

STRAIN-ENGINEERED BISMUTH-BASED OXIDE THIN FILMS FOR MULTIFUNCTIONALITIES

by

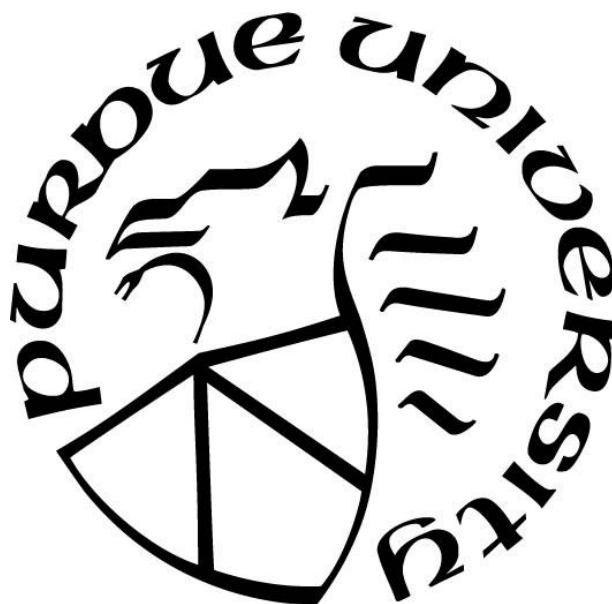
Han Wang

A Dissertation

Submitted to the Faculty of Purdue University

In Partial Fulfillment of the Requirements for the degree of

Doctor of Philosophy



School of Materials Engineering

West Lafayette, Indiana

August 2019

THE PURDUE UNIVERSITY GRADUATE SCHOOL
STATEMENT OF COMMITTEE APPROVAL

Dr. Haiyan Wang, Chair

School of Materials Engineering

Dr. Lia Stanciu

School of Materials Engineering

Dr. R. Edwin García

School of Materials Engineering

Dr. Xinghang Zhang

School of Materials Engineering

Approved by:

Dr. David Bahr

Head of the Graduate Program

To my grandmother

ACKNOWLEDGMENTS

I sincerely thank my advisor, Professor Haiyan Wang, for her patient guidance throughout my Ph.D. study at Purdue University. She is an outstanding scientist, researcher and mentor. It has been an honor and privilege learning from her. She guides her students to become independent researchers by demanding excellence and acting with integrity. The given trust and freedom allow us to try new ideas and plan our own research course. Her support for her students extends beyond academics. She encourages us to have a healthy work-life balance with emphasis on personal development. I will be continuously inspired by her energy, curiosity, tenacity and passion for her work.

I would like to acknowledge all my committee members, Dr. Lia Stanciu, Dr. R. Edwin García, and Dr. Xinghang Zhang for their great help and attention on my research. I also want to thank my former and present group members, Dr. Fauzia Khatkhatay, Dr. Jie Jian, Dr. Wenrui Zhang, Dr. Liang Jiao, Dr. Jijie Huang, Dr. Clement Jacob, Dr. Meng Fan, Xing Sun, Xingyao Gao, Zhimin Qi, Bruce Zhang, Matias Kalaswad, Shikhar Misra and Xin Li Phuah for their camaraderie and collaboration, in addition to the valuable insight I have gained through our many discussions. I extend my sincere gratitude to the staff at the School of Materials Engineering for their assistance with administrative and technical issues. I also would like to acknowledge the faculty and staff at the Birck Nanotechnology Center as well as the Life Science Microscopy Facility for their help and advice with equipment training, materials sample preparation, measurement, and analysis.

Finally, I want to thank my family for their continued support and encouragement for all my endeavors throughout my life. I really owe everything to them and their devotion.

TABLE OF CONTENTS

LIST OF TABLES	8
LIST OF FIGURES	9
NOMENCLATURE	13
ABSTRACT.....	14
CHAPTER 1. INTRODUCTION	16
1.1 Functional oxides and crystal structure	16
1.1.1 Overview of crystal structures.....	16
1.1.2 Perovskites.....	18
1.1.3 Layered perovskites.....	21
1.1.4 Spinel.....	23
1.2 Functionality and applications	24
1.2.1 Overview of functionality	24
1.2.2 Ferroelectricity	25
1.2.3 Ferromagnetic property	29
1.2.4 Multiferroicity	30
1.2.5 Optical Properties and Band Gap	31
1.3 Strain engineering in epitaxial perovskite oxide thin films	33
1.3.1 Epitaxial thin film and strain	33
1.3.2 Strain engineered ferroelectric oxide thin films	36
1.3.3 Strain engineered ferromagnetic oxide thin films	41
1.3.4 Strain effect on the optical properties of thin films.....	41
1.3.5 Novel layered structure induced by strain	42
1.3.6 Strain effect in superlattice and vertically aligned nanocomposites	43
CHAPTER 2. RESEARCH METHODOLOGY	50
2.1 Pulsed laser deposition	50
2.1 Structural characterization.....	53
2.1.1 X-Ray diffraction	53
2.2.2 Transmission electron microscopy.....	55
2.2.3 Scanning electron microscopy.....	59

2.3 Materials properties	62
2.3.1 Magnetic properties measurement.....	62
2.3.2 Polarization-electric field measurement	63
CHAPTER 3. STRAIN TUNING OF FERROELECTRIC AND OPTICAL PROPERTIES OF	
RHOMBOHEDRAL-LIKE BiFeO ₃ THIN FILMS ON SrRuO ₃ -BUFFERED SUBSTRATES..	
3.1 Overview	65
3.2 Introduction	66
3.2 Experimental	68
3.3 Results and discussion.....	69
3.3.1 BFO thin films growth	69
3.3.2 Microstructure characterization.....	72
3.3.3 Strain analysis.....	73
3.3.4 Electrical measurements.....	75
3.3.5 Optical measurements	77
3.3.6 Conclusions	79
3.3.7 Supplementary	79
CHAPTER 4. EFFECTIVE DOPING CONTROL IN Sm-DOPED BiFeO ₃ THIN FILMS VIA	
DEPOSITION TEMPERATURE	
4.1 Overview	81
4.2 Introduction	81
4.3 Experimental	83
4.4 Results and Discussion.....	84
4.4.1 BSFO thin film growth.....	84
4.4.2 Microstructure characterization.....	86
4.4.4 Ferroelectric measurements.....	89
4.4.5 Conclusions	90
4.4.6 Supplementary.....	91
CHAPTER 5. TWO-PHASE ROOM-TEMPERATURE MULTIFERROIC NANOCOMPOSITE	
WITH BiMnO ₃ TILTED NANOPILLARS IN Bi ₂ W _{1-x} Mn _x O ₆ MATRIX	
5.1 Overview	92
5.2 Introduction	93

5.3 Experimental	95
5.4 Results and discussion.....	97
5.4.1 BWMO-BMO thin film growth	97
5.4.2 Microstructure characterization.....	99
5.4.3 Magnetic and electrical characterization	104
5.3.4 Optical measurements	107
5.4 Conclusions	108
5.5 Supplementary.....	109
CHAPTER 6. MULTIFERROIC VERTICALLY ALIGNED NANOCOMPOSITE WITH	
CoFe ₂ O ₄ NANOCONES EMBEDDED IN LAYERED Bi ₂ WO ₆ MATRIX.....	112
6.1 Overview	112
6.2 Introduction	113
6.3 Experimental	115
6.4 Results and discussion.....	116
6.4.1 BWO:CFO film growth.....	116
6.4.2 Microstructure characterization.....	118
6.4.3 Electric and magnetical characterization.....	122
6.4.4 Conclusion.....	125
6.4.5 Supplementary.....	126
CHAPTER 7. SUMMARY AND FUTURE WORK	
REFERENCES	130

LIST OF TABLES

Table 1.1 The category of common functional oxide crystal structures	17
Table 1.2 Crystallographic classification of point groups according to centrosymmetry and polarity. ³⁰	25
Table 1.3 Summary of reported VAN systems	45
Table 1.4 Summary of functionalities in VAN systems	49
Table S3.1 EDS Analysis for Bi and Fe elements	80
Table S3.2 The FWHM of BFO (002).....	80
Table S5.1 STEM-EDS Analysis for W and Mn elements.....	109
Table S5.2 SEM-EDS Analysis for W and Mn elements	110

LIST OF FIGURES

Fig. 1.1 (a) Schematic of the ReO_3 cubic unit cell with cubic structure. (b) The corner-sharing octahedra in ReO_3 . (c) Perovskite ABO_3 structure from the cubic ReO_3 . (d) A unit cell of ABO_3 perovskite structure.	19
Fig. 1.2 Bulk BiFeO_3 with $R3c$ structure, represented by (a) hexagonal unit cell; (b) two pseudocubic unit cells; and (c) $2 \times 2 \times 2$ supercell. ¹⁵	21
Fig. 1.3 Crystal structures of layered perovskites: Dion–Jacobson $\text{KCa}_2\text{Nb}_3\text{O}_{10}$, Ruddlesden–Popper $\text{Sr}_4\text{Ti}_3\text{O}_{10}$ and Aurivillius $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. ¹⁷ Reproduced from Ref. 17 with permission from the Royal Society of Chemistry.	22
Fig. 1.4 Crystal structure of BWO.	23
Fig. 1.5 (a) The spinel crystal structure. (b) The crystal structure of CFO. ²⁸ Reproduced from Ref. 28 with permission from the Royal Society of Chemistry.	24
Fig. 1.6 The perovskite structure and two possible polarization states caused by the ionic movement of the B-site cation. ³³	28
Fig. 1.7 Ferromagnetic M-H loop corresponding to the two ways of domain alignment, randomly and parallelly.	29
Fig. 1.8 Multiferroics that exhibit ferromagnetic and ferroelectric properties simultaneously. ⁵³	31
Fig. 1.9 Band structures of Bi_2WO_6 photocatalyst. ⁶⁷	32
Fig. 1.10 Heteroepitaxial film growth: (a) lattice-matched, (b) coherently strained lattice-mismatched, and (c) incoherent growth-relaxed epitaxy.	34
Fig. 1.11 Epitaxial perovskite thin films and various perovskite substrates displayed above and below the number line, respectively. The number line represents the pseudocubic/pseudotetragonal a -axis lattice constants. ⁶⁹	35
Fig. 1.12 Various crystal structures of BFO thin films under the strain effect. ⁸⁶	37
Fig. 1.13 (a) Remnant polarization vs in-plane strain for BiFeO_3 films. (b) The spontaneous polarization direction of the rhombohedral (R) and monoclinic (MA and MB) phases of BFO. ⁸⁷ (c) Ab initio calculations of structure (c/a ratio) as a function of epitaxial strain of BFO films; (d) High resolution TEM image of the mixed T and R phase BFO on LAO substrate. ⁷³	38
Fig. 1.14 (a) Phase diagram of BaTiO_3 films as a function of temperature and substrate in-plane strain. ⁶⁹ (b) temperature dependent c lattice parameter of BaTiO_3 thin films grown with different laser fluences. ⁹²	39
Fig. 1.15 (a) Phase diagram of rare earth-doped BFO (Re-BFO) thin film. ⁹⁶ (b) d_{33} of BSFO thin films determined at various Sm doping. ⁹⁷	40
Fig. 1.16 STEM images of BFMO films on STO and LAO substrates under the same deposition conditions. ¹⁰³	42

Fig. 1.17 (a) Low magnification STEM image, (b) HR-STEM image and (c) atomic models of BaTiO ₃ /SrTiO ₃ superlattices. ¹⁰⁰	44
Fig. 1.18 Schematic representation of (a) relaxed unit cells of the substrate and the individual VAN phases; (b) substrate induced strain at the film-substrate interface and (c) vertical strain due to coupling between the two phases in the VAN film. ¹¹⁸	47
Fig. 1.19 Out-of-plane matching relationships between (a) BaTiO ₃ -YMnO ₃ (YMO) ¹³¹ and (b) La _{0.7} Sr _{0.3} MnO ₃ -CeO ₂ VAN films grown on SrTiO ₃ substrates (La _{0.7} Sr _{0.3} MnO ₃ = LSMO). ¹⁴³	48
Fig. 1. 20 A schematic showing theoretical out-of-plane strain matching relationship for various coupled two phase VAN structures. ¹¹⁸	48
Fig. 2.1 A schematic of the PLD system. ¹⁵¹	51
Fig. 2.2 A schematic of the interaction of high power laser with target. ¹⁵³	52
Fig. 2.3 Basic growth modes of thin films. ¹⁵⁵	53
Fig. 2.4 A schematic description of Bragg's Law for a set of crystal planes with d interplanar spacing. ¹⁵⁶	54
Fig. 2.5 Major components of TEM. ¹⁵⁸	56
Fig. 2.6 Two basic modes of operation in a TEM: (a) diffraction and (b) imaging. ¹⁵⁹	57
Fig. 2.7 Schematic diagram showing the (a) bright-field, (b) dark-field and high-resolution TEM imaging modes ¹⁶⁰	58
Fig. 2.8 The major components and their layout in a SEM. ¹⁶¹	60
Fig. 2.9 Relative escape depths for different secondary species created due to interaction. ¹⁶²	61
Fig. 2.10 PPMS basic components with an illustration of VSM part. ^{163,164}	62
Fig. 2.11 (a) The original Sawyer-Tower circuit ¹⁶⁵ and (b) a schematic of the Sawyer-Tower measurement. ¹⁶⁶	63
Fig. 3.1 (a) θ -2 θ XRD scans of BFO on SRO/LAO, SRO/STO, SRO/MgO and SRO/TiN/Sisubstrates. Au and TiO ₂ peaks are denoted as “*” and “#”. (b) Local XRD scan of BFO (002) peak. (d)-(f) Reciprocal space map (RSM) results of BFO (103) peak on SRO/LAO, SRO/STO and SRO/MgO, respectively.	69
Fig. 3.2 (a)-(d) Cross-sectional TEM images of BFO on SRO/LAO, SRO/STO, SRO/MgO and SRO/TiN/Si substrates, respectively. The inset shows the corresponding (SAED) pattern of BFO thin films. White arrows mark the interface between each layer.	72
Fig. 3.3 (a1)-(a2) Cs-corrected high-resolution STEM images of BFO on SRO/LAO and SRO/MgO substrates, and (b1)-(b2) their corresponding GPA ϵ_{xx} (in-plane strain) maps and (c1)-(c2) ϵ_{yy} (out-of-plane strain) maps.	73
Fig. 3.4 (a) Comparison of polarization hysteresis measurements for BFO on SRO/LAO, SRO/STO, SRO/MgO and SRO/TiN/Si. (b) Amplitude switching behavior as a function of tip bias with (c) their corresponding phase switching behavior.	75

Fig. 3.5 (a) Optical transmission spectrums of BFO on SRO/LAO, SRO/STO and SRO/MgO substrates. (b) The corresponding plot of $(\alpha h\nu)^2$ versus $h\nu$. The inset shows the summary of optical bandgap versus pseudocubic substrate lattice constant.....	77
Fig. S3.1 Comparison of pseudocubic lattice parameters. Epitaxial BFO thin film and substrates displayed above and below the number line, respectively.....	79
Fig. 4.1 (a) θ - 2θ XRD spectra of BSFO film deposited at 670 °C, 640 °C and 600 °C. (b) The summary of out-of-plane lattice parameter. (c)-(e) Reciprocal space map (RSM) results of BSFO (103) peaks.....	84
Fig. 4.2 (a) (c) Cross-sectional TEM images of BSFO thin films on STO substrates. (b) (d) High resolution TEM images. The insets in (a) and (c) show the corresponding (SAED) pattern of BSFO thin films. The insets in (b) and (d) show the fast-Fourier transformed (FFT) images from the blue squared region.	86
Fig. 4.3 (a) HR-STEM image of BSFO film deposited at 670 °C. (b) Enlarged view of the yellow dashed square area from (a). The intensity line profile is inserted along the marked blue line. ..	88
Fig. 4.4 (a)-(c) Polarization hysteresis measurements for BSFO film deposited at 670 °C, 640 °C and 600 °C. (d) Polarization hysteresis measurements for BFO film.	89
Fig. S4.1 HAADF image (a) with EDS mapping of Bi (b) and Sm (c) for BSFO thin film. The overlays in (a) shows the EDS line-scan profiles of Sm across the white line.....	91
Fig. 5.1 (a) Schematic crystal structure of Bi_2WO_6 (BWO). (b) θ - 2θ XRD scans of BWMO-BMO and BWO on LAO substrates.	97
Fig. 5.2 (a, c) Cross-sectional TEM images of BWMO-BMO and BWO thin films on LAO substrates. (b, d) The corresponding SAED patterns of thin films.	99
Fig. 5.3 Microstructure study of BWMO-BMO. (a) plan-view STEM image of a selected area of the film, with (b) EDS mapping and (c) atomic-scale high-resolution image of the marked area. (d) Cross-sectional STEM image of a selected area of the film with (e) EDS mapping and (f) atomic-scale high-resolution STEM image of pillar-like structure. Atomic model was used to illustrate the matrix and nanodomain area. (g) 3D construction of the film, in which the red pillars represent the BMO nanodomains and the blue area signifies the BWMO matrix.....	101
Fig. 5.4 (a) In-plane (IP) and (b) Out-plane (OP) magnetization hysteresis loops of BWMO-BMO and BWO at 300K. (c) Polarization hysteresis measurement for BWMO-BMO.(d) Amplitude and phase switching behavior of BWMO-BMO.	104
Fig. 5.5 Optical transmission spectrums of BWMO-BMO and BWO. The inset shows the corresponding plot of $(\alpha h\nu)^2$ versus $h\nu$	107
Fig. S5.1 HR-STEM of the film-substrate interface.	110
Fig. S5.2 (a) STEM image of the enlarged pillar-like area. (b) The corresponding (004) fast Fourier filtered image.	111
Fig. S5.3 The XPS spectrum of Mn $2p_{3/2}$	111

Fig. S5.4 Room temperature polarization vs magnetic field of BWMO-BMO. The black solid line indicates the result of linear fitting.	111
Fig. 6.1(a) Atomic models of Bi_2WO_6 (BWO), CoFe_2O_4 (CFO) and LaAlO_3 (LAO). (b) Schematic diagram of VAN structure. CFO phase is represented by red pillars and denoted with C, while BWO is the rest green area. (c) θ - 2θ XRD scans of BWO:CFO, BWO and CFO on LAO substrates, respectively.	116
Fig. 6.2 (a) Cross-sectional TEM image of BWO:CFO. (b) The corresponding SAED pattern from thin film area. BWO phase is denoted with B. (c) HRTEM image along the interface between BWO and CFO. The insets show the fast-Fourier transformed (FFT) images from BWO and CFO phases. (d) The corresponding FFT filtered image (the dashed line guides the interface).	118
Fig. 6.3 Microstructure study of BWO:CFO. (a) plan-view STEM image of a selected area of the film, with (b) EDS mapping of the marked area and (c) atomic-scale high resolution image of one pillar interface. (d) Cross-sectional STEM image of a selected area of the film with (e) the corresponding EDS mapping and (f) atomic-scale high resolution STEM image of BWO:CFO interface. (g) The atomic models of the coupling between BWO and CFO. (h) 3D construction of the film.	120
Fig. 6.4 (a) In-plane (IP) and Out-plane (OP) magnetization hysteresis loops of BWO:CFO and pure CFO at 300K. (b) Polarization hysteresis measurement for BWO:CFO and pure BWO. (c) Amplitude and phase switching behavior of BWO:CFO.	122
Fig. S6.1 XRD θ - 2θ scans of BWO:CFO deposited at 2Hz and 10Hz.	126
Fig. S6.2 (a, c) Cross-sectional TEM images of pure BWO and CFO phases. (c, d) The corresponding SAED patterns.	127

NOMENCLATURE

AFM	Antiferromagnetic
DME	Domain matching epitaxy
EDS	Energy-dispersive X-ray spectroscopy
FE	Ferroelectric
FM	Ferromagnetic
HAADF	High angle annular dark field
IP	In-plane
OP	Out-of-plane
PFM	Piezoelectric force microscopy
PLD	Pulsed laser deposition
PM	Paramagnetic
RSM	Reciprocal space mapping
SEM	Scanning electron microscopy
STEM	Scanning transmission electron microscopy
T_C	Curie temperature (ferromagnetic or ferroelectric)
TEM	Transmission electron microscopy
VAN	Vertically aligned nanocomposites
VSM	Vibrating sample magnetometer

ABSTRACT

Author: Wang, Han. PhD

Institution: Purdue University

Degree Received: August 2019

Title: Strain-engineered Bismuth-based Oxide Thin Films for Multifunctionalities

Committee Chair: Prof. Haiyan Wang

Multifunctional characteristics of Bismuth-based oxides offer great opportunities to design a variety of devices exploiting either a single functionality or the synergistic multifunctionalities. In the past decades, strain engineering of thin films arose as a solution for fabrication of novel structures with highly desired properties. In this thesis, strain engineering has been applied to Bismuth-based oxides to explore the strain effect on thin film structures and functionalities.

BiFeO_3 (BFO) serves as the first study platform, because of its strain-induced phase transition and the corresponding diverse polarization properties. The strain effect of SrRuO_3 (SRO)-buffered substrates on ferroelectric and optical properties of BFO thin films has been investigated. A wide range of strain states have been achieved in BFO films. The ferroelectricity and bandgap have been effectively tuned even with partial strain relaxation. However, pure BFO suffers from high leakage current and large coercive field. To overcome these limitations, Sm-doped BFO (BSFO) systems emerged and has been used in controlling the microstructure and properties of BFO. Our detailed structure analysis proves the Sm doping amount in BSFO thin films can be tuned effectively via deposition temperature. Consequently, the Sm dopant influences phase formation of BSFO and the macroscopic ferroelectric properties.

Another member in Bismuth-based oxide family, Bi_2WO_6 (BWO), has been selected as the base material for the design of the two-phase nanocomposites, because of its unique layered structure and ferroelectric property. To introduce ferromagnetic component into BWO, two

methods have been explored. The first method incorporates Mn cations into the BWO matrix (BWMO), and the second method couples CoFe_2O_4 (CFO) as secondary phase with BWO to form a vertically aligned nanocomposite (VAN) system. Both systems exhibit robust ferromagnetic and ferroelectric response at room temperature and demonstrate their promise as room temperature multiferroics for future spintronics and memory applications.

The studies in this dissertation demonstrate the great structure flexibility and tunable functionalities of BFO and BWO systems. It shows the potential structure modification and property control of other Bi-based oxides. In the last chapter, new experimental plans and directions are proposed. The connections between the strain engineering and the tunable material properties are being built for various applications.

CHAPTER 1. INTRODUCTION

Functional oxides play important roles in technological advances, owing to their chemical diversity and their wide range of functionalities. For example, ZnO with a wide bandgap is ideal for optoelectronic applications such as UV and blue laser diodes; BaTiO₃ with high dielectric permittivity and ferroelectricity has been considered as potential gate oxide materials in transistor. Single phase multiferroics include BiFeO₃ and BiMnO₃ which combine ferroelectric and ferromagnetic properties together are attractive for researchers. It is an exciting prospect for memory applications, combining the properties of and offering functionalities beyond both. These functionalities are determined largely by the crystal structures, bonding, and defects in the material.

Advances in nanotechnology and fabrication have enabled precise control of device dimensions down to the nanoscale, where unique functionalities have been realized, while not observed in bulk materials. Strain engineering of thin films arose as a solution for fabrication of novel structures with highly desired properties. According to the origin of the strain, there are three approaches on strain tuning: substrate induced strain, multilayer induced strain and vertically aligned nanocomposite (VAN) induced strain. In the following chapter, a brief review on the oxide structure and their functionalities will be given. Then each strain tuning approach is introduced. Detailed examples of oxides will be used to illustrate how these strain tuning approaches could enhance the ferroelectricity, multiferroicity and optical properties of thin films.

1.1 Functional oxides and crystal structure

1.1.1 Overview of crystal structures

Crystal structure is the basis for analyzing and subsequently controlling materials' properties and functionalities. The various crystal structures are largely due to the bonding effect,

with the bonding in functional oxides being predominantly ionic. The covalency of constituent atoms has a direct impact on physical properties. There are mainly two kinds of functional oxides based on the components: binary and ternary oxides. Table 1.1 briefly lists representative functional oxides of the two kinds with their corresponding structures. Binary oxides occupy a wide range of structures and the common structures include rock salt, wurtzite, rutile, fluorite, bixbyite, and corundum. Ternary oxides exist in more complex chemical structures, which include ilmenite ((AB)O₃; A, B = metal), spinel (AB₂O₄), perovskite (ABO₃), and perovskite-derived structures like the layered-perovskites, Ruddlesden–Popper (A_{n+1}B_nO_{3n+1}), Aurivillius ([Bi₂O₂]-[ABO₇]) and Dion-Jacobson phases (A[A'_{n-1}B_nO_{3n+1}]).¹ These ternary oxides display interesting properties like piezoelectricity, ferroelectricity, ferromagnetism, multiferroicity, superconductivity and thermoelectricity.

Table 1.1 The category of common functional oxide crystal structures

System	Structure	Representative Materials
Binary oxides	Rock salt	CoO, Eu ₂ O ₃ , MgO, MnO, Nd ₂ O ₃ , NiO, Sm ₂ O ₃ , TiO, VO, ZrO
	Wurtzite	ZnO, BeO
	Fluorite	CeO ₂ , HfO ₂ , ZrO ₂ , PrO ₂ , TbO ₂ , ThO ₂
	Antifluorite	Li ₂ O, Na ₂ O, K ₂ O, Rb ₂ O
	Cuprite	Cu ₂ O, Ag ₂ O, Pb ₂ O

Table 1.1 continued

	Rutile	TiO ₂ , IrO ₂ , MoO ₂ , RuO ₂ , SnO ₂ , WO ₂
	Bixbyite	Pr ₂ O ₃ , Tl ₂ O ₃
	Corundum	Al ₂ O ₃ , V ₂ O ₃ , Cr ₂ O ₃
Ternary oxides	Ilmenite	(Fe, Co, Ni, Mn)TiO ₃ , CoMnO ₃ , LiNbO ₃ , NiMnO ₃
	Spinel	(Co, Ni, Mn)Fe ₂ O ₄ , LiTi ₂ O ₄ , MgAl ₂ O ₄ ,
	Perovskite	SrTiO ₃ , BaTiO ₃ , BiFeO ₃ , La _x Sr _{1-x} MnO ₃
Perovskite-derived oxides	Layered perovskite	YBa ₂ Cu ₃ O _{7-δ}
	Ruddlesden-popper series	Sr ₂ RuO ₄ , Sr ₃ Ru ₂ O ₇
	Aurivillius phases	Bi ₂ WO ₆ , Bi ₃ TiNbO ₉
	Dion-Jacobson series	KLaNb ₂ O ₇ , CsLaNb ₂ O ₇

1.1.2 Perovskites

Perovskite exhibits a general structure and occupies a large part of ternary oxides. Its chemical formula is ABO₃ and built based on the ReO₃ structure as shown in Fig.1.1(a).² The lattice parameter of ReO₃ is 3.8 Å. Fig.1.1(b) illustrates another way for describing ReO₃ structure as corner-sharing octahedral structure. The assemblage of ReO₃ corner shared cubic produces perovskite structure. Cation A replaced the position of Re and cation B occupies the center of oxygen octahedra. The final perovskite structure is shown from Fig.1.1(c)-(d). Cations A and B cations are coordinated by 12 and 6 oxygen ions, respectively.

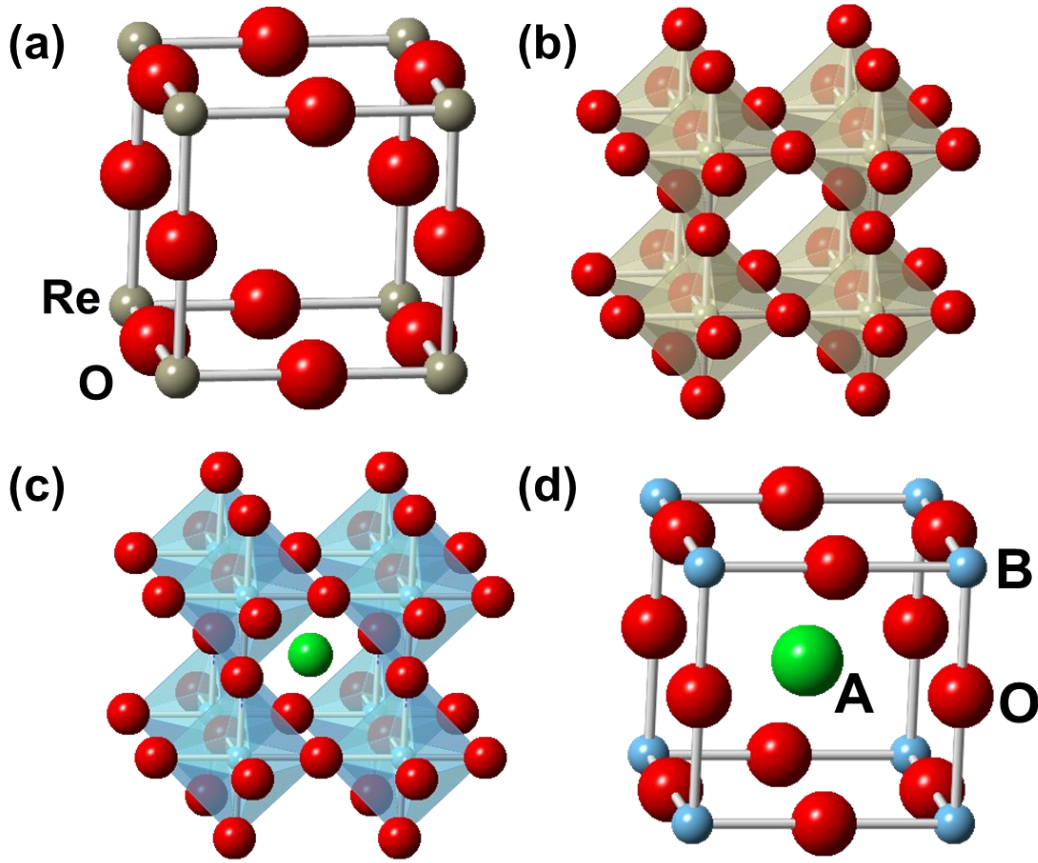


Fig. 1.1 (a) Schematic of the ReO_3 cubic unit cell with cubic structure. (b) The corner-sharing octahedra in ReO_3 . (c) Perovskite ABO_3 structure from the cubic ReO_3 . (d) A unit cell of ABO_3 perovskite structure.

In an ideal cubic perovskite, the lattice parameter a geometrically related to its three component ionic radii, r_A , r_B , and r_O as described in the following equation³:

$$a = \sqrt{2}(r_A + r_O) = 2(r_B + r_O) \quad (1-1)$$

The ratio of the two expressions above is called Goldshmidt's tolerance factor t and can be used for the estimation of structure distortion, given by the equation⁴:

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \quad (1-2)$$

SrTiO_3 (STO) exhibits an ideal cubic prototype perovskite structure, where $r_{\text{A/Sr}} = 1.44 \text{ \AA}$, $r_{\text{B/Ti}} = 0.605 \text{ \AA}$, and $r_{\text{O}} = 1.40 \text{ \AA}$, resulting in $t = 1$. A deviation from the unity in the value of t represents a distortion of the cubic unit cell. With the exception of STO, most ABO_3 perovskites have a distortion in the cubic cell structure.

The covalence diversity of A and B cations introduces various structures in perovskite, but it can still be categorized into three types: $\text{A}^{+1}\text{B}^{+5}\text{O}_3$ ($\text{A} = \text{Na, K, Ag}$; $\text{B} = \text{I, Nb, Ta}$), $\text{A}^{+2}\text{B}^{+4}\text{O}_3$ ($\text{A} = \text{Ca, Sr, Ba, Pb}$; $\text{B} = \text{Ti, Zr, Fe, Mn, Sn, Mo, Hf}$), and $\text{A}_{+3}\text{B}_{+3}\text{O}_3$ ($\text{A} = \text{Y, Bi, La, Pr, Sm}$; $\text{B} = \text{Al, Ti, V, Fe, Co, Mn, Cr}$). Oxides from the third class are mostly (anti)ferromagnetic (BiFeO_3 , $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$), while those from the first two classes are ferroelectric (BaTiO_3 , NaNbO_3).

BiFeO_3 (BFO) has been studied extensively among various perovskites, due to its room temperature multiferroic property, e.g., strong ferroelectric polarization and magnetoelectric coupling.^{5,6} The first report of BFO was published in 1957, and its crystal structure was first characterized by neutron technology after six years later.⁷⁻⁹ BFO belongs to the rhombohedral $R3c$ space group (R phase), where Bi cations occupy the 12 coordinate A site and Fe cations sit the 6 coordinate B site. BFO has lattice parameters $a = 3.965 \text{ \AA}$, $\alpha = 89.45^\circ$, so it can be referred as pseudocubic structure.^{10,11} Fig.1.2 shows three different ways to illustrate the bulk BFO with rhombohedral structure. The perovskite structures of BFO are remarkably flexible and allows distortion. Many factors of variation, such as temperature, strain and composition, are utilized for structure modification. As temperature increases to 1100 K, BFO transits from R phase to orthorhombic($Pbnm$) phase with first-order phase transition.¹²⁻¹⁴ BFO in thin film format also exhibits a plethora of structural transition and correspondingly it generates unexpected behaviors, as will be discussed later.

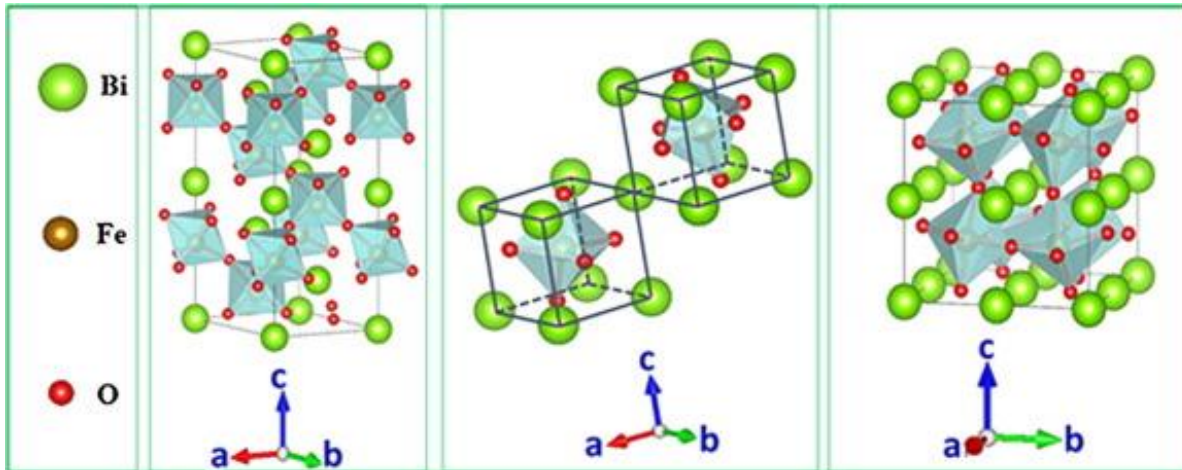


Fig. 1.2 Bulk BiFeO_3 with $R3c$ structure, represented by (a) hexagonal unit cell; (b) two pseudocubic unit cells; and (c) $2 \times 2 \times 2$ supercell.¹⁵

1.1.3 Layered perovskites

Layered perovskites are built by perovskite ABO_3 layers interleaved with thin sheets of A or B cations. Based on the thickness of motifs, there are mainly three types of layered perovskites: Dion-Jacobson, Ruddlesden-Popper and Aurivillius phases, illustrated by Fig. 1.3.^{16,17} The structure of Aurivillius phases is built from $(\text{Bi}_2\text{O}_2)^{2+}$ layers alternating with $(\text{A}_{n+1}\text{B}_n\text{O}_{3n+1})^{2-}$ blocks of perovskites, where A is a large 12-coordinated cation and B is a small cation with 6 coordinate. One important and intriguing feature of Aurivillius phases is the compositional flexibility of A site, such as Na^+ , K^+ , Sr^{2+} , Ca^{2+} , Bi^{3+} , Ba^{2+} , Ln^{3+} , Y^{3+} , U^{4+} , and B site, such as Fe^{3+} , Ga^{3+} , Ti^{4+} , Nb^{5+} , W^{6+} . In addition, n represents the number of BO_6 octahedra layers.¹⁸ These compounds show ferroelectric properties, which is considered due to the transition metal cations in perovskite layer.¹⁹ The high transition temperature encourages the materials to be applied in capacitors, sensors, condensers, transducers, memory storage and electro-optical devices.^{20,21}

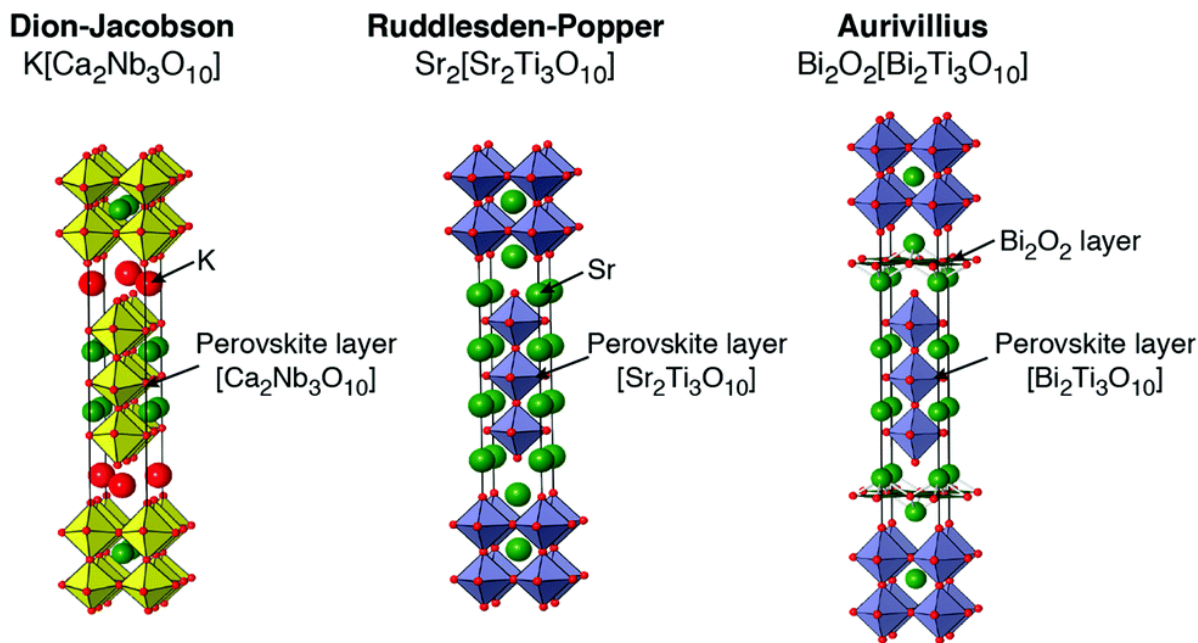


Fig. 1.3 Crystal structures of layered perovskites: Dion–Jacobson $KCa_2Nb_3O_{10}$, Ruddlesden–Popper $Sr_4Ti_3O_{10}$ and Aurivillius $Bi_4Ti_3O_{12}$.¹⁷ Reproduced from Ref. 17 with permission from the Royal Society of Chemistry.

Bi_2WO_6 (BWO) is the simplest member in the Bi-based layered structure family with only one layer of Bi_2O_2 . It displays orthorhombic crystal structure with parameters: $a = 5.457 \text{ \AA}$, $b = 5.436 \text{ \AA}$, $c = 16.427 \text{ \AA}$ and belongs to $P2_1ab$ space group.²² The crystal structure is shown in Fig. 1.4. It shows ferroelectricity at room temperature and has a high Curie temperature (T_c) of $960 \text{ }^\circ\text{C}$.²³ The ferroelectricity is attributed to the displacement of W cation from the oxygen octahedron.²⁴

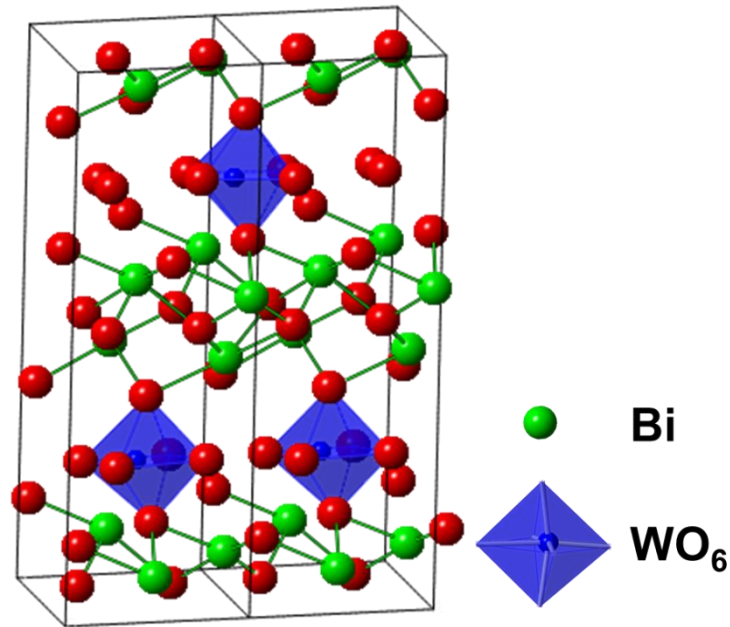


Fig. 1.4 Crystal structure of BWO.

