 217603 (2009).
- 50 X. He, Y. Wang, N. Wu, A. N. Caruso, E. Vescovo, K. D. Belashchenko, P. A. Dowben, and C. Binek, *Nat. Mater.* **9**, 579 (2010).
- 51 H. M. Christen, J. H. Nam, H. S. Kim, A. J. Hatt, and N. A. Spaldin, *Phys Rev B* **83**, 144107 (2011).
- 52 J. X. Zhang, et al., *Physical Review Letters* **107**, 147602 (2011).
- 53 Z. Chen, et al., *Phys Rev B* **84**, 094116 (2011).
- 54 Z. Chen, et al., *Adv Funct Mater* **21**, 133 (2011).
- 55 A. J. Hatt, N. A. Spaldin, and C. Ederer, *Phys Rev B* **81** (2010).
- 56 C. H. Yang, et al., *Nat. Mater.* **8**, 485 (2009).
- 57 Z. Zhang, P. Wu, L. Chen, and J. Wang, *Appl Phys Lett* **96**, 012905 (2010).
- 58 G. L. Yuan and S. W. Or, *Journal of Applied Physics* **100**, 024109 (2006).
- 59 I. Levin, S. Karimi, V. Provenzano, C. L. Dennis, H. Wu, T. P. Comyn, T. J. Stevenson, R. I. Smith, and I. M. Reaney, *Physical Review B* **81**, 020103 (2010).
- 60 D. Kan, L. Palova, V. Anbusathaiah, C. J. Cheng, S. Fujino, V. Nagarajan, K. M. Rabe, and I. Takeuchi, *Adv Funct Mater* **20**, 1108 (2010).
- 61 V. L. Mathe, *Journal of Magnetism and Magnetic Materials* **263**, 344 (2003).
- 62 S. Fujino, M. Murakami, V. Anbusathaiah, S. H. Lim, V. Nagarajan, C. J. Fennie, M. Wuttig, L. Salamanca-Riba, and I. Takeuchi, *Appl Phys Lett* **92** (2008).
- 63 C. J. Cheng, D. Kan, S. H. Lim, W. R. McKenzie, P. R. Munroe, L. G. Salamanca-Riba, R. L. Withers, I. Takeuchi, and V. Nagarajan, *Phys Rev B* **80** (2009).
- 64 C.-J. Cheng, D. Kan, V. Anbusathaiah, I. Takeuchi, and V. Nagarajan, *Appl Phys Lett* **97**, 212905 (2010).
- 65 C. J. Cheng, A. Y. Borisevich, D. Kan, I. Takeuchi, and V. Nagarajan, *Chem Mater* **22**, 2588 (2010).
- 66 D. Kan, R. Suchoski, S. Fujino, and I. Takeuchi, *Integr Ferroelectr* **111**, 116 (2009).
- 67 D. Kan, *J. Appl. Phys.* **110**, 014106 (2011).

- 68 D. Kan, V. Anbusathaiah, and I. Takeuchi, *Adv Mater* **23**, 1765 (2011).
- 69 W. F. Liu and X. B. Ren, *Phys Rev Lett* **103** (2009).
- 70 S. Yang, et al., *Phys Rev Lett* **104**, 197201 (2010).
- 71 S. O. Leontsev and R. E. Eitel, *Sci Technol Adv Mat* **11** (2010).
- 72 S. Bhattacharjee, S. Tripathi, and D. Pandey, *Applied Physics Letters* **91**, 042903 (2007).
- 73 W. M. Zhu, H. Y. Guo, and Z. G. Ye, *Physical Review B* **78**, 014401 (2008).
- 74 S. O. Leontsev and R. E. Eitel, *Journal of the American Ceramic Society* **92**, 2957 (2009).
- 75 S. O. Leontsev and R. E. Eitel, *Journal of Materials Research* **26**, 9 (2011).
- 76 H. Amorín, C. Correias, P. Ramos, T. Hungria, A. Castro, and M. Algueró, *Applied Physics Letters* **101**, 172908 (2012).
