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Synchrotron Investigations on $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ Heterostructures.

Jinling Zhou

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Synchrotron Investigations on $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ Heterostructures

Jinling Zhou

**Dissertation submitted
to the Eberly College of Arts and Sciences
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**Doctor of Philosophy in
Physics**

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Abstract

Synchrotron investigations on $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ heterostructures

Jinling Zhou

This dissertation is devoted to understanding the $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO)/ $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ (PZT) magnetoelectric interface through synchrotron x-ray absorption and other techniques.

The word magnetoelectric (ME) describes the coupling effects in certain materials that exhibit a change of the magnetic (electric) order with the change of the electric (magnetic) field. Materials that are ME could potentially advance current technology. Faster, more sensitive, and more energy efficient devices can be built with ME materials as compared to the present systems. Practical ME materials are essential for the realization of this advancement. Single phase ME materials are rare and the known few do not have strong coupling effects at ambient temperatures. Bilayer (or multilayer) systems, however, provide a feasible alternative because they sometimes exhibit ME coupling effects at the interface(s).

As an example of multilayer systems, ME coupling effects were previously reported by Vaz *et. al.* in between ferromagnetic LSMO and ferroelectric PZT, where the Mn valence changed with the varying external electric field. Through the use of a programmable shutter, small thickness gradients were created in both LSMO and PZT layers grown by pulsed laser deposition. A few flat samples were also grown for comparison. These samples were characterized by synchrotron methods including fluorescence mapping, micro x-ray diffraction (μXRD), x-ray absorption near edge spectroscopy (XANES), x-ray magnetic circular dichroism (XMCD), and photoemission electron microscopy (PEEM) as well as non-synchrotron based lab techniques such as atomic force microscopy (AFM) and scanning transmission electron microscopy (STEM). Wedge samples were locally smooth over experimental spot sizes and had uniform thickness gradients. Interfaces were sharp, exhibiting epitaxial growth. The magnetization increased with LSMO thickness. Mn valence in LSMO is associated with the LSMO magnetization states and was extensively studied in this dissertation. With the increase of LSMO thickness, Mn valence increased. A depth dependent valence model was developed to fit the LSMO thickness dependent valence results. The Mn charges were found to rearrange at the LSMO/PZT interface, and the effects of the ferroelectric polarization and polar interface on this interfacial valence were theoretically treated. In order to understand the effects of PZT on LSMO, Mn valence was measured at varied PZT thickness. Mn valence was found to be smaller when the PZT thickness was under 65 nm and decreased with decreasing PZT thickness in the PZT thickness region of 0 to 65 nm. Piezoresponse force microscopy (PFM) showed a transformation in PZT from polydomain to monodomain with decreasing thickness. Charges within the LSMO layer drawn to the interface to screen the PZT surface charge should theoretically vary with PZT domain structures, and would lead to a PZT thickness dependent Mn valence. This ferroelectric modulation of Mn valence charge was confirmed by measuring Mn valence in locally poled PZT. These discoveries agree with a charge

modulated interfacial ME coupling mechanism. This thickness dependence study additionally indicates that thin PZT is preferred to avoid in-plane ferroelectric domain orientations and to maximize the coupling effect with LSMO. In order to understand the relation of the magnetic domains to the ferroelectric domains on the microscopic scale appropriate for devices, linear and circular dichroic images were taken by PEEM at both the Mn and Ti absorption L-edges. At these interfaces, uncompensated spins were first seen in images taken with circularly polarized x-rays at the Ti absorption L-edge. These spins preferred to orient perpendicular to the LSMO ferromagnetic direction, consistent with magnetic biquadratic coupling.

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List of Symbols, Abbreviations & Nomenclature

ϵ_0 : dielectric constant

$\hat{\epsilon}$: electric susceptibility

$\hbar$: reduced Planck constant

μ : x-ray absorption coefficient

μ_0 : permeability

$\hat{\mu}$: magnetic susceptibility

AFM: atomic force microscopy

ALS: Advanced Light Source

CCD: charge coupled device

CO: charge ordering

EFM: electric force microscopy

EXAFS: extended x-ray absorption fine structures

FE: ferroelectric

FL: fluorescence

FM: ferromagnetic

JT: Jahn-Teller effect

LCP: left circularly polarized

LMO : LaMnO

LSMO: La_{0.7}Sr_{0.3}MnO₃

ME: magnetoelectric

MF: multiferroic

OO: orbital ordering

PEEM: photoemission electron microscopy

PFM: piezoresponse force microscopy

PZT: $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$

RCP: right circularly polarized

RHEED: reflection high energy electron diffraction

SPM: scanning probe microscopy

STEM: scanning transmission electron microscopy

STM: scanning tunneling microscopy

STO: SrTiO_3

TEY: total electron yield

μ XRD: micro x-ray diffraction

WVU: West Virginia University

XANES: x-ray absorption near edge structures

XAS: x-ray absorption spectroscopy

XMCD: x-ray magnetic circular dichroism

XPS: x-ray photoelectron spectroscopy

XRD: x-ray diffraction

Chapter One: Introduction

In this chapter, the background for the dissertation research is introduced. The history and classification of magnetoelectric (ME) materials, properties and characteristics of single material $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) and $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ (PZT), relevant theory and experimental results on bilayer ME systems are discussed.

1.1 Overview of the magnetoelectric coupling effect and materials

The magnetoelectric (ME) coupling effect describes the coupling between the magnetic and dielectric properties in matter, where internal magnetic (electric) order could be influenced by an external electric (magnetic) field. The relationship of ME materials with ferroelectrics, ferromagnets and other materials is given¹ in Figure 1 to assist the understanding of ME coupling effect. Among materials that respond to electric or magnetic fields, ferromagnetic (FM)/ferroelectric (FE) materials are special as they possess spontaneous magnetization/polarization without the presence of external fields. The materials that are both FE and FM are multiferroics, which by definition bear more than one primary ferroic order² including FE, FM, ferroelastic, etc. However, a material does not necessarily bear both FE and FM orders to be ME. Cr_2O_3 is, for example, an antiferromagnetic ME material without ferroelectric ordering.

The promising applications of ME coupling (such as electric control of magnetism) is unquestionably useful in a wide variety of devices from magnetic field sensors, hard drives, advanced logic devices, to tunable microwaves.^{3,4,5,6,7,8} By replacing traditional materials with ME coupled counterparts and equipped with alternative controlling systems, these apparatus could potentially process faster with higher sensitivity and lower cost.

Figure 1: Magnetoelectric materials among other materials. (Reference 9. Reproduced figure with permission by Nick Brookes at European Synchrotron Radiation Facility. Multiferroic materials combine magnetic and ferroelectrical properties. Retrieved from <http://www.esrf.eu/UsersAndScience/Publications/Highlights/2009/elecstrmag>.)

To target the ultimate goal of applicable ME materials, a brief review¹⁰ on the history of ME coupling effect and materials is helpful in developing a strategic research plan. The first observation of the ME coupling effect dated back to 1888, when Röntgen discovered that a moving dielectric was magnetized in an electric field,¹¹ followed by a theoretical prediction that ME coupling could exist in resting crystals in 1894 by Curie.¹² Seventeen years later, the reverse effect that a moving dielectric was polarized in a magnetic field was observed¹³ by Wilson. The term “magnetoelectric” was not introduced until 1926 by Debye.¹⁴ No experimental evidence, however, of a static ME coupling effect was reported in those times.

A breakthrough of ME research occurred in the sixties. Landau and Lifshitz¹⁵ pointed out in 1957 that ME coupling would only occur in time-asymmetric media. The antiferromagnet Cr_2O_3 was proposed by Dzyaloshinskii¹⁶ from the perspective of symmetry in 1959 and was soon

confirmed experimentally^{17,18,19} to be magnetoelectric a couple of years later. Other ME materials such as Ti_2O_3 ,²⁰ GaFeO_3 ,²¹ LiCoPO_4 ,²² TbPO_4 ,²³ etc. were identified subsequently. The focus of ME research transited from looking for the coupling media to the enhancement of the coupling effect.