1.1.4 Spinel

Spinel structure exhibits a close-packed array of eight FCC cells and has a general formula AB_2O_4 . Each spinel unit cell consists of 32 oxygen atoms, 8 A cations and 16 B cations, as shown in Fig. 1.5 (a). For the inverse spinel structure, the A sites and B sites switch places. $CoFe_2O_4$ (CFO) is a well-known member in magnetic oxides, due to the high coercivity and moderate magnetization.²⁵ CFO exhibits an inverse spinel structure with lattice parameter $a = b = c = 8.39$ Å.²⁶ It resides in the $Fd\bar{3}m$ space group (no. 227), where Fe^{3+} cations occupy the tetrahedral sites and half of the octahedral sites, whereas Co^{2+} ions are located at the remaining octahedral sites.²⁷ The CFO crystal structure is illustrated in Fig. 1.5 (b).²⁸

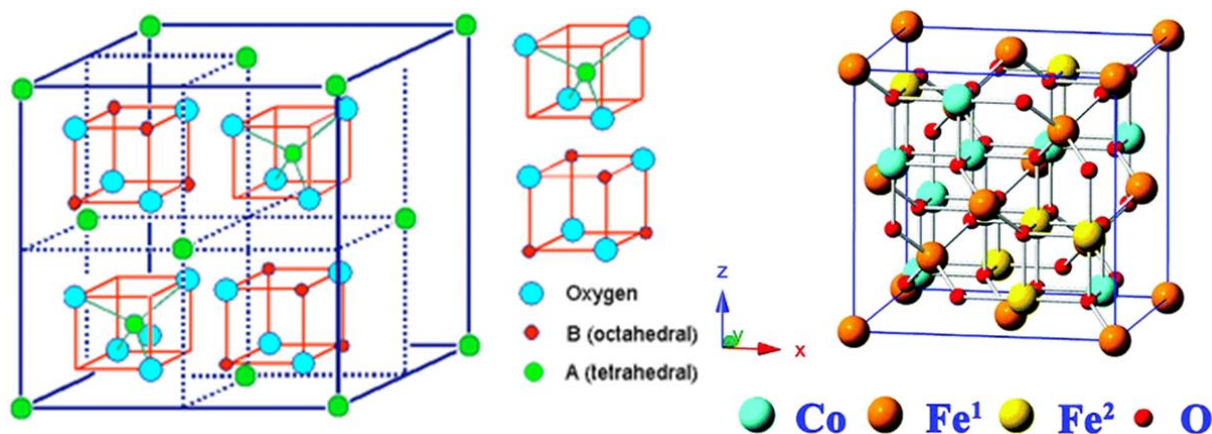


Fig. 1.5 (a) The spinel crystal structure. (b) The crystal structure of CFO. ²⁸ Reproduced from Ref. 28 with permission from the Royal Society of Chemistry.

1.2 Functionality and applications

1.2.1 Overview of functionality

Functional oxides with various crystal structures, (a)symmetry, and defects form the basis for smart materials whose properties can be altered by external conditions. The fascinating properties include dielectric, optical, ferroelectric, ferromagnetic, multiferroic, and resistance switching properties. Ferroelectricity is a property which a material possesses a spontaneous polarization that can be reversed by an applied electric field. Ferromagnetic materials develop a spontaneous magnetization in the absence of a magnetic field. Multiferroic property which couples the ferroelectric and ferromagnetic properties together offers the possibility of using electric field to control the magnetism. The electronic structure is responsive to the external perturbation such as strain, electric field and magnetic field, and moderately influences the optical properties. These phenomena will be discussed in further detail.

Table 1.2 Continued

polar (10)	non-centro (10)			6mm	6	4mm	4	3m	3	mm2	2 m	1
---------------	--------------------	--	--	-----	---	-----	---	----	---	-----	--------	---

The shaded groups are piezoelectric, while those within the bold line are pyroelectric.

Several parameters are considered when evaluating the piezoelectric properties of a material:³⁰

The piezoelectric strain constant d (also called the piezoelectric charge coefficient) relates the induced polarization P to the applied mechanical stress X in the direct piezoelectric effect by

$$P = dX \quad (1-3)$$

d also relates the induced strain x to the external electric field E in the converse piezoelectric effect by

$$x = dE \quad (1-4)$$

d has units of C/N for the direct effect and m/V in the case of the converse effect. d is typically written as d_{ij} , indicating that the coefficient relates the polarization perpendicular to the i direction due to a mechanical stress applied in the j direction. For example, d_{33} denotes coefficient for the polarization generated in the vertical direction due to a stress applied in the vertical direction, and d_{31} denotes the coefficient for the polarization in the vertical direction due to a stress applied in the lateral direction. A similar notation is used for other variables defined in this section.

E is related to the externally applied stress X by the piezoelectric voltage constant g by

$$E = gX \quad (1-5)$$

The relationship between d and g is given by

$$g = \frac{d}{\epsilon_0 \epsilon} \quad (1-6)$$

where ε is the permittivity of the piezoelectric material (also known as the dielectric constant) and ε_0 is the permittivity of free space.

An important gauge for the rate of conversion between mechanical energy and electrical energy is the electromechanical coupling factor k given by

$$k^2 = \frac{\text{stored mechanical energy}}{\text{input electrical energy}} = \frac{\text{stored electrical energy}}{\text{input mechanical energy}} = \frac{d}{\varepsilon_0 \varepsilon s} \quad (1-7)$$

where s is the elastic compliance of the material. Of the 20 piezoelectric crystal classes, 10 spontaneously form permanent dipoles depending on the operating temperature.³⁰ These materials are designated as pyroelectrics because the magnitude of the spontaneous polarization is temperature dependent. Within the lattice of these crystal classes there exists a unique polar axis, which is why they are also referred to as polar materials.³³ Ferroelectrics are a subgroup of pyroelectrics, which possess a spontaneous polarization that can be reversed by the application of an external electric field. The perovskite group, or the oxygen octahedral group, is the most commonly implemented family of ferroelectric materials. In the typical ABO_3 unit cell, the polarization reversibility is primarily due to the displacement of the body centered B-site atom, housed within the corner-linked oxygen octahedral.³³ Upon the application of an electric field, the B-site atom assumes its new position along the direction of this field, corresponding to one of six polarization states depending on the direction of the applied field, polarization up and polarization down, shown in Fig. 1.6. The small ionic movement results in a change in the dimensions of the unit cell and consequently the ceramic material. The material is said to be ferroelectric when the dipoles are oriented parallel to each other. In cases where they are oriented in an antiparallel arrangement, the material is antiferroelectric. The ferroelectric materials can be used for the fabrication of transistors.

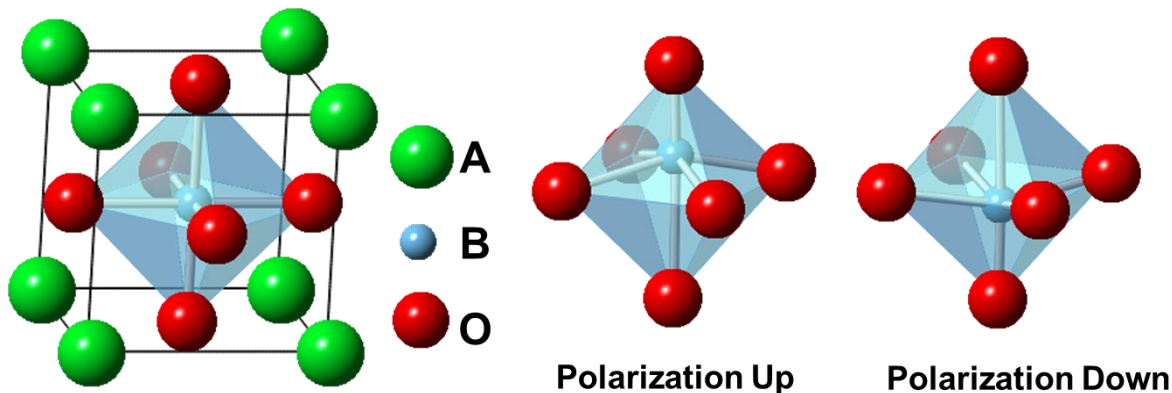


Fig. 1.6 The perovskite structure and two possible polarization states caused by the ionic movement of the B-site cation.³³

In 1970, the spontaneous polarization measurement was applied on BFO single crystal firstly and it turns out $3.5 \mu\text{C}/\text{cm}^2$ along the $\langle 001 \rangle$ direction.³⁴ In 2003, a larger spontaneous polarization of $50 \sim 60 \mu\text{C}/\text{cm}^2$ was shown by epitaxial BFO thin films at room temperature, which have been of great experimental interest as lead-free ferroelectrics.³⁵ A much larger spontaneous polarization of $90 \sim 100 \mu\text{C}/\text{cm}^2$ was predicted in 2005 by density functional theory.³⁶ The large ferroelectric polarization was attributed to the instability caused by Bi 6s lone pair structure and was proven as an intrinsic behavior.^{34,37} In the past decades, many efforts have been paid to tune the structure and ferroelectric properties of BFO thin films. For example, Ga doped BFO thin films were predicted to exhibit a giant polarization up to $\sim 230 \mu\text{C}/\text{cm}^2$, which may be due to the super-tetragonal phases with a giant c/a ratio of 1.25.^{38,39}

Aurivillius phases are also well known for their ferroelectric properties. They display low dielectric constants, high Curie temperatures and low fatigue.^{40,41} In the Aurivillius phase where perovskite layers are sandwiched by two $(\text{Bi}_2\text{O}_2)^{2+}$ layers, the Bi layers play a key role in the space charge compensation and insulation, which is also thought of as a barrier for the leakage current.

⁴² The strong anisotropy of ferroelectric properties is also correlated with the crystalline structure.

^{43,44} The integer number n , representing the number of perovskite layers, can determine the

spontaneous polarization (P_s). If n is even, the material will only exhibit P_s along the a axis, due to the symmetry and the sliding planes perpendicular to the b and c axis. The layered structure and ferroelectric properties offer great opportunities to tailor properties with incorporation of ions or another material.

1.2.3 Ferromagnetic property

Magnetic materials are made of atoms with partially filled shells. Due to the electrons having unpaired spins, these materials will have a net magnetic moment. When these unpaired dipoles (spins) tend to align with an external magnetic field, the phenomenon is known as the paramagnetic effect. Interestingly, ferromagnetism has an additional phenomenon where the dipoles can align spontaneously even in the absence of a magnetic field, which gives rise to spontaneous magnetization. Fig. 1.7 shows the magnetic hysteresis loop and alignments of domains under the external magnetic field.

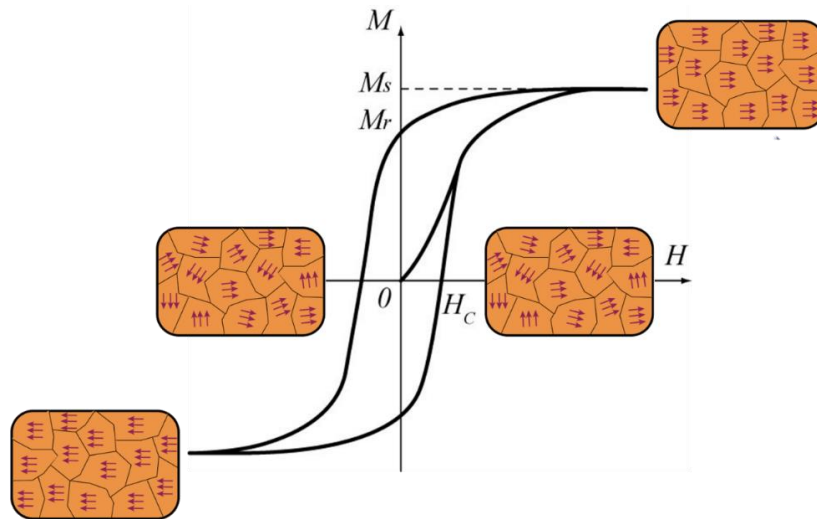


Fig. 1.7 Ferromagnetic M-H loop corresponding to the two ways of domain alignment, randomly and parallelly.

Rhombohedral BFO has a high Néel temperature T_N of 640K.⁴⁵ However, it possesses weak antiferromagnetic property due to the spin canting that is induced by the tilting of the oxygen

octahedra.⁴⁶ CFO is well known for its stable ferromagnetic property with a high magnetic saturation (M_S) of 400 emu/cm³ and the high Curie temperature T_C of 860K.^{47,48} In addition, it possesses a positive magnetocrystalline anisotropy constant $K_1 \sim 3 \times 10^6$ ergs/cm³, which is greater than other spinel structure ferrites and results in a high coercivity (H_C).⁴⁹ BMO exhibits various structure with different O stoichiometry, which controls the magnetic properties.

The unique magnetic properties of CFO make it a great candidate for magnetic spin filters and spintronics devices.^{50,51} It has commonly been used as the ferromagnetic materials in of read/write heads and in commercial magnetic recording media.⁵² Research on ferromagnetic materials continues to gather attention as spintronic devices are considered among the class of the so-called “next-generation” memory devices and potential candidates for “universal” memory devices to replace current CMOS technology. Multilayer devices have been engineered to exhibit interesting structures and properties based on the combination of ferromagnetic, insulating, nonmagnetic, and antiferromagnetic materials.

1.2.4 Multiferroicity

Multiferroic materials simultaneously display the properties of ferroelectricity and ferromagnetism, making it possible to change the magnetization by an applied electric field or to change the polarization by an applied magnetic field. Fig. 1.8 is an illustration of multiferroic materials.⁵³ Multiferroic properties were first demonstrated in $\text{Ni}_3\text{B}_7\text{O}_{13}\text{I}$ in the late 1960s.⁵⁴ The coupling between the magnetization and electric field gives one more degree of freedom for materials design used in actuators and storage devices. The most common single phase multiferroic perovskites include BiFeO_3 , BiMnO_3 , YMnO_3 , and $\text{Pb}(\text{Fe,Nb})\text{O}_3$. More recently, composite films of ferroelectric and ferromagnetic materials have been engineered to explore their magnetoelectric coupling, e.g. CoFe_2O_4 with ferroelectrics such as BiFeO_3 and BaTiO_3 .

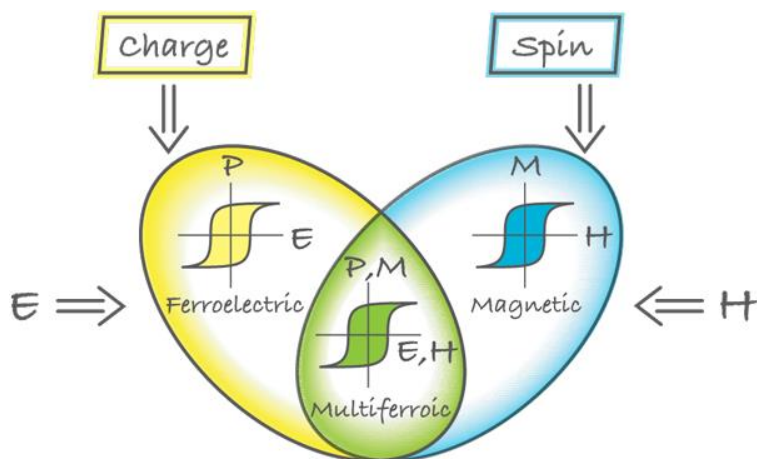


Fig. 1.8 Multiferroics that exhibit ferromagnetic and ferroelectric properties simultaneously.⁵³

Aurivillius phase is a potential candidate for multiferroic materials design, due to its original ferroelectric properties. The main barrier for obtaining the magnetic property is the built-in magnetic ions. However, the chemical structure of the Aurivillius compound is flexible. A study on $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ shows there are two main ways for creating magnetic Aurivillius structure: one way is to focus on the compound with a higher number of perovskite layers ($m > 4$); the other way is to increase the magnetic cations in the structure.⁵⁵ For example, ferromagnetism was observed in $\text{Bi}_5\text{Ti}_3\text{Fe}_{0.5}\text{Ni}_{0.5}\text{O}_{15}$ after half of the Fe cations in $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ ($m = 4$) were substituted by Ni ions.⁵⁶

1.2.5 Optical Properties and Band Gap

Semiconductor material BFO has a lower band gap, around 2.75 eV, than most other ABO_3 perovskites, such as BaTiO_3 .^{57,58} There has been evidence of BFO having a direct band gap, which may be due to a rather flat valence band.⁵⁹ In addition, BFO has demonstrated a strong photovoltaic effect and larger electro-optic coefficients than any ferroelectric materials, and thus gained great interests for its potential applications in photonics and plasmonics.⁶⁰⁻⁶² BFO thin films are birefringent, comparable to its bulk properties.^{63,64} The large birefringence endows BFO

with a potential for optical or plasmonic modulators. Bulk photovoltaic (BPV) effect is also exhibited by BFO thin films. Experiments suggest a strong coupling between its ferroelectric and optical properties, which makes BFO an ideal candidate for advanced photonic devices such as electro-optical modulators (EOMs) and oxide-based solar cells.^{65,66}

In semiconductor oxides, most materials exhibit a narrow band gap, which is due to the deep valence band from the O 2p. This phenomenon limits the development of visible-light-driven photocatalysts. However, it has been reported that the valence band formed by Bi 6s in BWO determines the bandgap effectively. Additionally, the hybridization of Bi 6s and O 2p could make the valence band more dispersed, which determines that the bandgap of BWO is in the visible light range, estimated as 2.7 eV.^{67,68} The band structures of Bi₂WO₆ are roughly described in Fig. 1.9, which have attracted research interests and shown potential as visible-light-driven photocatalysts.

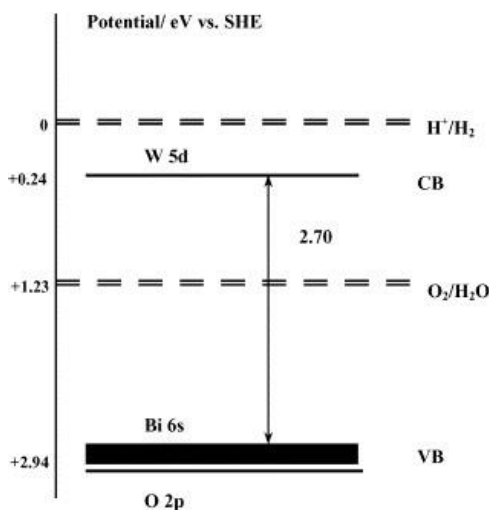


Fig. 1.9 Band structures of Bi₂WO₆ photocatalyst.⁶⁷

1.3 Strain engineering in epitaxial perovskite oxide thin films

1.3.1 Epitaxial thin film and strain

Epitaxial thin films refer to the ordered single-crystal growth of a film onto a substrate which, in most cases, is also single-crystal. For epitaxial film growth on a single-crystal substrate, there is typically a special relationship between the film orientation relative to that of the substrate. Homoepitaxy refers to the case where the film and substrate are of the same material. In heteroepitaxy, the film is of a different material with the substrate. The lattice mismatch f arises and is given by

$$f = 2 \times \left(\frac{a_f - a_s}{a_f + a_s} \right) \quad (1-8)$$

a_f and a_s are the unstrained lattice parameters of the film and substrate. Three modes arise in heteroepitaxial film growth based on the value of f , shown in Fig. 1.10. In the lattice matched mode in Fig. 1.10(a), where the lattice misfit is small ($f < 1\%$), films grow similarly to homoepitaxy. When the mismatch f becomes larger, but still less than 7%, the film is coherently strained so that the in-plane lattice parameter of the film $a_{f\parallel}$ matches a_s , without relaxation or generation of misfit dislocations, shown in Fig. 1.10(b).

The in-plane strain can be calculated as

$$\varepsilon_{\parallel} = \frac{a_{f\parallel} - a_f}{a_f} \quad (1-10)$$

As a result of the change in the value of $a_{f\parallel}$, the value of the out-of plane lattice parameter is changed to $a_{f\perp}$.

The resulting out-of-plane strain is calculated as

$$\varepsilon_{\perp} = \frac{a_{f\perp} - a_f}{a_f} \quad (1-11)$$

Beyond a certain critical thickness (h_c), the misfit dislocations form in the film and it transforms from a coherent strained structure to a relaxed incoherent structure.

When the misfit strain f is large ($f > 7\%$), the strain is too large for coherent film growth and strain relaxation is preferred. Interestingly, domain matching epitaxy (DME) is possible, as shown in Fig. 1.10(c). DME is a special case where domains of m lattice planes of the film are matched to n lattice planes of the substrate, resulting in epitaxial growth. Lattice mismatch within the domains then becomes

$$f = 2 \times \left(\frac{ma_f - na_s}{ma_f + na_s} \right) \quad (1-9)$$

where m and n are integers such that $n = m \pm 1$.

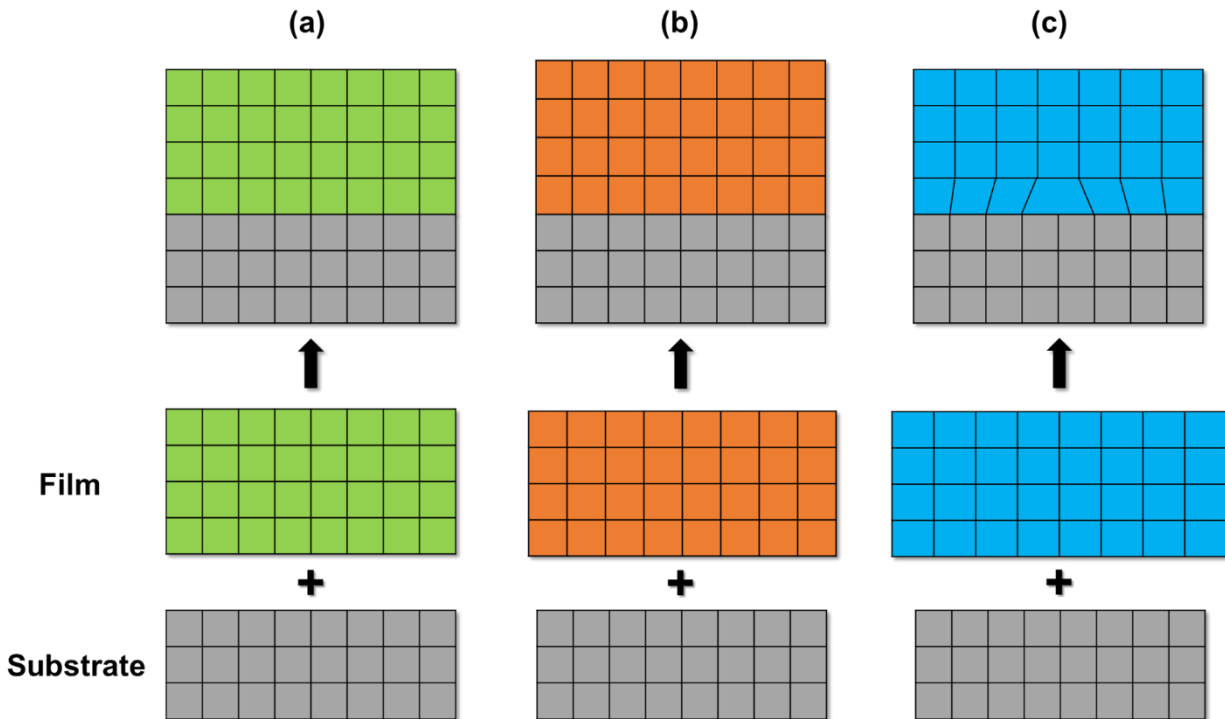


Fig. 1.10 Heteroepitaxial film growth: (a) lattice-matched, (b) coherently strained lattice-mismatched, and (c) incoherent growth-relaxed epitaxy.

Due to the epitaxial strain caused by lattice mismatch and differences in thermal expansion coefficients between thin film materials and the substrates, as well as defects formed during film growth, a unique opportunity presents itself to achieve enhanced functionalities in oxide thin films.⁶⁹ Additionally, much larger strains, up to several percent, can be accommodated in thin films unlike bulk materials. Strain engineered growth, however, requires high-quality single-crystal substrates that are suitable, both, structurally and chemically. Strain engineering has been employed in many applications, for example, enhancing semiconductor carrier mobility in strained SiGe_{1-x} films.^{70,71} In ZnO films grown epitaxially on GaN, the electrical resistivity has been increased with increasing strain, while the optical bandgap becomes wider and narrower for compressive and tensile strain, respectively.⁷² The in-plane lattice constants of some perovskite and related substrate materials including SrTiO_3 , LaAlO_3 , GdScO_3 , NdGaO_3 , and YAlO_3 are shown in Fig. 1.11.⁶⁹

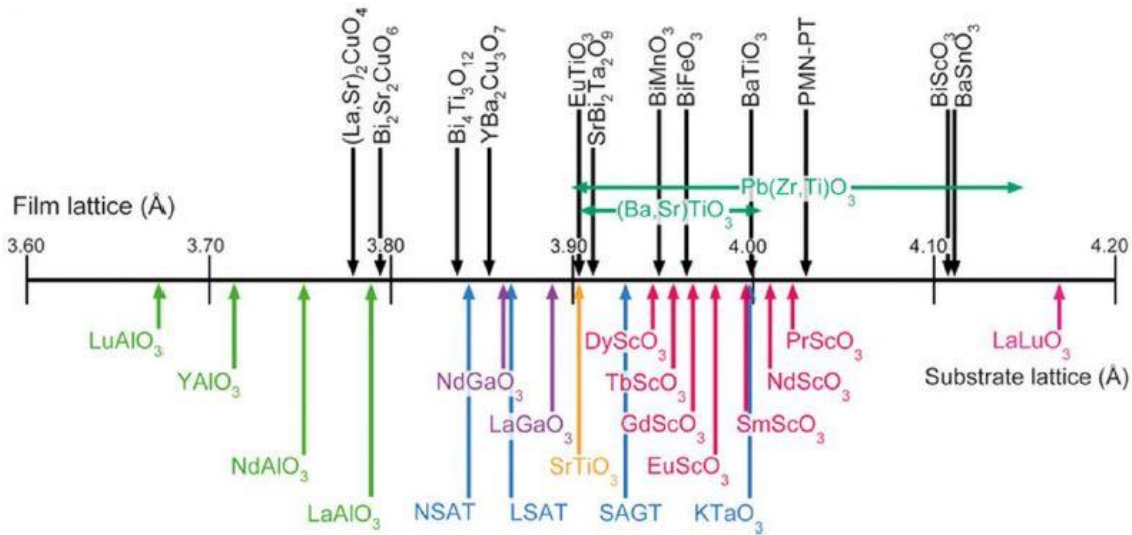


Fig. 1.11 Epitaxial perovskite thin films and various perovskite substrates displayed above and below the number line, respectively. The number line represents the pseudocubic/pseudotetragonal a -axis lattice constants.⁶⁹

1.3.2 Strain engineered ferroelectric oxide thin films

Ferroelectric materials exhibit field switchable stable and spontaneous electronic polarization. This has wide applications in sensors, actuators, memories, and transistors, and thus form an important component of today's materials. Most common ferroelectrics are ABO_3 perovskite oxides, like $PbTiO_3$, $BaTiO_3$, $BiFeO_3$, etc.^{73,74}. During the development, strain engineering has been widely investigated and demonstrated critical influence on the phase contents and properties of ferroelectrics.^{75,76}

$BiFeO_3$ (BFO) is the one of the most studied lead-free ferroelectric materials due to its large polarization of $\sim 100 \mu C/cm^2$ and multiferroic property (coexistence of ferroelectricity and antiferromagnetic) at room temperature.^{5,77} Its unique ferroelectricity is believed to be driven by lone-pair electrons of the Bi ion. The structure of BFO shows remarkable flexibility, hence, lots of factors, such as temperature, strain and doping, have been used in the structure modification. As temperature reaches as high as 1100 K, BFO transits from R phase to $GdFeO_3$ -like $Pbnm$ phase or probable orthorhombic γ phase with a first-order phase transition.¹²⁻¹⁴ For the epitaxial BFO films, the crystal structure can be modulated by the strain effect with the selection of substrates. It experiences from R into monoclinic (M_A , M_B , M_C),^{78,79} tetragonal or tetragonal-like,^{73,80} rhombohedral,^{81,82} orthorhombic,^{83,84} and even triclinic⁸⁵. Fig. 1.12 shows the phase transformation of BFO thin films under a range of strain effect. The plethora of possible symmetries of BFO generate unexpected ferroelectric behaviors.⁸⁶

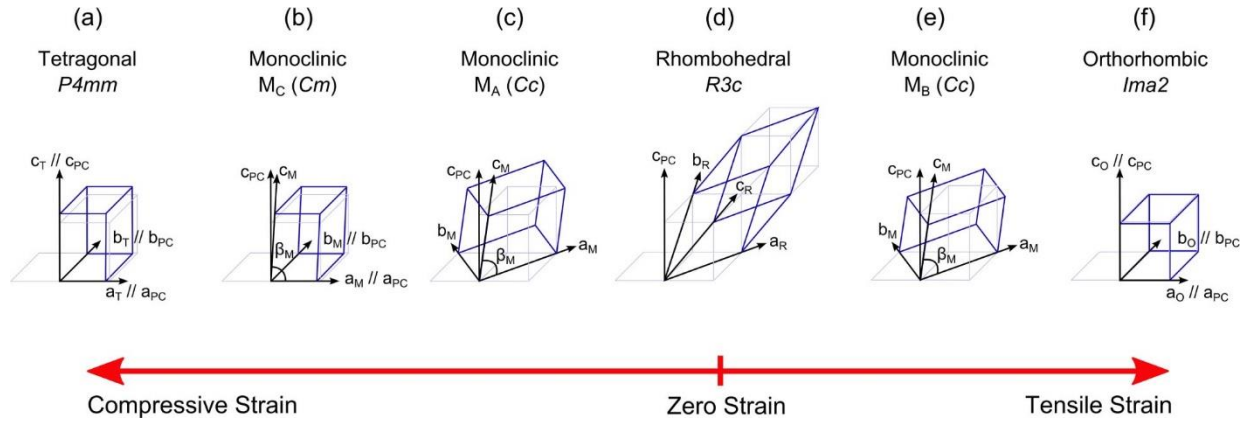


Fig. 1.12 Various crystal structures of BFO thin films under the strain effect.⁸⁶

Under moderate compressive or tensile strain, BFO shows distorted rhombohedral structure, and have polarization direction along [111] with polarization of $\sim 100 \mu\text{C}/\text{cm}^2$, similar with its bulk value⁸⁷, while compressive strain rotates the [111] polarization toward out-of-plane, making the [001] polarization larger, and tensile strain rotates the polarization to in-plane, giving smaller out-of-plane polarization, shown in Fig. 1.13 (a, b).⁸⁷ However, BFO can show a unique tetragonal structure (T phase) with a large c/a ratio of ~ 1.25 when grown on substrates that can give compressive epitaxial strain exceeds $\sim 4\%$ ^{73,88,89}, such as LaAlO_3 (LAO), YAlO_3 (YAO), which is summarized and shown in Fig. 1.13 (c).⁷³ The summary of c/a this new T phase is predicted and experimentally determined to have a giant polarization of $\sim 150 \mu\text{C}/\text{cm}^2$, higher than any other perovskite.⁸⁹ Partially relaxed highly strained BFO films show coexistence of multiple polymorphs, and remarkable stripe-like domain patterns^{73,88,89}, makes it a promising component for probe-based data storage and actuator devices. Recent work also shows that the highly strained BFO films, 45nm BFO on LAO, can undergo a transition to a true tetragonal high-temperature state at 430°C , with an estimated Curie temperature above 800°C . While S' polymorph is needed for piezoelectric switching, restricting the switching temperature no higher than 300°C .⁸⁸ The epitaxial strain could be utilized for the formation of morphotropic phase boundary (MPB) in BFO

system with ferroelectric-antiferroelectric (FE-AFE) boundaries. Fig. 1.13 (d) shows the HR-STEM image of boundaries between T and R.⁹⁰ Long-axis tetragonal phase of BFO forms under in-plane compressive strain and morphotropic phase transition between its T and R is also observed at the intermediate strains position.

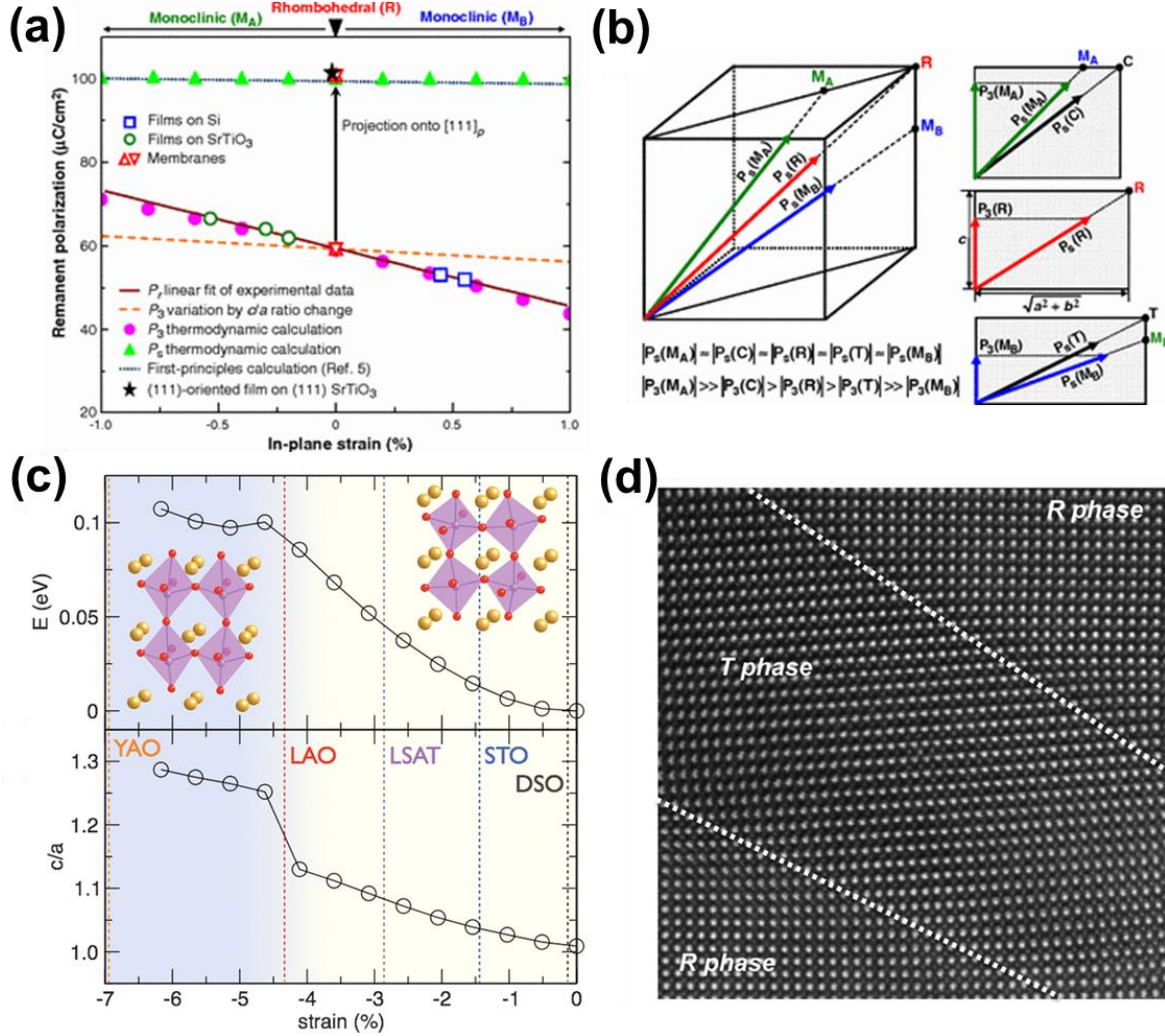


Fig. 1.13 (a) Remnant polarization vs in-plane strain for BiFeO₃ films. (b) The spontaneous polarization direction of the rhombohedral (R) and monoclinic (M_A and M_B) phases of BFO.⁸⁷ (c) Ab initio calculations of structure (c/a ratio) as a function of epitaxial strain of BFO films; (d) High resolution TEM image of the mixed T and R phase BFO on LAO substrate.⁷³

Strain effect has also been utilized to enhance the Curie temperature of ferroelectric materials. Phase field simulation shows that both tensile and compressive strain can elevate the Curie temperature (T_c) of BaTiO_3 .^{76,91} Fig. 1.14 (a) shows strain-temperature phase diagram of epitaxial BaTiO_3 thin film.⁶⁹ With increasing in-plane strain, T_c of BaTiO_3 thin films was increased and could achieve $\sim 540^\circ\text{C}$ on DyScO_3 substrate, comparable with the bulk value of 130°C .⁹¹ However, the magnitude of strain that can be applied is limited by available substrates and strain relaxation. Recent work demonstrated that epitaxial strain can control process induced defect dipoles' ordering, inducing additional vertical strains and enhancing T_c without need to change substrates.⁹² Fig. 1.14 (b) gives temperature-dependence of out of plane c lattice parameters of BaTiO_3 films grown at different laser fluences.⁹² There are two regimes of thermal expansion separated by a kink which indicates a phase transition. BaTiO_3 films grown by combining PLD growth process and GdScO_3 (110) substrate strain shows T_c over 800°C according to this work.⁹²

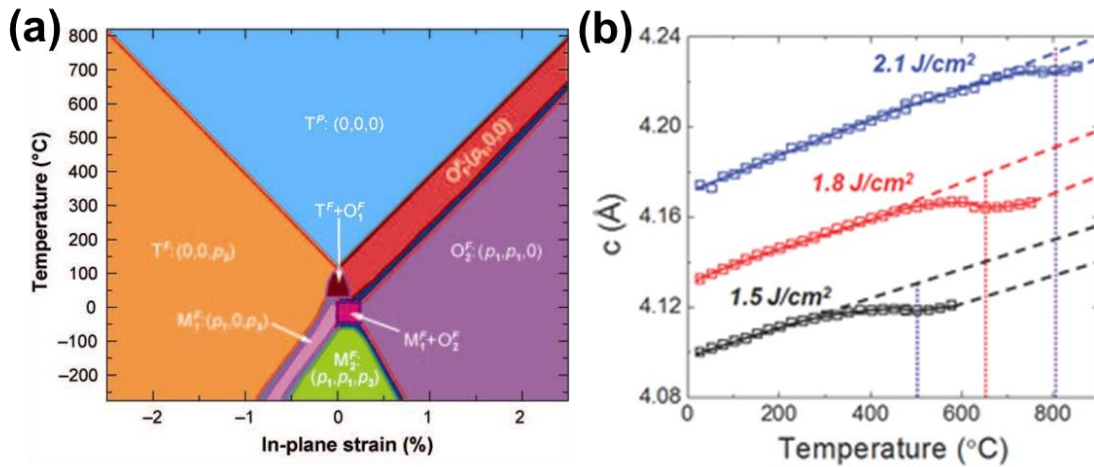


Fig. 1.14 (a) Phase diagram of BaTiO_3 films as a function of temperature and substrate in-plane strain.⁶⁹ (b) temperature dependent c lattice parameter of BaTiO_3 thin films grown with different laser fluences.⁹²

By adjusting the strain, it is possible to induce ferroic properties out of conventional non-ferroic material. Biaxial strain can tune SrTiO_3 to perform ferroelectricity and shift the T_c to room

temperature⁹³, which has been demonstrated experimentally with development of thin film growth technique and invention of substrates with different lattice constant.^{94,95}

Besides the epitaxial strain, chemical substitutions is another way to control the phase stability and transition temperatures in BFO system. Both ways aim to induce a mixed state, in order to improve its dielectric and electromechanical response, even though by different means: mechanical pressure and chemical pressure. The general phase diagram of rare earth-doped BFO (Re-BFO) thin film is shown in Fig. 1.15 (a).⁹⁶ Fig. 1.15 (b) shows the piezoelectric constant d_{33} measured at different doping amount of Sm is Sm-BFO (BSFO) thin films.⁹⁷ The maximum d_{33} value is at round 0.14, which corresponds to the MPB composition.

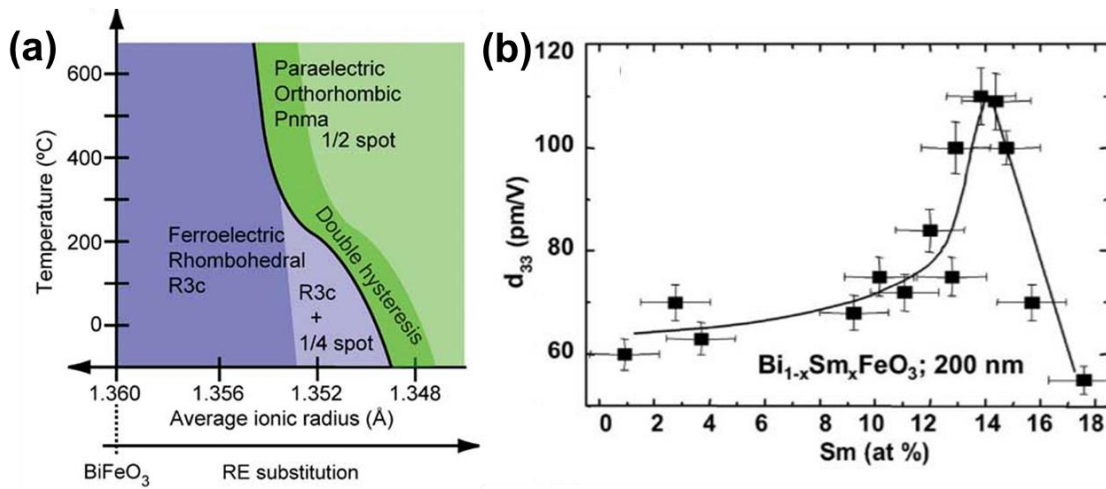


Fig. 1.15 (a) Phase diagram of rare earth-doped BFO (Re-BFO) thin film.⁹⁶ (b) d_{33} of BSFO thin films determined at various Sm doping.⁹⁷

1.3.3 Strain engineered ferromagnetic oxide thin films

Strain can also induce ferroic properties out of conventional non-ferroic material. What's more, magnetically ordered insulators EuTiO_3 that are neither ferroelectric nor ferromagnetic can be transformed into ferroelectric ferromagnets under proper strain.⁹⁸ Experimental measurements confirmed that EuTiO_3 grown on (110) DyScO_3 substrate shows strong ferroelectric and ferromagnetic properties.

Materials with magnetic anisotropy have an easy magnetization direction, which is called as the magnetic easy axis. The epitaxial strain in thin film has been used to tailor the magnetic easy axis and control the magnetic response. CFO has been under research interest due to its (100) magnetic easy axis.⁹⁹ In addition, a preferential perpendicular magnetization and anisotropy in CFO are necessary for a variety of application. However, it is still a significant challenge to precisely control the magnetic easy axis and obtain perpendicular anisotropy of the CFO thin film deposited on an inexpensive substrate; therefore, effective efforts have been placed on developing strategic approach.