- 77 J.-H. Lee, M.-A. Oak, H. J. Choi, J. Y. Son, and H. M. Jang, *Journal of Materials Chemistry* **22**, 1667 (2012).
- 78 H. Yang, C. Zhou, X. Liu, Q. Zhou, G. Chen, H. Wang, and W. Li, *Materials Research Bulletin* **47**, 4233 (2012).
- 79 D. Damjanovic, *Applied Physics Letters* **97**, 062906 (2010).
- 80 W. Liu and X. Ren, *Physical Review Letters* **103**, 257602 (2009).
- 81 S. Fujino, M. Murakami, V. Anbusathaiah, S.-H. Lim, V. Nagarajan, C. J. Fennie, M. Wuttig, L. Salamanca-Riba, and I. Takeuchi, *Applied Physics Letters* **92** (2008).
- 82 C.-J. Cheng, D. Kan, V. Anbusathaiah, I. Takeuchi, and V. Nagarajan, *Applied Physics Letters* **97** (2010).
- 83 D. Kan, L. Pálová, V. Anbusathaiah, C. J. Cheng, S. Fujino, V. Nagarajan, K. M. Rabe, and I. Takeuchi, *Advanced Functional Materials* **20**, 1108 (2010).
- 84 D. Kan, C.-J. Cheng, V. Nagarajan, and I. Takeuchi, *Journal of Applied Physics* **110** (2011).
- 85 D. V. Karpinsky, I. O. Troyanchuk, M. Tovar, V. Sikolenko, V. Efimov, and A. L. Kholkin, *Journal of Alloys and Compounds* **555**, 101 (2013).
- 86 D. A. Rusakov, A. M. Abakumov, K. Yamaura, A. A. Belik, G. Van Tendeloo, and E. Takayama-Muromachi, *Chemistry of Materials* **23**, 285 (2010).
- 87 I. O. Troyanchuk, et al., *Physical Review B* **83**, 054109 (2011).
- 88 I. O. Troyanchuk, D. V. Karpinsky, M. V. Bushinsky, O. S. Mantyskaya, N. V. Tereshko, and V. N. Shut, *Journal of the American Ceramic Society* **94**, 4502 (2011).
- 89 O. E. González-Vázquez, J. C. Wojdeł, O. Diéguez, and J. Íñiguez, *Physical Review B* **85**, 064119 (2012).
- 90 P. R. Willmott, *Progress in Surface Science* **76**, 163 (2004).
- 91 P. R. Willmott and J. R. Huber, *Rev Mod Phys* **72**, 315 (2000).
- 92 P. Thibault and V. Elser, *Annual Review of Condensed Matter Physics* **1**, 237 (2010).
- 93 J. Stephen and et al., *Nanotechnology* **17**, 1615 (2006).
- 94 A. Gruverman, O. Auciello, and H. Tokumoto, *Annual Review of Materials Science* **28**, 101 (1998).
- 95 A. Gruverman, H. Tokumoto, A. S. Prakash, S. Aggarwal, B. Yang, M. Wuttig, R. Ramesh, O. Auciello, and T. Venkatesan, *Applied Physics Letters* **71**, 3492 (1997).
- 96 D. H. Lowndes, D. B. Geohegan, A. A. Puretzky, D. P. Norton, and C. M. Rouleau, *Science* **273**, 898 (1996).
- 97 M. N. R. Ashfold, F. Claeysens, G. M. Fuge, and S. J. Henley, *Chemical Society Reviews* **33**, 23 (2004).

98 B. Dam, J. H. Rector, J. Johansson, J. Huijbregtse, and D. G. De Groot, *Journal of*
 Applied Physics **83**, 3386 (1998).
 99 T. Ohnishi, M. Lippmaa, T. Yamamoto, S. Meguro, and H. Koinuma, *Applied*
 Physics Letters **87**, 241919 (2005).