The upper limit for the strength of magnetoelectric coupling effect can be derived by expanding the free energy in terms of external electric and magnetic fields. The free energy F in the external electric ($\mathbf{E}$) and magnetic ($\mathbf{H}$) fields is

$$F(\mathbf{E}, \mathbf{H}) = F_0 - P_i^s E_i - M_i^s H_i - \frac{1}{2} \epsilon_0 \epsilon_{ij} E_i E_j - \frac{1}{2} \mu_0 \mu_{ij} H_i H_j - \alpha_{ij} E_i H_j - \frac{1}{2} \beta_{ijk} E_i H_j H_k - \frac{1}{2} \gamma_{ijk} H_i E_j E_k - \dots, \quad (1.1)$$

where F_0 is the free energy of the system under zero electric and magnetic fields, $\mathbf{P}^s$ and $\mathbf{M}^s$ are the spontaneous polarization and magnetization, ϵ_0 and μ_0 are the dielectric constant and permeability, $\hat{\epsilon}$ and $\hat{\mu}$ are the electric and magnetic susceptibility tensors, other symbols such as α, β, γ are the higher order expansion coefficients. The polarization of the material can be obtained by taking the derivative of the free energy with respect to an applied electric field,

$$P_i(\mathbf{E}, \mathbf{H}) = -\frac{\partial F}{\partial E_i} = P_i^s + \epsilon_0 \epsilon_{ij} E_j + \alpha_{ij} H_j + \frac{1}{2} \beta_{ijk} H_j H_k + \dots. \quad (1.2)$$

Likewise, we get the magnetization of the material

$$M_i(\mathbf{E}, \mathbf{H}) = -\frac{\partial F}{\partial H_i} = M_i^s + \mu_0 \mu_{ij} H_j + \alpha_{ji} E_j + \frac{1}{2} \gamma_{ijk} E_j E_k + \dots. \quad (1.3)$$

The induced polarization due to external magnetic field are the terms depending on the external magnetic fields,

$$P_i^I(\mathbf{E}, \mathbf{H}) = \alpha_{ij}H_j + \frac{1}{2}\beta_{ijk}H_jH_k + \dots \quad (1.4)$$

The induced magnetization due to the external electric field likewise is

$$M_i^I(\mathbf{E}, \mathbf{H}) = \alpha_{ji}E_j + \frac{1}{2}\gamma_{ijk}E_jE_k + \dots \quad (1.5)$$

Free energy decreases when a material transforms to a more stable state. While phase transitions of ME materials under external fields are plausible,¹⁰ a stable ME material, which does not undergo a phase change when the external fields are present, should have a smaller free energy under the external fields. Therefore the sum of the second order terms should be smaller than zero for a stable ME material when the higher order terms are negligible. We obtain

$$-\frac{1}{2}\epsilon_0\epsilon_{ij}E_iE_j - \frac{1}{2}\mu_0\mu_{ij}H_iH_j - \alpha_{ij}E_iH_j + \dots \leq 0. \quad (1.6)$$

By comparison to

$$(Ax + By)^2 \geq 0, \quad (1.7)$$

The upper bound of the magnetoelectric susceptibility $\hat{\alpha}$ is obtained as²⁴

$$\alpha_{ij}^2 \leq \epsilon_0\mu_0\epsilon_{ii}\mu_{jj}. \quad (1.8)$$

This relationship indicates that stable ME materials with large coupling effects must have high permittivity and permeability, which are commonly found in FE and FM materials.

The coexistence of FM and FE in single phase (single phase means there is only one phase present) materials is rare.^{1,25,26} From the perspective of symmetry,²⁷ the electric polarization (for example, a dipole moment) is time invariant and spatially asymmetric while magnetization, represented by a current in an orbit, is time asymmetric and spatially invariant. The two symmetries

are incompatible with each other. If seen from the view of electronic structures, FE materials maintain the separation of charge and are typically non-conductive; FM materials whose magnetism is from transition metals have incompletely filled d or f orbital which typically makes them conductive. Most of the few known single phase FE-FM ME materials, such as CoCr_2O_4 , DyFeO_3 , have very low transition temperatures which renders them impractical.^{28,29} Some room temperature antiferromagnetic-FE ME materials such as BiFeO_3 are also studied by Ramesh³⁰ but the weak coupling effect in the systems is still a concern.

The weak coupling effect and low T_c in single phase ME materials were repeatedly shown in many experimental results and left little room for improvement.³¹ As a result, some researchers are seeking other possibilities. Two-phase composite systems were predicted to generate a large ME coupling effect at the interface³² as early as 1976 but this was hindered by the difficulty to grow smooth interfaces. With the advances in atomic layer fabrication, it is now possible to manufacture low dimensional two phase composite heterostructures^{33,34} exceeding the impasse of single phase ME materials.³⁵

FE and FM materials are good candidates for building two phase systems. The FE and FM properties in each phase could be optimized individually and the interface between the two could be magnetoelectric. FE materials are piezoelectric, where the change in strain also changes the polarization states. By putting a magnetostrictive or piezomagnetic material on top of a FE material, the strain could couple the FM order in one material to the FE order in the other. Surface charges from FE material meanwhile also impose an electric field on the FM material. The Fermi level changes as a result of the charge accumulation at the FE/FM interface, which in turn changes the density of states at the Fermi level. The magnetization, which is proportional to the density of states at the Fermi level, could be modified accordingly. The $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$

(LSMO)/PbZr_{0.2}Ti_{0.8}O₃ (PZT) heterostructures included in this dissertation are one of such systems where PZT is a piezoelectric FE material and LSMO is a magnetostrictive FM material. While the strain effect will be investigated further in future research, the charge modulation in LSMO from neighboring PZT has been observed in the x-ray absorption spectroscopy (XAS) results. XAS is a technique sensitive to the valence states of each specific element and is referred to as “the finger print” of valences. The change in valence states reflect the change in the density of states of electrons. The discrepancy between the sum of the density of states of spin up and spin down electrons around the Fermi level in Mn is manifested as the LSMO magnetization. Direct observation of the interactions between the LSMO magnetization and PZT polarization confirms the magnetoelectric coupling effect. However, by investigating the change of Mn valence with the change of PZT physical properties such as thickness, the physics behind the coupling mechanism might be revealed and understood. Mn valences detected by XAS were found to increase with increasing PZT thickness, where the PZT domain structure was transformed from single domain to polydomain. The PZT surface charge, which varies with the domain structure, may cause the increase of Mn valence. Mn valence was tested at two polarization states of PZT. Mn valences were consistently larger when the PZT ferroelectric polarization was pointing away from LSMO than when it was pointing towards LSMO.

1.2 Properties of employed materials

Single phase LSMO and PZT are room temperature FM and FE materials respectively with similar lattice parameters ideal for epitaxial growth. Both of them have been extensively studied and the past research data on the two single materials aid the understanding of the constructed two phase system.

Figure 2: Perovskite ABO_3 . (Reference 36. Figure from a public domain.)

$(La,Sr)MnO_3$ and $Pb(Zr,Ti)O_3$ come from the family called perovskites with a general chemical formula ABO_3 . The unit cell of an ideal perovskite structure³⁶ has a cubic symmetry as shown in Figure 2 where A is in the body center, B is at the corner, and oxygens on side centers. They are generally viewed as eight corner-shared octahedral BO_6 cages with a 12-coordinated A cations. Minerals with perovskite structure have exhibited rich and interesting properties from colossal magnetoresistance, ferroelectricity to superconductivity and remain one of robust material groups in research. In the following paragraphs, the individual properties of LSMO and PZT are reviewed.

1.2.1 Single phase LSMO

LSMO does not have the simple cubic perovskite structure but rather a distorted one due to the mismatch of A-site and B-site radii. A tolerance factor

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)} \quad (1.9)$$

has been introduced by Goldschmidt to describe this kind of mismatch,³⁷ where R_A , R_B and R_O are the radii for the A cation, B cation and oxygen anion. Materials will have the simple cubic

perovskite structure when $t=1$. For LSMO, $t=0.936$,³⁸ which corresponds to a rhombohedral structure. If the equivalent t decreases even more, the bond angle of Mn-O-Mn will deviate from 180° resulting in reduced carrier mobility.

The prominent physical characters of LSMO are discussed below in comparison to other compounds in the family group with a chemical formula $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (where $x=0$ to 1).

Jahn-Teller Effect

While cation size is the main cause of lattice distortion, Jahn-Teller (JT) effect³⁹ may also distort the lattice. JT effect is an effect in which the lattice distortion can lower the total energy. Perovskites under this effect often result in an orthorhombic structure.⁴⁰ In $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, the oxygen anions surrounding Mn cations create a crystal field which splits the Mn d orbitals into two degenerate orbitals called e_g and t_{2g} orbitals. When these degenerate orbitals are occupied by the same number of the electrons, the lattice would not deform; but if they are occupied by different number of electrons, the lattice may deform to lift the energy degeneracy for a lower total energy. When the lattice deforms, these e_g and t_{2g} orbitals are compressed/elongated. The energies of the compressed orbitals are raised while the energies of the elongated orbitals are lowered. For Mn ($1s^2 2s^2 p^6 3s^2 p^6 d^5 4s^2$) element, Mn^{3+} cations have three electrons in t_{2g} orbitals and one electron in e_g orbitals (shown in Figure 3), favoring the lifting of degeneracy and thus a strong JT effect. Mn^{4+} loses one more electron than Mn^{3+} and has unoccupied e_g orbitals and half-filled t_{2g} orbitals. Lattice distortion would not change the total energy of Mn^{4+} cations. Mn^{4+} is therefore JT inactive.

In LaMnO_3 (LMO), each of the three oxygens prefer two electrons; the group three element La gives away three electrons to oxygen; three more electrons would come from Mn. Because Mn^{3+} cations are present in LMO, the JT distortion is favored. Because zero Mn^{4+} is present in the

lattice, the JT distortion is prevalent throughout the whole crystal creating a stabilized distorted state. The distortion localizes Mn e_g electrons and prevents them from hopping between neighboring Mn sites leading to an insulating state. When LMO is doped with Sr, the group two element Sr only gives away 2 electrons. Some of the Mn cations will lose one more electron. As the Mn^{4+} cations dilute the concentration of Mn^{3+} in the materials, the JT effect would be localized. Electrons can hop more between neighboring Mn sites due to the differing Mn valences. The mobility of electrons increases.

Figure 3: The splitting of the Mn^{3+} $3d^4$ orbitals and the lattice distortions due to JT effect.

Electronic structures of LSMO

Figure 4: The electronic structures of Mn 3d electrons subject to different factors. E stands for energy. The dotted lines are Fermi levels. (Reference 41. Reproduced figure with permission from J. Kautz, Master thesis, “The structural, magnetic and electrical behavior of (110) oriented LSMO” (2009).)