1.3.4 Strain effect on the optical properties of thin films

Multiferroic BFO thin films respond moderately to external perturbations such as strain, electric and magnetic field. The strain effect on the optical properties, albeit slightly, has been reported. Fan et al. investigated the tensile strain effect in BFO thin films and predicted larger band gap with the increased tensile strain.³⁸ Tetragonal-like BFO films own an even larger band gap, at 3.1 eV, presumably due to the change in band gap structure, caused by lower valence O 2p orbitals or higher conduction Fe 3d orbitals.^{100,101} A detailed experimental study of the microstructure, optical properties correlating with strain is required.

1.3.5 Novel layered structure induced by strain

Strain engineering can be used for promoting novel structures, such as the self-assembly bismuth-based supercell (SC) structure. Introducing the biaxial strain through the substrate in thin film epitaxy growth has been proved as a very effective way to manipulate the film microstructure and physical properties.^{69,102} Strain effect from the substrates has been proven as the driving force for the formation of supercell structure in multiferroic $\text{Bi}_3\text{Fe}_2\text{Mn}_2\text{O}_x$ (BFMO322) thin films.¹⁰³ Films were directly deposited on single-crystalline SrTiO_3 (STO) and LaAlO_3 (LAO) substrates under the identical deposition condition. Highly strained BFMO grown on LAO formed the supercell structure, while BFMO on STO only shown the conventional pseudo-perovskite structure. The structure was analyzed by the high-resolution STEM (HR-STEM) and shown in Fig. 1.16.¹⁰³

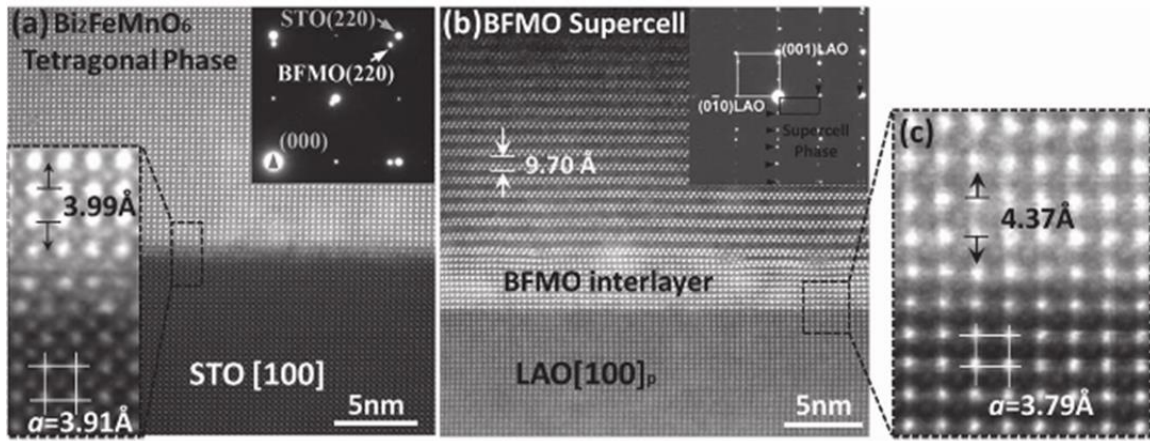


Fig. 1.16 STEM images of BFMO films on STO and LAO substrates under the same deposition conditions.¹⁰³

BFMO322 supercell structure on LAO has a much pronounced lattice mismatch (-2.0%) than that on STO substrate (-0.6%), which means that BFMO is under larger compressive strain on LAO.¹⁰³ The strain analysis has also shown that appropriate interfacial reconstruction is necessary for the growth of the novel BFMO322 supercell structure, besides the lattice misfit from

substrates. However, the new transitional interfacial phases behaving like coherent film layers only happens within critical thickness.¹⁰⁴ Similar interfacial structure has also been observed in supercell structure of $\text{Bi}_2\text{AlMnO}_6$.¹⁰⁵ In the new proven $\text{Bi}_2\text{NiMnO}_6$ (BNMO) systems with layered structure, in-plane rotation has been demonstrated to exist between the Bi-based slabs and Mn-O/Ni-Mn-O octahedral slabs. It contributes to the strain energy release and is helpful for the layer stacking of two sublattices along the out-of-plane direction.¹⁰⁶ The strain effect in the Bi-based layered structure prepared by PLD challenges the conventional understanding in existing epitaxial growth model.

1.3.6 Strain effect in superlattice and vertically aligned nanocomposites

An effective method of strain control, the superlattice structure, is also repeating sequence of two or more materials, but in this case the individual layers thicknesses are on the order of a few nanometers, less than the critical thickness for misfit dislocation formation, as shown in the example of $\text{BaTiO}_3/\text{SrTiO}_3$ superlattices in Fig. 1. 17.¹⁰⁷ In this structure, the in-plane lattice parameter is constrained to match that of the substrate, keeping the film completely coherent with the substrate, with the overall properties of the superlattice film determined by the elastic strain.

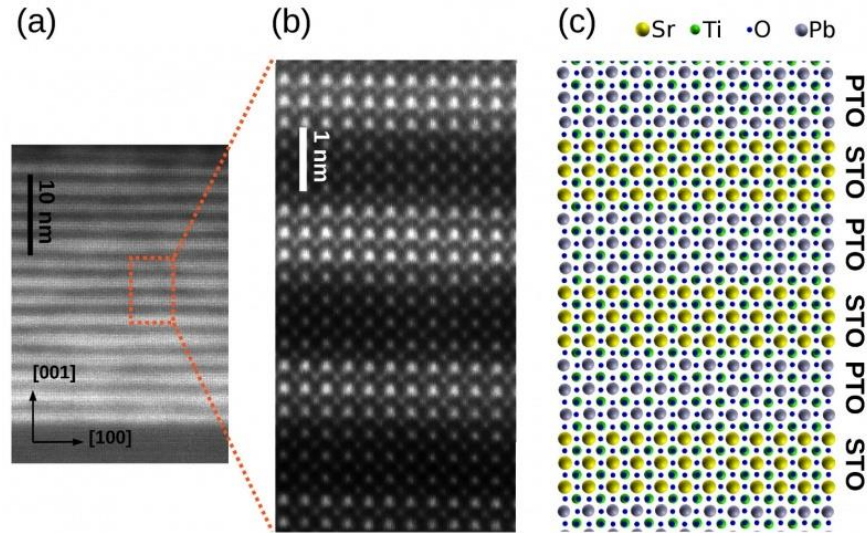


Fig. 1.17 (a) Low magnification STEM image, (b) HR-STEM image and (c) atomic models of $\text{BaTiO}_3/\text{SrTiO}_3$ superlattices.¹⁰⁰

As mentioned earlier, coherently strained epitaxial films begin to form misfit dislocations beyond a critical film thickness, after which the film becomes relaxed and incoherent. This maximum thickness for coherency varies from a few nanometers to a few tens of nanometers, depending on the film material and the growth conditions. However, in some materials, there is a minimum thickness above which it exhibits its particular functionality, eg. ferroelectricity, making it difficult to tailor the strain in thicker films.¹⁰⁸ A solution to this conundrum is the emergent architecture of vertically aligned nanocomposites (VAN) films, consisting of simultaneously grown two different epitaxial phases on a single substrate. This architecture offers the advantages of strain insensitivity to film thickness and very large vertical interfaces, over conventional single phase epitaxial strain.

The VAN system was first introduced in 2002, a composite film of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3:\text{MgO}$ grown by a solution based technique.¹⁰⁹ Tunability of the magnetotransport properties of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ was reported, attributed to mechanical strain coupling with the surrounding MgO. Following this, a multiferroic system of ferromagnetic CoFe_2O_4 pillars in a ferroelectric BaTiO_3

matrix was demonstrated using single composite ceramic target by PLD.¹¹⁰ Shortly after, strain control was reported in a checkerboard structure of $\text{BiFeO}_3\text{:Sm}_2\text{O}_3$ and then in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3\text{:ZnO}$. Following these pioneering works, several different two-phase systems have been demonstrated,¹¹¹ with significant enhancement in their functionalities for variety of applications like multiferroics, spintronics, superconductors, solid oxide fuel cells, and electrically tunable dielectrics.^{110,112-117} Summarized in Table 1.3 is a broad summary of reported VAN systems.¹¹⁸

Table 1.3 Summary of reported VAN systems

Crystal structure	VAN systems	References
Perovskite-body centered cubic	$\text{LaSrFeO}_4\text{:Fe}$	119
	$\text{BaTiO}_3\text{:Au}$	120
Perovskite-hexagonal close-packed	$\text{BaZrO}_3\text{:Co}$	121
Perovskite-rock salt	$\text{BiFeO}_3\text{:Sm}_2\text{O}_3$	122-124
	$\text{BiFeO}_3\text{:Nd}_2\text{O}_3$	118
	$\text{BiFeO}_3\text{:Eu}_2\text{O}_3$	118
	$\text{BaTiO}_3\text{:Sm}_2\text{O}_3$	75
	$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3\text{:MgO}$	125
	$\text{SrTiO}_3\text{:MgO}$	118
Perovskite-wurtzite	$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3\text{:ZnO}$	122,126,127
Perovskite-fluorite	$\text{BaTiO}_3\text{:CeO}_2$	128
	$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3\text{:CeO}_2$	129
	$\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3\text{:Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$	130

Table 1. 3 Continued

Perovskite-perovskite	BiFeO ₃ :BaZrO ₃	118
Perovskite-perovskite	BaTiO ₃ :YMnO ₃	131
Perovskite-layered perovskite	BaZrO ₃ :YBa ₂ Cu ₃ O _{7-δ}	132
	BaSnO ₃ :YBa ₂ Cu ₃ O _{7-δ}	133
Perovskite-spinel	BiFeO ₃ :CoFe ₂ O ₄	134,135
	BiFeO ₃ :NiFe ₂ O ₄	136
	BaTiO ₃ :CoFe ₂ O ₄	137
	BaTiO ₃ : NiFe ₂ O ₄	138
	PbTiO ₃ :CoFe ₂ O ₄	139
	La _{0.7} Sr _{0.3} MnO ₃ :Mn ₃ O ₄	140
Double perovskite- fluorite	PrBaCo ₂ O _{5+x} : Ce _{0.9} Gd _{0.1} O _{1.95}	141
Layered perovskite-spinel	Bi ₅ Ti ₃ FeO ₁₅ :CoFe ₂ O ₄	142

VAN thin films have two types of strain; horizontal strain induced by the substrate at the film-substrate interface and the vertical strain along the interfaces between the two phases, shown in Fig. 1.18.¹¹⁸ The substrate induced strain relaxes beyond a certain critical film thickness. However, the strain between the two phases in the VAN system can be tailored by material selection and material composition. The differences in the out-of-plane lattice parameter, crystal orientation, and crystal structure results in one phase to be under tensile strain and the other to be under compressive strain in the vertical direction. The immense sensitivity of the material properties is due to the large ratio of the surface area of the interfaces to the volume of the nanostructure phases.

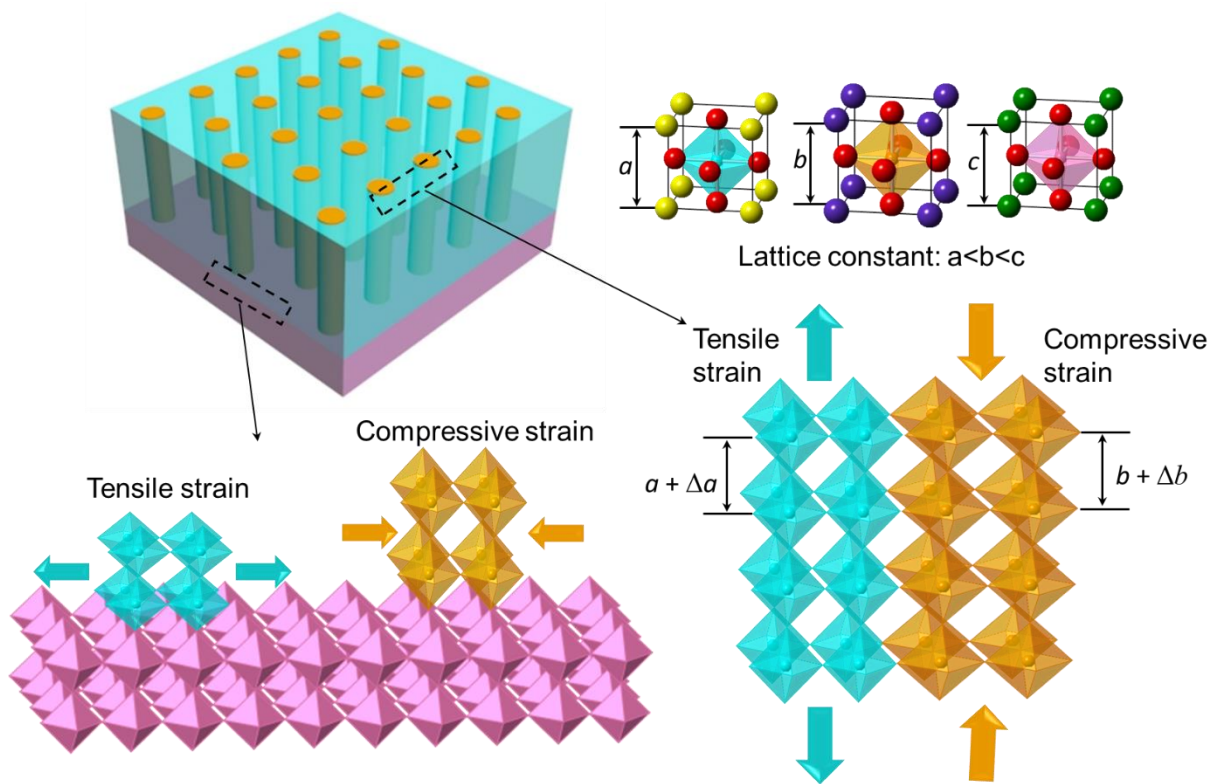


Fig. 1.18 Schematic representation of (a) relaxed unit cells of the substrate and the individual VAN phases; (b) substrate induced strain at the film-substrate interface and (c) vertical strain due to coupling between the two phases in the VAN film.¹¹⁸

Fig. 1.19 shows the out-of-plane matching relationships between the two phases and the in-plane matching relationships of the individual phases with the SrTiO_3 substrates for the BaTiO_3 - YMnO_3 (BTO-YMO) and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ - CeO_2 (LSMO- CeO_2) VAN systems. In the case of BTO-YMO, the out-of-plane lattice parameter is changed to $7.36 \text{ \AA}$ from the bulk value of $6.149 \text{ \AA}$ corresponding to a large out-of-plane tensile strain of 9.78% due to the presence of BTO.¹³¹ For LSMO- CeO_2 , the LSMO out-of-plane lattice parameter is changed from $3.87 \text{ \AA}$ to $3.789 \text{ \AA}$ corresponding to an out-of-plane compressive strain of -2.09% . Based on this, the strain in VAN systems can be tuned by selecting appropriate second phase materials. Shown in Fig. 1.20 is a

diagram with the theoretical out-of-plane strain matching relationship for various coupled two phase VAN structures.¹¹⁸

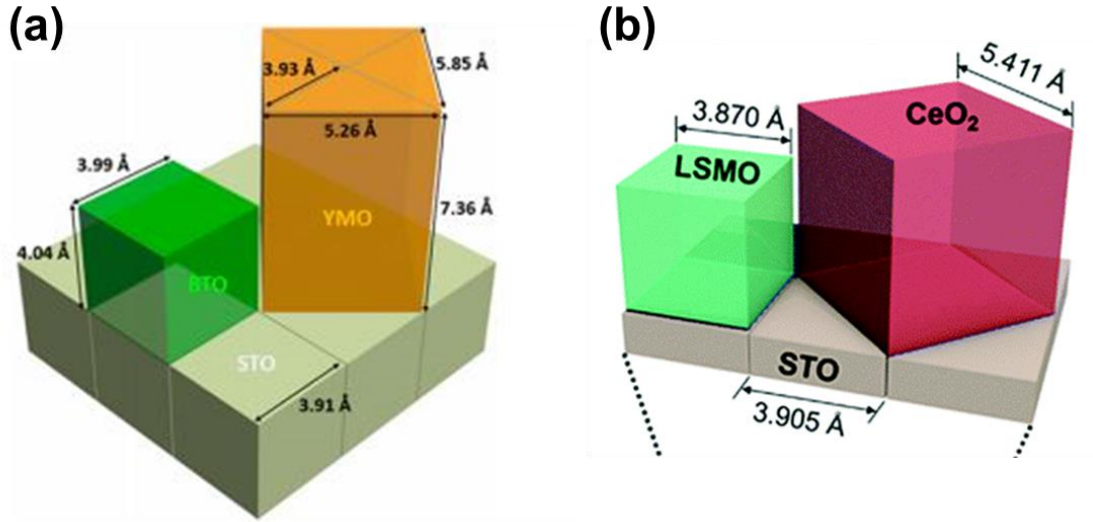


Fig. 1.19 Out-of-plane matching relationships between (a) $\text{BaTiO}_3\text{-YMnO}_3$ (YMO)¹³¹ and (b) $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3\text{-CeO}_2$ VAN films grown on SrTiO_3 substrates ($\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3 = \text{LSMO}$).¹⁴³

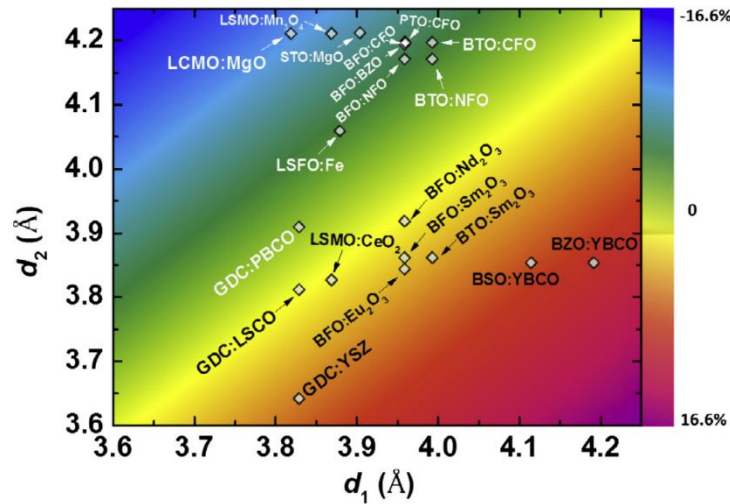


Fig. 1.20 A schematic showing theoretical out-of-plane strain matching relationship for various coupled two phase VAN structures.¹¹⁸

Two phase VAN systems using a variety of perovskite materials have been explored for property enhancement. Table 1.4 summarizes the functionalities in several VAN systems. $\text{BaTiO}_3\text{-Sm}_2\text{O}_3$ and $\text{BaTiO}_3\text{-CeO}_2$ have been used to enhance the ferroelectric response in BaTiO_3 by

reducing dielectric loss and leakage current and increasing the T_C .^{75,144} Ferroelectrics are coupled with ferromagnetics for exploration of multiferroic properties like magnetoelectric coupling in $\text{BaTiO}_3\text{:CoFe}_2\text{O}_4$,^{137,145} and magnetic anisotropy in $\text{BiFeO}_3\text{:CoFe}_2\text{O}_4$ systems.^{134,135} In solid oxide fuel cell applications, a VAN electrolyte of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}\text{-Zr}_{0.92}\text{Y}_{0.08}\text{O}_{1.96}$ showed an enhancement in the out-of-plane ionic conductivity,¹¹⁶ while an interlayer of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}\text{-Zr}_{0.92}\text{Y}_{0.08}\text{O}_{1.96}$ between the electrode and electrolyte increased the oxygen catalytic properties.¹⁴⁶ Low field magnetoresistance properties have been enhanced in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3\text{-ZnO}$ and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3\text{-CeO}_2$ due to the out-of-plane strain induced in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ by incorporating the second phase.^{113,147} The incorporation of CoFe_2O_4 as nanoparticles in superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, as well as in a VAN buffer layer with CeO_2 has provided a unique approach for analyzing the flux pinning properties in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.^{115,148} In several instances, two different material properties have been combined for advanced functionalities. A VAN system of $\text{CoFe}_2\text{O}_4\text{-SrRuO}_3$ has been shown to reveal a light-induced change in magnetization in the CoFe_2O_4 .¹⁴⁹

Table 1.4 Summary of functionalities in VAN systems

Functionalities	VAN systems	References
Ferroelectricity	$\text{BaTiO}_3\text{:Sm}_2\text{O}_3$	75
	$\text{BaTiO}_3\text{:CeO}_2$	128
	$\text{BiFeO}_3\text{:Sm}_2\text{O}_3$	122-124
Multiferroicity	$\text{BiFeO}_3\text{:CoFe}_2\text{O}_4$	134,135
	$\text{BaTiO}_3\text{:CoFe}_2\text{O}_4$	137,145
	$\text{BiFeO}_3\text{:NiFe}_2\text{O}_4$	136
	$\text{BaTiO}_3\text{:YMnO}_3$	131
	$\text{Bi}_5\text{Ti}_3\text{FeO}_{15}\text{:CoFe}_2\text{O}_4$	142

CHAPTER 2. RESEARCH METHODOLOGY

2.1 Pulsed laser deposition

Physical vapor deposition (PVD) refers to a variety of thin film deposition methods that involve vaporized materials from a solid target and deposition on desired substrates in a vacuum chamber. Pulsed laser deposition (PLD) is one PVD technique that uses high power laser beam as the energy source. It has become the preferred thin film deposition technique, since Dr. Venkatesan's research group first realized the deposition of $\text{YBa}_2\text{Cu}_3\text{O}_7$ via PLD in 1987.¹⁵⁰ Fig. 2.1 shows the schematic of a PLD system. It basically consists of a target manipulator, a heated substrate holder and a vacuum chamber. The target manipulator could hold single or multiple targets and do simple rotation. The laser beam strikes target surface at an angle of 45° , while the substrate holder is positioned 4-5 cm directly in front of the target. The vacuum is maintained at least 1.0×10^{-6} mbar by turbo-molecular pumping systems. Excimer lasers are the popular sources among common PLD laser sources. The output wavelength depends on the gas species; ArF, KrF, Nd:YAG produce wavelength of 193 nm, 248 nm, and 355 nm, respectively. Optical components including mirrors and lenses are placed between the laser and the vacuum chamber to direct and focus beam. For the thin film growth, the laser power density is varied from 3 J/cm^2 to 5 J/cm^2 and the laser is operated in a pulsed mode with a pulse duration of 20-25 ns. The following parameters can be used to control the film quality like laser energy density, pulse repetition rate, substrate temperature, target-substrate distance, working gas partial pressure, and gas species.

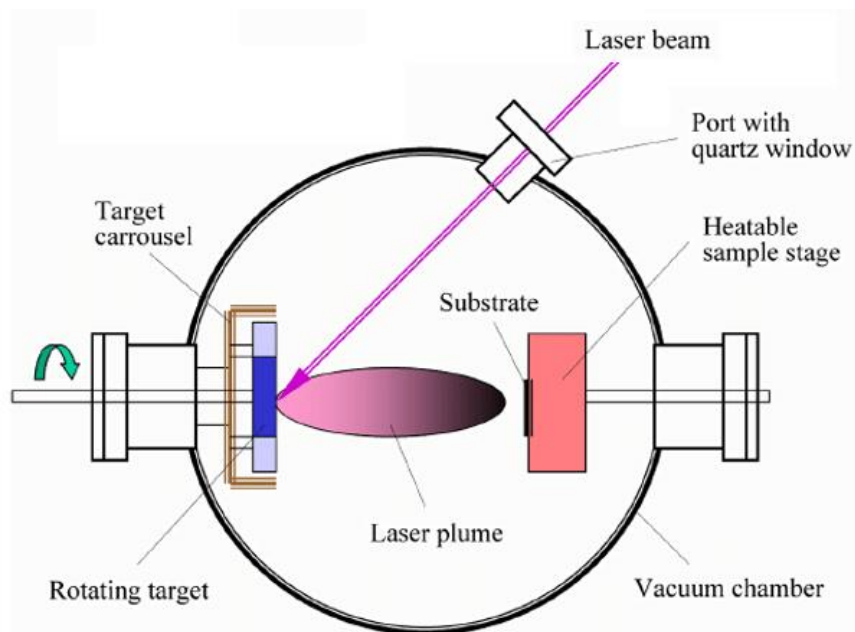


Fig. 2.1 A schematic of the PLD system.¹⁵¹

The physical process of the laser-target interaction can be divided into three steps: (1) interaction of the laser beam with the target materials, (2) plasma formation and (3) adiabatic plasmas expansion and deposition. The first two steps begin from the start of the laser and last through its duration. while the third step occurs after the laser pulse terminates.¹⁵² Fig. 2.2 illustrates the laser-target interaction. The electromagnetic energy from the laser pulse is absorbed by the target surface and converted to thermal, chemical and mechanical energy which will cause local melting and evaporation. The interaction between the laser beam and the evaporated materials produce the plasma. It consists of small particles, molted globules, clusters, molecules, atoms, ions, and electrons. As the target continues absorbing energy, the plume begins to isothermally expand outward. The adiabatic plasma expansion occurs after the end of pulse and gives rise to the deposition on the substrate.

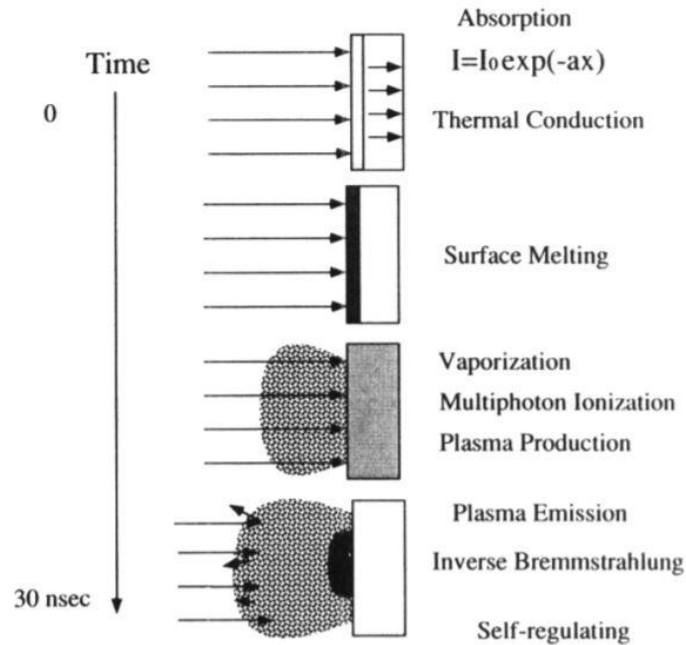


Fig. 2.2 A schematic of the interaction of high power laser with target.¹⁵³

The nucleation and growth of thin films onto substrate surface can be described into three primary modes including (1) Volmer-Weber (island growth), (2) Frank-van der Merwe (layer-by-layer growth), and (3) Stranski-Krastanov (island + layer growth). Each mode is illustrated in Fig. 2.3.¹⁵⁴ In island growth, the adatoms prefer to stick together and form clusters or islands, which is attributed to the stronger bonding between adatoms than adatoms with substrate surface. The layer-by-layer growth is 2D where adatoms attach to the surface and grow into smooth layers. The island + layer growth is characterized by the island and layer growth. The island begins to grow at a critical layer thickness, depending on the properties of thin films and substrates.

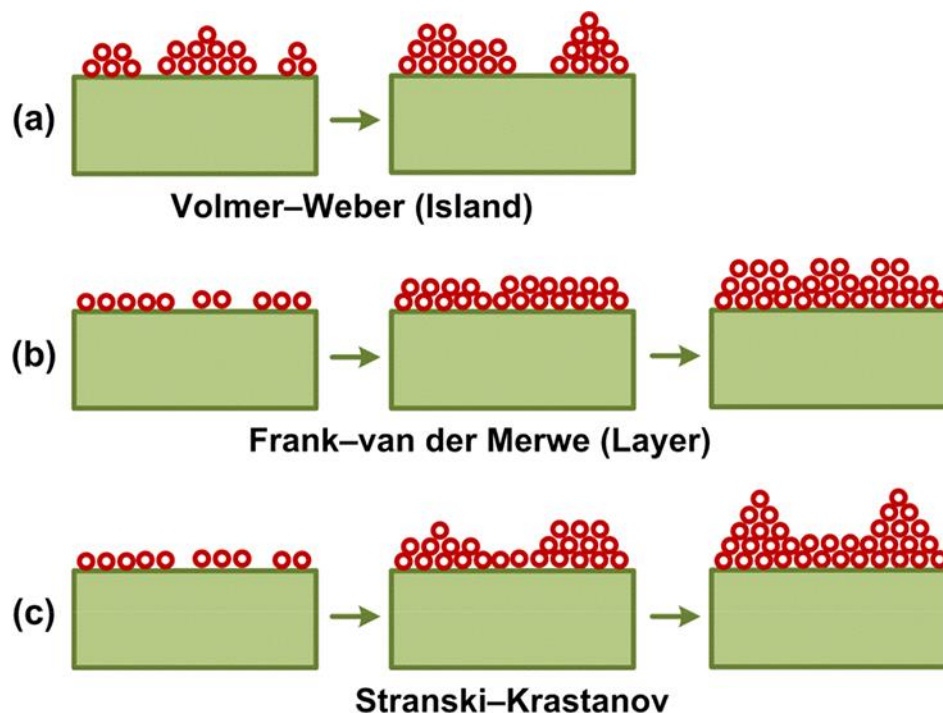


Fig. 2.3 Basic growth modes of thin films.¹⁵⁵

Some PLD systems are equipped with Reflection High Energy Electron Diffraction (RHEED) for monitoring the film quality. It is operated under a very high vacuum and can gather the real time lattice information, which is a helpful apparatus for the in-depth studies of the film growth mechanisms.

2.1 Structural characterization

2.1.1 X-Ray diffraction

X-ray diffraction (XRD) is a non-destructive technique to investigate the structure of crystalline materials. It can be used to identify the crystal orientation, crystallite size and stress in thin film materials. X-rays are diffracted by specimen and form a convergent beam at the receiving slits before they enter a detector. The diffraction, or Bragg diffraction, occurs due to the

constructive interference between the reflected X-rays from adjacent crystal planes. The basic principle behind X-ray diffraction is Bragg's Law as

$$n\lambda = 2d \sin \theta \quad (2-1)$$

where λ is the wavelength of coherent incident X-rays, n is a whole number, and θ is the incident angle. Fig. 2.4 is a schematic description of Bragg's Law. Same type of atoms is located on their respective parallel planes with interplanar spacing d . The separation between planes creates interferences giving rise to changes in intensity (depending of the direction). These intensity changes allow us to get information on the structure of atoms that form the crystal.

Advanced XRD techniques include grazing incidence diffraction, reciprocal space mapping, pole figure, reflectivity etc. They can be used to characterize thin films with phase information, strain, texture, mosaicity and surface roughness.

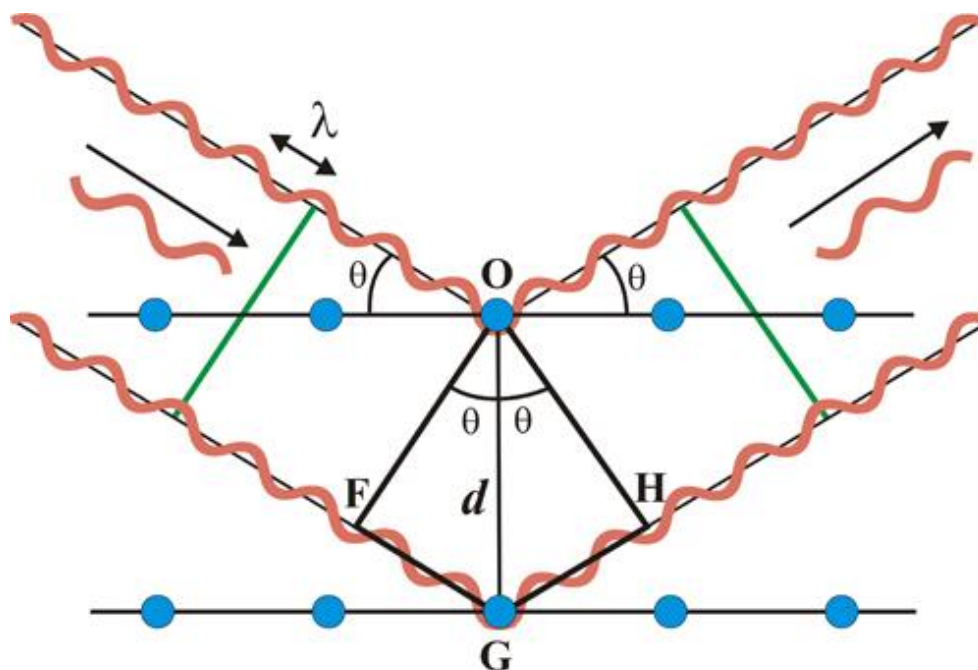


Fig. 2.4 A schematic description of Bragg's Law for a set of crystal planes with d interplanar spacing.¹⁵⁶

2.2.2 Transmission electron microscopy

Transmission electron microscopy (TEM) is a powerful tool for characterization of materials, which offers more information on the structure in sub-nanometer resolution. It is developed to overcome the limited resolution of optical microscopy. TEM has the ability to investigate the internal structure underneath the surface as the electron beam transmits an ultra-thin sample ($\sim 100\text{nm}$). It can also provide projection of microstructure in atomic level. TEM characterization on thin films offers information on sample morphology, crystallography, and chemistry sub-nanometer resolution etc. The resolving power or spatial resolution limit of the microscope is theoretically based on the Rayleigh criterion as uses the electron beam as the light source

$$R = \frac{0.612\lambda}{n \sin\alpha} \quad (2-2)$$

where λ is the wavelength of the light, n is the refractive index of the lens ($n=1$ for vacuum), and α is the half angle of the maximum cone of light that can enter or exit the lens. The product $n \sin\alpha$ is also referred to as the numerical aperture of the lens. The TEM uses coherent electron as the illuminating source with a short wavelength in the order of $0.01 \text{ \AA}$, which contributes to a much higher resolution than optical microscopes.

The wavelength λ of an electron beam at an accelerating voltage V is given by

$$\lambda = \frac{1.22}{\sqrt{V}} \quad (2-3)$$

Typically, an accelerating voltage of 200 kV is used, resulting in an electron beam wavelength of 0.0027 nm .

Shown in Fig. 2.5 is a schematic view of TEM column. A typical TEM mainly contains four main components: the electron source, the system of electromagnetic lenses, the sample stage and the image acquisition systems. They are all maintained in high vacuum, which is backed up

by a high vacuum pump system. It consists of the mechanical pump, turbo pump or diffusion pump.¹⁵⁷ The coherent electron beam is produced by the thermal emission guns or field emission guns and then accelerated by the extraction voltage. The electron beam is then focused and confined by condenser lens and apertures to provide illumination for the specimen. The objective, intermediate, and projector lenses as well as their apertures focus the transmitted beam and project the magnified images on to the phosphorescent screen and CCD camera.

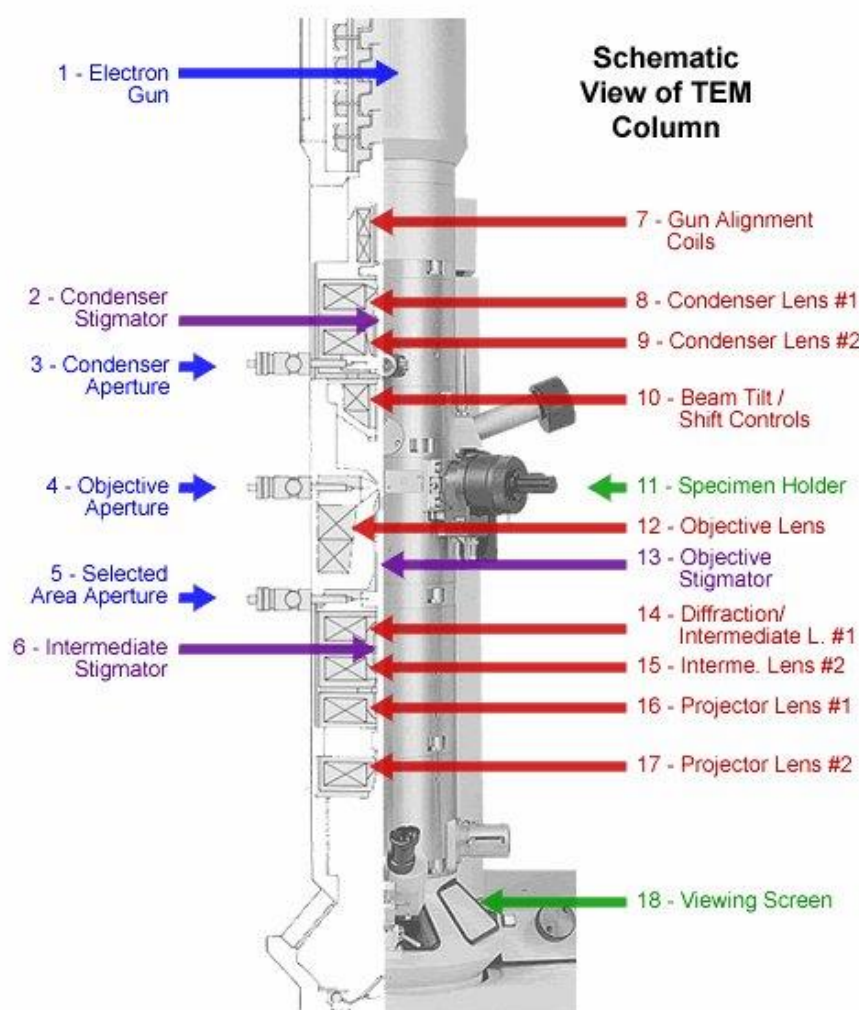


Fig. 2.5 Major components of TEM.¹⁵⁸

The TEM has two basic modes of operation; namely the diffraction mode and the imaging mode, as shown in Fig. 2.6 diagrams. Each mode can be controlled by changing the focal length of the intermediate lens. In the diffraction mode, the beam is refocused on the back focal plane of objective lens. The diffraction pattern is projected on the view screen with the selected area diffraction (SAD) aperture inserted. While in the imaging mode, the image plane coincides with the image plane of objective lens.

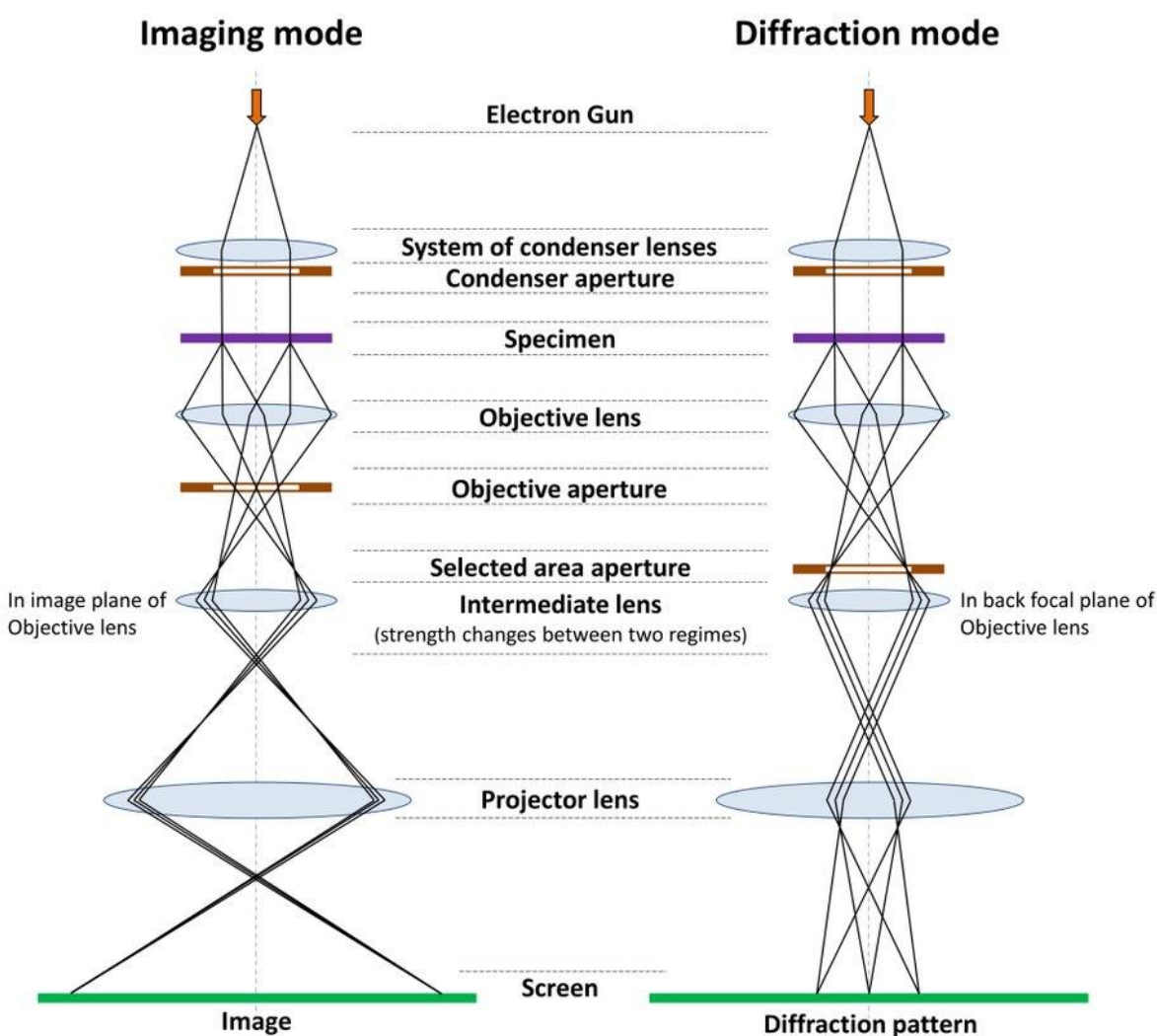


Fig. 2.6 Two basic modes of operation in a TEM: (a) diffraction and (b) imaging.¹⁵⁹

The contrast in the imaging mode can be adjusted by inserting the appropriate objective apertures at the back focal plane of the projective lens. It will form bright field (BF) and dark field (DF) images, shown in Fig. 2.7. When only direct transmitted electrons are allowed to pass, a BF image is formed; when only certain diffracted electrons are allowed, a DF image can be obtained.