 100 T. Ohnishi, K. Shibuya, T. Yamamoto, and M. Lippmaa, *Journal of Applied Physics*
103, 103703 (2008).
 101 E. Breckenfeld, R. Wilson, J. Karthik, A. R. Damodaran, D. G. Cahill, and L. W.
 Martin, *Chemistry of Materials* **24**, 331 (2012).
 102 E. Breckenfeld, N. Bronn, J. Karthik, A. R. Damodaran, S. Lee, N. Mason, and L. W.
 Martin, *Physical Review Letters* **110**, 196804 (2013).
 103 E. Breckenfeld, A. B. Shah, and L. W. Martin, *Journal of Materials Chemistry C* **1**,
 8052 (2013).
 104 E. Breckenfeld, R. B. Wilson, and L. W. Martin, *Applied Physics Letters* **103**, 082901
 (2013).
 105 A. R. Damodaran, E. Breckenfeld, Z. Chen, S. Lee, and L. W. Martin, *Advanced*
 Materials **26**, 6341 (2014).
 106 D. R. Lide, *CRC Handbook of Chemistry and Physics, 84th Edition*. (CRC Press,
 Boca Raton, Florida, 2003).
 107 S. M. Selbach, M.-A. Einarsrud, and T. Grande, *Chemistry of Materials* **21**, 169
 (2009).
 108 H. Béa, et al., *Applied Physics Letters* **87**, 072508 (2005).
 109 J. F. Ihlefeld, et al., *Applied Physics Letters* **92**, 142908 (2008).
 110 Z.-G. Mei, S. Shang, Y. Wang, and Z.-K. Liu, *Applied Physics Letters* **98**, 131904
 (2011).
 111 K. Feng, L.-C. Wang, J. Lu, Y. Wu, and B.-G. Shen, *CrystEngComm* **15**, 4900 (2013).
 112 L. You, N. T. Chua, K. Yao, L. Chen, and J. Wang, *Physical Review B* **80**, 024105
 (2009).
 113 Q. M. Zhang, H. Wang, N. Kim, and L. E. Cross, *Journal of Applied Physics* **75**, 454
 (1994).
 114 F. Xu, S. Trolier-McKinstry, W. Ren, B. Xu, Z.-L. Xie, and K. J. Hemker, *Journal of*
 Applied Physics **89**, 1336 (2001).
 115 V. Nagarajan, A. Roytburd, A. Stanishevsky, S. Prasertchoung, T. Zhao, L. Chen, J.
 Melngailis, O. Auciello, and R. Ramesh, *Nat Mater* **2**, 43 (2003).
 116 Y. H. Chu, et al., *Advanced Materials* **19**, 2662 (2007).
 117 J. F. Ihlefeld, C. M. Folkman, S. H. Baek, G. L. Brennecke, M. C. George, J. F.
 Carroll, and C. B. Eom, *Applied Physics Letters* **97**, 262904 (2010).
 118 J. W. Park, S. H. Baek, P. Wu, B. Winchester, C. T. Nelson, X. Q. Pan, L. Q. Chen, T.
 Tybell, and C. B. Eom, *Applied Physics Letters* **97**, 212904 (2010).
 119 H. W. Jang, et al., *Advanced Materials* **21**, 817 (2009).
 120 Y. H. Chu, et al., *Advanced Materials* **18**, 2307 (2006).
 121 Y. H. Chu, Q. He, C. H. Yang, P. Yu, L. W. Martin, P. Shafer, and R. Ramesh, *Nano*
 Letters **9**, 1726 (2009).
 122 C. M. Folkman, et al., *Applied Physics Letters* **94** (2009).
 123 S. H. Baek, et al., *Nat. Mater.* **9**, 309 (2010).
 124 V. Shelke, D. Mazumdar, G. Srinivasan, A. Kumar, S. Jesse, S. Kalinin, A. Baddorf,
 and A. Gupta, *Advanced Materials* **23**, 669 (2011).
 125 P. Yu, et al., *Proceedings of the National academy of Sciences of the United States of*
 America **109**, 9710 (2012).