The forming of Mn electronic structures in LSMO due to multiple factors is summarized⁴¹ in Figure 4. Dominant factors are on the left. Start from the left, a Mn atom in free space has degenerate 3d orbitals. The oxygen octahedron around the Mn in the LSMO structure creates a crystal field which splits the Mn 3d bands into degenerate e_g and t_{2g} bands. These bands are then divided into spin-up and spin-down groups because the electrons tend to fill up all 3d empty orbitals with the same spin before pairing up (Hund’s rule). Jahn Teller distortions in LMO break further the degeneracy of e_g and t_{2g} bands and inhibit the mobility of e_g electrons, creating a Mott insulator. Finally, the doping of Sr into LMO introduces holes to the Mn sites⁴² which lowers the Fermi level and localizes the JT distortion.

Super exchange and double exchange

Magnetic behavior can be explained through exchange coupling between magnetic atoms. Direct exchange happens when neighboring magnetic atoms interact directly through their valence electrons, which is described by the Heisenberg exchange Hamiltonian

$$H_{\text{ex}} = - \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j , \quad (1.10)$$

where J_{ij} is the exchange constant between spin $\mathbf{S}_i$ and $\mathbf{S}_j$. If $J_{ij} > 0$, parallel spins are favored, forming a FM state; otherwise, antiparallel configurations are more energetically favorable, creating anti-FM states.

Figure 5: Illustration of (a) super exchange and (b) double exchange. (Reference 43. Reprinted from Mater. Sci. Eng. R-Rep., 68, L. W. Martin, Y.-H. Chu, and R. Ramesh, Advances in the growth and characterization of magnetic, ferroelectric, and multiferroic oxide thin films, 89, Copyright (2010), with permission from Elsevier)

However, because of the existence of oxygen in between neighboring Mn atoms, the spins in LSMO crystals are coupled indirectly. In Figure 5, two indirect exchange mechanisms^{43,44}—super exchange and double exchange—are illustrated. The $3d^4$ core electrons of Mn are aligned parallel to the valence electrons in the Mn^{3+} cation due to Hund's rule. Super exchange happens when the valence electron of the adjacent Mn^{3+} cations are sharing the same orbital through the oxygen anions in between, which forces the spins of the sharing electrons on each side to align antiparallel to fulfill the Pauli exclusion principle. Thus the nearby Mn cations have opposite spin

moments which gives LMO an antiferromagnetic (AF) state. When La is replaced by Sr, LMO is hole doped. Mn has mixed 3+ and 4+ valence states, in which the hopping of e_g electrons without flipping the spin directions among Mn cations leads to a lower energy state. In this case, spins of all Mn cations align parallel. Carriers in LSMO are in principle 100% spin polarized which attracts enormous research interest.

Now that the general microscopic picture has been clarified, it is worthwhile to summarize them into a phase diagram⁴⁵ with regard to Sr doping levels in LMO, which is shown in Figure 6. The final property of each $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ compound is a balanced result of correlations among charge, spin, orbitals and lattices. At a doping level of $x = 0.3$, LSMO is a FM with a very high transition temperature, which is precisely the reason that LSMO is used to build the two-phase ME materials in the current research. Valence, as a macroscopic representation for microscopic charge densities, is explored extensively in this dissertation to understand the coupling mechanism of the system.

Figure 6: Phase diagram of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ at varied doping levels. (Reference 45. Reprinted figure with permission from J. Hemberger, A. Krimmel, T. Kurz, H.-A. Krug von Nidda, V. Ivanov, A. Mukhin, A. Balbashov, and A. Loidl, Phys. Rev. B, 66, 094410 (2002). Copyright (2002) by the American Physical Society.)

1.2.2 Single phase PZT

Despite the fact that most FE materials are not oxides⁴³ and lead-free FE materials have been proposed for health concerns, $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ are among the most extensively studied FE materials due to robust properties, their large polarization at high Ti content⁷ and great potential for practical applications.

Figure 7: Structure phase diagram of $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$. (Reference 47. Reprinted figure with permission from S. Yang, H. Bao, C. Zhou, Y. Wang, X. Ren, Y. Matsushita, Y. Katsuya, M. Tanaka, K. Kobayashi, X. Song, and J. Gao, *Phys. Rev. Lett.*, 104, 197201 (2010). Copyright (2010) by the American Physical Society.)

Crystal Structure of PZT

Similar to LSMO, PZT is a solid solution with two end members:⁴⁶ antiferroelectric PbZrO_3 and ferroelectric PbTiO_3 . The structural phase diagram⁴⁷ of $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ is shown in Figure 7. At high temperatures, $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ has a cubic symmetry, which is common for most perovskites at high temperature. At low temperatures, $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ with higher Zr content is rhombohedral while higher Ti content leads to tetragonal structures. Approximately halfway (~50% doping of Ti), there is a narrow composition region called the morphotropic phase boundary (MPB), where many different ferroelectric phases exist.

Polarization in PZT

The polarization of PZT originates from the dislocation of Ti/Zr cations with regard to the center of the oxygen octahedron. The breaking of centrosymmetry creates a dipole moment pointing from the electron clouds to the cations. The displacement of the cations is along the elongated side of the tetragonal PZT as illustrated⁴⁸ in Figure 8. Note that the polarization direction

is pointing up in Figure 8 but there is an equal probability for it to point downwards.

Figure 8: Origin of PZT polarization. Displacement of cations from the geometric center causes polarization in the material. (Reference 48. Figure from a public domain.)

Domain structure of PZT

PZT is piezoelectric. When applying strain to the lattice, an electric field will be generated by PZT because of the displacement of Ti and Zr cations; and alternatively, when an electric field is applied to a piece of PZT, the forces between charges will strain the material and change its shape. Possible domain structures have been proposed by Alpay *et al.*⁴⁹ in relation to the tetragonality and effective misfit strain, which are shown in Figure 9 as the domain stability map. This map was constructed based on their experimental results of a 400 nm PZT film grown on a (001) SrTiO₃ (STO) substrates. The effective misfit strain in the figure is calculated by

$$\overline{\varepsilon}_M = \frac{a - \overline{a}_s}{\overline{a}_s}. \quad (1.11)$$

The tetragonality ε_T is defined as

$$\varepsilon_T = \frac{c - a}{a}, \quad (1.12)$$

where a and c are the unconstrained lattice parameters of the film, $\bar{a}_s$ is the modified effective lattice parameters of the substrate. This modified effective lattice parameter takes into account the misfit dislocation relaxation at the deposition temperature and the critical thickness below which dislocations do not form. Detailed discussions and formulas can be found in their publication⁴⁹ and the citations within. They also studied the domain structures of PZT with top and bottom $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (LSCO) electrodes and similar PZT domain structures were observed. Therefore the domain stability map in Figure 9 may also apply to PZT samples with electrodes.

Figure 9: Domain stability map for PZT deposited at 650° on (001) STO (Reference 49. Reprinted from J. Appl. Phys. 85, 3271 (1998), with the permission of AIP Publishing). Filled circles are the theoretical values at different temperatures for a 400 nm PZT. c -domain fraction are constant on the thin lines in the $\dots c/a/c/a \dots$ region.

Alpay *et al.*⁴⁹ mentioned that dislocations do not typically form below a critical thickness, suggesting that the physical properties of PZT might be thickness dependent. The thickness dependence of PZT domain structures have been reported by Kwon *et al.*,⁵⁰ stating that a domains

were absent below 49.5 nm and appeared only in thicker films. Similar thickness dependence also occurred in PbTiO_3 films.⁵¹

1.2.3 Substrate STO

STO substrate was used for most of our samples, while Si substrate was used on some of the samples for electric testing. The STO substrate has a perovskite structure like PZT and LSMO, but with a cubic symmetry and a lattice parameter⁷ of $a=3.905\text{\AA}$. STO is available in very high crystalline quality and is popularly used as a substrate for epitaxial growth. A reflection high energy electron diffraction (RHEED) image of the STO substrate is included in the Appendix. When LSMO is grown on STO, the in-plane lattice mismatch is negligible.⁴⁴ The lattice parameter of each material⁵² in their bulk form has been listed in Table 1.

Table 1: Lattice parameters of LSMO, PZT and STO. (*This is the psuedocubic lattice parameter of LSMO, for detailed lattice information, please refer to reference 52)

Compound	Bulk lattice parameters	
	a ($\text{\AA}$)	c ($\text{\AA}$)
LSMO	$\sim 3.885^*$	$\sim 3.885^*$
PZT	3.935	4.135
STO	3.905	3.905

1.3 Previous investigations on similar heterostructures

Single materials LSMO and PZT are introduced in the previous section. They are stable FM and FE materials, respectively. Their sister materials with different doping levels in the $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ and $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ families might be in anti-FM or anti-FE states in order to maintain a balance among parameters such as spin, charge, orbit and lattice. Both charge and strain could

be responsible for the interfacial ME coupling.⁵³ A brief review of existing research on similar heterostructure is helpful to put the research direction in perspective.