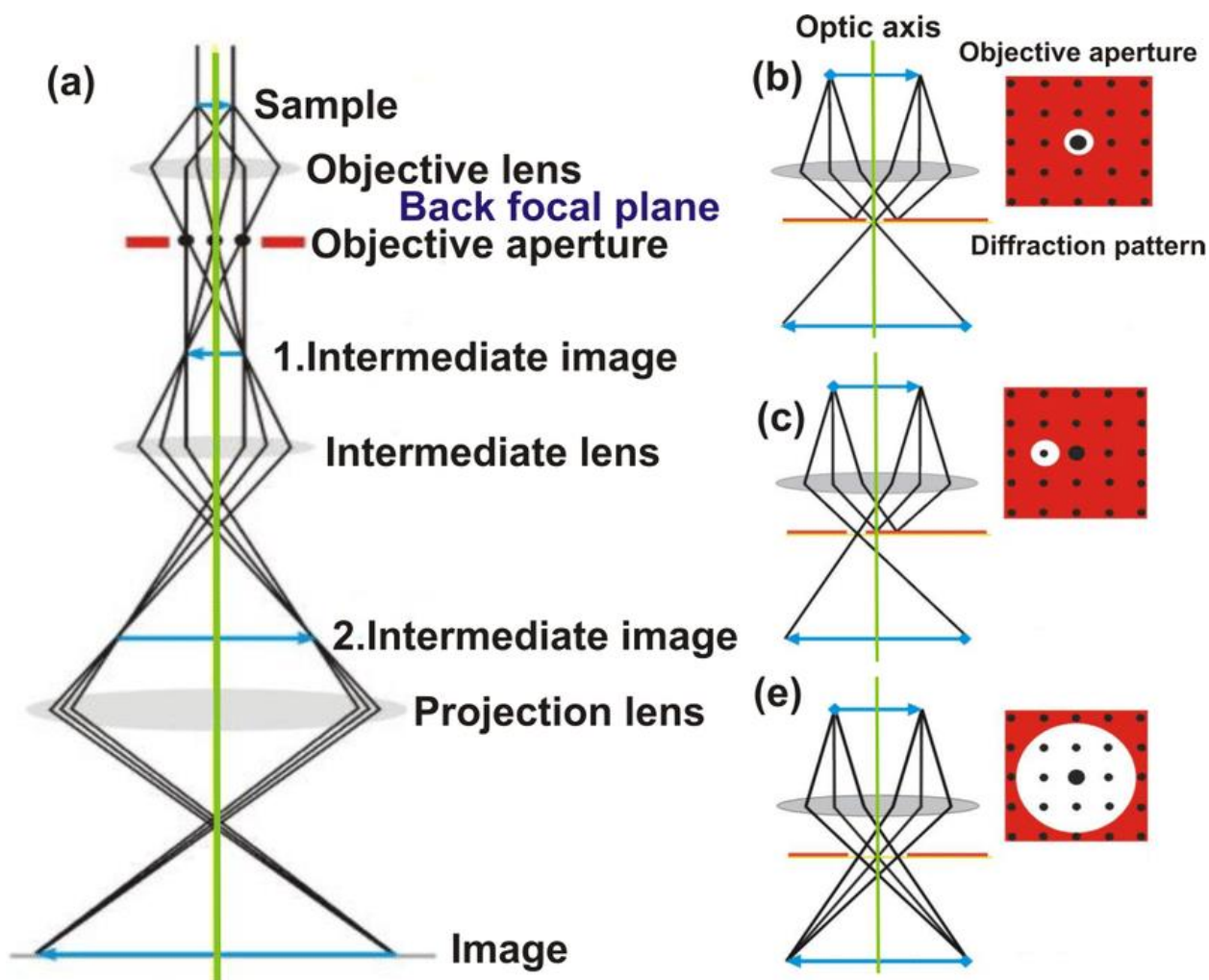


Fig. 2.7 Schematic diagram showing the (a) bright-field, (b) dark-field and high-resolution TEM imaging modes¹⁶⁰

Addition analytical techniques of TEM can provide detailed structure information even at single atomic scale. High-resolution TEM (HRTEM) allows atomic scale imaging and resolution of the sample possible. The operating mode is shown by Fig. 2.7(e). In this mode, image contrast

is highly dependent on the conditions of microscope and its components. Appropriate accelerating voltage, focal lengths and aperture sizes must be selected to minimize the spherical aberration, chromatic aberration, and astigmatism. Another helpful imaging mode is scanning transmission electron microscopy (STEM), where a focused beam is scanned over the sample in a raster illumination system. It makes other analytical techniques possible, such as Z-contrast (Z, atomic number) annular dark-field imaging, energy dispersive X-ray spectroscopy (EDS), and electron energy loss spectroscopy (EELS). These signals allow direct correlation of images and spectroscopic data.

2.2.3 Scanning electron microscopy

Scanning electron microscopy (SEM) consists in an electron source, electromagnetic lens and an electron detector. It uses a focused beam of high energy electrons as the illumination source. The layout and components of SEM is mostly similar with TEM, however, it has a different working principle. Rather than utilizing the transmitted electrons, SEM collects various types of secondary electrons and photons which are formed by the interaction between electron beam and sample surface. Therefore, SEM could provide the information of the topography and chemical composition of the sample. In addition, the resolution of SEM can reach 0.4 nm, which is lower than that of TEM. Shown in Fig. 2.8 is the schematic showing the layout and components in a SEM. Unlike the TEM, the objective lens and associated apertures are situated before the sample.

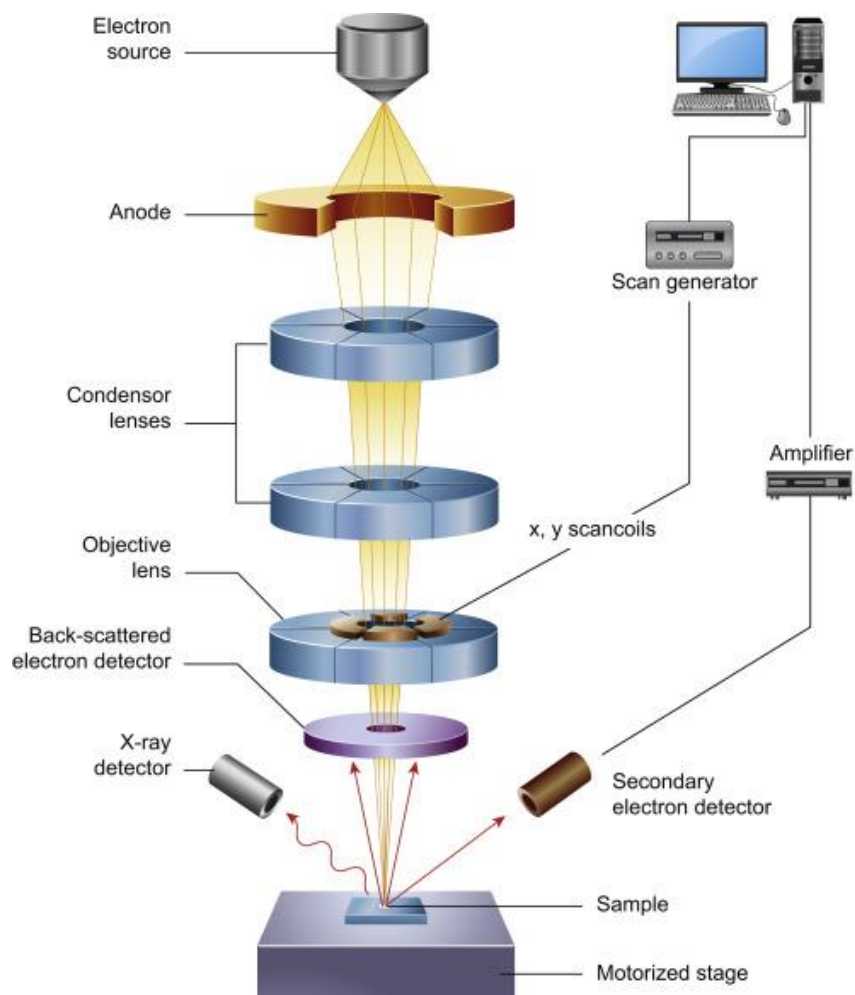


Fig. 2.8 The major components and their layout in a SEM.¹⁶¹

The electron beam is focused to a fine probe and scan across the sample in a raster scan pattern. The position of the beam is combined with the detected intensity of the secondary species of electrons to produce an image. When the incident electrons impinge in the solid sample, several interactions occur due to different electron interaction volumes, which produces a variety of signals as shown in Fig. 2.9. There are three primary types of signals in SEM: secondary electron (SE), backscattered electron (BSE) and X-rays. SEs are inelastic electrons with energy of less than 50 eV, which are commonly used for the topographical information of the sample. The energy of

BSEs is higher than 50 eV. They are closely related with the atoms with high atomic number Z , so the BSE images are valuable for illustrating composition information, especially for the analysis of the composite. The X-rays are produced when incident electrons hit the electrons on discrete shells in the sample inelastically. As the excited electrons return to the lower energy shell, they yield X-ray photons with a fixed wavelength. They are related to the different energy levels of electrons on different shells. Thus, X-rays are produced for each element and used for characterization. The working principle is same with the characteristic X-rays in TEM. SEM analysis is a non-destructive technology; in other words, X-rays generated by electron interactions do not lead to volume loss of the sample, so it allows for the repeated analysis of the same sample.

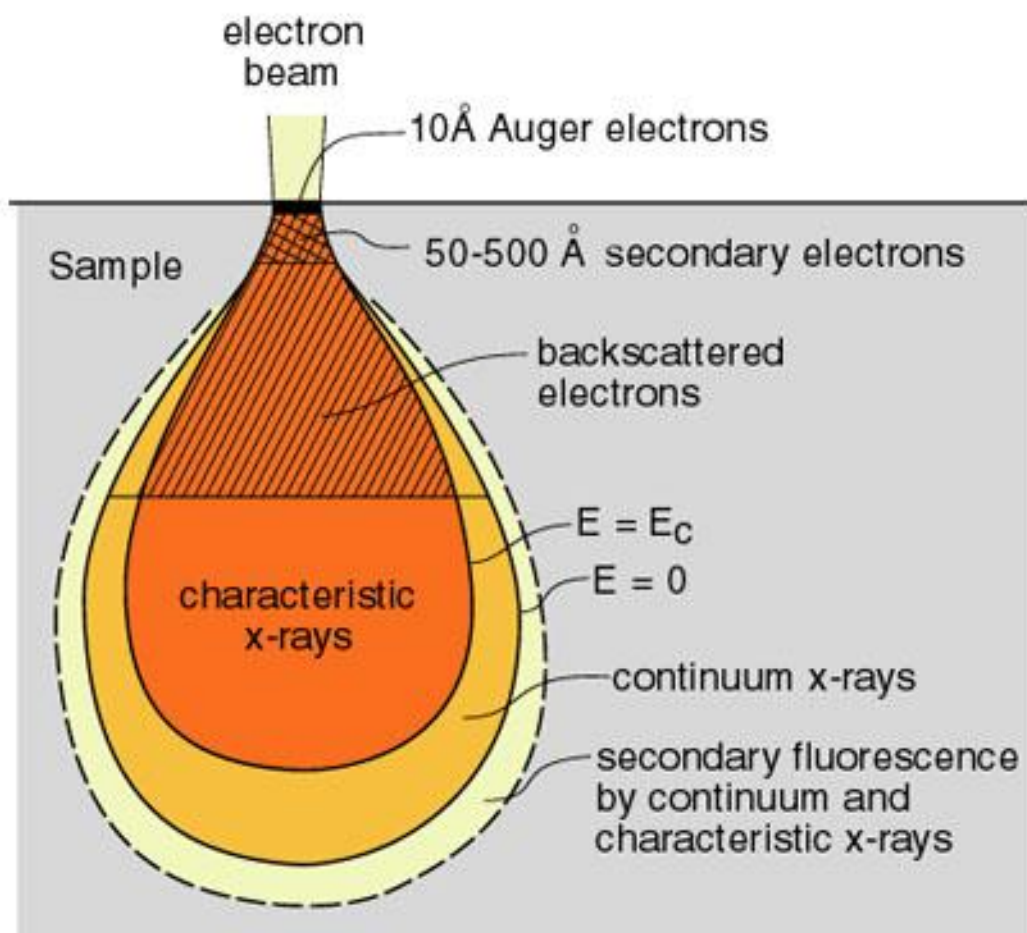


Fig. 2.9 Relative escape depths for different secondary species created due to interaction.¹⁶²

2.3 Materials properties

2.3.1 Magnetic properties measurement

The magnetization measurements are performed by Physical Property Measurement System (PPMS Quantum Design DynaCool) with a vibrating sample magnetometer (VSM) head. The system can achieve magnetic fields up to ± 9 tesla and a temperature range of 1.8 – 400 K. The VSM measurement noise is less than 5×10^{-7} emu. Fig. 2.10 shows the PPMS basic components with VSM option. After loading the VSM sample in center of the magnet also near a detection coil, the induced voltage can be detected by oscillating the sample. There are two different types of VSM measurements. The first type is studying the magnetization vs. magnetic field ($M-H$) of perovskite oxide thin films. In these measurements, a magnetic field is applied parallelly or perpendicularly (out-of-plane) to the sample. Usually, the in-plane magnetization shows easy axis and the out-of-plane magnetization exhibits a hard axis. The second type measurement is magnetization vs. temperature ($M-T$).



Fig. 2.10 PPMS basic components with an illustration of VSM part.^{163,164}

2.3.2 Polarization-electric field measurement

Ferroelectric P-E measurements are typically performed using sophisticated commercially available testers. In addition to the P-E measurement, several other measurements can be performed, like retention, imprint, fatigue, capacitance-voltage, and leakage current measurements on ferroelectrics, as well as resistive and dielectric materials. The basic measurement circuit is a modified version or the original circuit used by Sawyer and Tower for their measurements on Rochelle salt. Shown in Fig 2. 11(a) is the original Sawyer- Tower circuit.

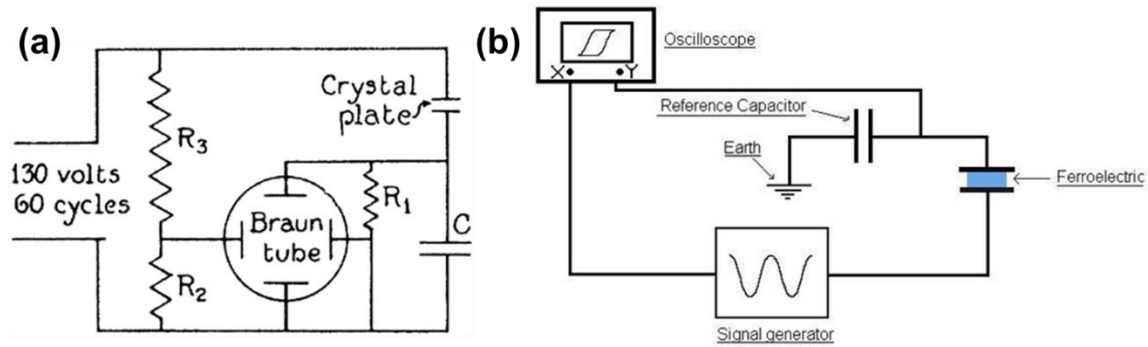


Fig. 2.11 (a) The original Sawyer-Tower circuit¹⁶⁵ and (b) a schematic of the Sawyer-Tower measurement.¹⁶⁶

From the simplified Sawyer-Tower circuit in Fig. 2.11 (b), a voltage source is connected to the ferroelectric capacitor C_F which is connected in series to a sense capacitor C_1 of known capacitance such that $C_1 \gg C_F$.

The charge Q across a parallel plate capacitor is given by

$$Q = CV \quad (2-4)$$

where C is the capacitance and V is the applied voltage. The charge can also be written as

$$Q = 2P_r A \quad (2-5)$$

where A is the cross-sectional area.

From Eqns. 2-4 and 2-5, the relationship between the capacitance and polarization is given by

$$C \propto \frac{dP_r}{dV} \quad (2-6)$$

Thus, the polarization is measured by monitoring the change in the voltage across the reference capacitor in Fig. 2.11 (b).

CHAPTER 3. STRAIN TUNING OF FERROELECTRIC AND OPTICAL PROPERTIES OF RHOMBOHEDRAL-LIKE BiFeO_3 THIN FILMS ON SrRuO_3 -BUFFERED SUBSTRATES

3.1 Overview

Rhombohedral-like (R-like) BiFeO_3 (BFO) thin films with a SrRuO_3 (SRO) buffer layer have been deposited on a range of lattice mismatched substrates, including single crystalline (001)-oriented LaAlO_3 (LAO), SrTiO_3 (STO), MgO and TiN-buffered Si substrates. A wide range of strain states in BFO films have been achieved on these substrates. Ferroelectric measurements indicate that the film strain state affects the polarization of the BFO films. The bandgap of R-like BFO films follows the trend that highly compressive strain in BFO thin films leads to a larger bandgap. This study indicates that the physical properties including bandgap and ferroelectricity of BFO films, can be effectively tuned on large lattice mismatch substrates even with partial strain relaxation. Furthermore, the integration of ferroelectric BFO on SRO-buffered Si substrates suggests the possible application of strained BFO in Si-based electronic and optical devices.

This chapter is reprinted with permission from “Strain tuning of ferroelectric and optical properties of rhombohedral-like BiFeO_3 thin films on SrRuO_3 -buffered substrates” by H. Wang, *et al*, Materials Research Bulletin, 110, 120(2019). Copyright © 2019 by Elsevier.

3.2 Introduction

Multiferroic BiFeO₃ (BFO) has been intensively studied, because of its strong ferroelectric polarization and magnetoelectric coupling at room temperature^{77,167}. BFO also attracts strong interest for its applications in photonics and plasmonics, owing to its band gap (~ 2.7 eV) in the visible range¹⁶⁸, strong photovoltaic effect¹⁶⁹ and large electro-optic coefficients⁶¹. The observed multi-functionalities make BFO an ideal candidate for advanced photonic devices such as electro-optical modulators (EOMs)¹⁷⁰ and oxide-based solar cells. Strain engineering presents as a powerful approach through which most of these physical properties of BFO thin films can be tuned via structural symmetry^{171,172}. There has been particular interest on the influence of substrate-induced strain on structure, spontaneous polarization, and magnetization of BFO thin films¹⁷³. It has been demonstrated that BFO could experience tetragonal (T) - monoclinic type-C (M_C) - monoclinic type-A (M_A) - rhombohedral (R) symmetry transition sequence through applied biaxial strain from substrates¹⁷⁴. Strain-driven morphotropic phase boundaries (MPBs) have been discovered in BFO thin films^{171,175}. Epitaxial BFO thin films on SrTiO₃ (STO) possess a monoclinic phase and show a remanent polarization of (50 to 60 $\mu\text{C}/\text{cm}^2$) and enhanced magnetization¹⁷⁶, which is comparable to the bulk¹⁷⁷. The enhancement is attributed to the polarization rotation induced by the compressive epitaxial strain in BFO thin films¹⁷³. It was suggested that epitaxial strain, in either compressive or tensile state, can substantially influence the spontaneous polarizations and Curie temperatures of BFO thin films^{173,178,179}. BFO thin films deposited on LaAlO₃ (LAO) substrate exhibits a giant c/a ratio of 1.23 under compressive strain. It exhibits a large bandgap (~ 3.02 eV) and could keep both strong ferroelectric¹⁸⁰ and ferromagnetic properties at room temperature¹⁸¹. There is also an increase of the bandgap (~ 2.80 eV) in tensile-strained BFO thin films¹⁸². The remarkable ferroelectric and optic properties, and

the coupling between them revealed by BFO thin films, hence, lead to rich tunability and potential technological applications in these systems.

Towards the practical applications of BFO, (001)-oriented LAO and MgO substrates are more ideal than STO, because of their lower dielectric constant and loss tangent values ¹⁸³. Considering the high cost of LAO, STO and MgO substrates, there are also great needs for oxide integration on silicon (Si) substrates towards multifunctional oxide devices on Si ^{184,185}. SrRuO₃ (SRO) has been widely used as a bottom electrode in ferroelectric testing and switching of BFO thin films, for it shows conductive without doping and undergoes minimal structural change under the influence of strain ^{186,187}. In addition, SRO is often chosen as the buffer layer to control nanoscale domain architecture in BFO ¹⁸⁸. It is, hence, desired to investigate the strain state, ferroelectric and optical property tuning of BFO thin films with the SRO buffer layer on various substrates.

In this study, (001)-oriented LAO, STO, MgO and Si substrates with a wide range of lattice mismatch varied from compressive to tensile for the proposed tuning study (from + 4.51 % on LAO, + 1.52 % on STO, and – 6.00 % on MgO, and – 31.20 % on Si (without domain matching epitaxy)). The lattice parameters of BFO and substrates are compared and shown in Fig. 3. S1. A thin SRO buffer layer of 15-20 nm has been deposited for this strain tuning study on STO, LAO, MgO and TiN-buffered Si substrates. TiN/Si has been selected since TiN ($a=4.242 \text{ \AA}$) has been reported to minimize the large lattice mismatch with Si ($a=5.431 \text{ \AA}$) to around 4.1% through domain matching epitaxy (i.e., 4 of (200) TiN match with 3 of (200) Si very well) ^{189,190}. Such TiN/Si is helpful for the epitaxial growth of SRO buffer layer and the functional oxides ¹⁹¹. We explored the epitaxial strain effects of SRO/substrate on the overall BFO film quality, and, the corresponding ferroelectric and optical properties to probe the overall tunability of the materials.

The mechanisms of strain-controlled optical and ferroelectric properties of BFO films are discussed.

3.2 Experimental

The Bi-rich $\text{Bi}_{1.1}\text{FeO}_3$ and SRO targets were prepared by a conventional solid-state sintering method. The TiN targets (Plasmaterials, Inc) was hot-pressed stoichiometric TiN. The TiN seed layer was deposited on (001)-oriented Si substrate with the conditions ¹⁹⁰. The epitaxial BFO and SRO thin films were deposited on single-crystal (001)-oriented LAO, STO, MgO and TiN-buffered Si substrates by pulsed laser deposition (PLD) using a KrF excimer laser ($\lambda = 248$ nm). The SRO buffer layer was deposited at a pulse rate of 5 Hz, while the deposition rate of BFO thin films was 10 Hz. All depositions were under an optimized oxygen partial pressure of 50 mTorr. Substrate temperature of 700 °C and 670 °C were maintained during SRO and BFO deposition. Following BFO deposition, the composite thin films were annealed in 500 Torr oxygen at a cooling rate of 5 °C/min. 100 nm thick Au top contacts of 0.1 mm² area, were deposited by a custom-built magnetron sputtering system using a 99.99% pure Au sputter target from Williams Advanced Materials.

The EDS analysis was conducted using a scanning electron microscope (SEM) (FEI Nova NanoSEM). The pseudocubic index is used throughout this paper unless otherwise specified. The microstructure of as-deposited films was investigated with X-ray diffraction (XRD, PANalytical Empyrean) and transmission electron microscopy (TEM, FEI TALOS T200X) operated at 200 kV. Asymmetric reciprocal space mapping (RSM) of BFO (103) peak was used to analyze the phase details. The Bragg peak of (103) has been selected for the RSM scans. A two-dimensional (ω , 2θ) intensity map was collected and then converted to RS coordinate (Q_x , Q_z). The high-resolution scanning transmission electron microscopy (HRSTEM) images in high angle annular dark-field

(HAADF) mode (also called Z-contrast imaging) were obtained using a FEI Titan G2 80–200 STEM with a Cs probe corrector operated at 200 kV and a modified FEI Titan STEM TEAM 0.5 with a convergence semi-angle of 17 mrad operating at 300 kV. Ferroelectric polarization-electric field (P-E loops) measurements were conducted by Precision LC II Ferroelectric Tester (Radiant Technologies, Inc.). The phase and amplitude *hysteresis loops* were collected with atomic force microscopy (AFM, Bruker Dimension Icon). Bruker SCM-PIT Cr-Pt coated silicon cantilevers were adopted in the piezoelectric force microscopy (PFM) measurements. The transmission measurement was performed using Hitachi U-4100 UV-Vis-NIR spectrophotometer.

3.3 Results and discussion

3.3.1 BFO thin films growth

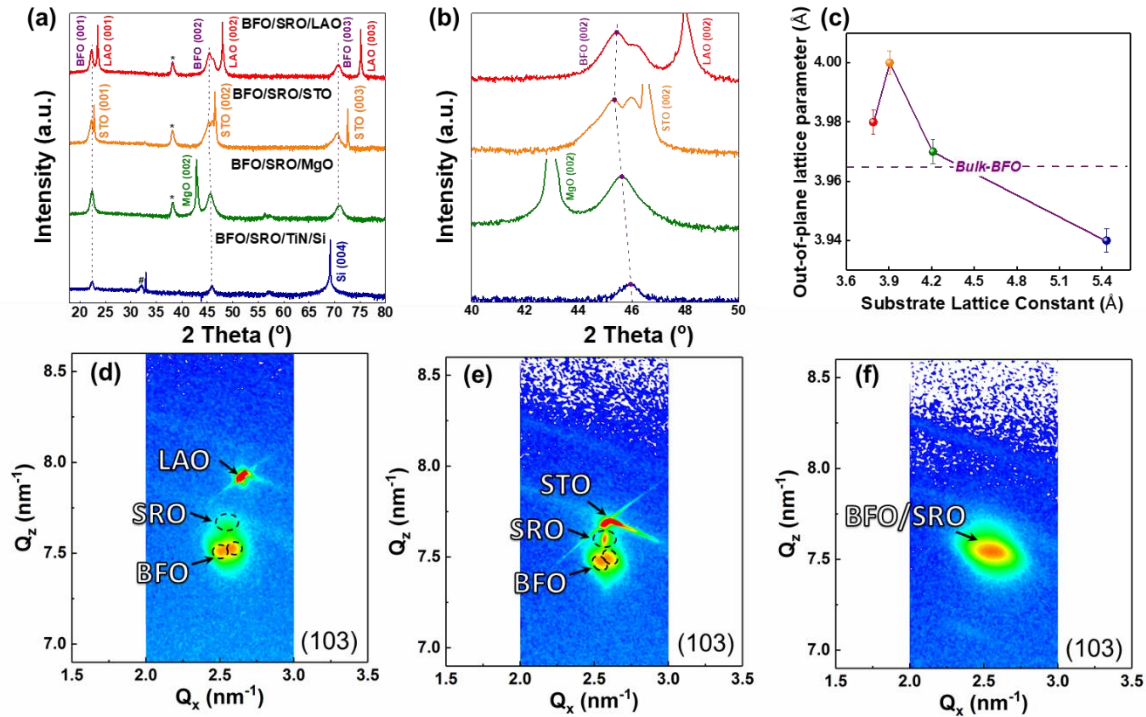


Fig. 3.1 (a) θ -2 θ XRD scans of BFO on SRO/LAO, SRO/STO, SRO/MgO and SRO/TiN/Si substrates. Au and TiO₂ peaks are denoted as “*” and “#”. (b) Local XRD scan of BFO (002) peak. (d)-(f) Reciprocal space map (RSM) results of BFO (103) peak on SRO/LAO, SRO/STO and SRO/MgO, respectively.

SEM–EDS analysis was conducted on several samples to determine the Bi and Fe content. The average of Bi/Fe ratio is 1.0, as displayed in the Table 3. S1. It shows the necessity of using Bi-rich $\text{Bi}_{1.1}\text{FeO}_3$ target for the BFO deposition for the possible Bi loss during target processing and deposition. Fig. 3.1(a) shows the XRD θ - 2θ scans of BFO thin films on SRO-buffered LAO, STO, MgO and TiN/Si substrates. The R-like BFO phase is evidenced by the BFO (00 l) diffractions, which are marked by the dashed line for all samples. SRO (00 l) peaks partially overlap with BFO ones. To examine the strain-driven lattice parameter variation in BFO, fine XRD spectra of BFO (002) peak is shown in Fig. 3.1(b). The full width at half maximum (FWHM) of BFO (002) was measured and summarized in Table 3. S2. The variation of the FWHM values indicates that BFO on SRO-buffered LAO, STO and MgO have better texture quality, compared to the one on the SRO-buffered TiN/Si. This could be explained by lower epitaxial quality of the BFO films in the very large lattice mismatched case of TiN/Si substrate. The out-of-plane lattice parameters were calculated and plotted in Fig. 3.1(c). They are 3.98 Å, 4.00 Å, 3.97 Å and 3.94 Å on SRO/LAO, SRO/STO, SRO/MgO and SRO/TiN/Si substrates, respectively. The lattice parameter of rhombohedral BFO (3.965 Å) is plotted as the reference. Based on the out-of-plane strain analysis, BFO on SRO/ LAO, SRO/STO and SRO/MgO are under compressive strain, while the one on Si exhibits tensile strain. This result is inconsistent with the expectation following the calculated lattice mismatch, which indicates that SRO buffer layer lessens the strain effect from pure substrates. The buffer layer could keep the strain states well on STO, due to the relatively small lattice mismatch of $\sim +0.6\%$. Larger lattice mismatch exists in SRO/LAO ($\sim +2.0\%$) and SRO/MgO ($\sim -6.9\%$), and thus partial strain relaxation has happened in the SRO buffer layer. For the case of Si, another buffer layer, TiN, was introduced to minimize the large lattice mismatch between SRO and Si by domain matching^{188,189}. The low intensity of the SRO peak indicates low

epitaxial quality of SRO layer on TiN/Si, but in a strained state, which consequently led to tensile strain in the out-of-plane of BFO.

To reveal the phase features of BFO, asymmetric reciprocal space mapping (RSM) around the BFO (103) peak position was performed and the results are shown in Fig. 1(d)-(f). Both BFO films on SRO/LAO and SRO/STO (Fig. 3.1(d)-(e)) exhibit an obvious peak splitting, which are marked by two black dashed circles. It implies the existence of a Rhombohedral-like (R-like) phase with monoclinic structure in BFO thin films¹⁹². No splitting was observed for the BFO (103) on SRO/MgO (Fig. 3.1(f)), which suggests the BFO structure is very close to the bulk structure for this case. It is, however, hard to conclude that the film is fully relaxed considering the calculated out-of-plane data. The strain analysis is further conducted using strain mapping by STEM imaging and discussed later.

3.3.2 Microstructure characterization

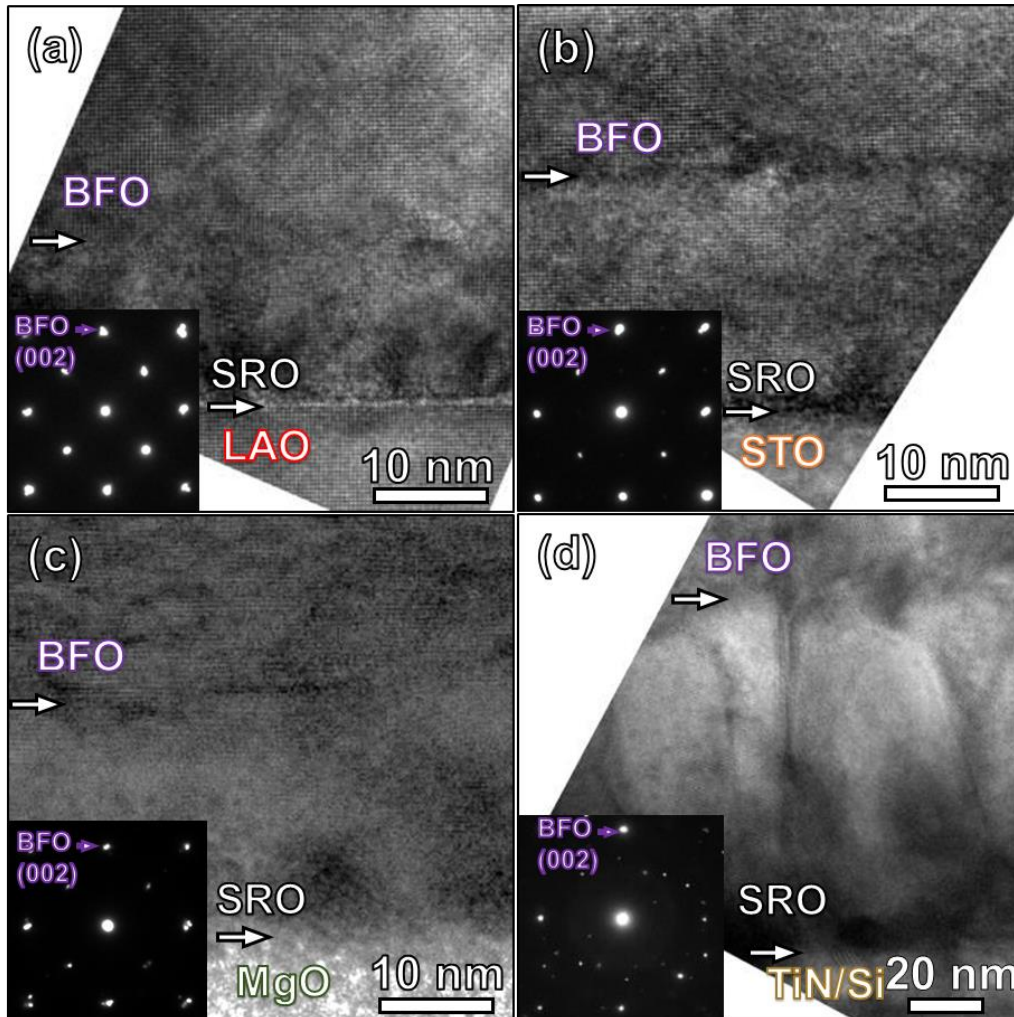


Fig. 3.2 (a)-(d) Cross-sectional TEM images of BFO on SRO/LAO, SRO/STO, SRO/MgO and SRO/TiN/Si substrates, respectively. The inset shows the corresponding (SAED) pattern of BFO thin films. White arrows mark the interface between each layer

Cross-sectional TEM images in Fig. 3. 2(a)-(d) show the overall film stacks of BFO and SRO on LAO, STO, MgO and TiN/Si where the interfaces between each layer are marked by arrows. For the LAO, STO and MgO substrates, clear and flat interfaces are exhibited, and the thickness of the SRO buffer is 15 ~ 20 nm. The SRO buffer layer on TiN/Si is relatively thick around 100 nm to ensure improved texture for the growth of BFO. The inset shows the corresponding selected area electron diffraction (SAED) patterns including the BFO thin films and

SRO buffer layers. It is **obvious** that BFO films all grow epitaxially and the ones on SRO/LAO, SRO/STO and SRO/MgO are of higher epitaxial quality than that on SRO/TiN/Si. Combining the XRD and TEM results, it suggests that the strain relaxation happened in BFO on SRO/TiN/Si substrate.

3.3.3 Strain analysis

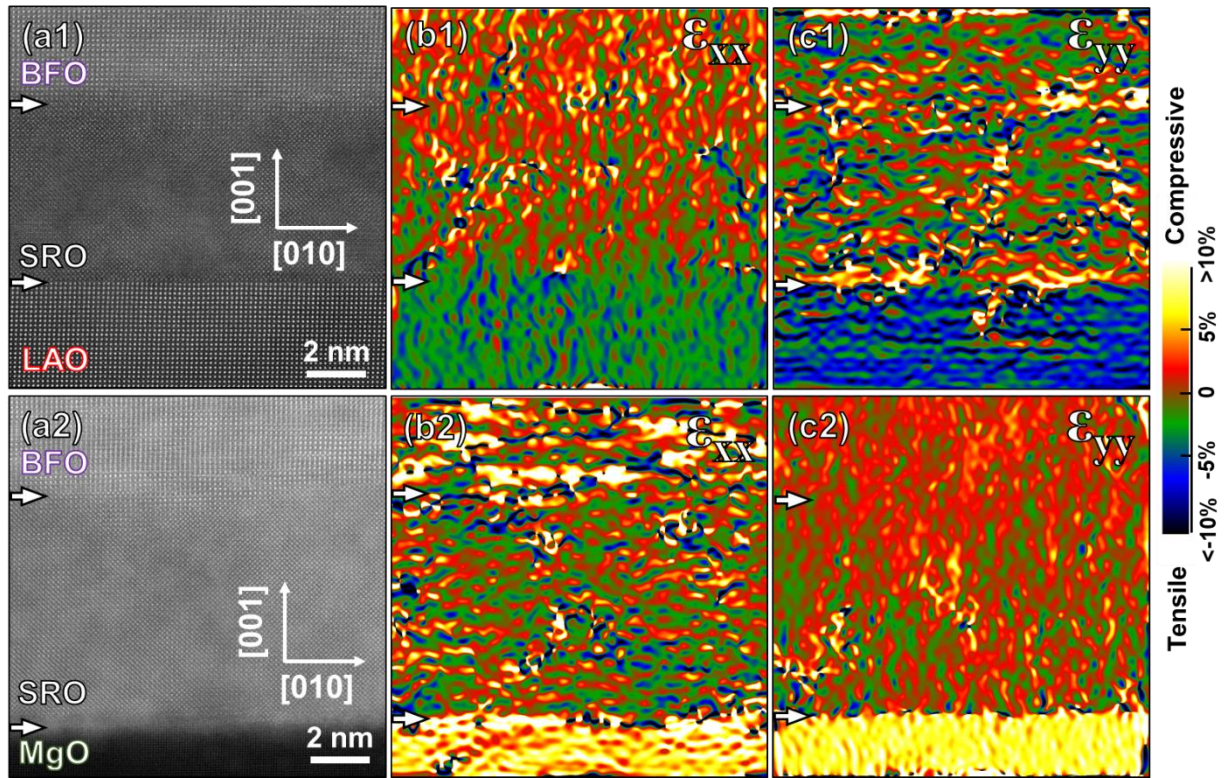


Fig. 3.3 (a1)-(a2) Cs-corrected high-resolution STEM images of BFO on SRO/LAO and SRO/MgO substrates, and (b1)-(b2) their corresponding GPA ϵ_{xx} (in-plane strain) maps and (c1)-(c2) ϵ_{yy} (out-of-plane strain) maps.

Fig. 3.3 (a1)-(a2) show the high-resolution scanning transmission electron microscopy (HR-STEM) images of BFO on SRO/LAO and SRO/MgO substrates. White arrows mark the interfaces between the BFO, SRO and substrates. The out-of-plane lattice parameters of the BFO lattice near the interface are measured to be 4.07 Å on SRO/LAO and 3.87 Å on SRO/MgO. It

suggests that the BFO near the interface area undergoes an in-plane compressive strain on SRO/LAO, while it presents an in-plane tensile strain on SRO/MgO. This is inconsistent with the above XRD results as the STEM study focuses on the film/substrate interface area, while XRD covers the entire film thickness and a large area. In-plane (ϵ_{xx}) and out-of-plane (ϵ_{yy}) epitaxial lattice strain has been further analyzed using geometric phase analysis (GPA) based on the HRSTEM images. The mapping data is presented in Fig. 3. 3(b1), (b2), (c1) and (c2) with the SRO buffer layer as the reference lattice. A gradual strain variation can be seen across the interface of SRO/LAO (Fig. 3. 3 (b1)-(b2)), while an obvious strain jump, color coded from yellow to red, is identified across the interface of SRO/MgO. It is evident that more strain relaxation is in the case of SRO buffer layer on MgO than that of the LAO one. The strain contour across the BFO/SRO interface is in a uniform color, implying BFO maintained the strain state through SRO. The strain state of BFO also suggests that SRO buffer layer could remain in-plane compressive strain rather than in-plane tensile strain.

3.3.4 Electrical measurements

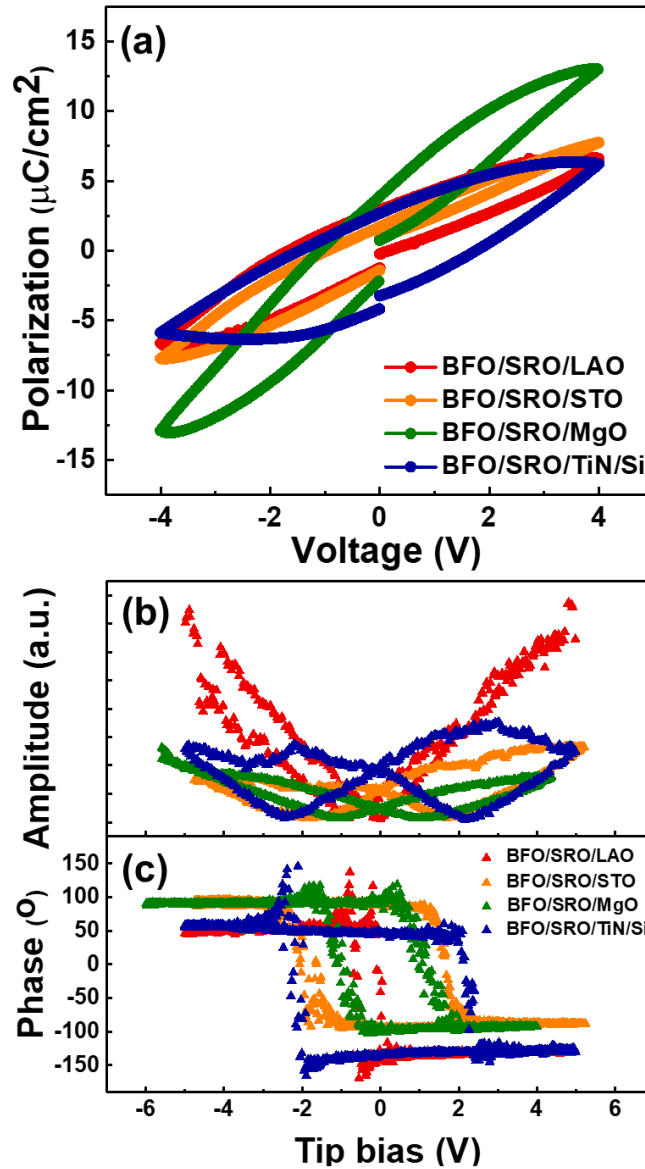


Fig. 3.4 (a) Comparison of polarization hysteresis measurements for BFO on SRO/LAO, SRO/STO, SRO/MgO and SRO/TiN/Si. (b) Amplitude switching behavior as a function of tip bias with (c) their corresponding phase switching behavior.