126 B. Winchester, P. Wu, and L. Q. Chen, *Applied Physics Letters* **99** (2011).
 127 R. J. Sichel, A. Grigoriev, D.-H. Do, S.-H. Baek, H.-W. Jang, C. M. Folkman, C.-B.
 Eom, Z. Cai, and P. G. Evans, *Applied Physics Letters* **96**, 051901 (2010).
 128 T. H. Kim, et al., *Applied Physics Letters* **98**, 022904 (2011).
 129 C. Ederer and N. A. Spaldin, *Physical Review Letters* **95**, 257601 (2005).
 130 D. H. Kim, H. N. Lee, M. D. Biegalski, and H. M. Christen, *Applied Physics Letters*
92, 012911 (2008).
 131 K. Uchino, in *Ferroelectric Devices 2nd Edition* (CRC Press, 2009), p. 45.
 132 Y. Kui and F. Eng Hock Tay, *Ultrasonics, Ferroelectrics, and Frequency Control*,
IEEE Transactions on **50**, 113 (2003).
 133 R. Seshadri and N. A. Hill, *Chemistry of Materials* **13**, 2892 (2001).
 134 J. B. Neaton, C. Ederer, U. V. Waghmare, N. A. Spaldin, and K. M. Rabe, *Physical*
Review B **71**, 014113 (2005).
 135 P. Ravindran, R. Vidya, A. Kjekshus, H. Fjellvåg, and O. Eriksson, *Physical Review*
B **74**, 224412 (2006).
 136 V. M. Goldschmidt, *Naturwissenschaften* **14**, 477 (1926).
 137 A. Glazer, *Acta Crystallographica Section B* **28**, 3384 (1972).
 138 H. D. Megaw and C. N. W. Darlington, *Acta Crystallographica Section A* **31**, 161
 (1975).
 139 P. Fischer, M. Polomska, I. Sosnowska, and M. Szymanski, *Journal of Physics C:*
Solid State Physics **13**, 1931 (1980).
 140 F. Kubel and H. Schmid, *Acta Crystallographica Section B* **46**, 698 (1990).
 141 R. Shannon, *Acta Crystallographica Section A* **32**, 751 (1976).
 142 S. Geller and E. A. Wood, *Acta Crystallographica* **9**, 563 (1956).
 143 A. Y. Borisevich, et al., *Nat Commun* **3**, 775 (2012).
 144 M. Khodabakhsh, C. Sen, H. Khassaf, M. A. Gulgun, and I. B. Misirlioglu, *Journal of*
Alloys and Compounds **604**, 117 (2014).
 145 M. Guennou, P. Bouvier, G. S. Chen, B. Dkhil, R. Haumont, G. Garbarino, and J.
 Kreisel, *Physical Review B* **84**, 174107 (2011).
 146 A. F. Devonshire, *The London, Edinburgh, and Dublin Philosophical Magazine and*
Journal of Science **42**, 1065 (1951).
 147 D.-J. Kim, J.-P. Maria, A. I. Kingon, and S. K. Streiffer, *Journal of Applied Physics*
93, 5568 (2003).
 148 Y. Q. Jia, *J Solid State Chem* **95**, 184 (1991).
 149 F. Bai, N. Wang, J. Li, D. Viehland, P. M. Gehring, G. Xu, and G. Shirane, *J Appl*
Phys **96**, 1620 (2004).
 150 Y. Qi, et al., *Appl Phys Lett* **99**, 132905 (2011).
 151 Z. Chen, et al., *Appl Phys Lett* **97**, 242903 (2010).
 152 Z. H. Chen, L. You, C. W. Huang, Y. J. Qi, J. L. Wang, T. Sritharan, and L. Chen,
Appl Phys Lett **96** (2010).
 153 B. Cordero, V. Gomez, A. E. Platero-Prats, M. Reves, J. Echeverria, E. Cremades, F.
 Barragan, and S. Alvarez, *Dalton Transactions*, 2832 (2008).