Experimental results

An experimental interfacial magnetoelectric coupling coefficient of 6.2×10^{-3} Oe cm V⁻¹ at 100 K in a La_{0.8}Sr_{0.2}MnO₃ and PZT bilayer was reported.⁵⁴ Interfacial Mn valence was observed to change upon the application of an external electric field. In Figure 10 (a), the Mn *K*-edge x-ray absorption spectra (XAS) under two states of PZT polarization are shown, where the shift of Mn *K*-edge signifies a change in the Mn valence (Chapter 4, section 1). Figure 10 (b) shows that the XAS intensity at a single energy $E = 6549.7$ eV varied like a hysteresis loop with regards to the applied gate voltage on PZT. Because the applied gate voltage controlled the PZT polarization, this graph proved that the Mn valence changes with the PZT polarization. Mn valence change itself indicates the changes of the charge carrier densities in LSMO. Mn valence, however, also plays an important role in the magnetic properties of (La,Sr)MnO₃ systems. As it has been discussed earlier, Mn³⁺ favors super-exchange coupling leading to an antiferromagnetic phase in LaMnO₃, while mixed Mn³⁺ and Mn⁴⁺ in LSMO promote the double-exchange mechanism resulting in a FM phase. The behavior of the Mn valence influences and indicates the competition between the super-exchange and double-exchange coupling mechanisms. Because the change in Mn valence is associated with the change in the LSMO physical properties, the change of Mn valence due to PZT change, such as PZT thickness, may help determine the interfacial coupling mechanism.

Theoretical results

Burton and Tsymbal⁵⁵ carried out first principal simulations on the similar system of La_{1-x}A_xMnO₃/BaTiO₃. They found that the polarization direction of ferroelectric BaTiO₃ could

change the charge carrier density across the interface and induce a FM-antiferromagnetic phase change of $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ at $x = 0.5$. This result indicated theoretically that the magnetization of $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ is sensitive to the charge density and the charge effect plays an important role in the interfacial ME coupling in $\text{La}_{1-x}\text{A}_x\text{MnO}_3/\text{FE}$ composite systems.

Figure 10: (a) Mn K -edge XAS under two PZT polarization states at room temperature. (b) Variation of XAS at a fixed x-ray energy, $E = 6549.7$ eV, with the change of the applied gate voltage. The error bars reflect counting statistics (Reference 54. Figure adapted with permission from C. A. F. Vaz, J. Hoffman, Y. Segal, J. W. Reiner, R. D. Grober, Z. Zhang, C. H. Ahn, and F. J. Walker, *Phys. Rev. Lett.*, 104, 127202 (2010). Copyright (2010) by American Physical Society).

These former works indicated that the interfacial ME coupling could be studied through Mn valence. The magnetoelectric interface, however, is buried at some depth into the sample. Separating the interface signals from the rest of the heterostructure is important for a better understanding of the interfacial coupling mechanism. In this dissertation, a depth dependent Mn valence was established through modeling the valence data obtained from two techniques with

drastically different probing depth. Additionally, the induced spin structure at the interface with PZT was imaged through photoemission electron microscopy (PEEM) imaging method at the Ti *L*-edge. The results support the hypothesis that PZT and LSMO are coupled through the charge screening effect, where the interfacial Mn valence changes to screen the PZT polarization and in turn possibly creates a reversible magnetization change at the interface. Uncompensated spin structures of PZT were found oriented perpendicular to the LSMO ferromagnetic direction from statistical analysis of PEEM images, indicating a biquadratic coupling.

In summary, this chapter discussed the background of the dissertation research – ME coupling. Due to the fact that single ME materials are rare and not practical, LSMO/PZT heterostructures were grown to create ME coupled interfaces. Double exchange and super exchange coupling mechanisms in LSMO are directly correlated to the Mn valence. Previous research on similar heterostructures also suggest that FE materials can modulate the charge density at the interface and Mn valence was sensitive to FE polarization. These prior results indicate that ME coupling in LSMO/PZT systems could be studied through Mn valence. Because ME coupling most likely happens close to the LSMO/PZT interface, research designed and devoted especially for the interface region is worthwhile for in-depth understanding of the coupling mechanism and may also bear broad interest for scientists studying other types of interfaces.

Chapter Two: Synchrotron Techniques

This chapter starts with an introduction to the synchrotron facilities followed by the synchrotron techniques including x-ray absorption spectroscopy (XAS), x-ray magnetic circular dichroism (XMCD), photoemission electron microscopy (PEEM), and micro x-ray diffraction (μ XRD).

2.1 Synchrotron facilities

Although non-synchrotron based lab techniques have also been used to test our samples, results from synchrotron facilities are the center of discussions in this dissertation. In order to understand their importance for the current work, I will start with the introduction of the synchrotron facility. A synchrotron facility is a cyclic particle accelerator where the magnetic field and the electric field are synchronized to a particle beam. To generate radiation, the particle beam is accelerated in a linear accelerator and enters a storage ring with a speed very close to that of light. The storage ring consists of both curved and straight sections. The particle beam circles through the curved sections under strong magnetic field and radiates in the tangential direction. The wavelength of radiation is tuned by an array of magnets called wigglers and undulators. X-rays are a common product from the radiation. In comparison to lab x-rays, the light from a synchrotron facility is much brighter. The brightness of these photons shortens the experimental time because each spectra produced by synchrotron light is many times higher in intensity than those produced in lab. For the same reason, small samples and small effects could be tested and detected with high resolutions at synchrotron facilities. Besides the high brightness, the energy and polarization of x-rays in synchrotron facilities could be tuned, which provides a unique tool to study the magnetic properties of materials.

Figure 11: Photo of ALS located on the Berkeley hills and overseeing the San Francisco Bay. (Reference 57. Photo courtesy of Lawrence Berkeley National Laboratory. Credit: Roy Kaltschmidt.)

The data contained in this dissertation were collected at one of the brightest sources for ultraviolet and x-ray light in the world—a third generation synchrotron⁵⁶ facility, the Advanced Light Source (ALS) (Figure 11)⁵⁷ of Lawrence Berkeley National Lab in California. Funded by U.S. Department of Energy, ALS cost \$99.5 million to construct, has an annual budget of \$60 million and has been in operation since 1993. An overview⁵⁸ about the facility and the accelerator information are adopted from the official website and shown in Figure 12. The electron current inside the ring is kept at 500 mA in a separation of 2 ns in multibunch mode; 2×17.5 mA and 328 ns in two bunch mode (used for time resolved studies, not discussed here). Being one billion times brighter than the sun, x-rays generated at ALS offers unique research opportunities to nationwide and international users from physics, materials science, geosciences, environmental sciences, energy sciences, chemistry and biology. A broad range of research topics from crystal and electronic structures, chemical reaction dynamics to 3-dimensional biological imaging are done at the facility. Synchrotron techniques used for this dissertation research are reviewed in the following sections. They include x-ray absorption spectroscopy, photoemission electron microscopy, x-ray magnetic circular dichroism, and micro x-ray diffraction. Fluorescence mapping

is introduced in Chapter 3.

Figure 12: a) facility facts and b) accelerator information of ALS. (Reference 58. Courtesy of the Advanced Light Source, Lawrence Berkeley National Laboratory.)

2.2 X-ray interactions with matter

When light interacts with a material, it can be scattered or absorbed. X-rays are electromagnetic waves with a wavelength of 0.1 to 100 Å. Because the lattice spacing of solid state materials is comparable to the wavelength of x-rays, the scattered x-rays from a material produce a diffraction pattern of constructive and destructive light. The energy range of x-rays is from 120

eV to 120 keV. At certain wavelengths/energies, x-rays are absorbed by the core electrons of the elements within the materials and produce an absorption spectrum. These interactions of x-rays with materials are utilized and formulated in varied settings in scientific research to target a range of material properties. Several of the synchrotron associated techniques are discussed specifically in the following sections.

2.3 X-ray absorption spectroscopy (XAS)

X-ray absorption process

When x-rays can provide enough energy to excite core electrons to unoccupied states, they are absorbed. After the excited electrons move above the Fermi level, core holes are left in the original core shells, as illustrated⁵⁹ in Figure 13 (a). The ejected electrons from this process are called photoelectrons. The produced core holes, however, are unstable. They recombine with electrons from higher states and release energy by radiating fluorescent x-rays or promoting other electrons to above the Fermi level. Figure 13 (b) shows the second case where the promoted electrons are called Auger electrons along with the creation of additional holes. The recombination of these holes and the inelastic electron-electron scattering of Auger electrons lead to a cascade of secondary electrons in Figure 13 (c). Because x-ray absorption happens only at certain incident energies, which is tied to the core level of a specific element, x-ray absorption spectra are named after the element and the core level from which they originate. The nomenclatures of absorption peaks corresponding to each core level are shown in Table 2. The peaks are normally referred to as edges in x-ray absorption spectroscopy.

Figure 13: X-ray absorption process. (Reference 59. Reproduced figure with permission from H. Ohldag, Ph.D dissertation, “Exchange coupling of Co and Fe on antiferromagnetic NiO investigated by dichroism x-ray absorption spectromicroscopy” (2003).)

Table 2: Nomenclature of x-ray absorption peaks.

ABSORPTION EDGE	CORE LEVEL
K	1s
L _I	2s
L _{II}	2p _{1/2}
L _{III}	2p _{3/2}
M _I	3s
M _{II}	3p _{1/2}
M _{III}	3p _{3/2}
M _{IV}	2d _{3/2}
M _V	2d _{5/2}

Measurement modes

Figure 14: TEY and FL modes. The color gradient of the sample illustrates the depth sensitivity of each mode.