The ferroelectric behaviors under a bias of ± 4 V in BFO films on SRO/LAO, SRO/STO, SRO/MgO and SRO/TiN/Si substrates are shown in Fig. 3. 4(a). The well-defined hysteresis loops clearly confirm that BFO thin films, even with partial strain relaxation in SRO, exhibit strong

ferroelectric behavior at room temperature. The remanent polarization values are lower for SRO/STO, while higher for SRO/LAO and SRO/MgO. Based on the structure characterization, BFO films on SRO/LAO and SRO/STO are mostly in monoclinic structure. This crystal structure provides further degrees of freedom for the polarization direction and amplitude related to the rotation of the oxygen octahedral as previously reported¹⁸¹. The wider P-E loop of BFO on TiN/Si may be due to its lower epitaxial quality as indicated in the XRD results. PFM measurements have been performed on BFO and complete polarization switching has been observed for all the substrates as shown in Fig. 3. 4(b)-(c). The BFO film on SRO/LAO substrate has the most obvious amplitude enhancement and sharp phase switching by 180°, which indicates that the switched polarization remains after the bias removal. As previously suggested by Mazumdar *et al.*, it is possible for the appearance of intermediate states during the polarization switching process in R-like BFO on LAO substrate¹⁸⁰.

3.3.5 Optical measurements

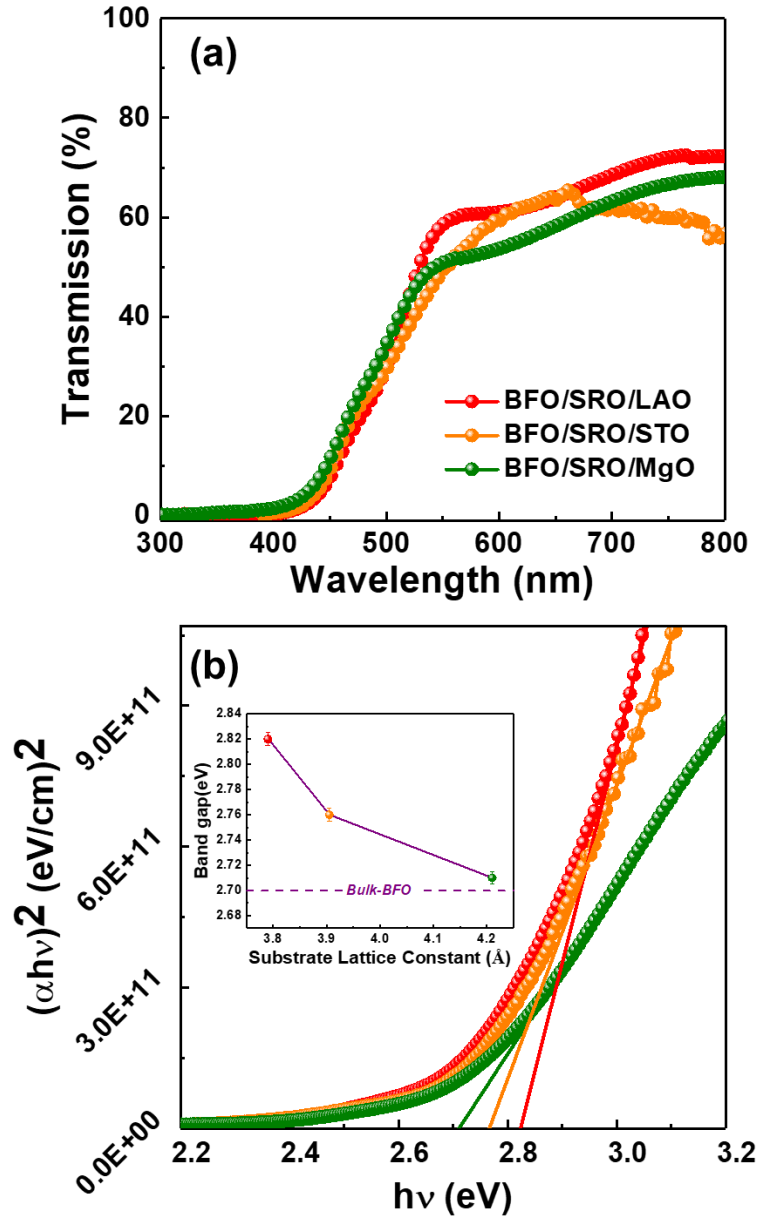


Fig. 3.5 (a) Optical transmission spectrums of BFO on SRO/LAO, SRO/STO and SRO/MgO substrates. (b) The corresponding plot of $(\alpha h\nu)^2$ versus $h\nu$. The inset shows the summary of optical bandgap versus pseudocubic substrate lattice constant.

Fig. 3.5(a) presents the optical transmission spectrums of the BFO on SRO/LAO, SRO/STO and SRO/MgO, and (b) their corresponding Tauc plots. The classical Tauc formula is shown as follows ¹⁹³:

$$\alpha h\nu^2 = \text{Constant} \cdot (h\nu - E_g)$$

where α is the optical absorption coefficient, h is the Planck's constant, ν is the frequency of incident photons, E_g is the optical band gap, the constant is called the band tailing parameter, and the index of 2 corresponds to the direct transition for BFO, respectively. The plot of $\alpha h\nu^2$ versus $h\nu$ gives a straight line in a certain region. The bandgap value E_g is therefore determined by extrapolating the linear portion of the plot relating $\alpha h\nu^2$ verse $h\nu$ to 0. As shown in Fig. 5(b), the linear extrapolation gives the E_g values of 2.82, 2.76 and 2.71 eV for BFO thin films on SRO/LAO, SRO/STO and SRO/MgO substrates, respectively. The bandgap of SRO estimated by work function is 5.2 eV ¹⁹⁴, which can't overlap with the bandgap of BFO. The inset summarizes the optical bandgap versus substrate lattice constant. Compressive strain results in an increase of the optical bandgap for R-like BFO, which is consistent with the previous report ¹⁸². The BFO on SRO/MgO has the lowest bandgap, which is related to the compressive strain in BFO induced by the strain-relaxed SRO buffer layer on MgO. In addition, the above analysis of the strain mapping suggests that part of the BFO films is still under tensile strain. The balance between the tensile and compressive strain states will give rise to the final bandgap values. The overall trend of the bandgap values as a function of substrate lattice is that, as the substrate lattice increases, the bandgap value decreases. The bandgap variation could be attributed to the distortion of Fe^{3+} local field and the shifts in the O 2p orbitals, which is induced by the strain effect and structure symmetry breaking ¹⁹⁵. Combined with the XRD and RSM result, the tuning in bandgap suggests that the SRO-buffered substrates have strong effects on the optical behavior of BFO thin films.

Further experimental work on the substrate-induced strain in a systematic way is necessary to clarify the effect of BFO monoclinic structure in the distorted rhombohedral phase.

3.3.6 Conclusions

In summary, the BFO thin films show high epitaxial quality on various lattice mismatched substrates, such as STO, LAO, MgO and TiN-buffered Si, all with an SRO buffer layer. The ferroelectric polarization of the films on LAO, MgO and TiN/Si is comparable to the case of STO substrate with a good lattice matching. The in-plane compressive strain leads to narrow bandgaps in BFO thin films. The feasibility of tuning ferroelectric and optical properties of BFO via the substrate-induced strain with SRO buffer layer is critical for future practical applications of BFO. The demonstration of BFO integrated on SRO/TiN buffered Si, with a pronounced ferroelectric response, enables broad applications of BFO thin films in Si-based electronic and optical devices.

3.3.7 Supplementary

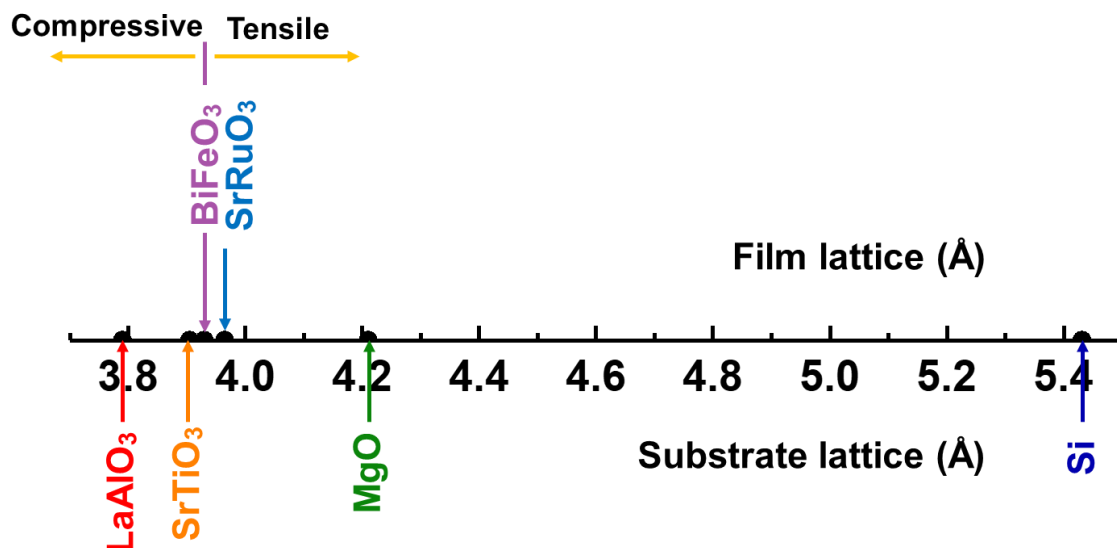


Fig. S3.1 Comparison of pseudocubic lattice parameters. Epitaxial BFO thin film and substrates displayed above and below the number line, respectively.

Table S3.1 EDS Analysis for Bi and Fe elements

Sample	Bi (Atomic %)	Fe (Atomic %)	Bi/Fe Ratio
BFO/SRO/LAO	6.43	6.43	1.00
	6.35	6.54	0.97
BFO/SRO/STO	10.01	9.15	1.09
	9.8	9.27	1.06
BFO/SRO/MgO	6.5	6.39	1.02
	6.46	6.41	1.01
Average			1.02

Table S3.2 The FWHM of BFO (002)

Sample	FWHM of BFO (002), (°)
BFO/SRO/LAO	0.53
BFO/SRO/STO	0.48
BFO/SRO/MgO	0.41
BFO/SRO/TiN/Si	0.75

CHAPTER 4. EFFECTIVE DOPING CONTROL IN Sm-DOPED BiFeO₃ THIN FILMS VIA DEPOSITION TEMPERATURE

4.1 Overview

Sm-doped BiFeO₃ (Bi_{0.85}Sm_{0.15}FeO₃, or BSFO) thin films have been deposited on single-crystal LaAlO₃ (LAO) (001) substrates over a range of substrate temperatures. The Sm doping amount could be effectively tuned via the temperature. Detailed microstructure analysis via STEM first proves the existence of Sm in BSFO. It also demonstrates phase information of BSFO could be controlled with Sm doping and then correspondingly effects the ferroelectric properties. This demonstration paves a way for controlling the phase information and ferroelectric property of BSFO with Sm doping amount to meet the practical applications.

4.2 Introduction

BiFeO₃ (BFO) has attracted enormous research interest, due to its multiferroic property (coexistence of ferroelectric and antiferromagnetic ordering). In addition, the various phase structure and the morphotropic phase boundary (MPB) behavior of BFO thin films contribute to remarkably enhanced piezoelectric response^{196,197}. Therefore, BFO has been considered as a promising alternative lead-free piezoelectric material and shows great device potentials in actuators, acoustic sensors, etc⁸⁶. Epitaxial strain imposed by a wide range of substrates has been used to control the MPB formation in BFO thin films⁹⁰. However, substrate induced strain is limited and only effective up to 10-20 nm. Further increasing the thickness leads to the strain relaxation. In addition, it suffers from high-leakage current and large coercive fields, as well as the electromechanical coefficients not large enough to compete with most conventional ferroelectrics

¹⁹⁸. In order to overcome the above mentioned defects, rare-earth doped BFO (Re-BFO) systems emerged and been widely used in controlling the microstructure and properties of BFO.

As the polarization is mainly induced by Bi^{3+} ions, rare-earth elements have been doped into the Bi-site of BFO to improve the overall ferroelectric response ¹⁹⁹. It showed that La- or Sm-doping could decrease the leakage current and improve the piezoelectric activity of BFO thin films ²⁰⁰. In addition, Re-BFO exhibits a number of phase structures or phase boundaries established by doping foreign elements or forming solid solutions ²⁰⁰⁻²⁰². Preliminary phase diagrams of $\text{Bi}_{1-x}\text{Ln}_x\text{FeO}_3$ (Ln=La, Nd, Sm, Gd) systems were proposed ^{203,204}. The present results show that Sm-doped BFO has unique properties compared to the more popular La or Nd-doped BFO systems. Sm^{+3} has a much smaller ionic size than La^{+3} . The existence of a low symmetry phase at MPB is expected to enhance the piezoelectric properties as the polarization vector is no longer constrained to lie along a symmetry axis but instead can rotate within a suitable plane. The Sm-doped BFO thin films also exhibit high values of out-of-plane piezoelectric coefficient ($d_{33} \sim 110$ pm/V) and enhanced dielectric constant, because of the MPB between rhombohedral and pseudo-orthorhombic phases ^{97,205}.

In this work, $\text{Bi}_{0.85}\text{Sm}_{0.15}\text{FeO}_3$ (BSFO) was selected as the model system. To explore how the Sm doping element tune the microstructures and ferroelectric properties of BSFO thin films, three different substrate temperatures has been used in the thin film deposition. Deposition temperature has been proven as an effective deposition parameter in controlling the thin film microstructure and the related properties. For example, in Ag-doped ZnO (SZO) system, deposition temperature directly controls the density of stacking faults and finally affect the conductivity property ²⁰⁶. Studies on the effect of deposition temperature on the growth of BSFO thin films are missing, so this work will help enrich the knowledge of BSFO system. Detailed

microstructures of BSFO were analyzed and the corresponding ferroelectric properties were characterized, which were also compared with the pure BFO to demonstrate the effectiveness of Sm doping in tuning the structure and physical properties.

4.3 Experimental

The BSFO target was synthesized by a conventional solid-state sintering method using high-purity Bi_2O_3 (99.99%), Fe_2O_3 (99.95%) and Sm_2O_3 (99.90%) powders. The epitaxial thin films were deposited on single-crystal (001)-oriented STO substrates by pulsed laser deposition (PLD) using a KrF excimer laser ($\lambda = 248$ nm). Thin films were deposited at three different substrate temperatures of 670 °C, 640 °C and 600 °C. For all depositions, the deposition rate was 5 Hz under an optimized oxygen partial pressure of 200 mTorr. Following the deposition, the films were cooled down to room temperature in 200 Torr oxygen atmosphere and at a cooling rate of 10 °C/min. 100 nm thick Au top contacts of 0.1 mm² area were deposited by a custom-built magnetron sputtering system using a 99.99% pure Au sputter target from Williams Advanced Materials.

X-ray diffraction (XRD) spectra were measured using a PANalytical Empyrean with Cu K_α radiation. An FEI TALOS F200X TEM/STEM with ChemiSTEM technology (X-FEG and SuperX EDS with four silicon drift detectors) operated at 200 kV was used for microstructure characterization and energy-dispersive X-ray spectroscopy (EDS) chemical mapping. Ferroelectric polarization-electric field (P-E loops) measurements were conducted by Precision LC II Ferroelectric Tester (Radiant Technologies, Inc.).

4.4 Results and Discussion

4.4.1 BSFO thin film growth

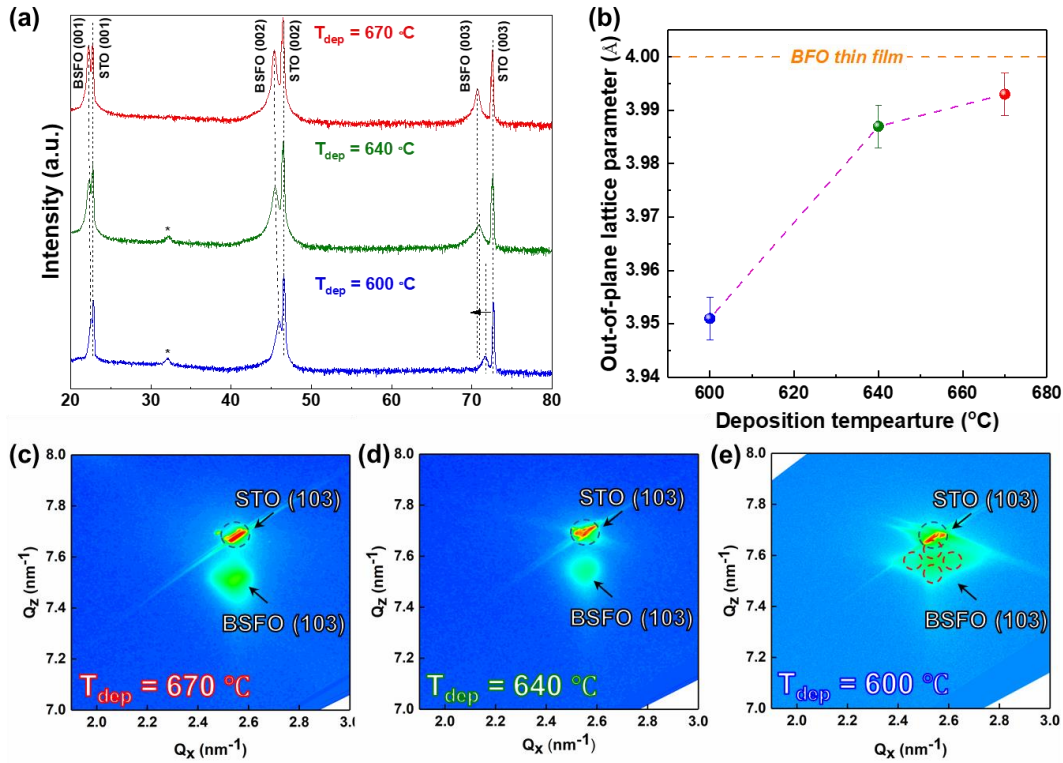


Fig. 4.1 (a) θ -2 θ XRD spectra of BSFO film deposited at 670 °C, 640 °C and 600 °C. (b) The summary of out-of-plane lattice parameter. (c)-(e) Reciprocal space map (RSM) results of BSFO (103) peaks.

The microstructural information was first acquired by X-ray diffraction (XRD). Fig. 4. 1(a) shows the θ -2 θ XRD spectra of 670 °C, 640 °C and 600 °C samples. All films mainly show (00 l) diffractions, indicating high epitaxial quality of BSFO along c -axis. It is interestingly observed that BSFO (003) peak shifts from 71.616° (T_{dep} =600 °C), to 70.817° (T_{dep} =640 °C) and to 70.699° (T_{dep} =670 °C) as the deposition temperature increases. The corresponding out-of-plane lattice parameters are calculated as 3.951 Å, 3.987 Å and 3.993 Å, and they are summarized in Fig.1(b). Compared with the out-of-plane lattice parameter of pure BFO film (~ 4.000 Å), three BSFO samples show smaller lattice parameter. The Sm^{3+} ion (radius=0.958 Å) has a smaller radius than

the Bi^{3+} ion (radius=1.030 Å) ²⁰⁷. It suggests that the partial Bi^{3+} ions have been substituted by Sm^{3+} ions. The BSFO peaks at around 32.155° comes from Rhombohedral (110) peak and denoted as “*” in the figure. With the deposition temperature increase, the peak disappears in the 670 °C sample. The above results indicate that the deposition temperature controls the Sm doping amount and then influence the BSFO crystal structure.

To further analyze the detailed phase information, asymmetric reciprocal space mapping (RSM) of (103) peak position was performed on all three samples and the results are shown in Fig. 1(c)-(e). The RSM pattern of ($T_{\text{dep}} = 600^\circ\text{C}$) exhibits obvious four domains, which are marked by four red dashed circles. It indicates the existence of four structural domains of a rhombohedral phase ²⁰⁸. For the other two samples ($T_{\text{dep}}=670^\circ\text{C}$ and $T_{\text{dep}}=640^\circ\text{C}$), peak split of the domains along Q_x direction is not obvious. It is also shown by the narrower width ($T_{\text{dep}}=670^\circ\text{C}$ and $T_{\text{dep}}=640^\circ\text{C}$) along Q_x direction than that of the sample ($T_{\text{dep}}=600^\circ\text{C}$), indicating the improvement of crystalline quality in BSFO films deposited at higher temperature. These results provide direct evidence that the deposition temperature significantly affects the domain structure of the BSFO film.

4.4.2 Microstructure characterization

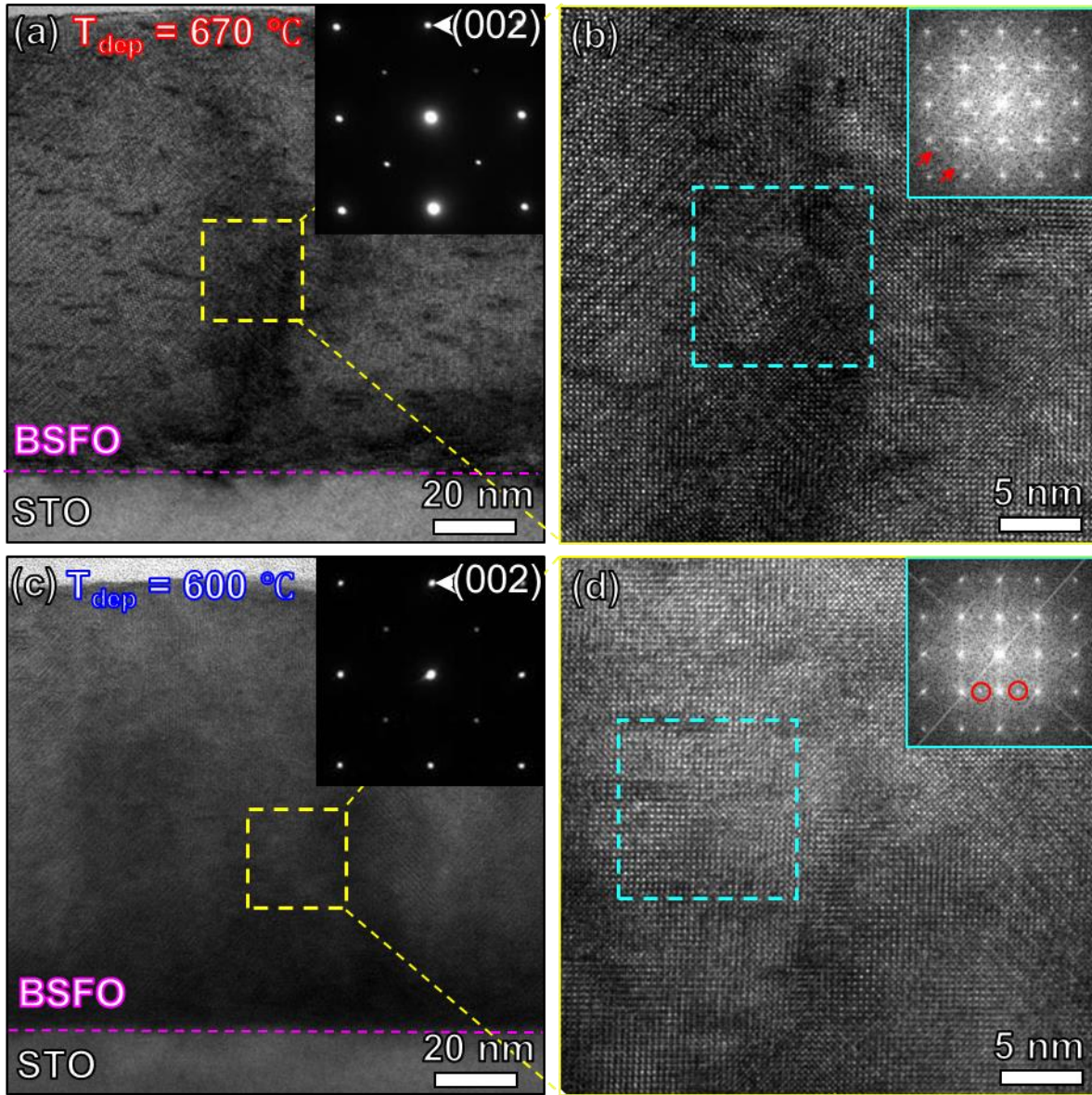


Fig. 4.2 (a) (c) Cross-sectional TEM images of BSFO thin films on STO substrates. (b) (d) High resolution TEM images. The insets in (a) and (c) show the corresponding (SAED) pattern of BSFO thin films. The insets in (b) and (d) show the fast-Fourier transformed (FFT) images from the blue squared region.

In order to analyze the microstructure structure, TEM analysis has been applied on two samples ($T_{\text{dep}}=670\text{ }^{\circ}\text{C}$ and $T_{\text{dep}}=600\text{ }^{\circ}\text{C}$). Fig. 4. 2 (a) and (c) show the overall films stacks of BSFO on STO substrates. The inset shows the corresponding selected area electron diffraction (SAED) patterns of BSFO thin film with only parent phases. The TEM image of high deposition

temperature sample ($T_{\text{dep}}=670\text{ }^{\circ}\text{C}$) exhibits a few dark lines. And the dark line density in the high deposition temperature sample is obviously higher than that of lower deposition temperature one. In TEM bright-field mode, image contrast is proportional to $\sim Z^2$ (Z , atomic number). The dark line is thus proposed be related to Sm, due to Z_{Sm} is larger than Z_{Bi} and Z_{Fe} . Fig. 4. 2 (b) and (d) are high resolution TEM (HR-TEM) images from local areas, which were analyzed by Fast Fourier Transform (FFT). The spots (marked by red arrows) in the FFT image of the sample ($T_{\text{dep}}=670\text{ }^{\circ}\text{C}$) correspond to the incommensurate phase, which is caused by the competition between FE and AFE. Different phase emerges in the sample ($T_{\text{dep}}=600\text{ }^{\circ}\text{C}$), and the corresponding spots $\frac{1}{2}\{010\}$ are marked by red circle. It has been proved as a none polar orthorhombic AFE phase, linked to the macroscopic AFE behavior. The phase information of $\text{Bi}_{0.85}\text{Sm}_{0.15}\text{FeO}_3$ thin film in this study is different from previous reported BSFO with only AFE phases²⁰⁹. This shows the effect of deposition temperature on the phase formation in BSFO system even with 15 atomic percent Sm.

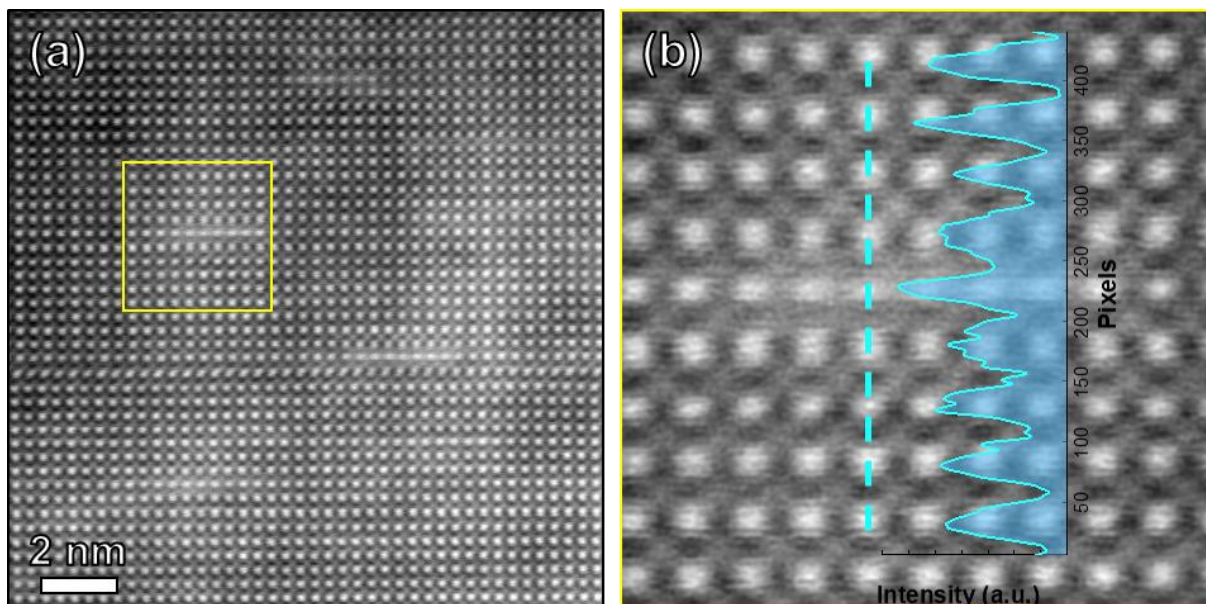


Fig. 4.3 (a) HR-STEM image of BSFO film deposited at 670 °C. (b) Enlarged view of the yellow dashed square area from (a). The intensity line profile is inserted along the marked blue line.

STEM analysis was then performed to resolve the composition information. Fig. 4. 3(a) shows the high resolution STEM (HR-STEM) image of the 670 °C sample. Under the high angle annular dark field mode (HAADF)in STEM (also called Z-contrast), the image contrast is proportional to $\sim Z^2$ (Z , atomic number). Thus, the white line areas in STEM image are corresponding to the dark lines in TEM images. We further examined the composition distribution across this Sm layer using the intensity line profile (Fig. 4.3(b)), which provides a direct interpretation of composition information in the HAADF imaging mode. It is obvious that the position near white line area has higher intensity than other areas. This result proves that Sm^{3+} ion has been successfully doped into BFO system. Energy dispersive spectroscopy (EDS) measurements have been further applied on the same area. The EDS mapping of Bi and Sm elements are shown in Fig. 4. S1 (b)-(c). A clear Sm-segregation across the white line was observed, as evidenced by the EDS line-scan of Sm in the inset of Fig. 4. S1(a). Both the TEM and STEM

results show that the higher deposition temperature BSFO sample ($T_{\text{dep}}=670\text{ }^{\circ}\text{C}$) has higher Sm doping amount.

4.4.4 Ferroelectric measurements

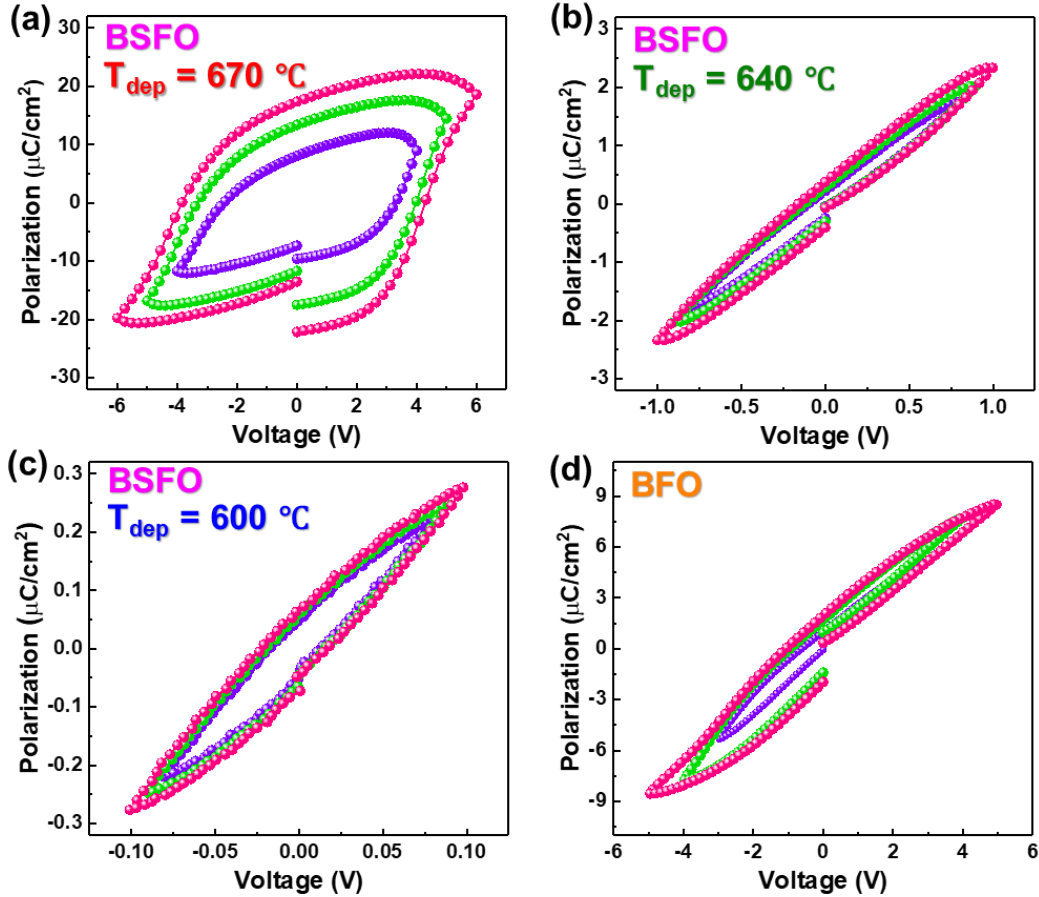


Fig. 4.4 (a)-(c) Polarization hysteresis measurements for BSFO film deposited at 670 $^{\circ}\text{C}$, 640 $^{\circ}\text{C}$ and 600 $^{\circ}\text{C}$. (d) Polarization hysteresis measurements for BFO film.

The ferroelectric behaviors were characterized by the polarization–electric field (P–E) hysteresis loops. Fig. 4. 4(a)-(c) show the P-E loops of BSFO samples with three different deposition temperatures, while Fig. 4. 4(d) shows the loop of BFO as a comparison. The BSFO sample ($T_{\text{dep}}=670\text{ }^{\circ}\text{C}$) with higher Sm doping amount exhibits obvious enhanced polarization. The remnant polarization (P_r) for the film is determined to be $17\text{ }\mu\text{C}/\text{cm}^2$, much larger than other two

BSFO samples and the BFO sample. It was proposed that the incorporation of Sm could break the short-range dipolar regions, surmount the local barrier and transform it to the long-range polar structure²¹⁰. The BFO film with four-variant domains exhibits a lower electric field and remnant polarization P_r ²¹¹. It was also found that the formation of bridging phase could enhance piezoelectric and dielectric properties of BSFO²¹². In this work, the BSFO sample ($T_{\text{dep}}=600\text{ }^{\circ}\text{C}$) shows four structural domain structure and the lowest P_r . With the increase amount of Sm doping amount, incommensurate phase appears in the $670\text{ }^{\circ}\text{C}$ sample. We conclude that the higher deposition temperature introduces the higher Sm doping amount, which assists the incommensurate phase formation and suppresses the AFE phase. Other rare earth doping elements such as La, Nd and Gd are also worthy of exploring with different deposition temperatures for the practical applications of Re-BFO in electronic devices.

4.4.5 Conclusions

This study proves that Sm doping amount in BSFO systems can be tuned effectively via deposition temperature. The Sm doping influences phase formation of $\text{Bi}_{0.85}\text{Sm}_{0.15}\text{FeO}_3$ and then the macroscopic ferroelectric properties. The appearance of incommensurate phase is beyond the reported Sm doping amount ($\text{Bi}_{0.86}\text{Sm}_{0.14}\text{FeO}_3$), which adds new data in the BSFO phase diagram. More interestingly, existence of Sm doping element in BSFO thin film has first been shown by detailed STEM and EDS analysis.

4.4.6 Supplementary

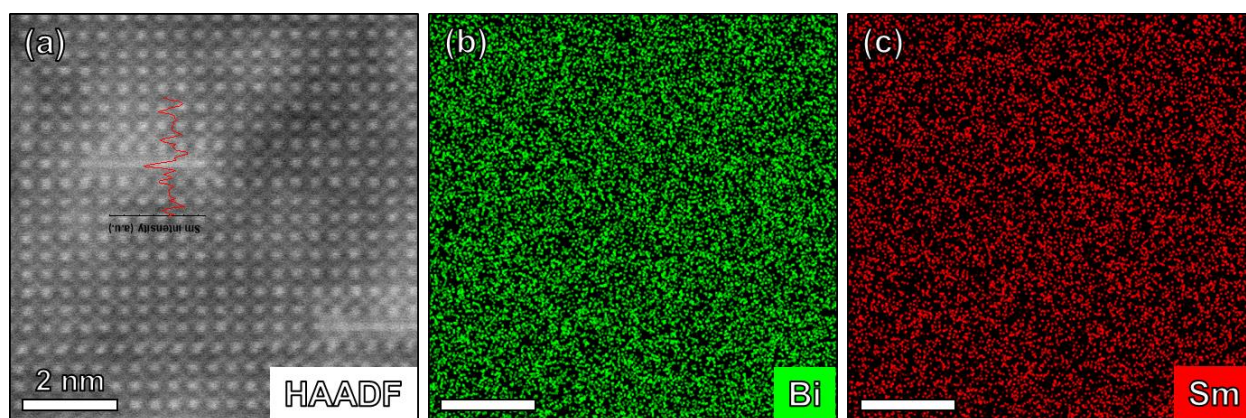


Fig. S4. 1HAADF image (a) with EDS mapping of Bi (b) and Sm (c) for BSFO thin film. The overlays in (a) shows the EDS line-scan profiles of Sm across the white line

CHAPTER 5. TWO-PHASE ROOM-TEMPERATURE MULTIFERROIC NANOCOMPOSITE WITH BiMnO_3 TILTED NANOPILLARS IN $\text{Bi}_2\text{W}_{1-x}\text{Mn}_x\text{O}_6$ MATRIX

5.1 Overview

Single phase multiferroics are scarce due to the fact that the coexistence of magnetism (spin order) and ferroelectricity (electric dipole order) in a single-phase material may be limited. Taking the advantage of nanocomposite design, combining a ferroelectric phase and a ferromagnetic phase presents enormous opportunities in multiferroic material exploration. In this work, a new 2D layered framework of $\text{Bi}_2\text{W}_{1-x}\text{Mn}_x\text{O}_6$ - BiMnO_3 (BWMO-BMO) in nanocomposite thin film form has been demonstrated and shows obvious room temperature multiferroic properties, i.e., ferroelectric and ferromagnetic at room temperature. The BMO phase forms a unique tilted domain structure in the BWMO matrix and both phases are with excellent epitaxial quality. The ferroelectric response originates from the layered Aurivillius phase of BWMO matrix, and the ferromagnetic properties mainly arise from the BMO nanodomains. Moreover, the band gap of BWMO-BMO nanocomposite is effectively tuned to 3.10 eV from its original 3.75 eV of BWO. This study demonstrates a new design of nanocomposite using layered oxides towards future multifunctional oxides for nanoscale devices.

This chapter is reprinted with permission from “Two-phase room-temperature multiferroic nanocomposite with BiMnO_3 tilted nanopillars in $\text{Bi}_2\text{W}_{1-x}\text{Mn}_x\text{O}_6$ matrix” by H. Wang, *et al*, ACS Applied Materials & Interfaces, (2019). Copyright © 2019 by American Chemical Society.

5.2 Introduction

Multiferroic materials with the coexistence of ferroelectricity and magnetism have gained considerable attention over the past few decades.^{213,214} Such materials are interesting because of their potential applications in non-volatile data storage, sensors and microwave devices.²¹⁵⁻²¹⁷ BiFeO₃ is currently one of the most well studied lead-free single-phase multiferroics. Its large polarization²¹⁸ and high Curie temperature (~ 820 °C)²¹⁹ make it appealing for applications in ferroelectric non-volatile memories and high temperature electronics. However, single-phase multiferroic materials are scarce in both natural forms and synthesized products,²²⁰ due to the fact that the coexistence of magnetism (spin order) and ferroelectricity (electric dipole order) in a single-phase material may be limited. Thus, great attention has been placed on the design of novel multiferroic materials by exploring either new families of materials^{105,221} or nanocomposite design.^{222,223}

Aurivillius phases are a class of materials worthy of exploration, because of their unique layered structures, and excellent ferroelectric properties with low leakage current and fatigue compared to BiFeO₃.^{40,224} The overall chemical formula is $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$, where many different cations can be incorporated in the A and B sites within the perovskite-like layers.²²⁵ It offers great potential for tailoring specific properties by varying both ionic composition and the number of layer structures. For example, enhanced ferromagnetic properties at room temperature have been reported for materials based on the bulk four-layer compound Bi₅FeTi₃O₁₅, with half of the Fe cations substituted by either Co or Ni.^{56,226} In addition, a new single-phase multiferroic material, SrBi₅Fe_{0.5}Co_{0.5}Ti₄O₁₈, was created by the insertion of magnetic BiFe_{1-x}Co_xO₃ into Aurivillius phase SrBi₄Ti₄O₁₅.²²⁷ However, it should be noted that in many cases the observed polarization and magnetization were reported in the bulk form, and depend strongly on the synthesis methods.²²⁸

For functional device integration of Aurivillius compounds, thin films growth methods are desired for functionality tuning and control of the layers.

Another approach for multiferroic material design is through combining a ferromagnetic phase with a ferroelectric one. Various two-phase nanocomposites have been demonstrated to show multiferroic properties including $\text{BiFeO}_3\text{:CoFe}_2\text{O}_4$, $\text{BaTiO}_3\text{:CoFe}_2\text{O}_4$, and $\text{BaTiO}_3\text{:YMnO}_3$.^{137,229,230} The vertically aligned nanocomposite (VAN) structures provide effective vertical strain coupling along vertical interfaces which allows enhanced ferroelectric properties and ferromagnetic properties compared to their single-phase counter parts.^{229,231}

In this work, a new layered Aurivillius compound of bismuth tungstate, Bi_2WO_6 (BWO), has been incorporated into a thin film structure with excess MnO_2 composition for the growth of $\text{Bi}_2\text{W}_{1-x}\text{Mn}_x\text{O}_6\text{-BiMnO}_3$ (BWMO-BMO) nanocomposite. Bi_2WO_6 (BWO) is selected for this work because it is one of the simplest layered oxide compounds and the most studied systems in the Aurivillius family.²² It is constructed by alternating $(\text{Bi}_2\text{O}_2)^{2+}$ slabs and $(\text{WO}_4)^{2-}$ perovskite layers, as shown in Fig. 5. 1(a).²³² Because of the layered perovskite structure, it shows directional spontaneous polarization depending on the crystallinity.²³³ In addition, considerable attention has been paid on the optical behavior of BWO, owing to its narrow band gap (2.6–2.8 eV) and its potentials in photocatalytic activity in the visible regime.^{234,235} However, up to date, magnetic composition incorporated in BWO has not yet been reported. In this work, we report the room temperature multiferroic properties in the BWMO-BMO nanocomposite thin film as the first two-phase nanocomposite system in layered oxide structure. The microstructure, magnetic, ferroelectric and optical properties have been characterized and compared with the pure BWO to demonstrate the effectiveness of Mn incorporation in tuning the physical properties.