 154 O. Diéguez, O. E. González-Vázquez, J. C. Wojdeł, and J. Íñiguez, *Physical Review*
B **83**, 094105 (2011).
 155 C.-S. Woo, et al., *Physical Review B* **86**, 054417 (2012).
 156 Z. Chen, L. You, C. Huang, Y. Qi, J. Wang, T. Sritharan, and L. Chen, *Applied*
Physics Letters **96**, 252903 (2010).

- ¹⁵⁷ A. R. Damodaran, S. Lee, J. Karthik, S. MacLaren, and L. W. Martin, *Physical Review B* **85**, 024113 (2012).
- ¹⁵⁸ L. You, Z. Chen, X. Zou, H. Ding, W. Chen, L. Chen, G. Yuan, and J. Wang, *ACS Nano* **6**, 5388 (2012).
- ¹⁵⁹ R. People and J. C. Bean, *Applied Physics Letters* **47**, 322 (1985).
- ¹⁶⁰ A. R. Damodaran, E. Breckenfeld, A. K. Choquette, and L. W. Martin, *Applied Physics Letters* **100** (2012).
- ¹⁶¹ K.-E. Kim, B.-K. Jang, Y. Heo, J. Hong Lee, M. Jeong, J. Y. Lee, J. Seidel, and C.-H. Yang, *NPG Asia Mater* **6**, e81 (2014).
- ¹⁶² M. D. Rossell, R. Erni, M. P. Prange, J. C. Idrobo, W. Luo, R. J. Zeches, S. T. Pantelides, and R. Ramesh, *Physical Review Letters* **108**, 047601 (2012).

List of Publications

1. Weigang Chen, Lu You, Gaofeng Chen, Yating Chua, Ong Hock Guan, Xi Zou, Junling Wang, Lang Chen, Nanoscale Polarization Relaxation of Epitaxial BiFeO₃ Thin Film, *Thin Solid Films*, 518 (2010) e169-e173.
2. Weigang Chen, Wei Ren, Lu You, Yurong Yang, Zuhuang Chen, Yajun Qi, Xi Zou, Junling Wang, Thirumany Sritharan, Ping Yang, L. Bellaiche, and Lang Chen, Domain structure and in-plane switching in a highly strained Bi_{0.9}Sm_{0.1}FeO₃ film, *Appl Phys Lett* **99** (22), 222904 (2011).
3. Yang Wang, Weigang Chen, Zuhuang Chen, Rami Chukka, Junling Wang, Lang Chen, Effective Control of Polarity in Bi_{0.9}La_{0.1}FeO₃ Thin Films by Dopant-related Internal Bias, *Phys Status Solidi A*, 208(2011), p919-23.
4. Lu You, Zuhuang Chen, Xi Zou, Hui Ding, Weigang Chen, Lang Chen, Guoliang Yuan, and Junling Wang, Characterization and Manipulation of Mixed Phase Nanodomains in Highly Strained BiFeO₃ Thin Films, *ACS Nano* (6), 5388 (2012).
5. Lu You, Shintaro Yasui, Yoshitaka Ehara, Xi Zou, Hui Ding, Zuhuang Chen, Weigang Chen, Lang Chen, Hiroshi Funakubo, and Junling Wang, Domain tuning in mixed-phase BiFeO₃ thin films using vicinal substrates, *Appl Phys Lett* **100** (20), 202901 (2012).
6. Xi Zou, Lu You, Weigang Chen, Hui Ding, Di Wu, Tao Wu, Lang Chen, and Junling Wang, Mechanism of Polarization Fatigue in BiFeO₃, *ACS Nano* (6), 8997 (2012).
7. Xi Zou, Hock Guan Ong, Lu You, Weigang Chen, Hui Ding, Hiroshi Funakubo, Lang Chen, and Junling Wang, Charge trapping-detrapping induced resistive switching in (Ba_{0.7}Sr_{0.3})TiO₃, *AIP Adv* 032166(2012) .