The x-ray absorption process occurs when the energy of the incident x-rays matches the energy difference between core holes and the Fermi energy. The end products of this process are

ejected electrons, fluorescence x-rays, and remnant x-rays. The absorption information could be therefore obtained accordingly through these three measurement modes: total electron yield (TEY), fluorescence (FL) and transmission. Figure 14 is a cartoon illustrating what TEY and FL mode are measuring. Figure 15 shows an example setup for the three modes. In the exact setup for the TEY measurement, the sample is grounded and put in a biased electric cage to pull the electrons out. The lost electrons from the sample surface are replenished by the ground and the photocurrent is measured. Silver paint is used to make an electric contact between the sample surface and substrate. Because not all excited electrons can escape from the sample, electrons buried deep inside the sample are not detected. The detection depth of a measurement depends on the attenuation of the incident x-rays and the attenuation of the exiting electrons/x-rays in a material. Low energy (generally smaller than 12 keV) x-rays are classified as “soft” x-rays and have shorter penetration depths than high energy “hard” x-rays. Electrons travel a significantly shorter distance than any x-rays inside solid state materials. As a result, the sampling depth in TEY mode is predominantly determined by the electron mean free path, which is about a few nanometers, making TEY a surface sensitive technique⁶⁰; the sampling depth in fluorescence mode is frequently as deep as several microns. The drastic difference of the measurement depth in these two modes are combined in the current research to map the depth dependence of Mn valence. Detailed discussions on the attenuation depth are included in Chapter 4.

Figure 15: Cartoon for the setup of the three XAS measurement modes: total electron yield (I_e), fluorescence (I_f) and transmission (I_t). UHV stands for ultrahigh vacuum.

The information obtained from each mode is related but not identical. The generation of fluorescence x-rays and yield of electrons is directly proportional to the absorption probabilities of the photons. The x-ray absorption spectrum in these two modes is therefore proportional to the absorption coefficient with regard to incident photon energy. The fluorescence light generated deep inside the sample, however, has far greater chances to be detected than the ejected electrons. For that reason, deeply buried layers contributing to the FL result may not contribute to the TEY result.

The absorption coefficient measures how much light is absorbed. The transmission mode on the contrary measures the attenuation of x-rays, which is described by Beer's law

$$I = I_0 e^{-\mu t}, \quad (2.1)$$

where I is the transmitted x-ray intensity, I_0 is the incident intensity, μ is the attenuation coefficient, t is the sample thickness. The raw spectrum obtained in transmission mode is normally the ratio of transmitted intensities to incident intensities vs. photon energy. The result is converted through equation (2.1) for the attenuation coefficient. Transmission mode requires ultrathin samples and a non-opaque substrate in order for the x-rays to pass through. In the assumption of ultrathin samples, the attenuation coefficient is a good approximation for the absorption coefficient⁶¹ and they are often used interchangeably by researchers. For simplicity, the same symbol μ is used for the absorption coefficient in the following paragraphs.

X-ray absorption spectra

X-ray attenuation coefficient μ depends on the sample density ρ , the atomic number Z , the atomic mass A , the x-ray energy E and is roughly estimated by the relationship

$$\mu \approx \frac{\rho Z^4}{AE^3}. \quad (2.2)$$

Mass attenuation coefficients μ/ρ for different elements⁶² are shown in Figure 16. Elements with small atomic numbers such as Si, Al, and O are out of the range of the graph. The K edges in the graph are from elements with atomic numbers 20 to 58. They all have distinct edge peaks. Because of this element specific character of x-ray absorption spectra, x-rays are useful for multiple imaging applications including medical diagnosis.

Figure 16: Mass attenuation coefficients (μ/ρ) for various elements. (Reference 62. Republished with permission of Geosphere, from “Quantitative 3D petrography using X-ray tomography 3: Documenting accessory phases with differential absorption tomography”, G. Gualda, A. Pamukcu, L. Claiborne, and M. Rivers, 6, 6, 782 (2010); permission conveyed through Copyright Clearance Center, Inc.)

X-ray absorption spectra, i.e. the x-ray absorption/attenuation coefficient dependence on energy, have fine structures and normally are divided into two regions: the near-edge region and the extended edge region. The edge refers to the abrupt change of absorption when the incident x-ray energy is sufficient for a core electron to have a transition to an energy level above the Fermi level. Correspondingly, in Figure 16, the edge is shown as the abrupt jump in each curve. The near-edge region is approximately 50 eV around the edge, and the extended region ranges from around 50 eV up to about several hundreds of eV above the edge. The spectra in these two regimes are frequently termed as x-ray absorption near-edge structures (XANES) and extended x-ray absorption fine structures (EXAFS), though other alternative names exist. A sample spectrum is shown in Figure 17 with illustration of XANES and EXAFS regions.⁶³ “White line” is a historical

name for XAS peaks because XAS peaks showed up as a white line on the detector when photographic plates were used.

Figure 17: Sample x-ray absorption raw spectra. (Reference 63. Reprinted by Permission, ASA, CSSA, SSSA.)

The sources of EXAFS fine structures are from the scattering and absorption of ejected electrons among neighboring atoms. Destructive and constructive interference are formed when the incoming x-rays have an energy above the element's absorption edge. With proper modeling, it is possible to determine nearest neighbor types and distances.

EXAFS spectra are normally decomposed to the background contribution and the atomic contribution of individual atoms. A breakdown⁶⁴ of an EXAFS spectrum is shown in Figure 18. The experimental absorption coefficients μ_{exp} is decomposed into background and atomic contributions which causes the fine structure. Fine structure χ is theoretically determined by the sum of the scattering process and it is described as

$$\chi(k) = \sum_j \frac{N_j S_0^2 f_j(k) e^{-2k^2 \sigma_j^2} e^{-2R_j/\lambda(k)}}{k R_j^2} \sin[2kR_j + \delta_j(k)], \quad (2.3)$$

Figure 18: EXAFS breakdown. (Reference 64. Reproduced figure with permission from Alexei Kuzmin. Retrieved from http://www.dragon.lv/exafs/about_exafs.htm.)

where j is the j th shell of identical neighboring atoms at approximately the average distance R from the center atom that absorbs an x-ray, N is the number of these identical atoms, $f(k)$ and $\delta(k)$ represent the scattering amplitude and phase shift, S_0^2 is the amplitude reduction term due to the relaxation of electrons to the core holes, σ^2 is the disorder in the neighbor distance R , λ is the mean free path of the photoelectrons. The variable, k , is the wave number of the photoelectron defined by

$$k = \sqrt{\frac{2m(E-E_0)}{\hbar^2}}, \quad (2.4)$$

where m is the electron mass, $\hbar$ is the reduced Planck constant, E is the incident x-ray energy, E_0 is the energy difference between the initial state and the final state of the photoelectron. By fitting the experimental results to equation (2.3), local structural information such as bond distances,

coordination numbers and local disorder are obtained. Equation (2.3) successfully interprets EXAFS. However, as the incident x-ray energy approaches the absorption edge, less excess energy is transferred to the photoelectron. Because $\chi(k)$ breaks down at small k , the equation is inapplicable to XANES. The decomposition of XANES, however, is the same as that of EXAFS (Figure 18).

The chemical environment modifies the unoccupied states of the absorbing atoms and shapes their electronic structures and XANES. The quantum theory descriptions of x-ray absorption are given in the next section for a better understanding of the absorption process. XMCD and PEEM are built on the near edge structures and are discussed after the quantum theory descriptions.

2.4 Quantum theory descriptions of x-ray absorption

X-ray absorption includes a one electron absorption process and multiple resonant scattering processes. In a one electron absorption process, an electron absorbs the x-ray energy and is excited to a higher empty state. In the resonant scattering processes, electrons decay to the holes at lower energy levels by exciting other electrons. A transition from a state $|i\rangle$ to a state $|f\rangle$ can occur by a direct transition from $|i\rangle$ to $|f\rangle$, or via a range of intermediate states $|n\rangle$. The transition probability per unit time T_{if} was derived by Kramers and Heisenberg⁶⁵ and by Dirac.⁶⁶ Its formula to second order is

$$T_{if} = \frac{2\pi}{\hbar} \left| \langle f | H_{int} | i \rangle + \sum_n \frac{\langle f | H_{int} | n \rangle \langle n | H_{int} | i \rangle}{\varepsilon_i - \varepsilon_n} \right|^2 \delta(\varepsilon_i - \varepsilon_f) \rho(\varepsilon_f), \quad (2.5)$$

where ε_i , ε_f , and ε_n are the energies at each state, $\rho(\varepsilon_f)$ is the density of the final state and the interaction Hamiltonian H_{int} is a perturbation term describing the reaction of electrons from an

electromagnetic wave (x-rays). H_{int} consists of the product of the electron momentum operator $\mathbf{p}$ and the electric vector potential $\mathbf{A}$,⁶⁷

$$H_{int} = \frac{e}{m_e} \mathbf{p} \cdot \mathbf{A}. \quad (2.6)$$

The vector potential in the Coulomb gauge can be expressed as

$$\mathbf{A} = A_0 \boldsymbol{\varepsilon} e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)}, \quad (2.7)$$

where A_0 is the amplitude, $\boldsymbol{\varepsilon}$ is the unit photon polarization vector, $\mathbf{k}$ is the photon wave vector, $\mathbf{r}$ is the position vector, ω is the frequency and t is the time. In the dipole approximation, the size of atomic shells is assumed to be much smaller than the x-ray wavelength. For a typical 2 p to 3 d transition case, the 2 p core shell has a radius of about 0.01 nm, which is smaller than the incident x-ray wavelength ($\lambda = hc/E$, $\lambda \sim 1.2$ nm for $E = 1000$ eV).⁶¹ The electromagnetic field which drives the electronic transitions is therefore approximately constant over the atomic shell. The interaction Hamiltonian is

$$H_{int} = \frac{A_0 e}{m_e} \mathbf{p} \cdot \boldsymbol{\varepsilon} e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} = \frac{A_0 e}{m_e} \mathbf{p} \cdot \boldsymbol{\varepsilon} (1 + i\mathbf{k} \cdot \mathbf{r} + \dots) \approx \frac{A_0 e}{m_e} \mathbf{p} \cdot \boldsymbol{\varepsilon}, \quad (2.8)$$

and transition matrix in the dipole approximation is

$$\langle f | \mathbf{p} \cdot \boldsymbol{\varepsilon} | i \rangle = i m_e \omega \langle f | \mathbf{r} \cdot \boldsymbol{\varepsilon} | i \rangle. \quad (2.9)$$