5.3 Experimental

The targets of BWO incorporated with MnO_2 (molar ratio of Mn:W is 1:1) and pure BWO have been prepared by a conventional solid-state sintering method. The epitaxial thin films were grown on single-crystal (001)-oriented LaAlO_3 (LAO) substrates by pulsed laser deposition (PLD). All the thin films were deposited via a KrF excimer laser ($\lambda = 248 \text{ nm}$) and with 2 Hz repetition rate. The substrate was maintained at 600°C and under an optimized oxygen partial pressure of 200 mTorr during the deposition. Following the deposition, the films were annealed with an oxygen pressure of 200 Torr oxygen and a cooling rate of $10^\circ\text{C}/\text{min}$ to room temperature. Au contacts, each have 0.1 mm^2 area, were deposited on the film surface by a custom-built magnetron sputtering system with shadow mask method. Au sputter target (99.99% pure) was purchased from Williams Advanced Materials.

The crystallinity of as-deposited films was analyzed with X-ray diffraction (XRD, PANalytical Empyrean) first. Then transmission electron microscopy (TEM, FEI TALOS T200X) operated at 200 kV was used for microstructure characterization. The high-resolution scanning transmission electron microscopy (HR-STEM) images in high angle annular dark-field (HAADF) mode (also called Z-contrast imaging) were obtained using TEAM 1, a modified FEI Titan TEM with a Cs probe corrector operating at 300 kV. The chemical composition was investigated using X-ray photoelectron spectroscopy (XPS) system (Kratos Axis Ultra DLD) with monochromatic Al $K\alpha$ radiation (1486.6 eV). The magnetic properties of the thin films were investigated using the vibrating sample magnetometer (VSM) option in a commercial Physical Properties Measurement System (PPMS 6000, Quantum Design). During the measurements, the out-of-plane and in-plane magnetization were recorded under 1T magnetic field perpendicular and parallel to the film plane. The polarization-electric field (P-E) loops were measured by Precision LC II Ferroelectric Tester (Radiant Technologies, Inc.). The magnetoelectric (ME) coupling was characterized by Magneto-

electric Bundle (Radiant Technologies, Inc.) The piezoresponse force microscopy (PFM) loop measurements were carried out by atomic force microscopy (AFM, Bruker, Dimension Icon) with SCM-PIT Cr-Pt coated silicon cantilevers. The transmittance spectrums were collected by Hitachi U-4100 UV-Vis-NIR spectrophotometer.

5.4 Results and discussion

5.4.1 BWMO-BMO thin film growth

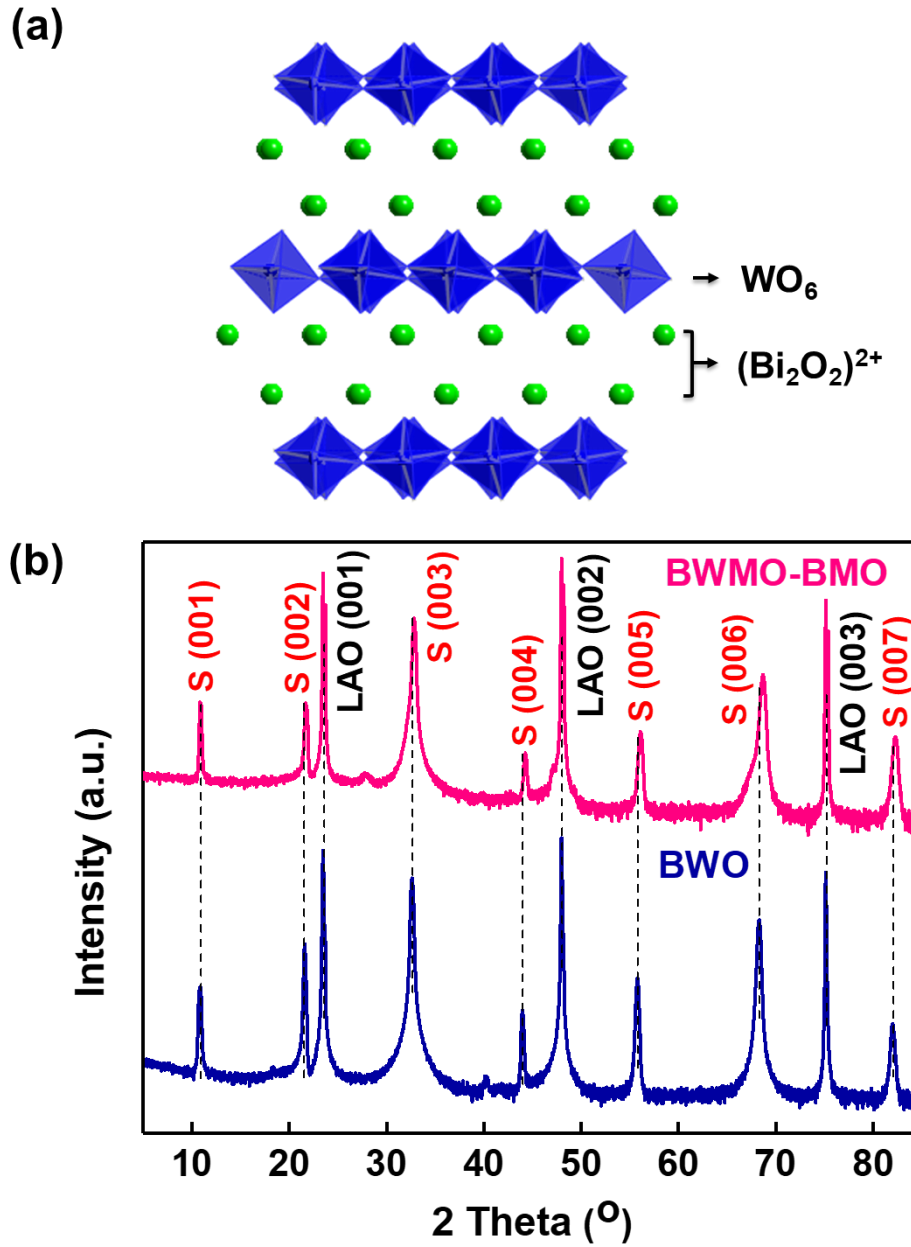


Fig. 5.1 (a) Schematic crystal structure of Bi_2WO_6 (BWO). (b) θ - 2θ XRD scans of BWMO-BMO and BWO on LAO substrates.

XRD analysis was first conducted to characterize the crystallinity of the BWMO-BMO nanocomposite and pure BWO thin films on (001)-LAO substrates, as shown in Fig. 5. 1(b). Different from the reported orthorhombic structure of BWO,²³⁶ both thin films mainly present a series of (00*l*)-type diffraction peaks. The new set of diffractions belongs to the layered supercell (SC) structure,¹⁰³ which are marked by the dashed line and indexed with S (00*l*). It suggests highly epitaxial growth of thin films and Bi₂O₂ layered structure along the out-of-plane direction. An obvious peak shifting has been observed from the BWMO-BMO sample compared with the peaks from the BWO SC structure. The out-of-plane d-spacing is then calculated to be 8.19 Å for BWMO-BMO, which is smaller than 8.24 Å for BWO. This could suggest the effective incorporation of Mn ions in the SC structure as the ionic radius of Mn⁴⁺ (67 pm) is smaller than that of W⁶⁺ (74 pm). In addition, the full width at half maximum (FWHM) of the SC peaks is wider for BWMO-BMO than that for BWO, which suggests slightly lower crystallinity and the possibility of domain formation.

5.4.2 Microstructure characterization

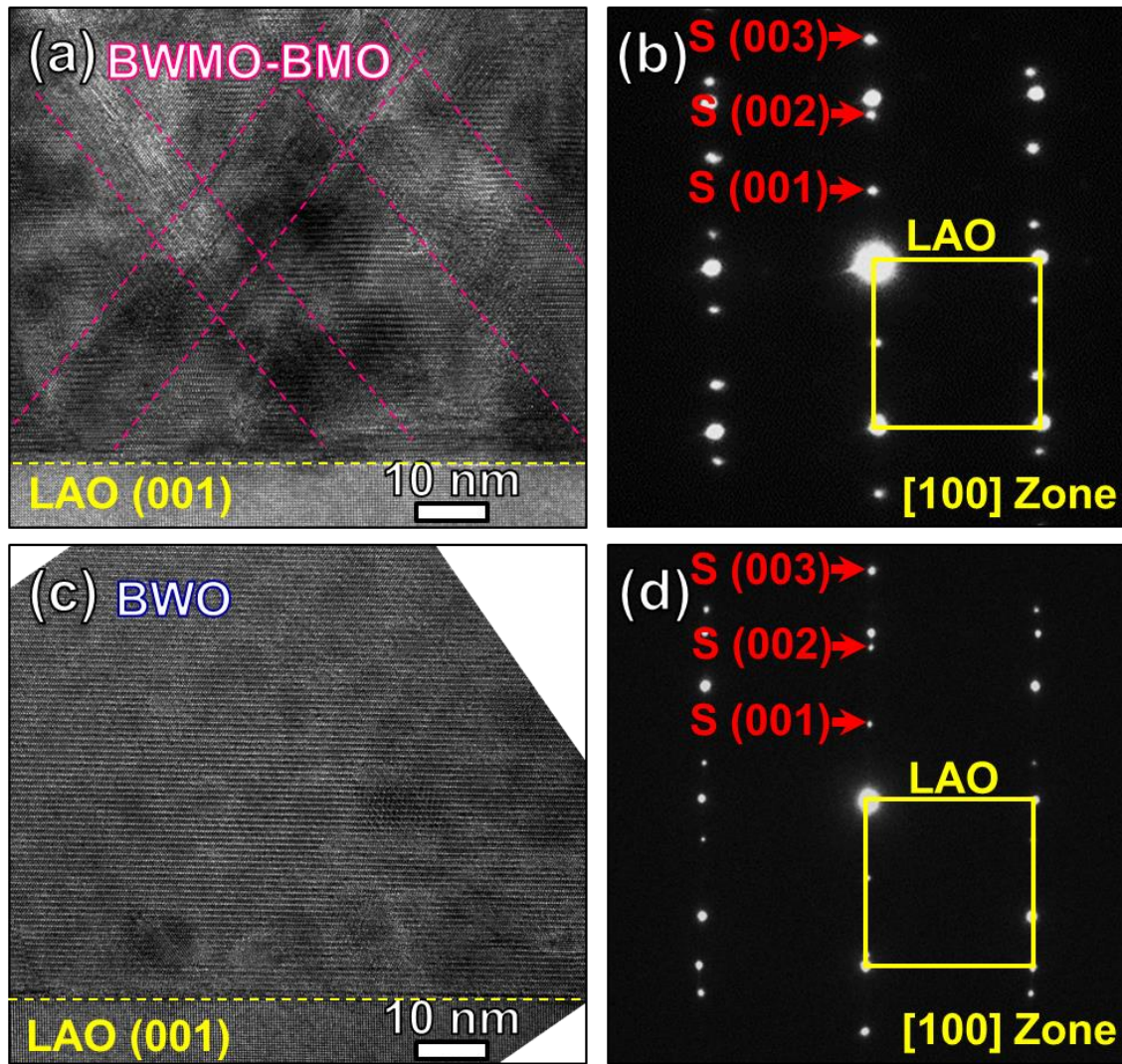


Fig. 5.2 (a, c) Cross-sectional TEM images of BWMO-BMO and BWO thin films on LAO substrates. (b, d) The corresponding SAED patterns of thin films.

Cross-sectional TEM analysis was conducted on both the nanocomposite and pure BWO thin films to better understand the microstructure details, as shown in Fig. 5. 2. TEM images (Fig. 5. 2(a, c)) show the overall film stacks of BWMO-BMO and BWO on LAO, where the interfaces between films and substrates are marked by yellow dashed line. BWMO-BMO and BWO both exhibit obvious layered SC structure with the lattice planes parallel to the LAO substrate.

Interestingly, tilted pillar-like structures are formed in BWMO-BMO, as marked by the dashed line. The nanopillars formed after the initial few monolayers. Fig. 5. 2(b, d) show the corresponding selected area electron diffraction (SAED) patterns taken along the substrate [100] zone axis. The satellite diffraction again confirms the highly epitaxial nature of the BWMO-BMO and BWO thin films on substrate. It is noted that the SAED pattern of BWMO-BMO only shows one set of patterns. Combining with the observed pillar-like structure in TEM images, the formation of domain structure is proposed during the growth of BWMO-BMO.

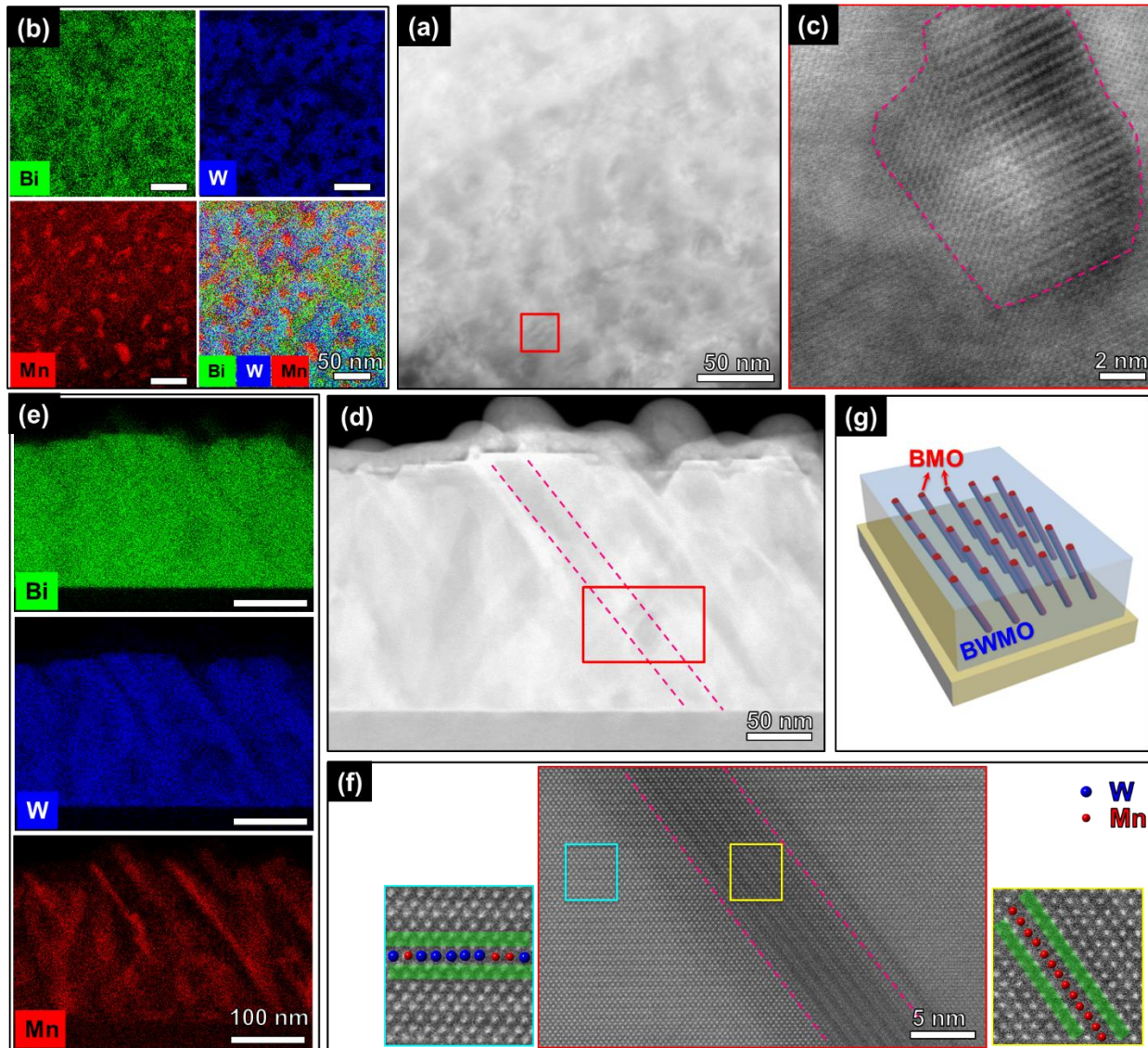


Fig. 5.3 Microstructure study of BWMO-BMO. (a) plan-view STEM image of a selected area of the film, with (b) EDS mapping and (c) atomic-scale high-resolution image of the marked area. (d) Cross-sectional STEM image of a selected area of the film with (e) EDS mapping and (f) atomic-scale high-resolution STEM image of pillar-like structure. Atomic model was used to illustrate the matrix and nanodomain area. (g) 3D construction of the film, in which the red pillars represent the BMO nanodomains and the blue area signifies the BWMO matrix.

Furthermore, scanning transmission electron microscopy (STEM) imaged in high angle annular dark-field (HAADF) mode, coupled with EDS mapping, was used to resolve the nanodomain evolution in BWMO-BMO. A low-magnification plan-view STEM image and the corresponding EDS elemental mapping of Bi, W and Mn are presented in Fig. 5. 3(a) and Fig. 5.

3(b), respectively. The mapping results show that Bi is distributed uniformly throughout the film, while Mn exhibits segregation in BWMO-based matrix. The Mn segregation regions are circular and correspond to the dark contrast area in the plan-view STEM image. Detailed EDS analysis has been applied on the BWMO matrix area. As listed in the supplementary Table S5. 1, the x in the $\text{Bi}_2\text{W}_{1-x}\text{Mn}_x\text{O}_6$ matrix is roughly equal to 0.06. High-resolution STEM (HR-STEM) was carried out on a typical area, as shown in Fig. 5. 3(c). The boundary along the dark contrast area (roughly marked by the dashed line) is blurred, due to the image overlap caused by tilt angles of nanopillars. In order to obtain the complete structure information, cross-sectional STEM imaging (Fig. 5. 3(d)) coupled with EDS mapping (Fig. 5. 3(e)) was performed. The chemical mapping data confirms the uniform distribution of Bi in the entire film. Mn EDS map shows that the Mn appears segregation in the pillar-like areas, and also exists in the BWMO-based matrix with lower concentration. Hence, the overall film structures are attributed to $\text{Bi}_2\text{W}_{1-x}\text{Mn}_x\text{O}_6$ matrix and BiMnO_3 nanodomains (BWMO-BMO).

The STEM image also shows that the formation of BMO nanopillars happens after the few layers deposition. This suggests the initial pseudomorphic growth of the highly strained layer because of the substrate strain effect. After the initial substrate strained region, the strain relaxed and caused the formation of the BMO nanopillars in BWMO matrix. As displayed by the HR-STEM image in Fig. S5. 1, the BMO nanopillars show up after the initial deposition stage, which is around 9 nm above the substrate-film interface. In addition, the tilted BMO nanopillars formed due to the large mismatch between the BWO and BMO phases. Specifically, the out-of-plane lattice parameter of pure BWO is $\sim 16.427 \text{ \AA}$, while the out-of-plane lattice parameter is $\sim 28.03 \text{ \AA}$ for layered BMO with 2-Bi layers.³⁵ The out-of-plane strain was calculated to be as large as 12.87% considering 3:2 lattice matching between BWO and BMO. The in-plane lattice parameters of pure

BWO are $a = 5.457 \text{ \AA}$ and $b = 5.436 \text{ \AA}$ ($5.457 / \sqrt{2} = 3.859 \text{ \AA}$). The lattice parameter of pseudocubic LAO is $3.79 \text{ \AA}$. The lattice mismatch between the film and substrate can be calculated as 1.80%. This value is much smaller than the out-of-plane lattice mismatch, which suggests that the large out-of-plane strain effect could trigger the decomposition of BWMO-BMO nanocomposite. Tilted BMO nanopillars are formed to effectively minimize the mismatch strain out-of-plane. Such strain relaxation mechanism has been previously reported in the formation of other layered oxide systems after the initial pseudo-perovskite layer at the interface.²³⁷ Similar tilted nanopillars for minimizing the mismatch strain has also been reported in BaSnO₃-doped YBa₂Cu₃O_{7-x} VAN systems.¹³³

The HR-STEM image of one pillar-like area is shown in Fig. 5. 3(f). Since STEM intensity is proportional to Z^α (Z is the atomic number; $1.5 \leq \alpha \leq 2$; $Z_{\text{Bi}} = 83$; $Z_{\text{W}} = 74$; $Z_{\text{Mn}} = 25$), the bright layers in both the BWMO-based matrix and pillar-like area are Bi-based slabs. The dark contrast layers in the BWMO-based matrix area is W-rich, while the darker contrast layers are assigned as Mn-rich in the pillar-like areas. Enlarged images are also presented in Fig. 5. 3(f). The schematic model was overlaid on the top of enlarged atomic images. The successive Bi-layers are marked with green strip. Based on the above EDS mapping data, minor Mn doping happened in the BWMO phase. The dark layer hence in this area is illustrated by W atoms (blue circles) combined with Mn atoms (red circles). In the pillar-like area, Mn layers are sandwiched between Bi-layers. Detailed structure analysis was applied on a typical pillar-like area (Fig. S5. 2(a)) from Fig. 5. 3(f). The corresponding (004) fast Fourier filtered image (Fig. S5. 2(b)) shows coherent interfaces across the BWMO-BMO interface without any obvious misfit dislocations. It suggests the tilted BMO nanopillars could effectively release the out-of-plane strain with BWMO matrix. In addition, such coherent interface coupling between the two phases also explains why there are no separate XRD

diffraction peaks from BMO nanopillars. The composition of thin films has also been analyzed by EDS in SEM where a larger volume of the films is covered (see Table S5. 2). It shows that the molar ratio of Mn to W is 0.65:1, which is less than the ratio in target (1:1). The cation atomic ratio Bi/(W+Mn) is 1.41. The formation of BMO nanodomains may cause the stoichiometry difference between target and film. The final 3D structure is illustrated in the schematic drawing in Fig. 5. 3(g), in which the red pillars represent the BMO nanodomains and the blue area signifies the BWMO matrix.

5.4.3 Magnetic and electrical characterization

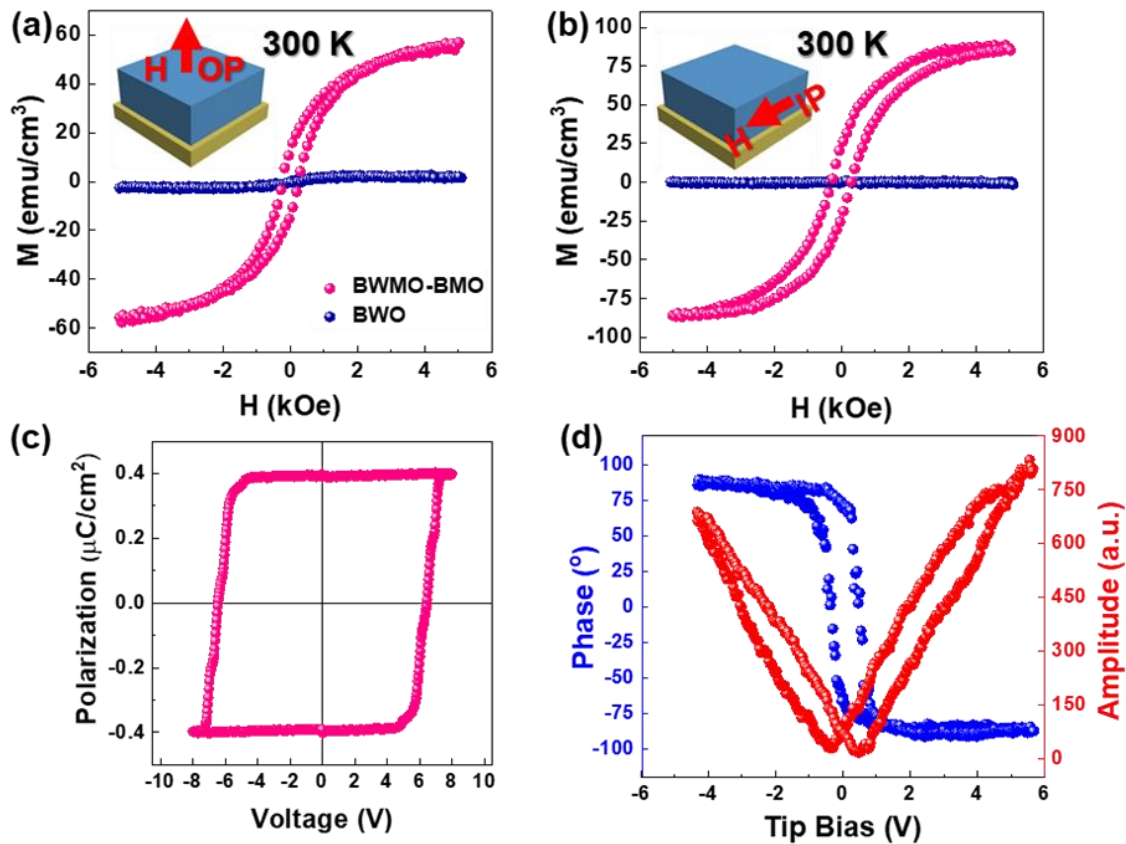


Fig. 5.4 (a) In-plane (IP) and (b) Out-plane (OP) magnetization hysteresis loops of BWMO-BMO and BWO at 300K. (c) Polarization hysteresis measurement for BWMO-BMO.(d) Amplitude and phase switching behavior of BWMO-BMO.

The ferromagnetic hysteresis loops along out-of-plane (OP) and in-plane (IP) are illustrated by Fig. 5. 4(a,b). The magnetization values were normalized to the entire films' volume and excluded the diamagnetic signals from the LAO substrates. The coercive fields from the OP and IP hysteresis loops were same and determined as ~ 260 Oe. The OP and IP saturation values of BWMO-BMO were measured as ~ 57 emu/cm³ and ~ 85 emu/cm³ under 5 kOe magnetic field at 300 K. No magnetic response has been observed in pure BWO SC. It has been reported that spontaneous magnetization of Bi-based oxides could be increased with Mn incorporation,²³⁸ hence the much stronger magnetization of BWMO-BMO could be induced by the net magnetic moment from Mn. The XPS analysis of Mn ions (Fig. S5. 3) indicates the existence of two oxidation states, Mn³⁺ and Mn⁴⁺. The ferromagnetic property of BMO SC has been proposed to be related with double-exchange interaction between different ionic status of Mn ions.^{106,239} Based on the above EDS mapping data, the nanopillar areas present a larger amount (86% atomic ratio) of Mn than that of the matrix. Therefore, the magnetism of BWMO-BMO could be mostly attributed to the BMO phase. In addition, the magnetic property of BWMO-BMO thin film is much better than that of pseudocubic BiMnO₃ thin film on LAO (001) with a low Curie temperature 50K.²⁴⁰ It indicates that the advantages of the SC structure of BMO over the pseudocubic one. The in-plane magnetization (~ 85 emu/cm³) of BWMO-BMO is smaller than that (~ 190 emu/cm³) of pure BMO with layered structure¹⁰⁶, which is possibly due to the tilted domain structure. The difference between the out-of-plane and in-plane magnetization demonstrates the magnetic anisotropy of BWMO-BMO. The similar anisotropic magnetization has been observed in other SC structures, such as BAMO and BMO.^{105,106} The structure anisotropy contributes to the magnetic anisotropy, due to the layered structure along in-plane direction is believed as an easy crystalline axis for magnetization.

To explore the ferroelectric properties of the BWMO-BMO, the ferroelectric hysteresis loop was measured and shown in Fig. 5. 4(c). It has been reported that BWO thin films with high crystallinity has poor ferroelectric property.²³³ In Bi-based materials, the Bi ions form strong covalent bonds with the surrounding O anions via the Coulomb force, which causes the Bi 6s² lone pair of electrons shift away from the centrosymmetric position. An electric dipole is then formed with the localized lobe-like distribution of the lone pair. It breaks the spatial inversion symmetry and introduces the ferroelectric distortion in Bi-based multiferroic materials.²⁴¹ In addition, the ferroelectric hysteresis loop is in a highly square shape, which is better than the other reported ferroelectric properties of Aurivillius phase thin films with thicker thickness.²⁴² It is possible that the nanodomains broke the long crystallinity and promote spontaneous polarization in a specific direction. To further explore the ferroelectric property, PFM measurements were also carried out on the BWMO-BMO sample. Fig. 5. 4(d) shows the obvious out-of-plane phase and amplitude switching image. The magnetoelectric (ME) measurement has been carried on the nanocomposite at room temperature. Fig. S5. 4 shows polarization plot with a varied magnetic field. The black solid line indicates the result of linear fitting. The slope of the plot indicates the ME charge coefficient α , which is around $1.08 \times 10^{-4} \mu\text{C}/(\text{cm}^2 \cdot \text{Oe})$ for this sample. The relationship between the ME charge coefficient α and ME voltage coefficient α_{ME} is $\alpha = \alpha_{\text{ME}} \epsilon_0 \epsilon_r$, where ϵ_0 is the permittivity of the vacuum ($\epsilon_0 \approx 8.85 \times 10^{-12} \text{ C/m} \cdot \text{V}$) and ϵ_r is the relative permittivity of the film. Since this material is a new system, the value of Bi₂WO₆ film was used as ϵ_r , which is around 55.²⁴³ The calculated α_{ME} is 22.19 V/(cm·Oe).

5.3.4 Optical measurements

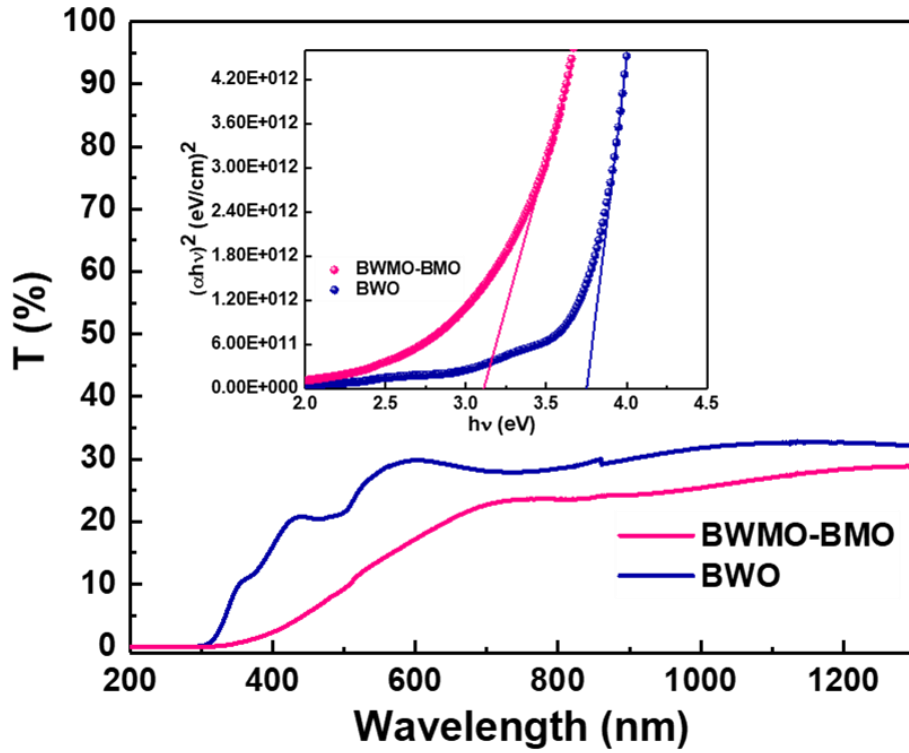


Fig. 5.5 Optical transmission spectrums of BWMO-BMO and BWO. The inset shows the corresponding plot of $(\alpha h\nu)^2$ versus $h\nu$.

Last, to explore the optical property tuning of BWMO-BMO, optical measurement has been carried out for the films. Fig. 5. 5 shows the optical transmittance spectrums of BWMO-BMO and BWO as a function of the wavelength. Based on the above discussion and the FFT analysis shown by Fig. S5. 2, it was proven that the interfaces between the BWMO and BMO are coherent without obvious misfit lattice formation. In addition, BMO only occupies small portion ($\sim 11\%$ volume percent estimated based on the Mn mapping data in Fig. 5. 3(b)) in this nanocomposite. The Tauc method was used for the band gap calculation. The details are shown below¹⁹³:

$$\alpha h\nu^2 = \text{Constant} \cdot (h\nu - E_g)$$

where α is the optical absorption coefficient, h is the Planck's constant, ϑ is the frequency of incident beam, E_g is the optical band gap, the constant is called the band tailing parameter, and the index 2 corresponds to the direct transition. The plot of $\alpha h\vartheta^2$ versus $h\vartheta$ gives a straight line in a certain region. The inset presents the corresponding direct band gap, where the bandgap is 3.10 eV for the BWMO-BMO, reduced from 3.75 eV for the BWO. Oxygen vacancy has been proposed as an effective way in narrowing the bandgap of BWO layer²⁴⁴ and thus it is possible that oxygen vacancies were introduced with Mn incorporation into BWO phase. The bandgap of BWO SC is out of the visible range and different from most previous studies (2.6–2.8 eV).²³⁵ It is comparable with the bandgap value of BWO thin film (3.76–3.79 eV) prepared by sol-gel method.²⁴⁵ In addition, the bandgap value of a porous BWO sample was reported to be 3.20 eV, which suggests bandgap variation depending on the microstructure. This result paves a new avenue to design Bi-layered SC and control its photonic bandgap energy.

The design and fabrication of a new nanocomposite with 2D layered structure in this work opens up a wide range of possibilities for exploration of nanocomposites. The Bi-layered SC structure and tilted nanodomain structure presents enormous versatility of the Bi-based oxide layered structures. Besides Mn ions, other magnetic elements, including Fe and Co, and nonmagnetic ones could also be incorporated into the BWO system to create new layered oxides with novel functionalities. In addition, it is highly expected to control the functionalities in preferred direction with systematic study of Bi-based layered structures.

5.4 Conclusions

In this work, a new layered oxide $\text{Bi}_2\text{W}_{1-x}\text{Mn}_x\text{O}_6\text{-BiMnO}_3$ (BWMO-BMO) in thin film form has been grown by PLD method on (001)-oriented LAO substrates. The epitaxial nanocomposite thin films consist of BWMO matrix and pillar-like BMO nanodomains. Robust

ferroelectricity and ferromagnetism (room temperature multiferroic responses) have been observed in this novel layered nanocomposite. In addition, unique tunable band gap has been demonstrated by the incorporation of Mn cation. This work holds great significance for the modification of magnetic and optical properties of BWO with other magnetic ions. It also presents the composition versatility of the layered Aurivillius phases and their great potentials in new layered nanocomposite design.

5.5 Supplementary

Table S5.1 STEM-EDS Analysis for W and Mn elements

Position	W (Atom %)	Mn (Atom %)	Mn/W+Mn
1	26.92	1.12	0.04
2	29.10	2.00	0.06
3	28.00	1.58	0.05
4	26.94	1.74	0.06
5	28.24	1.81	0.06
6	23.42	1.37	0.06
7	28.04	1.33	0.05
8	21.61	0.97	0.04
9	26.09	2.09	0.07
10	28.82	1.81	0.06
Average			0.06

Table S5.2 SEM-EDS Analysis for W and Mn elements

Position	Bi (Atom %)	W (Atom %)	Mn (Atom %)	Bi/(W+Mn)	Mn/W
1	9.57	4.03	2.71	1.42	0.67
2	9.09	3.93	2.78	1.35	0.71
3	9.47	4.07	2.73	1.39	0.67
4	9.43	4.01	2.82	1.38	0.70
5	9.43	4.13	2.54	1.41	0.62
6	9.52	4.06	2.41	1.47	0.59
7	9.55	4.12	2.98	1.35	0.72
8	9.34	4.11	2.29	1.46	0.56
9	9.54	4.08	2.43	1.47	0.60
10	9.42	4.15	2.7	1.38	0.65
Average				1.41	0.65

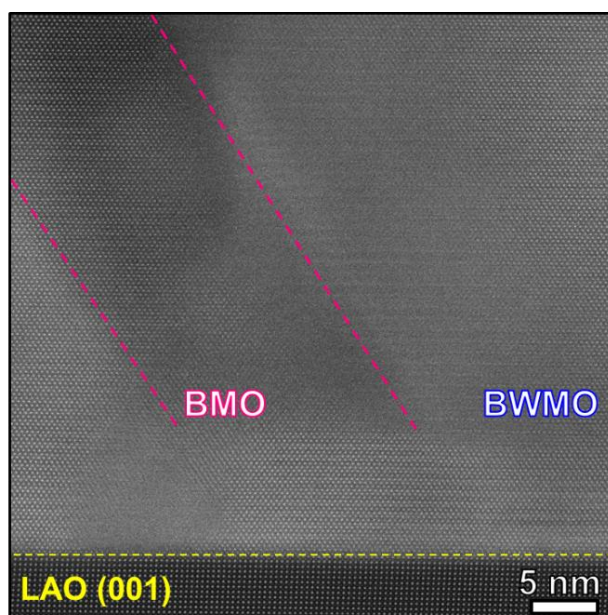


Fig. S5. 1 HR-STEM of the film-substrate interface.

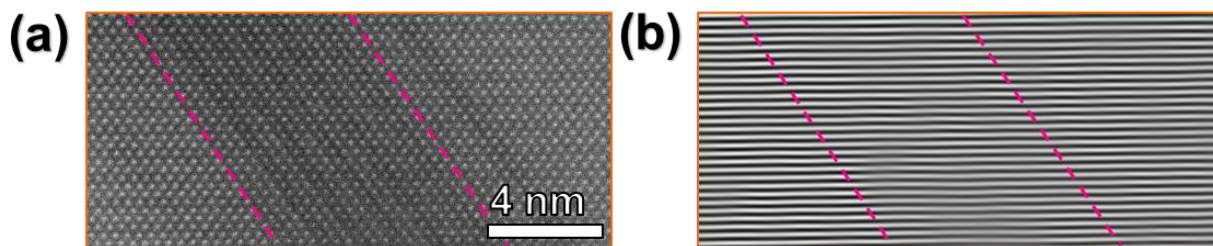


Fig. S5. 2 (a) STEM image of the enlarged pillar-like area. (b) The corresponding (004) fast Fourier filtered image.

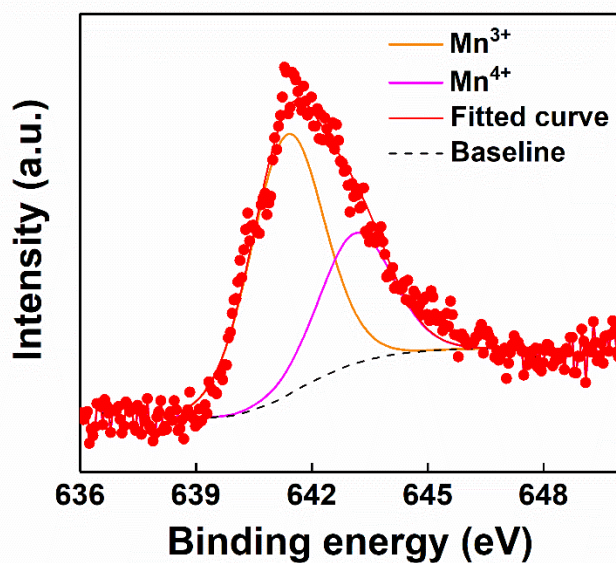


Fig. S5. 3 The XPS spectrum of Mn 2p_{3/2}.

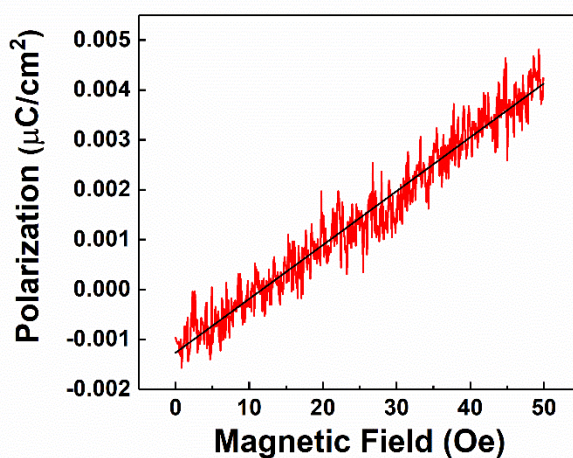


Fig. S5. 4 Room temperature polarization vs magnetic field of BWMO-BMO. The black solid line indicates the result of linear fitting.

CHAPTER 6. MULTIFERROIC VERTICALLY ALIGNED NANOCOMPOSITE WITH CoFe_2O_4 NANOCONES EMBEDDED IN LAYERED Bi_2WO_6 MATRIX

6.1 Overview

$\text{Bi}_2\text{WO}_6\text{:CoFe}_2\text{O}_4$ (BWO:CFO) vertically aligned nanocomposite (VAN) in epitaxial thin film form has been demonstrated on single-crystal LaAlO_3 (LAO) (001) substrates via pulsed laser deposition (PLD). CFO nanopillars exhibit a unique nanocone shape embedded in the epitaxial BWO matrix with an Aurivillius layered oxide structure. The growth direction of the CFO nanopillars is (004), different from that of its epitaxial single-phase counterpart (220), which is attributed to the interfacial strain effect. Magnetic measurements show robust and anisotropic magnetic properties from the CFO nanocone structures, and obvious ferroelectric responses are demonstrated in the BWO matrix, both at room temperature. The BWO:CFO VAN thin film combining a ferroelectric layered oxide matrix and magnetic vertical nanocone present a new hybrid material platform for room temperature multiferroics design towards nanoscale sensors and actuators.

This chapter is reprinted with permission from “Multiferroic vertically aligned nanocomposite with CoFe_2O_4 nanocones embedded in layered Bi_2WO_6 ” by H. Wang, *et al*, *Materials Research Letters*, 10, 418(2019). Copyright © 2019 by Talor & Francis.