The major transitions responsible for each absorption edge are identified through the calculation of the transition probability matrix. The total cross section is obtained by dividing the transition probability per unit time by the incident photon flux. The x-ray absorption intensity is directly proportional to the energy integral of the total cross section. By using the atomic spin orbitals $|R_{n,l}(r); l, m_l, s, m_s\rangle$ for the electron states,⁶⁷ a transition matrix among different atomic states is obtained and the nonvanishing terms can be summarized in the notation of $|n, l, m_l, s, m_s\rangle$

as

$$\begin{aligned}\Delta l &= l' - l = \pm 1, \\ \Delta m_l &= m_l' - m_l = q = 0, \pm 1, \\ \Delta s &= s' - s = 0, \\ \Delta m_s &= m_s' - m_s = 0,\end{aligned}$$

where $q\hbar$ is the x-ray angular momentum along its propagation direction.

Table 3: Selection rules in the notation of JJ and LS coupling. (Reference 68. Courtesy of National Institute of Standards and Technology.)

Selection rules for discrete transitions			
	Electric dipole (E1) ("allowed")	Magnetic dipole (M1) ("forbidden")	Electric quadrupole (E2) ("forbidden")
Rigorous rules	1. $\Delta J = 0, \pm 1$ (except $0 \nleftrightarrow 0$)	$\Delta J = 0, \pm 1$ (except $0 \nleftrightarrow 0$)	$\Delta J = 0, \pm 1, \pm 2$ (except $0 \nleftrightarrow 0$, $1/2 \nleftrightarrow 1/2$, $0 \nleftrightarrow 1$)
	2. $\Delta M = 0, \pm 1$ (except $0 \nleftrightarrow 0$ when $\Delta J = 0$)	$\Delta M = 0, \pm 1$ (except $0 \nleftrightarrow 0$ when $\Delta J = 0$)	$\Delta M = 0, \pm 1, \pm 2$
	3. Parity change	No parity change	No parity change
With negligible configuration interaction	4. One electron jumping, with $\Delta l = \pm 1$, Δn arbitrary	No change in electron configuration; i.e., for all electrons, $\Delta l = 0$, $\Delta n = 0$	No change in electron configuration; <i>or</i> one electron jumping with $\Delta l = 0, \pm 2$, Δn arbitrary
For LS coupling only	5. $\Delta S = 0$	$\Delta S = 0$	$\Delta S = 0$
	6. $\Delta L = 0, \pm 1$ (except $0 \nleftrightarrow 0$)	$\Delta L = 0$ $\Delta J = \pm 1$	$\Delta L = 0, \pm 1, \pm 2$ (except $0 \nleftrightarrow 0$, $0 \nleftrightarrow 1$)

The transition probability T_{if} in equation (2.5) is an approximation to the second order. Higher order terms in equation (2.5) and (2.8) yield transitions such as magnetic dipole transitions, electric quadrupole transitions, etc. The possibility of a magnetic dipole or electric quadrupole transition, however, is much smaller than an electric dipole transition. These unlikely transitions are therefore referred to as “forbidden” and are only considered when the electric dipole transition is zero. Table 3 summarizes the selection rules⁶⁸ in the notation of LS and jj coupling for electric dipole, magnetic dipole and electric quadrupole transitions for the readers’ reference.

In conclusion, the states of unoccupied holes (populations and spin) and the polarization states of incident photons determine the probabilities of absorption and shape the x-ray absorption structures. Take transition metals for example, the unoccupied d orbitals and the photon polarization states shape the *L*-edge x-ray absorption spectra.

2.5 X-ray magnetic circular dichroism (XMCD)

Figure 19: Origins of x-ray polarizations.

As we learnt from the last section, the absorption of x-rays is dependent on the x-ray polarization states. Figure 19 illustrates the origin of the x-ray polarizations from a synchrotron

source. The cycling electrons have an angular momentum L , which is transferred to the generated x-rays. L is positive, negative, or zero values along x-ray propagation directions. When x-rays travel in the same plane as the electron orbit, $L_z = 0$, where the x-rays are linearly polarized. When x-rays travel above or below the electron orbit plane, L_z will be either positive or negative leading to circularly polarized x-rays.

XMCD

Spin dependent XAS measurement is possible by using circularly polarized x-rays. Due to the conservation of momentum, the transition probability of a photoelectron to a higher state depends on the availability of holes with the right angular momentum at the right energy ($E_{\text{final}} = E_{\text{core electron}} + E_{\text{photon}}$). Photons with the same energy but opposite angular momentum excite transitions of different pairs of electron-holes. Circular dichroism happens when a material has different densities of states for spin-up and spin-down holes as it is the case in a ferromagnet (assuming the core shells are spherically symmetric). Therefore the technique described above is termed x-ray magnetic circular dichroism (XMCD). Because of the uneven absorption of optical spins, XMCD is a magneto-optical effect.⁶⁹

The absorption probability (reflected in XAS intensity) concerns only the relative orientation of the photon spins and the sample magnetization. Switching the x-ray polarization directions between left and right circular polarizations is therefore equivalent to switching the magnetization direction of the sample as shown in Figure 20.

Figure 20: Two equivalent ways of measuring XMCD: by changing the polarization directions of the incident or by changing the magnetization direction of the sample.

2.6 Photoemission electron microscopy (PEEM)

Other dichroic effects

XMCD is the dichroic absorption of circularly polarized x-rays due to the uneven spin up and spin down electron densities. However, XMCD is not the only dichroic effect. Anisotropic electron charge distribution also causes dichroic absorptions of linearly polarized x-rays. Non-magnetic materials such as FE materials and small molecules with directional covalent bonds have preferred direction for electron charge. Axial magnetic spins in magnetic materials will cause a spherically distributed electron cloud to elongate along the magnetic direction due to the spin-orbital coupling. The absorption of x-rays in these materials is dependent on the incident angles. The absorption of linearly polarized x-rays are typically the largest when the E component of x-rays is in the direction of the largest number of proper empty states. Depending on whether the charge anisotropy has a spin origin, these effects are termed as x-ray magnetic linear dichroism (XMLD) and x-ray natural linear dichroism (XNLD). Similarly, x-ray natural circular dichroism (XNCD) can happen if the charge distributions lack a center of inversion.

PEEM

XMCD, XMLD, XNLD, and XNCD are the spectroscopic ways to study dichroic effects. Photoemission electron microscopy (PEEM) records microscopy images of dichroic absorption over an area. Instead of taking two absorption spectra over an energy range, a PEEM image is taken at a fixed energy. The fixed energy is chosen from one of the energies at which a large dichroism could result among different domains, e.g. the domains pointing upwards vs. downwards in a FM material. The difference in x-ray absorption of these domains produces an image contrast in PEEM; the obtained PEEM image therefore reflects the domain structures of the material.

The major source of PEEM images are the secondary electrons generated in x-ray absorption. The generated electrons are accelerated by a high voltage external electric field. Their trajectories are controlled by curved electric field lines created by electronic lenses. These electronic lenses magnify the electronic images of electron distributions just as the optical lenses magnify optical images. At the end of their journey, the electrons are detected by a phosphor screen, which then emits visible light. The visible light images created by electrons are recorded using a cooled charge coupled device (CCD) camera. Each PEEM image is taken at a single incident energy with defined polarization at a fixed angle. A second PEEM image with opposite contrast is usually taken for image analysis. The opposite contrast is accomplished by using x-rays at a different energy, polarization state (for circular dichroism) or angle (for linear dichroism). The exact setup of PEEM measurement at beamline 11.0.1 of ALS is included in Chapter 4.

PEEM is a powerful tool to study multilayer thin films. PEEM can selectively image each layer by setting the incident x-rays at around an edge energy unique to that layer. PEEM can compare properties of different layers and interfaces at exactly the same location because the

sample can be kept at the same setup and location during the imaging process of all layers.

2.7 Micro X-ray diffraction (μ XRD)

X-ray diffraction

As mentioned in section 2.2, x-rays can be scattered and absorbed. When the scattered x-rays are in phase, the intensity of x-rays is amplified due to constructive interference. Otherwise, the intensity is greatly reduced and even annulled due to destructive interface. Figure 21 shows a cartoon for the scattering process. The constructive interference happens when the phase difference of outgoing x-rays is a multiple of x-ray wavelength (i.e. in phase), and the result is given by Bragg's law

$$n\lambda = 2d \sin \theta, \quad (2.10)$$

where λ is the wavelength of x-rays, d is the lattice spacing between crystal planes, and θ is the angle between the incident x-rays and the lattice planes. The technique making use of the x-ray diffraction patterns is called x-ray diffraction (XRD), which is commonly used in labs to study crystal structures.