6.2 Introduction

Multiferroic materials which exhibit ferroelectric and ferromagnetic response simultaneously have attracted significant interest in the past few decades¹³⁷. However, truly single-phase multiferroics are scarce, because the coexistence of magnetism (spin order) and ferroelectricity (electric dipole order) in a single-phase material may be limited. Hence, multiferroic nanocomposites that combine a ferroelectric phase and a magnetic phase have been introduced^{102,131,137,246}. Various two-phase nanocomposite thin films have been demonstrated to show multiferroic properties, including $\text{BaTiO}_3\text{:CoFe}_2\text{O}_4$ ¹³⁷, $\text{BiFeO}_3\text{:CoFe}_2\text{O}_4$ ²⁴⁶, and $\text{BaTiO}_3\text{:YMnO}_3$ ¹³¹. Some of the above nanocomposites were designed with vertically aligned nanocomposites (VAN) structure, which is a novel thin film architecture and where two immiscible phases co-grow epitaxially and vertically on substrates^{247,248}. Furthermore, the VAN systems provide effective vertical strain coupling along the vertical two-phase interfaces, which allows the growth of highly strained films and enhanced ferroelectric / ferromagnetic properties compared to their single-phase counterparts²³¹. However, the ferroelectric phases in the reported multiferroic VAN systems are mostly perovskite oxide structures¹⁰², for example, BaTiO_3 (BTO) and BiFeO_3 (BFO). These representative ferroelectric materials have some limitations: e.g., BTO was reported to have a low Curie temperature (T_c) of 120 °C to 130 °C, and BFO exhibits high leakage current. Studies on the growth and property characterizations of both BTO and BFO also suggested that both films are sensitive to processing conditions and their ferroelectric properties vary significantly among different reports²⁴⁹⁻²⁵¹.

Bismuth-based layered oxides (in an Aurivillius phase) have been reported as another family of ferroelectric materials, which exhibits robust polarization with low leakage current and resistant to fatigue⁴¹. Among various Aurivillius phases, orthorhombic Bi_2WO_6 (BWO) is one of the simplest members in the Bismuth-based layered oxide family. It is constructed by alternating

$(\text{Bi}_2\text{O}_2)^{2+}$ slabs and $(\text{WO}_4)^{2-}$ perovskite layers²³², as shown in the atomic model in Fig. 6.1(a). Because of the layered perovskite structure, it shows directional spontaneous polarization depending on the crystallinity²³³. The strong polarization anisotropy makes it unique for mastering the ferroelectric property by thin film strain effect. However, the work on BWO in thin film form is very scarce²⁵² and most of the BWO demonstrations have previously focused on dielectric and photocatalysis properties²⁵³⁻²⁵⁵.

On the other hand, CoFe_2O_4 (CFO) with a spinel structure (Fig. 6.1(a)) is an important ferromagnetic material with excellent magnetic property such as high coercivity, moderate saturation magnetization, as well as high chemical and structure stability^{256,257}. Furthermore, because of the high magnetostriction coefficient, it shows the possibility of tuning magnetization by lattice strain²⁵⁸. Therefore, CFO as the ferromagnetic component has been previously introduced into multiple heteroepitaxial nanocomposite systems, such as $\text{SrRuO}_3\text{:CFO}$ ²⁵⁹, $\text{BiFeO}_3\text{:CFO}$ ²⁶⁰ and $\text{PbTiO}_3\text{:CFO}$ ¹³⁹.

In this study, a new VAN system composed of the ferroelectric BWO layered oxide as the matrix and the ferromagnetic CFO as the secondary phase has been proposed and illustrated in Fig. 6.1(b). The red pillars represent the CFO phase, while the green area signifies the BWO matrix. (001)-oriented LaAlO_3 (LAO) substrates have been selected for the epitaxial growth of both phases. Compared to perovskite VAN systems such as BTO:CFO and BFO:CFO , the proposed BWO:CFO nanocomposites could present the following potential advantages: (1) high Curie temperature, low leakage current and high fatigue endurance; (2) the directional spontaneous polarization related with the layered structure; and (3) reliable ferroelectric properties presented by BWO. We thus investigated the microstructure, strain state, ferromagnetic and ferroelectric properties of the new

BWO:CFO VAN system and compared it with the single phase BWO and CFO films, with a focus on room temperature properties.

6.3 Experimental

The $\text{BWO}_{0.5}:\text{CFO}_{0.5}$ target was prepared by a conventional solid-state sintering method. The epitaxial thin films were deposited on single-crystal (001)-oriented LAO substrates by pulsed laser deposition (PLD) using a KrF excimer laser ($\lambda = 248 \text{ nm}$). The deposition rate of thin films was 2 Hz under an optimized oxygen partial pressure of 200 mTorr. Substrate temperature of 670 °C was maintained during the deposition. Following the deposition, the films were cooled down to room temperature in 200 Torr oxygen atmosphere at a cooling rate of 10 °C/min. 100 nm thick Au top contacts of 0.1 mm² area, were deposited by a custom-built magnetron sputtering system using a 99.99% pure Au sputter target from Williams Advanced Materials.

The microstructure of as-deposited films was investigated with X-ray diffraction (XRD, PANalytical Empyrean) and transmission electron microscopy (TEM, FEI TALOS T200X) operated at 200 kV. The high-resolution scanning transmission electron microscopy (HRSTEM) images in high angle annular dark-field (HAADF) mode (also called Z-contrast imaging) were obtained using TEAM 1.0, a modified FEI Titan TEM with a Cs probe corrector operated at 300 kV. The magnetic properties of the thin films were investigated using the vibrating sample magnetometer (VSM) option in a commercial Physical Properties Measurement System (PPMS 6000, Quantum Design). During the measurements, the out-of-plane and in-plane magnetization were recorded by applying a magnetic field of 1T perpendicular and parallel to the film plane, respectively. Ferroelectric polarization-electric field (P-E loops) measurements were conducted by Precision LC II Ferroelectric Tester (Radiant Technologies, Inc.). The phase and amplitude

hysteresis loops were collected with atomic force microscopy (AFM, Bruker Dimension Icon). Bruker SCM-PIT Cr-Pt coated silicon cantilevers were adopted in the piezoelectric force microscopy (PFM) measurements.

6.4 Results and discussion

6.4.1 BWO:CFO film growth

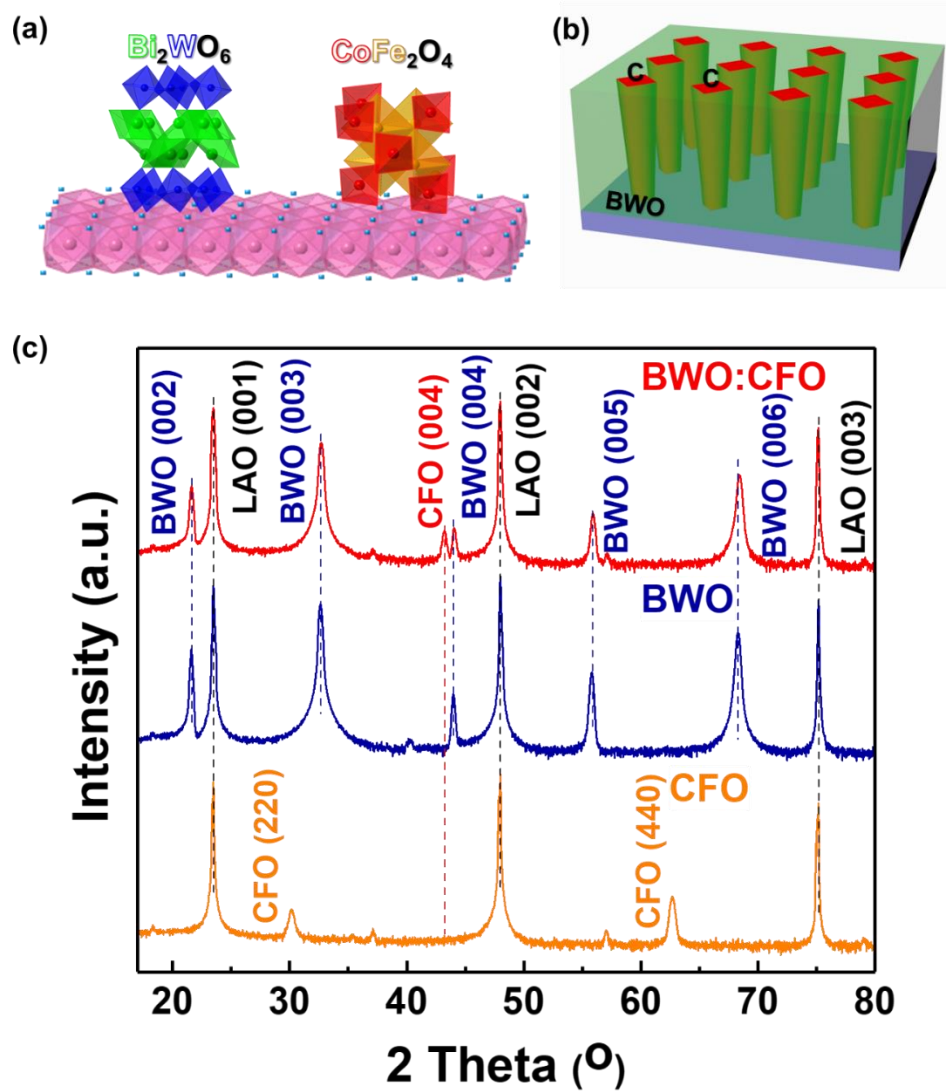


Fig. 6.1(a) Atomic models of Bi_2WO_6 (BWO), CoFe_2O_4 (CFO) and LaAlO_3 (LAO). (b) Schematic diagram of VAN structure. CFO phase is represented by red pillars and denoted with C, while BWO is the rest green area. (c) θ - 2θ XRD scans of BWO:CFO, BWO and CFO on LAO substrates, respectively.

XRD analysis was first carried out to check the crystallinity of the BWO:CFO film. Pure BWO and CFO films were also deposited and measured for comparison, as shown in Fig. 6. 1(c). The pattern of nanocomposite BWO:CFO presents BWO (00 l) and CFO (004) peaks. The BWO (00 l) peaks indicate the layered structure and are identical to that of the pure BWO on LAO. The lattice parameter of BWO (004) is calculated to be 8.213 Å, which is almost half of the bulk parameter 16.427 Å²². It indicates nearly perfect matching between BWO and CFO phases in the out-of-plane direction. In addition, it is clearly observed that BWO (004) matches with CFO (004) in the out-of-plane direction. However, the pure CFO on LAO shows (220) and (440) as the textured orientation, which is different from the preferred (004) texture of the CFO phase in the nanocomposite. Similar preferred (004) CFO growth orientation has been reported in the BFO:CFO system^{137,261}, where the interface of CFO (004) shares the {110}c-type interface with BFO matrix, due to the low interface energy between the octahedron in the perovskite and those in the spinel phase. Thus, the preferred orientation of (004) CFO in BWO:CFO nanocomposite compared with the pure CFO is highly due to the strain effect from BWO matrix. The out-of-plane lattice parameter of CFO in BWO:CFO can be calculated to be 8.367 Å compared to the bulk parameter of 8.39 Å²⁶, which indicates a minor compressive strain of – 0.27% in out-of-plane direction. The effect of deposition rate on the nanocomposite microstructure has also been explored. Fig. S6. 1 shows the XRD pattern of BWO:CFO deposited under the laser frequency of 10 Hz. CFO phase shows the (004) growth orientation and the out-of-plane lattice parameter is calculated as 8.359 Å, which is also under compressive strain. However, BWO phase shows more peaks, besides the primary (00 l) peaks, which are marked by “*”. It indicates other orientations of BWO phase have grown in the high deposition frequency sample. This result is similar to the previous bismuth-based oxides work that the layered structure is sensitive to the deposition rate²⁶².

Similarly, the film composition (i.e., two phase molar ratio) could also affect the overall film microstructure and the resulted film properties. It thus shall be further explored as future work.

6.4.2 Microstructure characterization

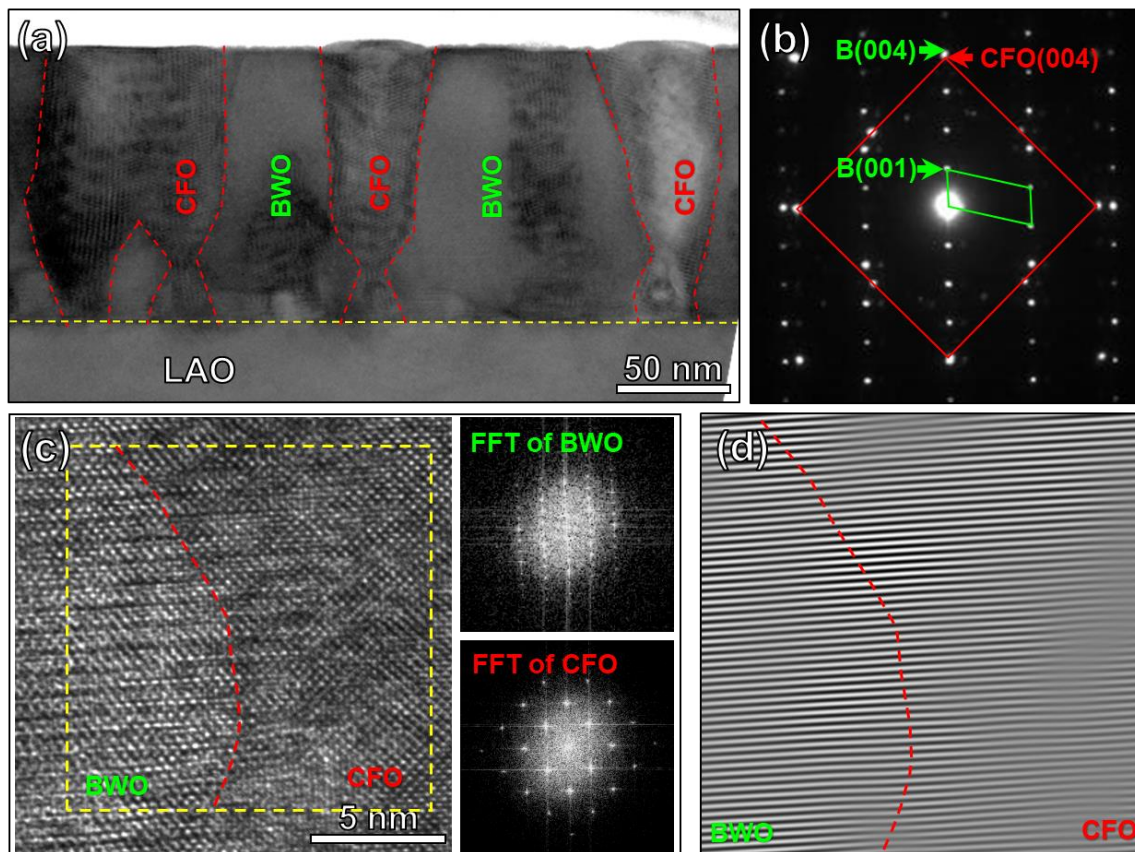


Fig. 6.2 (a) Cross-sectional TEM image of BWO:CFO. (b) The corresponding SAED pattern from thin film area. BWO phase is denoted with B. (c) HRTEM image along the interface between BWO and CFO. The insets show the fast-Fourier transformed (FFT) images from BWO and CFO phases. (d) The corresponding FFT filtered image (the dashed line guides the interface).

TEM was applied to further investigate the microstructure and strain status of the nanocomposite films. The cross-sectional TEM image (Fig. 6. 2(a)) shows that both phases grew as vertical domains from the substrate surface to the top of the film. The distinguished dots in the corresponding selective area electron diffraction (SAED) pattern (Fig. 6. 2(b)) exhibit only (00 l)-orientated BWO and (004)-oriented CFO phases, which agrees well with the previous XRD results.

The in-plane lattice parameter of CFO is then calculated to be $a = b = 8.404 \text{ \AA}$ and the corresponding in-plane strain is determined as 0.17%. It indicates that the CFO phase in BWO:CFO is under out-of-plane compressive strain (ϵ_{001}), which is calculated as -0.44% . As a comparison, pure BWO and CFO phases were also characterized and shown in Fig. S6. 2(a, c) by TEM. BWO wets the substrate completely and follows a layer-by-layer growth, which is identified by the satellite diffraction pattern (Fig. S6. 2(b)). In comparison, the pure CFO thin film follows islands growth with $(04\bar{4})$ as the out-of-plane orientation in the SAED pattern (Fig. S6. 2(d)). It suggests that the BWO phase in the nanocomposite facilitated the nucleation and growth of CFO (004). BWO:CFO heterointerface was investigated with high-resolution TEM (HRTEM) (Fig. 6. 2(c)). The two phases show excellent epitaxial quality. The BWO phase exhibits clear layered structure along the out-of-plane direction (c -axis). The insets are fast Fourier transform (FFT) images obtained from local BWO and CFO areas. They agree well with the SAED pattern. The corresponding fast Fourier filtered image (Fig. 6. 2(d)) confirms the well matching between 4 of BWO (00 l) and CFO (004) along the vertical interface, which is energy saving with small residual strain.

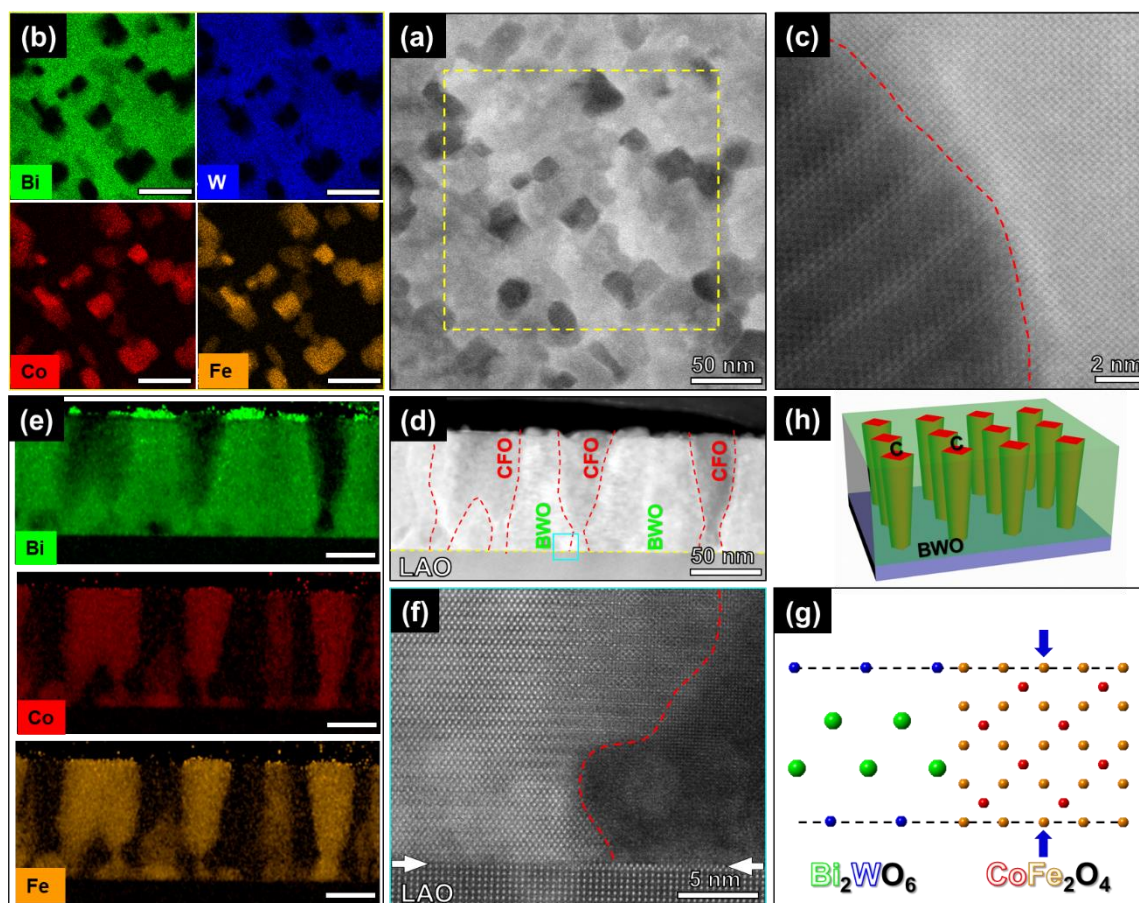


Fig. 6.3 Microstructure study of BWO:CFO. (a) plan-view STEM image of a selected area of the film, with (b) EDS mapping of the marked area and (c) atomic-scale high resolution image of one pillar interface. (d) Cross-sectional STEM image of a selected area of the film with (e) the corresponding EDS mapping and (f) atomic-scale high resolution STEM image of BWO:CFO interface. (g) The atomic models of the coupling between BWO and CFO. (h) 3D construction of the film.

Further microstructure analysis has been conducted to reveal the chemical composition distribution and the out-of-plane strain status of BWO:CFO. Fig. 6. 3(a) presents the plan-view low-mag STEM image, and Fig. 6. 3 (b) shows the corresponding EDS mapping data. The top view of CFO nanopillars shows a rectangular shape. Based on the high-resolution STEM (HRSTEM) (Fig. 6. 3(c)) and EDS results, the interfaces between the two phases are very sharp without any obvious inter-diffusions. Cross-sectional STEM (Fig. 6. 3(d)) and corresponding EDS

mapping (Fig. 6. 3(e)) were also carried out to explore the 3D nature of the film. The diameter of the CFO nanopillars increases along the growth direction and the pillars form an inverted cone shape, which could be related to the strain effects on CFO pillars from BWO matrix decrease as the film grows thicker. Similar inverted cone shape of CFO nanopillars has been reported in the $\text{BiFeO}_3\text{:CFO}$ nanocomposite, in which CFO nanopillars also grow along (001) direction²⁴⁶. Hence, the overall 3D structure of BWO:CFO VAN thin film is illustrated in Fig. 6. 3(h). HRSTEM was applied to explore the triple phase interface area between the substrate and the two phases, as shown in Fig. 6. 3(f). BWO shows very clear layered structure along the growth direction (*c*-axis). It is noted that four layers of BWO (a half unit cell thickness) are coupled with CFO (004) (a unit cell thick of CFO). The coupling is illustrated by the atomic model in Fig. 6. 3(g). Based on the above strain and structure analysis, parts of the octahedron in CFO phase is shown under out-of-plane compressive strain. The strain effect from BWO on CFO phase could lead to a pronounced change in the coupling behaviors.

6.4.3 Electric and magnetical characterization

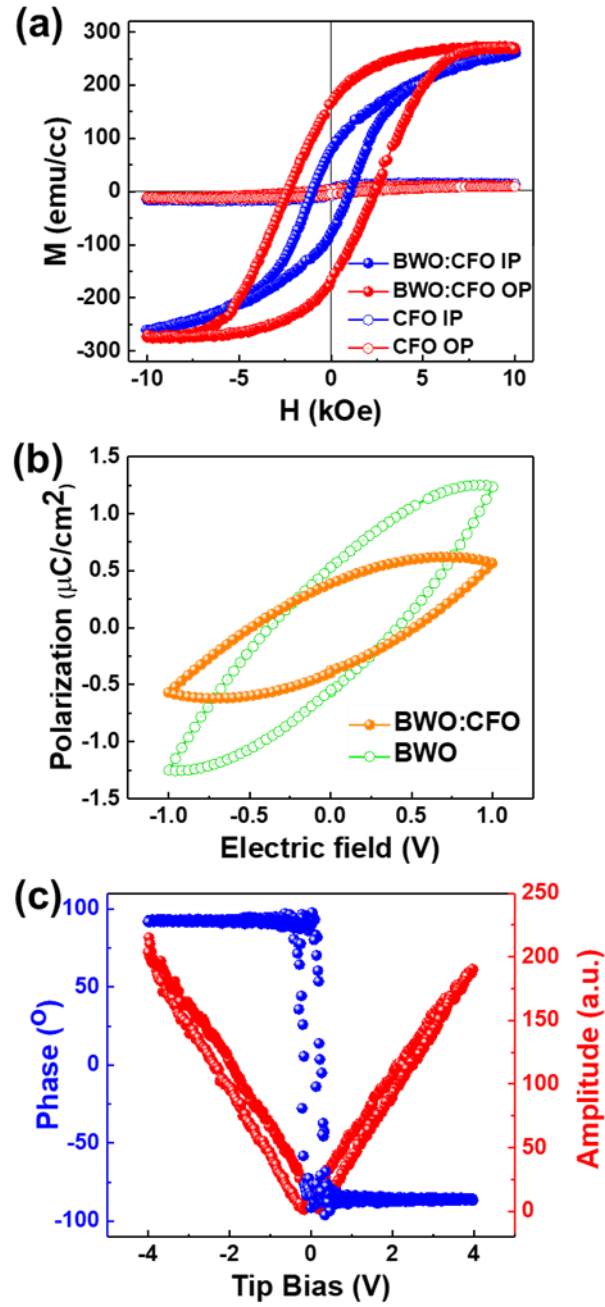


Fig. 6.4 (a) In-plane (IP) and Out-plane (OP) magnetization hysteresis loops of BWO:CFO and pure CFO at 300K. (b) Polarization hysteresis measurement for BWO:CFO and pure BWO. (c) Amplitude and phase switching behavior of BWO:CFO.

To demonstrate the multiferroic nature of the two-phase nanocomposite film, both magnetic and ferroelectric measurements have been conducted at room temperature. Fig. 6. 4(a) shows the in-plane (IP) and out-of-plane (OP) magnetic hysteresis (M-H) loops of BWO:CFO film measured at 300 K. The magnetization values were normalized to the volume fraction of CFO ($\sim 29\%$) approximately after subtracting the diamagnetic signals from the LAO substrates. This demonstrates the effectiveness of CFO as secondary phase into VAN systems to introduce ferromagnetic property. The ratio of remanence to saturation magnetization (M_r/M_s) for the out-of-plane (M_r/M_s) $_{\perp}$ is 61%, which is larger than that for the in-plane (M_r/M_s) $_{\parallel}$ value of 37%. Meanwhile, the coercive field (H_c) in out-of-plane direction is 2.39 kOe, which is also much larger than that of the in-plane direction of 1.07 kOe. The high magnetic anisotropy can be attributed to the anisotropic microstructure of the nanocomposite film, i.e., the CFO nanocone structures in the BWO matrix. The IP and OP magnetic hysteresis (M-H) loops of pure CFO are also shown in Fig. 6. 4(a), which suggests a lower magnetic response of (220)-oriented CFO pure film.

The magnetic anisotropy related with CFO phase has also been observed in other magnetic CFO nanopillar structures^{137,263}. One source for the magnetic anisotropy could be the magnetostriction effect, which stems from the compressive strain of CFO. The stress in CFO is given by the equation $\sigma = Y\varepsilon_{001}$, where Y is the Young's modulus (~ 141.6 Gpa)²⁶⁴ and ε_{001} is the strain along the [001] direction ($\sim -0.44\%$). The magnetoelectric energy(K_{me}) is calculated by $K_{me} = -3\lambda_{001}\sigma_{001}/2$, where λ_{001} is the magnetostrictive coefficient of CFO ($\sim -350 \times 10^{-6}$)²⁶⁴. Thus, the anisotropy energy for CFO in VAN is 3.27×10^6 erg/cm³. Another possible source for the magnetic anisotropy is the shape anisotropy of CFO. The anisotropy energy (K_s) is calculated based on a heterogeneous model $K_s = -2\pi M_s^2$ ²⁶⁵, which is -0.46×10^6 erg/cm³. The total anisotropy energy in BWO:CFO thin film is thus 2.81×10^6 erg/cm³. The anisotropy field is given

by $H_{stress} = 2K/M_s = 20.8$ kOe, which is larger than the experimental observed value of 10 kOe. The difference could be due to other possible sources for the magnetic anisotropy such as interface exchange anisotropy and magnetocrystalline anisotropy. In addition, the model used for the calculation of shape anisotropy energy is only a two-dimensional model without consideration of CFO nanocone structures, which need to be modified in future work.

Ferroelectric measurements demonstrate a well-defined P-E hysteresis loop of BWO:CFO, as shown in Fig. 6. 4(b). It is compared with the loop of pure BWO. The remanent polarization (P_r) of BWO:CFO is $0.40 \mu\text{C}/\text{cm}^2$ which is slightly lower than that of pure BWO with $0.53 \mu\text{C}/\text{cm}^2$. It is probably due to the incorporation of none-ferroelectric phase CFO in the system. In addition, PFM measurement was performed on BWO:CFO VAN thin film. Fig. 6. 4(c) shows the out-of-plane phase and amplitude switching plots as a function of the bias applied. An 180° phase transition with the change of tip bias direction can be seen in the phase switching curve while a perfect butterfly-like shape is shown in the amplitude curve. This demonstrates the ferroelectric response of the BWO:CFO VAN thin film at the room temperature.

The demonstration of multiferroic BWO:CFO paves a way to create new nanocomposites which combine a bismuth-based layered oxide with a spinel phase, beyond the conventional perovskite oxide systems. It also provides a practical approach for introducing magnetic components into the ferroelectric and piezoelectric layered oxides. BWO:CFO VAN exhibits a larger in-plane $(M_r/M_s)_{||}$ anisotropy in magnetic property compared with the reported BFO:CFO VAN films^{229,263}. The strong coupling effect between the layered BWO matrix and CFO could be the possible source. In addition, pure BWO thin films have been reported with directional polarization, which is highly dependent on the growth orientation²³³. Hence, the BWO:CFO VAN system is worthy of a systematic study on the influence of several experimental parameters, such

as the molar ratios and deposition rate. It is promising to control directional multiferroic properties in 3D materials with build-in layered structure and to incorporate the new hybrid material platform for spintronic devices, nanoscale sensors and actuators.

6.4.4 Conclusion

In summary, BWO:CFO VAN thin films with layered oxide VAN structure have been grown on (001)-LAO substrate by PLD. The CFO phase forms inverted cone-shaped nanopillars in BWO layered oxide matrix. The BWO:CFO VAN system shows robust multiferroic properties as a result of the vertical interface coupling between the ferroelectric BWO layered oxide matrix and the ferromagnetic CFO nanopillars, under room temperature. The BWO:CFO VAN thin films present a new hybrid layered oxide platform for room temperature multiferroics design towards nanoscale sensors and actuators.

6.4.5 Supplementary

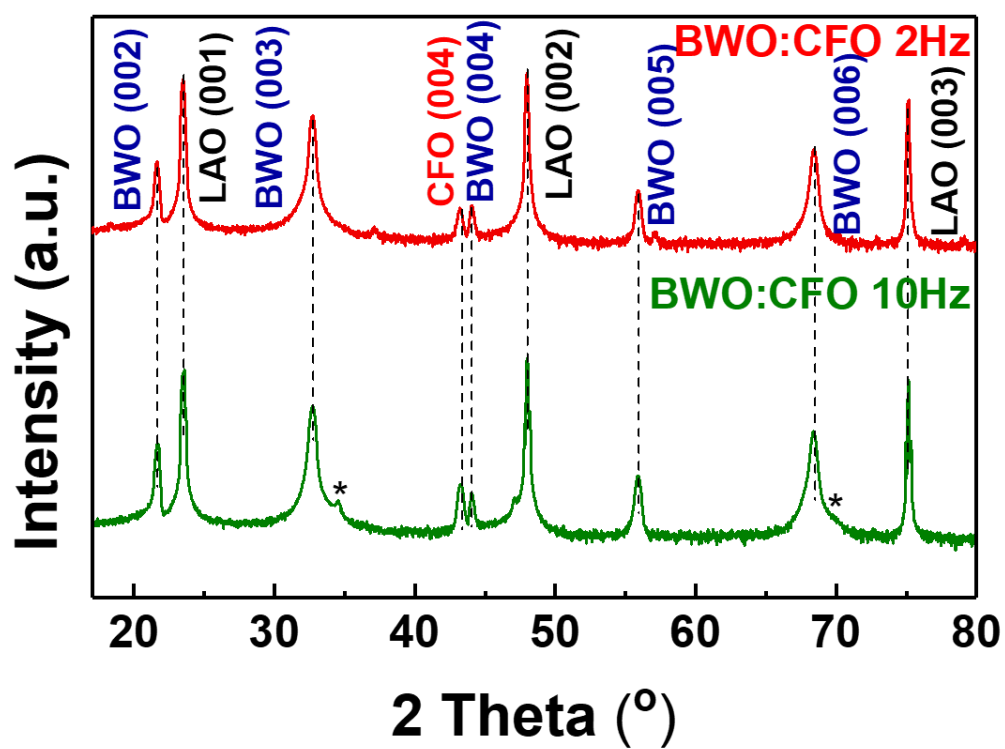


Fig. S6.1 XRD θ - 2θ scans of BWO:CFO deposited at 2Hz and 10Hz.

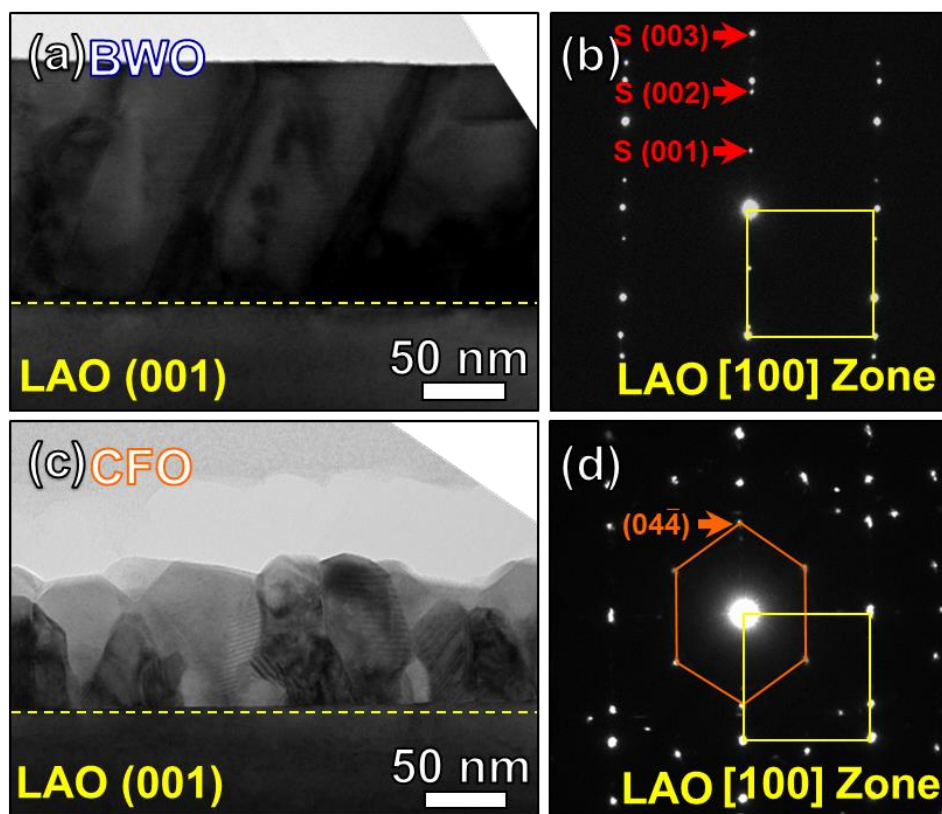


Fig. S6.2 (a, c) Cross-sectional TEM images of pure BWO and CFO phases. (c, d) The corresponding SAED patterns.

CHAPTER 7. SUMMARY AND FUTURE WORK

In this dissertation, we have exploited the structure and functionalities of Bi-based oxide thin films via strain engineering. For the first study system BiFeO_3 (BFO), we have deposited a set of BFO thin films on SRO-buffered substrates and then explored the buffered-substrate strain effects on ferroelectric and optical properties of the films. The tensile strain provides potential of narrowing band gap in BFO. Highly strained BFO thin films show lower coercive field, which owing to the coexistence of polar instabilities and the rotation of the oxygen octahedral. In addition, we have grown BFO on TiN-buffered Si substrates, which further proves the practical applications of BFO. Compared with pure BFO, a much higher polarization was measured in Sm-doped BFO (BSFO). We have tuned the structure and polariton of Sm-doped BFO systems via deposition temperature. It is the first demonstration of Sm dopant existence in BFO via STEM and EDS measurement.

For the second study system Bi_2WO_6 (BWO), we have incorporated magnetic cations Mn into BWO to create a new nanocomposite $\text{Bi}_2\text{W}_{1-x}\text{Mn}_x\text{O}_6\text{-BiMnO}_3$. Robust room temperature ferroelectric and ferromagnetic response (room temperature multiferroic responses) and unique tunable optical properties have been observed for this new layered structure. In addition, we have demonstrated a new VAN structure of BWO:CFO with layered structure. The new VAN system shows strong multiferroic properties as a result of the vertical interface coupling between the ferroelectric BWO layered oxide matrix and ferromagnetic CFO nanocones.

We have proven the structure flexibility and tunable functionality in BFO and how a vertically aligned structure can improve the ferromagnetic properties in BWO. Future work includes investigation on:

1. More property characterization and strain analysis of BSFO samples is required.
2. BWO-based VAN structure will be considered as new research project, since the horizontal stain effect has been explored on the structure and properties of BWO thin films. For example, other spinel phases are considered as a candidate for the second phase. Other properties such as optical can be characterized in the BWO-based VAN.
3. The work presents great potentials of layered oxides in terms of new VAN design.
4. The proved nanocomposite can be deposited on Si substrates and incorporated in the functional devices, such as nanoscale sensors and actuators.

REFERENCES

- 1 L. Martin, Y.-H. Chu, and R. Ramesh, *Materials Science and Engineering: R: Reports* **68**, 89 (2010).
- 2 R. Chintamani Nagesa Ramachandra and B. Raveau, *Transition metal oxides: structure, properties, and synthesis of ceramic oxides* (Wiley-VCH, 1998).
- 3 A. Bhalla, R. Guo, and R. Roy, *Materials research innovations* **4**, 3 (2000).
- 4 V. M. Goldschmidt, *Naturwissenschaften* **14**, 477 (1926).
- 5 R. Ramesh and N. A. Spaldin, *Nature Materials* **6**, 21 (2007).
- 6 J. C. Wojdel and J. Iniguez, *Physical Review Letters* **103**, 4 (2009).
- 7 P. Royen and K. Swars, *Angewandte Chemie* **69**, 779 (1957).
- 8 S. Kiselev, R. Ozerov, and G. Zhdanov, in *Detection of magnetic order in ferroelectric BiFeO₃ by neutron diffraction*, 1963, p. 742.
- 9 S. Kiselev, *Sov. Phys.* **7**, 742 (1963).
- 10 A. R. Damodaran, C. W. Liang, Q. He, C. Y. Peng, L. Chang, Y. H. Chu, and L. W. Martin, *Advanced Materials* **23**, 3170 (2011).
- 11 H. D. Megaw and C. Darlington, *Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography* **31**, 161 (1975).
- 12 D. C. Arnold, K. S. Knight, F. D. Morrison, and P. Lightfoot, *Physical Review Letters* **102**, 027602 (2009).
- 13 I. Levin, M. Tucker, H. Wu, V. Provenzano, C. Dennis, S. Karimi, T. Comyn, T. Stevenson, R. Smith, and I. Reaney, *Chemistry of Materials* **23**, 2166 (2011).
- 14 R. C. Lennox, M. C. Price, W. Jamieson, M. Jura, A. Daoud-Aladine, C. A. Murray, C. Tang, and D. C. Arnold, *Journal of Materials Chemistry C* **2**, 3345 (2014).
- 15 J. G. Wu, Z. Fan, D. Q. Xiao, J. G. Zhu, and J. Wang, *Progress in Materials Science* **84**, 335 (2016).
- 16 K. Kalantar-zadeh, J. Z. Ou, T. Daeneke, A. Mitchell, T. Sasaki, and M. S. Fuhrer, *Applied Materials Today* **5**, 73 (2016).
- 17 M. Osada and T. Sasaki, *Dalton Transactions* **47**, 2841 (2018).
- 18 F. Suhua, C. Wen, Z. Fengqing, and H. Guangda, *Journal of Rare Earths* **25**, 317 (2007).

- 19 B. Zulhadjri, A. Prijamboedi, N. Nugroho, A. Mufti, T. Fajar, and I. Palstra, *J Solid State Chem* **184**, 1318 (2011).
- 20 R. A. Golda, A. Marikani, and D. P. Padiyan, *Ceramics International* **37**, 3731 (2011).
- 21 T. Jardiel, A. Caballero, and M. Villegas, *Journal of the Ceramic Society of Japan* **116**, 511 (2008).
- 22 R. Wolfe, R. Newnham, and M. Kay, *Solid State Communications* **7**, 1797 (1969).
- 23 I. IG and F. Mirishli; *Vol. 14* (AMER INST PHYSICS CIRCULATION FULFILLMENT DIV, 500 SUNNYSIDE BLVD, WOODBURY ..., 1970), p. 636.
- 24 R. Withers, J. Thompson, and A. Rae, *Journal of Solid State Chemistry* **94**, 404 (1991).
- 25 M. V. Limaye, S. B. Singh, S. K. Date, D. Kothari, V. R. Reddy, A. Gupta, V. Sathe, R. J. Choudhary, and S. K. Kulkarni, *The Journal of Physical Chemistry B* **113**, 9070 (2009).
- 26 A. Ravindra, P. Padhan, and W. Prellier, *Applied Physics Letters* **101**, 161902 (2012).
- 27 C. Schmitz-Antoniak, D. Schmitz, P. Borisov, F. M. De Groot, S. Stienen, A. Warland, B. Krumme, R. Feyerherm, E. Dudzik, and W. Kleemann, *Nature communications* **4**, 2051 (2013).
- 28 X. Zeng, J. Zhang, S. Zhu, X. Deng, H. Ma, J. Zhang, Q. Zhang, P. Li, D. Xue, and N. J. Mellors, *Nanoscale* **9**, 7493 (2017).
- 29 A. F. Wells, *Structural inorganic chemistry* (Oxford university press, 2012).
- 30 K. Uchino, *Ferroelectric Devices 2nd Edition* (CRC press, 2009).
- 31 R. Calìò, U. Rongala, D. Camboni, M. Milazzo, C. Stefanini, G. De Petris, and C. Oddo, *Sensors* **14**, 4755 (2014).
- 32 S. R. Anton and H. A. Sodano, *Smart materials and Structures* **16**, R1 (2007).
- 33 G. H. Haertling, *Journal of the American Ceramic Society* **82**, 797 (1999).
- 34 J. R. Teague, R. Gerson, and W. J. James, *Solid State Communications* **8**, 1073 (1970).
- 35 J. Wang, J. Neaton, H. Zheng, V. Nagarajan, S. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. Schlom, and U. Waghmare, *Science* **299**, 1719 (2003).
- 36 J. Neaton, C. Ederer, U. Waghmare, N. Spaldin, and K. Rabe, *Physical Review B* **71**, 014113 (2005).
- 37 P. Ravindran, R. Vidya, A. Kjekshus, H. Fjellvåg, and O. Eriksson, *Physical Review B* **74**, 224412 (2006).