Figure 21: Formation of x-ray diffraction pattern. The phase difference of the outgoing x-rays $CB + BD$ equals to $2 d \sin \theta$. When the phase difference is a multiple of x-ray wavelength, the outgoing x-rays are in phase, which leads to the local maximum intensity of interference pattern.

Micro x-ray diffraction

XRD carried out in labs (lab XRD) and in synchrotron (μ XRD) facilities have different features. Lab XRD has fixed incident x-ray energy, while synchrotron x-ray sources can provide a range of x-ray energies. A large number of diffraction patterns can therefore be obtained with one shot of white beams, i.e. x-rays with a wide range of wavelengths. This capability provides an efficient way to study the grain orientations, phases, strain, etc. Lab XRD has a typical spot size of 1mm and low intensity while μ XRD has sub-micron spot sizes with high brightness. These distinct features make μ XRD a great tool to study ultra-thin wedge samples. Because the understanding and analysis of μ XRD is beyond the focus of the current dissertation, μ XRD is included in Chapter 3 only for sample quality characterization.

To conclude, this chapter discussed how x-rays interact with matter and the associated techniques from XAS, XMCD, PEEM imaging to XRD. Because x-rays are absorbed at specific energies unique to each element, x-ray can selectively detect one element at a time. Since the fine structure of an absorption spectrum is dependent on a material's spin structure, charge density, and the incident light polarization, x-rays can be controlled to identify the spin orientations and charge distributions in materials. X-rays are nevertheless useful for studying the crystal structure. Due to the fact that the scattered x-rays from atoms interfere with each other, the resulting diffraction pattern can be used to calculate the distance between the planes of atoms from which the x-rays are scattered. Useful information such as strain and PZT domain structures can be obtained from XRD and would deepen the understanding of ME coupling in the system, though it was not finalized in the current dissertation. The discussion of techniques in this chapter will help assist the understanding of the research results in the following chapters.

Chapter Three: Sample Characterization

Sample growth and characterization were introduced in this chapter. A laser-MBE with a programmable shutter was used to grow the samples. Atomic force microscopy, fluorescence mapping, XRD, μ XRD and scanning transmission electron microscopy were used for characterization.

3.1 Sample design and growth

Sample design

Figure 22: Sample scheme for LSMO/PZT heterostructures. Buffer layers of LSMO were grown before the deposition of PZT to promote high quality epitaxial growth. Double wedge (left): the orthogonal wedge directions of LSMO and PZT layers create a wide range of thickness combinations. Single LSMO wedge (middle) and flat bilayers (right) were also utilized. The buffer layer is always flat.

In order to create a large combination of PZT and LSMO thicknesses, a large number of our samples were grown with a thickness gradient. General sample schemes with exaggerated gradient angles are shown in Figure 22. Figure 22 (a) is a double wedge sample where thickness varies in both the LSMO and PZT layers. The direction of the PZT thickness gradient is along one side of the sample and perpendicular to that of the LSMO gradient. This design maximizes

thickness combinations and minimizes growth and measurement variations. Single wedge samples shown in Figure 22 (b) as well as flat bilayers in Figure 22 (c) were also grown.

The thickness gradient of the wedge samples were controlled by moving a shutter⁷⁰ mask in front of the substrate. The moving speed of the shutter is tested and programmed for different wedge thickness. Continuous movement is used for thin wedges while step by step movement is applied for thicker wedges. The actual gradients of the samples are extremely small. For the wedges with the largest gradients, LSMO thickness goes from 0 to 10 nm over a length of 3 mm; PZT goes from 0 to 300 nm over 6 mm. Therefore the wedge slope are on the order of 10^{-6} ; LSMO and PZT layers are locally flat in a region of study.

Sample growth

The samples were grown by a Laser-MBE system (shown in Figure 23) and provided by Ying-Hao Chu's group at National Chiao Tung University, Taiwan. The growth conditions were first calibrated with flat samples and then tested for wedges. The growth of flat samples were monitored by reflection high energy electron diffraction⁷¹ (RHEED) and the sample qualities were determined by atomic force microscopy (AFM), x-ray diffraction (XRD) and x-ray reflectivity (XRR). The obtained optimum growth conditions, which are summarized in Table 4, were used to grow wedges. Before the growth of PZT, a flat 5nm LSMO buffer layer was normally grown and calibrated by RHEED to promote high quality epitaxial growth and to potentially serve as a bottom electrode for electrical measurements. After a PZT wedge was grown, the substrate was rotated by 90° to deposit a LSMO wedge. On the edges of the wedge samples, about 1-2 mm wide stripes were kept flat for calibrations.

Figure 23: Cartoon for a Laser-MBE system. A shutter was used to create thickness gradient.

Table 4: Growth conditions

	Ambient Gas	P_{amb} (mTorr)	T_{sub} ($^{\circ}\text{C}$)	θ_{il} ($^{\circ}$)	D_{ts} (cm)	ν_{rep} (Hz)	E_p (mJ)
LSMO	O ₂	100	685	~ 45	6-8	10	300
PZT	O ₂	100	620	~ 45	6-8	15	320

Table legend:

P_{amb} : Pressure of ambient gas;

T_{sub} : Temperature of substrate;

θ_{il} : Angle between incident laser and the normal direction of target plane;

D_{ts} : Distance between the target and the substrate;

ν_{rep} : Pulse repetition rate of laser;

E_p : Output energy per pulse.

3.2 Sample Characterization

All of the wedge samples were grown on 10 mm by 5 mm STO or Si substrates. Table 5 lists the samples covered in this dissertation, though some other films were also measured.

Table 5: List of samples.

Samples	Sample construction (top layer)/.../(substrate)
1	LSMO wedge(0-200nm) / PZT (30nm) / LSMO (5nm) / STO
2	LSMO wedge (0-3nm) / PZT wedge (0-300nm) / LSMO (5 nm) / STO
3	LSMO wedge (0-10nm) / PZT wedge (0-300nm) / LSMO (5 nm) / STO
4	LSMO wedge (0-10nm) / PZT wedge (0-30nm) / LSMO (5 nm) / STO
5	PZT wedge (0-80nm) / LSMO wedge (5-20nm) / STO on Si
6	PZT (225 nm flat) / $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (15 nm flat) / LaAlO_3

3.2.1 Atomic Force Microscopy (AFM)

Figure 24: Van der Waals' force vs. Tip-sample separation.

AFM is an imaging technique that belongs to a group of characterization methods called scanning probe microscopy (SPM). The first SPM was scanning tunneling microscopy (STM)⁷² with atomic resolution. STM was created based on the fact that the tunneling current between an atomic tip and a conductive sample changes exponentially with their separation (~ a few angstroms). By maintaining a constant tunneling current while scanning, the tip's movement traces the topological features of the sample. However, the technique was restricted to conductors. The efforts to extend STM to non-conductive samples lead to the birth of AFM,⁷³ where the force

between a tip and a sample surface could be described by the Van der Waals' interaction (Figure 24). The tip is about several μm long with the tip diameter smaller than $100 \text{ \AA}$. The tip is on the free end of a cantilever which is attached to a chip for mounting purpose. Figure 25 is a cartoon for a typical AFM set up.⁷⁴ While several different detection methods exist, the system shown in the figure uses a laser beam, reflected from the reverse side of the tip into position sensitive photodetectors. The position information is processed by the feedback electronics to the piezodrivers which in turn decide the movement of the probe.

Figure 25: Cartoon for AFM setup. (Reference 74. Reprinted from Nano Today, 6, A. T. Ampere, Advancements and challenges in development of atomic force microscopy for nanofabrication, 493, Copyright (2011), with permission from Elsevier)

AFM generally works in three different modes: contact, non-contact, and tapping modes.⁷⁵

In a contact mode, the tip touches the sample surface and the cantilever is bent by the repulsive force. Either the deflection of the cantilever or the height of the scanner is kept constant through the feedback loop. A topologic image is produced by recoding the vertical movement of the scanner in a constant deflection scan. Or the deflection (i.e. variation of the tip height) of the cantilever is used in a constant height situation. Because the cantilever cannot be bent unlimitedly, the latter often requires relatively flat samples. In a non-contact mode, the cantilever oscillates at

around its resonance frequency above the surface while the oscillation amplitude is monitored. The shift of vibration behaviors derives from the change in the attractive force between the tip and sample, which in turn determines the topological information. In between a contact mode and a non-contact mode, a tapping mode is created by vibrating the tip in close vicinity of the sample surface that the tip occasionally touches the surface. The RMS (root mean square) voltage produced by the reflected laser into the photodiode is monitored in this mode.

A mode is selected based on the features of a specific sample. The non-contact mode and the tapping mode generally produce higher quality images than the contact mode in solid state studies. Figure 26 illustrates the generated surface topography in each mode along with the individual interactions between a tip and a sample. An AFM tip may drag and damage the sample surface in a contact mode while the other two do not alter the sample surface.

Figure 26: The interactions between the tip and the sample surface under the three modes: contact (left), non-contact (middle) and tapping mode (right). (Reference 75. Reprinted from Mechatronics, 14, N. Jalili and K. Laxminarayana, A review of atomic force microscopy imaging systems: application to molecular metrology and biological sciences, 907, Copyright (2004), with permission from Elsevier)

The setup of other SPM techniques is very similar to the operations of AFM, with minor modulations. Electric force microscopy (EFM) uses an electrically biased conductive tip to map the electrostatic force from the sample. EFM can image the out-of-plane electric domains. Piezoresponse force microscopy (PFM) utilizes the fact that ferroelectric materials change shape

upon the application of an external electric field and can also image the in-plane domains. Detailed information on PFM is discussed in the PFM section.