- 38 Z. Fan, J. Xiao, H. Liu, P. Yang, Q. Ke, W. Ji, K. Yao, K. P. Ong, K. Zeng, and J. Wang, ACS applied materials & interfaces **7**, 2648 (2015).
- 39 J. Yan, M. Gomi, T. Yokota, and H. Song, Applied Physics Letters **102**, 222906 (2013).
- 40 C.-P. De Araujo, J. Cuchiaro, L. McMillan, M. Scott, and J. Scott, Nature **374**, 627 (1995).
- 41 B. Park, B. Kang, S. Bu, T. Noh, J. Lee, and W. Jo, Nature **401**, 682 (1999).
- 42 S. K. Kim, M. Miyayama, and H. Yanagida, Materials Research Bulletin **31**, 121 (1996).
- 43 K. Zheng, Y. Zhou, L. Gu, X. Mo, G. R. Patzke, and G. Chen, Sensors and Actuators B: Chemical **148**, 240 (2010).
- 44 S. Jin, I. M. M. Salvado, and M. E. V. Costa, Materials Research Bulletin **46**, 432 (2011).
- 45 D. Sando, A. Agbelele, C. Daumont, D. Rahmedov, W. Ren, I. Infante, S. Lisenkov, S. Prosandeev, S. Fusil, and E. Jacquet, Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences **372**, 20120438 (2014).
- 46 D. Albrecht, S. Lisenkov, W. Ren, D. Rahmedov, I. A. Kornev, and L. Bellaiche, Physical Review B **81**, 140401 (2010).
- 47 S. Bellad and C. Bhosale, Thin Solid Films **322**, 93 (1998).
- 48 S. E. Shirsath, X. Liu, Y. Yasukawa, S. Li, and A. Morisako, Scientific reports **6**, 30074 (2016).
- 49 P. Thang, G. Rijnders, and D. H. Blank, Journal of Magnetism and Magnetic Materials **310**, 2621 (2007).
- 50 K. Inomata, N. Ikeda, N. Tezuka, R. Goto, S. Sugimoto, M. Wojcik, and E. Jedryka, Science and Technology of Advanced Materials **9**, 014101 (2008).
- 51 X. Gao, L. Liu, B. Birajdar, M. Ziese, W. Lee, M. Alexe, and D. Hesse, Advanced Functional Materials **19**, 3450 (2009).
- 52 V. Pillai and D. Shah, Journal of Magnetism and Magnetic Materials **163**, 243 (1996).
- 53 D. Khomskii, Physics **2**, 20 (2009).
- 54 E. Ascher, H. Rieder, H. Schmid, and H. Stössel, Journal of Applied Physics **37**, 1404 (1966).
- 55 A. Y. Birenbaum and C. Ederer, Physical Review B **90**, 214109 (2014).
- 56 X. Chen, J. Xiao, Y. Xue, X. Zeng, F. Yang, and P. Su, Ceramics International **40**, 2635 (2014).

- 57 J. Allibe, K. Bougot-Robin, E. Jacquet, I. Infante, S. Fusil, C. Carrétéro, J.-L. Reverchon,
B. Marcilhac, D. Creté, and J.-C. Mage, *Applied Physics Letters* **96**, 182902 (2010).
- 58 I. Grinberg, D. V. West, M. Torres, G. Gou, D. M. Stein, L. Wu, G. Chen, E. M. Gallo,
A. R. Akbashev, and P. K. Davies, *Nature* **503**, 509 (2013).
- 59 S. Clark and J. Robertson, *Applied physics letters* **90**, 132903 (2007).
- 60 J. Allibe, K. Bougot-Robin, E. Jacquet, I. C. Infante, S. Fusil, C. Carretero, J. L.
Reverchon, B. Marcilhac, D. Crete, J. C. Mage, A. Barthelemy, and M. Bibes, *Applied
Physics Letters* **96**, 3 (2010).
- 61 S. H. Chu, D. J. Singh, J. Wang, E. P. Li, and K. P. Ong, *Laser & Photonics Reviews* **6**,
684 (2012).
- 62 H. Dong, Z. Wu, S. Wang, W. Duan, and J. Li, *Applied Physics Letters* **102**, 072905
(2013).
- 63 D. Sando, P. Hermet, J. Allibe, J. Bourderionnet, S. Fusil, C. Carrétéro, E. Jacquet, J.-C.
Mage, D. Dolfi, and A. Barthélémy, *Physical Review B* **89**, 195106 (2014).
- 64 J.-P. Rivera and H. Schmid, *Ferroelectrics* **204**, 23 (1997).
- 65 T. Choi, S. Lee, Y. J. Choi, V. Kiryukhin, and S. W. Cheong, *Science* **324**, 63 (2009).
- 66 R. Nechache, C. Harnagea, S. Li, L. Cardenas, W. Huang, J. Chakrabartty, and F. Rosei,
Nature Photonics **9**, 61 (2015).
- 67 H. Fu, L. Zhang, W. Yao, and Y. Zhu, *Applied Catalysis B: Environmental* **66**, 100
(2006).
- 68 A. Kudo, K. Omori, and H. Kato, *Journal of the American Chemical Society* **121**, 11459
(1999).
- 69 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).
- 70 Y. Song, H. Zhou, Q. Xu, J. Luo, H. Yin, J. Yan, and H. Zhong, *Journal of electronic
materials* **40**, 1584 (2011).
- 71 K. J. Kuhn, A. Murthy, R. Kotlyar, and M. Kuhn, *ECS Transactions* **33**, 3 (2010).
- 72 R. Ghosh, D. Basak, and S. Fujihara, *Journal of Applied Physics* **96**, 2689 (2004).
- 73 R. Zeches, M. Rossell, J. Zhang, A. Hatt, Q. He, C.-H. Yang, A. Kumar, C. Wang, A.
Melville, and C. Adamo, *science* **326**, 977 (2009).
- 74 W. Eerenstein, N. Mathur, and J. F. Scott, *nature* **442**, 759 (2006).

- 75 S. A. Harrington, J. Zhai, S. Denev, V. Gopalan, H. Wang, Z. Bi, S. A. Redfern, S.-H. Baek, C. W. Bark, and C.-B. Eom, *Nature nanotechnology* **6**, 491 (2011).
- 76 Y. Li and L. Chen, *Applied physics letters* **88**, 072905 (2006).
- 77 T. Zhao, A. Scholl, F. Zavaliche, K. Lee, M. Barry, A. Doran, M. P. Cruz, Y. H. Chu, C. Ederer, N. A. Spaldin, R. R. Das, D. M. Kim, S. H. Baek, C. B. Eom, and R. Ramesh, *Nature Materials* **5** (2006).
- 78 G. Xu, H. Hiraka, G. Shirane, J. Li, J. Wang, and D. Viehland, *Applied Physics Letters* **86**, 182905 (2005).
- 79 Z. Chen, Y. Qi, L. You, P. Yang, C. Huang, J. Wang, T. Sritharan, and L. Chen, *Physical Review B* **88**, 054114 (2013).
- 80 D. Ricinschi, K.-Y. Yun, and M. Okuyama, *Journal of Physics: Condensed Matter* **18**, L97 (2006).
- 81 X. Qi, J. Dho, R. Tomov, M. G. Blamire, and J. L. MacManus-Driscoll, *Applied Physics Letters* **86**, 062903 (2005).
- 82 H. Béa, M. Bibes, X.-H. Zhu, S. Fusil, K. Bouzehouane, S. Petit, J. Kreisel, and A. Barthélémy, *Applied Physics Letters* **93**, 072901 (2008).
- 83 J. Yang, Q. He, S. Suresha, C. Kuo, C. Peng, R. Haislmaier, M. Motyka, G. Sheng, C. Adamo, and H. Lin, *Physical review letters* **109**, 247606 (2012).
- 84 J. H. Lee, K. Chu, A. A. Ünal, S. Valencia, F. Kronast, S. Kowarik, J. Seidel, and C.-H. Yang, *Physical Review B* **89**, 140101 (2014).
- 85 L. Yan, H. Cao, J. Li, and D. Viehland, *Applied Physics Letters* **94**, 132901 (2009).
- 86 D. Sando, A. Barthélémy, and M. Bibes, *Journal of Physics: Condensed Matter* **26**, 473201 (2014).
- 87 H. Jang, S. Baek, D. Ortiz, C. Folkman, R. Das, Y. Chu, P. Shafer, J. Zhang, S. Choudhury, and V. Vaithyanathan, *Physical review letters* **101**, 107602 (2008).
- 88 C. Beekman, W. Siemons, T. Z. Ward, M. Chi, J. Howe, M. D. Biegalski, N. Balke, P. Maksymovych, A. Farrar, and J. Romero, *Advanced Materials* **25**, 5561 (2013).
- 89 J. Zhang, Q. He, M. Trassin, W. Luo, D. Yi, M. D. Rossell, P. Yu, L. You, C. H. Wang, and C. Kuo, *Physical review letters* **107**, 147602 (2011).
- 90 R. J. Zeches, M. D. Rossell, J. X. Zhang, A. J. Hatt, Q. He, C. H. Yang, A. Kumar, C. H. Wang, A. Melville, C. Adamo, G. Sheng, Y. H. Chu, J. F. Ihlefeld, R. Erni, C. Ederer, V.

- Gopalan, L. Q. Chen, D. G. Schlom, N. A. Spaldin, L. W. Martin, and R. Ramesh, *Science* **326**, 977 (2009).
- 91 K. J. Choi, M. Biegalski, Y. Li, A. Sharan, J. Schubert, R. Uecker, P. Reiche, Y. Chen, X. Pan, and V. Gopalan, *Science* **306**, 1005 (2004).
- 92 A. R. Damodaran, E. Breckenfeld, Z. Chen, S. Lee, and L. W. Martin, *Advanced Materials* **26**, 6341 (2014).
- 93 Y. Li, S. Choudhury, J. Haeni, M. Biegalski, A. Vasudevarao, A. Sharan, H. Ma, J. Levy, V. Gopalan, and S. Trolier-McKinstry, *Physical Review B* **73**, 184112 (2006).
- 94 J. Haeni, P. Irvin, W. Chang, R. Uecker, P. Reiche, Y. Li, S. Choudhury, W. Tian, M. Hawley, and B. Craigo, *Nature* **430**, 758 (2004).
- 95 M. P. Warusawithana, C. Cen, C. R. Sleasman, J. C. Woicik, Y. Li, L. F. Kourkoutis, J. A. Klug, H. Li, P. Ryan, and L.-P. Wang, *Science* **324**, 367 (2009).
- 96 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).
- 97 S. Fujino, M. Murakami, V. Anbusathaiah, S.-H. Lim, V. Nagarajan, C. Fennie, M. Wuttig, L. Salamanca-Riba, and I. Takeuchi, *Applied Physics Letters* **92**, 202904 (2008).
- 98 L. June Hyuk, F. Lei, V. Eftihia, K. Xianglin, J. Young Woo, K. Lena Fitting, K. Jong-Woo, J. R. Philip, H. Tassilo, R. Martin, G. Veronica, B. Margitta, U. Reinhard, P. C. Hammel, M. R. Karin, K. Stanislav, S. Jürgen, W. F. John, A. M. David, J. F. Craig, S. Peter, G. Venkatraman, J.-H. Ezekiel, and G. S. Darrell, *Nature* **476**, 114 (2011).
- 99 E. S. Sagar, L. Xiaoxi, Y. Yukiko, L. Sean, and M. Akimitsu, *Scientific Reports* **6** (2016).
- 100 H. Dong, H. Liu, and S. Wang, *Journal of Physics D: Applied Physics* **46**, 135102 (2013).
- 101 P. Chen, N. Podraza, X. Xu, A. Melville, E. Vlahos, V. Gopalan, R. Ramesh, D. Schlom, and J. Musfeldt, *Applied Physics Letters* **96**, 131907 (2010).
- 102 W. Zhang, R. Ramesh, J. L. MacManus-Driscoll, and H. Wang, *MRS Bulletin* **40**, 736 (2015).
- 103 A. Chen, H. Zhou, Z. Bi, Y. Zhu, Z. Luo, A. Bayraktaroglu, J. Phillips, E. M. Choi, J. L. MacManus-Driscoll, and S. J. Pennycook, *Advanced Materials* **25**, 1028 (2013).
- 104 Y. Zhu, A. Chen, H. Zhou, W. Zhang, J. Narayan, J. L. MacManus-Driscoll, Q. Jia, and H. Wang, *APL materials* **1**, 050702 (2013).

- 105 L. Li, P. Boullay, P. Lu, X. Wang, J. Jian, J. Huang, X. Gao, S. Misra, W. Zhang, and O. Perez, *Nano letters* **17**, 6575 (2017).
- 106 L. Li, P. Boullay, J. Cheng, P. Lu, X. Wang, G. Steciuk, J. Huang, J. Jian, X. Gao, B. Zhang, S. Misra, X. Zhang, K. Yang, and H. Wang, *Materials Today Nano*, 100037 (2019).
- 107 D. Schlom, J. Haeni, J. Lettieri, C. Theis, W. Tian, J. Jiang, and X. Pan, *Materials Science and Engineering: B* **87**, 282 (2001).
- 108 J. Junquera and P. Ghosez, *Nature* **422**, 506 (2003).
- 109 O. I. Lebedev, J. Verbeeck, G. Van Tendeloo, O. Shapoval, A. Belenchuk, V. Moshnyaga, B. Damashcke, and K. Samwer, *Physical Review B* **66** (2002).
- 110 H. Zheng, J. Wang, S. E. Lofland, Z. Ma, L. Mohaddes-Ardabili, T. Zhao, L. Salamanca-Riba, S. R. Shinde, S. B. Ogale, F. Bai, D. Viehland, Y. Jia, D. G. Schlom, M. Wuttig, A. Roytburd, and R. Ramesh, *Science* **303**, 661 (2004).
- 111 A. P. Chen, M. Weigand, Z. X. Bi, W. R. Zhang, X. J. Lu, P. Dowden, J. L. MacManus-Driscoll, H. Y. Wang, and Q. X. Jia, *Scientific Reports* **4**, 7 (2014).
- 112 A. P. Chen, Z. X. Bi, Q. X. Jia, J. L. MacManus-Driscoll, and H. Y. Wang, *Acta Materialia* **61**, 2783 (2013).
- 113 A. P. Chen, Z. X. Bi, C. F. Tsai, J. Lee, Q. Su, X. H. Zhang, Q. X. Jia, J. L. MacManus-Driscoll, and H. Y. Wang, *Advanced Functional Materials* **21**, 2423 (2011).
- 114 W. Zhang, A. Chen, F. Khatkhatay, C. F. Tsai, Q. Su, L. Jiao, X. Zhang, and H. Wang, *ACS Appl Mater Interfaces* **5**, 3995 (2013).
- 115 C. F. Tsai, L. Chen, A. P. Chen, F. Khatkhatay, W. R. Zhang, and H. Y. Wang, *Ieee Transactions on Applied Superconductivity* **23** (2013).
- 116 Q. Su, D. Yoon, A. P. Chen, F. Khatkhatay, A. Manthiram, and H. Y. Wang, *Journal of Power Sources* **242**, 455 (2013).
- 117 O. Lee, S. A. Harrington, A. Kursumovic, E. Defay, H. Y. Wang, Z. X. Bi, C. F. Tsai, L. Yan, Q. X. Jia, and J. L. MacManus-Driscoll, *Nano Letters* **12**, 4311 (2012).
- 118 W. Zhang, A. Chen, Z. Bi, Q. Jia, J. L. MacManus-Driscoll, and H. Wang, *Current Opinion in Solid State and Materials Science* **18**, 6 (2014).
- 119 L. Mohaddes-Ardabili, H. Zheng, S. Ogale, B. Hannoyer, W. Tian, J. Wang, S. Lofland, S. Shinde, T. Zhao, and Y. Jia, *Nature materials* **3**, 533 (2004).

- 120 L. Li, L. Sun, J. S. Gomez-Diaz, N. L. Hogan, P. Lu, F. Khatkhatay, W. Zhang, J. Jian, J. Huang, and Q. Su, *Nano letters* **16**, 3936 (2016).
- 121 J. Huang, L. Li, P. Lu, Z. Qi, X. Sun, X. Zhang, and H. Wang, *Nanoscale* **9**, 7970 (2017).
- 122 J. L. MacManus-Driscoll, P. Zerrer, H. Wang, H. Yang, J. Yoon, A. Fouchet, R. Yu, M. G. Blamire, and Q. Jia, *Nature materials* **7**, 314 (2008).
- 123 H. Yang, H. Wang, J. Yoon, Y. Wang, M. Jain, D. M. Feldmann, P. C. Dowden, J. L. MacManus-Driscoll, and Q. Jia, *Advanced Materials* **21**, 3794 (2009).
- 124 Z. Bi, J. H. Lee, H. Yang, Q. Jia, J. L. MacManus-Driscoll, and H. Wang, *Journal of Applied Physics* **106**, 094309 (2009).
- 125 O. Lebedev, J. Verbeeck, G. Van Tendeloo, O. Shapoval, A. Belenchuk, V. Moshnyaga, B. Damashcke, and K. Samwer, *Physical Review B* **66**, 104421 (2002).
- 126 A. Chen, Z. Bi, C. F. Tsai, J. Lee, Q. Su, X. Zhang, Q. Jia, J. L. MacManus-Driscoll, and H. Wang, *Advanced Functional Materials* **21**, 2423 (2011).
- 127 B. Kang, H. Wang, J. MacManus-Driscoll, Y. Li, Q. Jia, I. Mihut, and J. Betts, *Applied physics letters* **88**, 192514 (2006).
- 128 F. Khatkhatay, A. Chen, J. H. Lee, W. Zhang, H. Abdel-Raziq, and H. Wang, *ACS applied materials & interfaces* **5**, 12541 (2013).
- 129 A. Chen, Z. Bi, H. Hazariwala, X. Zhang, Q. Su, L. Chen, Q. Jia, J. L. MacManus-Driscoll, and H. Wang, *Nanotechnology* **22**, 315712 (2011).
- 130 J. Yoon, S. Cho, J. H. Kim, J. Lee, Z. Bi, A. Serquis, X. Zhang, A. Manthiram, and H. Wang, *Advanced Functional Materials* **19**, 3868 (2009).
- 131 X. Gao, L. Li, J. Jian, H. Wang, M. Fan, J. Huang, X. Wang, and H. Wang, *ACS Applied Nano Materials* (2018).
- 132 C. Cantoni, Y. Gao, S. H. Wee, E. D. Specht, J. Gazquez, J. Meng, S. J. Pennycook, and A. Goyal, *Acs Nano* **5**, 4783 (2011).
- 133 Y. Zhu, C.-F. Tsai, J. Wang, J. H. Kwon, H. Wang, C. V. Varanasi, J. Burke, L. Brunke, and P. N. Barnes, *Journal of Materials Research* **27**, 1763 (2012).
- 134 F. Zavaliche, H. Zheng, L. Mohaddes-Ardabili, S. Yang, Q. Zhan, P. Shafer, E. Reilly, R. Chopdekar, Y. Jia, and P. Wright, *Nano letters* **5**, 1793 (2005).
- 135 F. Zavaliche, T. Zhao, H. Zheng, F. Straub, M. Cruz, P.-L. Yang, D. Hao, and R. Ramesh, *Nano letters* **7**, 1586 (2007).

- 136 Q. Zhan, R. Yu, S. Crane, H. Zheng, C. Kisielowski, and R. Ramesh, *Applied physics letters* **89**, 172902 (2006).
- 137 H. Zheng, J. Wang, S. Lofland, Z. Ma, L. Mohaddes-Ardabili, T. Zhao, L. Salamanca-Riba, S. Shinde, S. Ogale, and F. Bai, *Science* **303**, 661 (2004).
- 138 H. Luo, H. Yang, S. A. Baily, O. Ugurlu, M. Jain, M. E. Hawley, T. M. McCleskey, A. K. Burrell, E. Bauer, and L. Civale, *Journal of the American Chemical Society* **129**, 14132 (2007).
- 139 I. Levin, J. Li, J. Slutsker, and A. L. Roytburd, *Advanced Materials* **18**, 2044 (2006).
- 140 Z. Bi, E. Weal, H. Luo, A. Chen, J. L. MacManus-Driscoll, Q. Jia, and H. Wang, *Journal of Applied Physics* **109**, 054302 (2011).
- 141 S. Cho, Y. N. Kim, J. Lee, A. Manthiram, and H. Wang, *Electrochimica Acta* **62**, 147 (2012).
- 142 A. Imai, X. Cheng, H. L. Xin, E. A. Eliseev, A. N. Morozovska, S. V. Kalinin, R. Takahashi, M. Lippmaa, Y. Matsumoto, and V. Nagarajan, *Acs Nano* **7**, 11079 (2013).
- 143 X. Sun, J. Huang, J. Jian, M. Fan, H. Wang, Q. Li, J. L. Mac Manus-Driscoll, P. Lu, X. Zhang, and H. Wang, *Materials Horizons* **5**, 536 (2018).
- 144 F. Khatkhatay, A. P. Chen, J. H. Lee, W. R. Zhang, H. Abdel-Raziq, and H. Y. Wang, *Acs Applied Materials & Interfaces* **5**, 12541 (2013).
- 145 C. Schmitz-Antoniak, D. Schmitz, P. Borisov, F. M. F. de Groot, S. Stienen, A. Warland, B. Krumme, R. Feyerherm, E. Dudzik, W. Kleemann, and H. Wende, *Nature communications* **4**, 2051 (2013).
- 146 Q. Su, D. Yoon, Z. Sisman, F. Khatkhatay, Q. X. Jia, A. Manthiram, and H. Y. Wang, *International Journal of Hydrogen Energy* **38**, 16320 (2013).
- 147 A. P. Chen, Z. X. Bi, H. Hazariwala, X. H. Zhang, Q. Su, L. Chen, Q. X. Jia, J. L. MacManus-Driscoll, and H. Y. Wang, *Nanotechnology* **22** (2011).
- 148 J. J. Huang, C. F. Tsai, L. Chen, J. Jian, F. Khatkhatay, K. Y. Yu, and H. Y. Wang, *Journal of Applied Physics* **115** (2014).
- 149 H. J. Liu, L. Y. Chen, Q. He, C. W. Liang, Y. Z. Chen, Y. S. Chien, Y. H. Hsieh, S. J. Lin, E. Arenholz, C. W. Luo, Y. L. Chueh, Y. C. Chen, and Y. H. Chu, *Acs Nano* **6**, 6952 (2012).

- 150 D. Dijkkamp, T. Venkatesan, X. Wu, S. Shaheen, N. Jisrawi, Y. Min-Lee, W. McLean,
and M. Croft, *Applied Physics Letters* **51**, 619 (1987).
- 151 http://groups.ist.utl.pt/rschwarz/rschwarzgroup_files/PLD_files/PLD.htm},
- 152 R. K. Singh, O. Holland, and J. Narayan, *Journal of applied physics* **68**, 233 (1990).
- 153 J. Cheung and J. Horwitz, *MRS Bulletin* **17**, 30 (1992).
- 154 P. H. Le and C. W. Luo, in *Applications of laser ablation-thin film deposition, nanomaterial synthesis and surface modification* (IntechOpen, 2016).
- 155 P. H. Le and C. W. Luo, *Applications of laser ablation-thin film deposition, nanomaterial synthesis and surface modification* (2016).
- 156 http://www.xtal.iqfr.csic.es/Cristalografia/parte_05_5-en.html.
- 157 B. Fultz and J. M. Howe, *Transmission electron microscopy and diffractometry of materials* (Springer Science & Business Media, 2012).
- 158 F. Wu, (2014).
- 159 https://commons.wikimedia.org/wiki/File:Schematic_view_of_imaging_and_diffraction_modes_in_TEM..tif
- 160 E. P. Amaladass, (2008).
- 161 B. J. Inkson, in *Materials Characterization Using Nondestructive Evaluation (NDE) Methods*, edited by G. Hübschen, I. Altpeter, R. Tschuncky, and H.-G. Herrmann (Woodhead Publishing, 2016), p. 17.
- 162 <https://www2.nau.edu/micro-analysis/wordpress/index.php/signals/>.
- 163 <https://www.qd-latam.com/site/products/company/quantum-design/ppms-dynacool>.
- 164 https://qdusa.com/sitedocs/appNotes/vsmappnote_5-09.pdf.
- 165 C. B. Sawyer and C. H. Tower, *Physical Review* **35**, 0269 (1930).
- 166 https://www.doitpoms.ac.uk/tlplib/ferroelectrics/measuring_pol.php.
- 167 R. Ramesh and A. S. Nicola; *Vol. 6* (2007), p. 21.
- 168 H. Dong, Z. Wu, S. Wang, W. Duan, and J. Li, *Applied Physics Letters* **102** (2013).
- 169 T. Choi, S. Lee, Y. Choi, V. Kiryukhin, and S. W. Cheong, *Science (Washington)* **324**, 63 (2009).
- 170 J. Allibe, K. Bougot-Robin, E. Jacquet, I. C. Infante, S. Fusil, C. Carrétéro, J. L. Reverchon, B. Marilhac, D. Creté, J. C. Mage, A. Barthélémy, and M. Bibes, *Applied Physics Letters* **96** (2010).

- 171 H.-J. Liu, C.-W. Liang, W.-I. Liang, H.-J. Chen, J.-C. Yang, C.-Y. Peng, G.-F. Wang, F.-N. Chu, Y.-C. Chen, H.-Y. Lee, L. Chang, S.-J. Lin, and Y.-H. Chu, *Physical Review B (Condensed Matter and Materials Physics)* **85**, 014104 (2012).
- 172 R. Zeches, M. Rossell, J. Zhang, A. Hatt, C. H. Yang, A. Kumar, C. Wang, A. Melville, C. Adamo, G. Sheng, Y. H. Chu, J. Ihlefeld, R. Erni, C. Ederer, V. Gopalan, L. Chen, D. Schlom, and N. Spaldin, *Science (Washington)* **326**, 977 (2009).
- 173 C. Ederer and N. Spaldin, *arXiv.org* **95** (2005).
- 174 Z. Fu, Z. G. Yin, N. F. Chen, X. W. Zhang, Y. J. Zhao, Y. M. Bai, Y. Chen, H. H. Wang, X. L. Zhang, and J. L. Wu, *Applied Physics Letters* **104** (2014).
- 175 J. X. Zhang, B. Xiang, Q. He, J. Seidel, R. J. Zeches, P. Yu, S. Y. Yang, C. H. Wang, Y. H. Chu, L. W. Martin, A. M. Minor, and R. Ramesh, *Nature Nanotechnology* **6**, 98 (2011).
- 176 J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, *Science* **299**, 1719 (2003).
- 177 H. Béa, M. Gajek, M. Bibes, and A. Barthélémy, *Journal of Physics: Condensed Matter* **20**, 434221 (2008).
- 178 J. H. Jang, S. H. Baek, D. Ortiz, R. Das, C. H. Folkman, Y. H. Chu, P. Shafer, J. X. Zhang, C. S. V. Vaithyanathan, Y. B. Chen, D. A. Felker, M. D. Biegalski, M. Ryzhowski, X. Q. Pan, L.-Q. Chen, D. Schlom, R. Ramesh, and C.-B. Eom, *Physical Review Letters* **101** (2008).
- 179 I. C. Infante, S. Lisenkov, B. Dupé, M. Bibes, S. Fusil, E. Jacquet, G. Geneste, S. Petit, A. Courtial, J. Juraszek, L. Bellaiche, A. Barthélémy, and B. Dkhil, *Physical review letters* **105**, 057601 (2010).
- 180 D. Mazumdar, V. Shelke, M. Iliev, S. Jesse, A. Kumar, S. V. Kalinin, A. P. Baddorf, and A. Gupta, *Nano Lett* **10**, 2555 (2010).
- 181 H. Béa, B. Dupé, S. Fusil, R. Mattana, E. Jacquet, B. Warot-Fonrose, F. Wilhelm, A. Rogalev, S. Petit, V. Cros, A. Anane, F. Petroff, K. Bouzehouane, G. Geneste, B. Dkhil, S. Lisenkov, I. Ponomareva, L. Bellaiche, M. Bibes, and A. Barthélémy, *Physical review letters* **102**, 217603 (2009).

- 182 D. Sando, Y. Yang, E. Bousquet, C. Carretero, V. Garcia, S. Fusil, D. Dolfi, A.
Barthelemy, P. Ghosez, L. Bellaiche, and M. Bibes, *Nature Communications* **7** (2016).
- 183 V. Shelke, G. Srinivasan, and A. Gupta, *physica status solidi (RRL) – Rapid Research
Letters* **4**, 79 (2010).
- 184 S.-H. Baek and C.-B. Eom, *Acta Materialia* **61**, 2734 (2013).
- 185 J. Huang, A. Gellatly, A. Kauffmann, X. Sun, and H. Wang, *Crystal Growth and Design*
18, 4388 (2018).
- 186 K. J. Choi, S. H. Baek, H. W. Jang, L. J. Belenky, M. Lyubchenko, and C. B. Eom,
Advanced Materials **22**, 759 (2010).
- 187 W. Siemons, G. Koster, G. Rijnders, L. Klein, J. S. Dodge, P. C.-B. Eom, D. H. A. Blank,
and M. R. Beasley, *Reviews of Modern Physics* **84** (2012).
- 188 Y. H. Chu, Q. Zhan, L. Martin, M. Cruz, P. L. Yang, G. Pabst, F. Zavaliche, S. Y. Yang,
J. X. Zhang, L. Q. Chen, D. Schlom, I. N. Lin, T. B. Wu, and R. Ramesh, *Advanced
Materials (FRG)* **18**, 2307 (2006).
- 189 H. Wang, A. Sharma, A. Kvit, Q. Wei, X. Zhang, C. Koch, and J. Narayan, *Journal of
Materials Research* **16**, 2733 (2001).
- 190 J. Narayan, P. Tiwari, X. Chen, J. Singh, R. Chowdhury, and T. Zheleva, *Applied Physics
Letters* **61**, 1290 (1992).
- 191 F. Khatkhatay, A. P. Chen, J. Lee, W. Zhang, H. Abdel-Raziq, and H. Wang, *Acs
Applied Materials & Interfaces* **5**, 12541 (2013).
- 192 Z. Chen, Z. Luo, Y. Qi, P. Yang, S. Wu, C. W. Huang, T. Wu, J. Wang, C. Gao, T.
Sritharan, and L. Chen, *Applied Physics Letters* **97** (2010).
- 193 J. Tauc, *Amorphous and liquid semiconductors* (Springer Science & Business Media,
2012).
- 194 C. Yoshida, A. Yoshida, and H. Tamura, *Applied Physics Letters* **75**, 1449 (1999).
- 195 R. F. Berger, C. J. Fennie, and J. B. Neaton, *Phys. Rev. Lett.* **107** (2011).
- 196 H. Nagata, M. Yoshida, Y. Makiuchi, and T. Takenaka, *Japanese journal of applied
physics* **42**, 7401 (2003).
- 197 X.-h. Du, J. Zheng, U. Belegundu, and K. Uchino, *Applied Physics Letters* **72**, 2421
(1998).

- 198 S. Yang, F. Zavaliche, L. Mohaddes-Ardabili, V. Vaithyanathan, D. Schlom, Y. Lee, Y.
Chu, M. Cruz, Q. Zhan, and T. Zhao, *Applied physics letters* **87**, 102903 (2005).
- 199 D. Kan, C.-J. Cheng, V. Nagarajan, and I. Takeuchi, *Journal of Applied Physics* **110**,
014106 (2011).
- 200 G. Yuan, S. W. Or, and H. L. W. Chan, *Journal of Physics D: Applied Physics* **40**, 1196
(2007).
- 201 X. Chen, J. Wang, G. Yuan, D. Wu, J. Liu, J. Yin, and Z. Liu, *Journal of Alloys and
Compounds* **541**, 173 (2012).
- 202 G. Yuan and S. W. Or, *Applied physics letters* **88**, 062905 (2006).
- 203 S. Karimi, I. Reaney, Y. Han, J. Pokorny, and I. Sterianou, *Journal of materials science*
44, 5102 (2009).
- 204 S. Karimi, I. Reaney, I. Levin, and I. Sterianou, *Applied Physics Letters* **94**, 112903
(2009).
- 205 C.-J. Cheng, A. Y. Borisevich, D. Kan, I. Takeuchi, and V. Nagarajan, *Chemistry of
Materials* **22**, 2588 (2010).
- 206 M. Myers, V. Khranovskyy, J. Jian, J. Lee, H. Wang, and H. Wang, *Journal of Applied
Physics* **118**, 065702 (2015).
- 207 G. Yuan and S. W. Or, *Journal of applied physics* **100**, 024109 (2006).
- 208 H. W. Jang, D. Ortiz, S. H. Baek, C. M. Folkman, R. R. Das, P. Shafer, Y. Chen, C. T.
Nelson, X. Pan, and R. Ramesh, *Advanced materials* **21**, 817 (2009).
- 209 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, *Physical Review B* **80**, 014109 (2009).
- 210 N. Liu, R. Liang, Z. Zhou, and X. Dong, *Journal of Materials Chemistry C* **6**, 10211
(2018).
- 211 J. Park, S. Baek, P. Wu, B. Winchester, C. Nelson, X. Pan, L. Chen, T. Tybell, and C.
Eom, *Applied Physics Letters* **97**, 212904 (2010).
- 212 C.-J. Cheng, D. Kan, S.-H. Lim, W. McKenzie, P. Munroe, L. Salamanca-Riba, R.
Withers, I. Takeuchi, and V. Nagarajan, *Physical Review B* **80**, 014109 (2009).
- 213 D. I. Khomskii, *Journal of Magnetism and Magnetic Materials* **306**, 1 (2006).
- 214 R. Ramesh and N. A. Spaldin, *Nature materials* **6**, 21 (2007).

- 215 A. Zvezdin, A. Logginov, G. Meshkov, and A. Pyatakov, Bulletin of the Russian
Academy of Sciences: Physics **71**, 1561 (2007).
- 216 M. M. Vopson, Critical Reviews in Solid State and Materials Sciences **40**, 223 (2015).
- 217 J. Scott, Nature materials **6**, 256 (2007).
- 218 J. Dho, X. Qi, H. Kim, J. L. MacManus-Driscoll, and M. G. Blamire, Advanced Materials
18, 1445 (2006).
- 219 R. T. Smith, G. D. Achenbach, R. Gerson, and W. J. James, Journal of Applied Physics
39, 70 (1968).
- 220 W. Prellier, M. Singh, and P. Murugavel, Journal of Physics: Condensed Matter **17**, R803
(2005).
- 221 J. R. Sahu, C. R. Serrao, N. Ray, U. V. Waghmare, and C. Rao, Journal of Materials
Chemistry **17**, 42 (2007).
- 222 J. Huang, J. Macmanus-Driscoll, and H. Wang, Journal Of Materials Research **32**, 4054
(2017).
- 223 R. Comes, H. Liu, M. Khokhlov, R. Kasica, J. Lu, and S. A. Wolf, Nano letters **12**, 2367
(2012).
- 224 Y. Ahn, J. D. Seo, and J. Y. Son, Journal of Crystal Growth **422**, 20 (2015).
- 225 H. Yan, H. Zhang, M. J. Reece, and X. Dong, Applied Physics Letters **87**, 082911 (2005).
- 226 X. Mao, H. Sun, W. Wang, Y. Lu, and X. Chen, Solid State Communications **152**, 483
(2012).
- 227 J. Wang, Z. Fu, R. Peng, M. Liu, S. Sun, H. Huang, L. Li, R. J. Knize, and Y. Lu,
Materials Horizons **2**, 232 (2015).
- 228 X. Mao, W. Wang, H. Sun, Y. Lu, and X. Chen, Journal of Materials Science **47**, 2960
(2012).
- 229 W. Zhang, M. Fan, L. Li, A. Chen, Q. Su, Q. Jia, J. L. MacManus-Driscoll, and H. Wang,
Applied Physics Letters **107**, 212901 (2015).
- 230 X. Gao, L. Li, J. Jian, H. Wang, M. Fan, J. Huang, X. Wang, and H. Wang, ACS Applied
Nano Materials **1**, 2509 (2018).
- 231 A. Chen, Z. Bi, Q. Jia, J. L. MacManus-Driscoll, and H. Wang, Acta Materialia **61**, 2783
(2013).
- 232 B. Frit and J. Mercurio, Journal of alloys and compounds **188**, 27 (1992).

- 233 Y. Ahn and J. Y. Son, *Journal of Crystal Growth* **462**, 41 (2017).
- 234 Y. Zhou, Z. Tian, Z. Zhao, Q. Liu, J. Kou, X. Chen, J. Gao, S. Yan, and Z. Zou, *ACS applied materials & interfaces* **3**, 3594 (2011).
- 235 F. Amano, A. Yamakata, K. Nogami, M. Osawa, and B. Ohtani, *Journal of the American Chemical Society* **130**, 17650 (2008).
- 236 N. A. McDowell, K. S. Knight, and P. Lightfoot, *Chemistry – A European Journal* **12**, 1493 (2006).
- 237 Y. Y. Zhu, A. P. Chen, H. H. Zhou, W. R. Zhang, J. Narayan, J. L. MacManus-Driscoll, Q. X. Jia, and H. Y. Wang, *Apl Materials* **1**, 11 (2013).
- 238 D. K. Pradhan, R. Choudhary, C. Rinaldi, and R. Katiyar, *Journal of Applied Physics* **106**, 024102 (2009).
- 239 C. Zener, *Physical Review* **82**, 403 (1951).
- 240 J. Y. Son, B. G. Kim, C. H. Kim, and J. H. Cho, *Applied Physics Letters* **84**, 4971 (2004).
- 241 R. Seshadri and N. A. Hill, *Chemistry of materials* **13**, 2892 (2001).
- 242 S. Kooriyattil, R. K. Katiyar, S. P. Pavunny, G. Morell, and R. S. Katiyar, *Applied Physics Letters* **105**, 072908 (2014).
- 243 K. Ishikawa, T. Watanabe, and H. Funakubo, *Thin Solid Films* **392**, 128 (2001).
- 244 J. Hou, S. Cao, Y. Wu, F. Liang, Y. Sun, Z. Lin, and L. Sun, *Nano Energy* **32**, 359 (2017).
- 245 P. Wollmann, B. Schumm, and S. Kaskel, *Solid State Sciences* **14**, 1378 (2012).
- 246 H. Zheng, F. Straub, Q. Zhan, P. L. Yang, W. K. Hsieh, F. Zavaliche, Y. H. Chu, U. Dahmen, and R. Ramesh, *Advanced Materials* **18**, 2747 (2006).
- 247 J. Huang, J. L. MacManus-Driscoll, and H. Wang, *Journal of Materials Research* **32**, 4054 (2017).
- 248 J. L. MacManus-Driscoll, *Advanced Functional Materials* **20**, 2035 (2010).
- 249 A. P. Chen, F. Khatkhatay, W. Zhang, C. Jacob, L. Jiao, and H. Wang, *Journal of Applied Physics* **114**, 124101 (2013).
- 250 H. Yang, Y. Wang, H. Wang, and Q. Jia, *Applied Physics Letters* **96**, 012909 (2010).
- 251 H. Wang, F. Khatkhatay, J. Jian, J. Huang, M. Fan, and H. Wang, *Materials Research Bulletin* **110**, 120 (2019).
- 252 M. Hamada, H. Tabata, and T. Kawai, *Thin Solid Films* **306**, 6 (1997).

- 253 H. Fu, C. Pan, W. Yao, and Y. Zhu, The Journal of Physical Chemistry B **109**, 22432
(2005).
- 254 L. Zhang, W. Wang, L. Zhou, and H. Xu, Small **3**, 1618 (2007).
- 255 V. Utkin, Y. E. Roginskaya, V. Voronkova, V. Yanovskii, B. Sh. Galyamov, and Y. N.
Venevtsev, physica status solidi (a) **59**, 75 (1980).
- 256 R. M. Bozorth, Ferromagnetism, by Richard M. Bozorth, pp. 992. ISBN 0-7803-1032-2.
Wiley-VCH, August 1993., 992 (1993).
- 257 D. Mukherjee, M. Hordagoda, R. Hyde, N. Bingham, H. Srikanth, S. Witanachchi, and P.
Mukherjee, ACS applied materials & interfaces **5**, 7450 (2013).
- 258 W. Huang, J. Zhu, H. Zeng, X. Wei, Y. Zhang, and Y. Li, Applied physics letters **89**,
262506 (2006).
- 259 H.-J. Liu, L.-Y. Chen, Q. He, C.-W. Liang, Y.-Z. Chen, Y.-S. Chien, Y.-H. Hsieh, S.-J.
Lin, E. Arenholz, and C.-W. Luo, Acs Nano **6**, 6952 (2012).
- 260 N. Dix, R. Muralidharan, J.-M. Rebled, S. Estradé, F. Peiró, M. Varela, J. Fontcuberta,
and F. Sánchez, ACS nano **4**, 4955 (2010).
- 261 Y. H. Hsieh, J. M. Liou, B. C. Huang, C. W. Liang, Q. He, Q. Zhan, Y. P. Chiu, Y. C.
Chen, and Y. H. Chu, Advanced Materials **24**, 4564 (2012).
- 262 A. Chen, H. Zhou, Y. Zhu, L. Li, W. Zhang, J. Narayan, H. Wang, and Q. Jia, Journal of
Materials Research **31**, 3530 (2016).
- 263 W. Zhang, J. Jian, A. Chen, L. Jiao, F. Khatkhatay, L. Li, F. Chu, Q. Jia, J. L.
MacManus-Driscoll, and H. Wang, Applied Physics Letters **104**, 062402 (2014).
- 264 D. Bonnenberg, H. Landolt-Bornstein, J. B. Goodenough, D. Bonnenberg, and K. Enke,
Magnetic and other properties of oxides and related compounds (Springer-Verlag, 1970).
- 265 J. Dubowik, Physical Review B **54**, 1088 (1996).