Experimental results

Figure 27: AFM image at 5nm LSMO/200 nm PZT. (Reference 76. Reprinted from J. Zhou, V.Tra, S. Dong, R. Trappen, M. Marcus, C. Jenkins, C. Frye, E. Wolfe, R. White, S. Polisetty, J. Lin, J. LeBeau, Y. Chu and M. Holcomb, Appl. Phys. Lett., 107, 141603 (2015). with the permission of AIP Publishing.)

AFM measurements were carried out by sample growers after the growth. Terraces, which are common for LSMO AFM images,⁷⁷ were often seen on our samples (Appendix). Figure 27 is an image taken at 5 nm LSMO on top of 200 nm PZT on a double wedge sample. The width of the terrace is about 0.25 μm . The root mean square roughness is 0.266 nm, which is quite small given the thickness of the underlying PZT layer.

3.2.2 Fluorescence mapping and thickness estimation

While roughness is an important measure of sample quality, the sample thickness estimated with the help of fluorescence mapping is crucial for the thickness dependence study. The attenuation lengths of hard incident x-rays and the outgoing fluorescence x-rays are of the order of micrometers, the intensity of XAS signal is thus approximately proportional to the number of a specific element in the few nanometer thick samples. Fluorescence yield at specific incident x-ray

energy ranges can be collected while the x-rays are sweeping the sample surface in micrometer steps. The intensity map produced this way is called a micro-fluorescence element map. Because the samples are highly crystallized, the column density of the element unique to a layer is a good representation of the layer thickness. The setup for mapping is the same as the one for XAS FL measurement (Figure 15 in Chapter 2 and Figure 38 in Chapter 4). All fluorescence maps were taken at beamline 10.3.2 of ALS.

Figure 28: Micro-fluorescence element map of lead. The column density of lead is approximately proportional to the thickness of PZT. (Reference 76. Reprinted from J. Zhou, V. Tra, S. Dong, R. Trappen, M. Marcus, C. Jenkins, C. Frye, E. Wolfe, R. White, S. Polisetty, J. Lin, J. LeBeau, Y. Chu and M. Holcomb, *Appl. Phys. Lett.*, 107, 141603 (2015). with the permission of AIP Publishing.)

Figure 28 shows a typical fluorescence map where the variations of fluorescence yield intensity are shown as an intensity gradient. The post-edge intensities in XAS are relatively flat and less affected by the near edge structures. Therefore incident x-rays at post-edge energies are perfect for the purpose of element mapping. The incident x-rays' energy for the map shown in Figure 28 was set at 50 eV above the Pb L_3 edge (~ 13.035 keV). Because Pb is an element only present in the PZT, the column density of Pb shown in the map confirms the thickness gradient of the PZT layer. The orange curve is the fluorescence intensity along the PZT gradient direction. By matching the lowest intensity and highest intensity with the beginning and ending thickness of the

PZT wedge, the PZT thickness of each specific locations in the sample are determined. A typical Mn map is also included in the Appendix.

3.2.3 XRD

The working principle of XRD was introduced in Chapter 2 in the micro-XRD section. Lab XRD was carried out with the Bruker AXS D8 Discover high-resolution x-ray diffractometer at the Shared Research Facilities of West Virginia University. The x-ray source is the Cu K_α x-rays ($\lambda = 0.1541$ nm). XRD measurements were taken by Evan Wolfe. Typical XRD curves from a wedge sample are shown in Figure 29. This is a θ - 2θ scan, where the rotation of the detector is twice the rotation of the sample. The sample construction is 10 nm LSMO wedge/30 nm PZT wedge/5 nm LSMO buffer/STO. Figure 29 (a) displayed three curves taken at $t_{\text{PZT}} \approx 0.4$, 15 and 30 nm. As evidenced by the green curve ($t_{\text{PZT}} \approx 0.4$ nm), the substrate STO peaks (001), (002) and (003) corresponds to a lattice spacing of 3.905 nm, signifying the single crystalline cubic structure of STO. X-ray peaks of PZT (001), (002) and (003) were observed for $t_{\text{PZT}} > 0.4$ nm. The locations of these peaks match an out-of-plane c lattice spacing of 4.270 Å. The correspondent spacing in bulk PZT is 4.135 Å. The elongation of c spacing normally comes from the straining of in-plane lattice spacing, which is consistent with the epitaxial layer growth of tetragonal PZT⁷⁸ on STO substrate. With the increase of PZT thickness, the relative intensities of PZT peaks (00 l), where $l = 1, 2$ and 3 are enhanced; the full width at half maximum (FWHM) is reduced. The PZT thickness can be estimated from Scherrer's equation^{79,80} for crystallite sizes

$$B(2\theta) = \frac{K\lambda}{L\cos\theta}, \quad (3.1)$$

where B is the FWHM of the peak, λ is the x-ray wavelength, θ is the diffraction angle. L is the average crystal thickness along the plane normal. K is the Scherrer constant which depends on the

crystal shape and is 0.94 for spherical crystals with cubic symmetry. The PZT thickness was roughly estimated to be 13 nm for the blue curve and 32 nm for the red curve assuming $K \sim 1$, $\cos \theta \sim \cos 11 \sim 1$ from the PZT (001) peak.

(a)

(b)

Figure 29: Typical XRD curves at varied PZT and LSMO thicknesses. (Reference 76. Reprinted from J. Zhou, V. Tra, S. Dong, R. Trappen, M. Marcus, C. Jenkins, C. Frye, E. Wolfe, R. White, S. Polisetty, J. Lin, J. LeBeau, Y. Chu and M. Holcomb, Appl. Phys. Lett., 107, 141603 (2015). with the permission of AIP Publishing.)

Figure 29 (b) shows the XRD curves taken at the same PZT thickness but two LSMO thicknesses: 10 nm and ~ 0.4 nm. On top of the STO and PZT peaks, LSMO peaks $(001)_{pc}$ and $(002)_{pc}$ are also observed on the shoulders of STO peaks for the thick t_{LSMO} . Rhombohedral and cubic LSMO produce very similar XRD peaks.⁸¹ However, bulk LSMO is rhombohedral at room temperature and is only cubic at much higher temperatures. The observed LSMO peaks are probably due to the rhombohedral structure. STO has a cubic structure with a lattice parameter of 3.905 Å, LSMO is pseudocubic with an equivalent lattice parameter of 3.885 Å. Because of the straining from underlying layers, LSMO peaks falls on the right shoulder of STO peaks. The left shoulder LSMO peaks may due to the slightly relaxed LSMO lattice.⁸² Due to the large lab x-ray spot sizes (~ 0.1 to 1 millimeter) on the wedges, fringes frequently observed in thin films were barely seen.^{83,84} A smaller spot size is helpful to fully understand these films. Attempts to use pinholes to reduce the spot size on the lab XRD resulted in unsatisfactory intensity, thus synchrotron sources were sought.

3.2.4 μ XRD

Micro x-ray diffraction (μ XRD) spectra were taken at beamline 12.3.2 of the ALS. Figure 30 is the setup scheme⁸⁵ for beamline 12.3.2. It provides both monochromatic and polychromatic x-rays ranging from 5 to 22 keV. The spot size on the sample is about 0.6 μ m by 0.5 μ m. The high intensity and tiny beam size make μ XRD ideal to characterize ultrathin wedge samples. As it has been observed in the lab XRD results, the LSMO peaks severely overlapped with the STO peaks. Lab-based reciprocal space maps can be used on flat samples, but the large spot size is problematic for wedges. The capability to resolve these LSMO peaks is crucial to map the strain evolution of LSMO along wedges, which is helpful to uncover the strain effect on the ME coupling. Using synchrotron techniques, strain is normally studied in a two-step processes using both white beam

and monochromatic beams.⁸⁶ Due to the constraint of the current dissertation and that the understanding of the strain effect is still a work in progress, strain analysis is not covered. The μ XRD information is included here for a rough idea of the technique and results.

Figure 30: Setup scheme for beamline 12.3.2 at ALS. The x-rays from the bending magnet are refocused through the toroidal mirror at a ratio of 1:0.72. The silicon (111) monochromator consists of 2 identical channel cuts, which directs the monochromatic beam along the same axis as the white beam. After passing through the silicon crystals, the x-rays are focused by a set of Kirkpatrick-Baez mirrors (i.e. KB mirrors). The spot size on the sample is about $0.6 \mu\text{m}$ by $0.5 \mu\text{m}$. The diffracted x-rays are recorded by a CCD camera. (Reference 85. Credit: beamline 12.3.2 at the Advanced Light Source)

Figure 31 shows a typical set of μ XRD spectra. This set of spectra was taken at three thicknesses of the same wedge sample as in the lab XRD. Because the rotations of the sample would shift the x-ray beam to a different location on the wedge (Figure 30), an energy scan is used instead of the θ - 2θ scan. The red and the blue curves in Figure 31 were measured at the thinner part of the sample. The bottom red curve was taken before the start of the wedges. The middle blue was at 5 nm LSMO /15 nm PZT. The top green curve was taken at a thicker location with 5 nm LSMO and 30 nm PZT. Similar to what were observed in lab XRD, LSMO and PZT peaks emerge

and are enhanced as the layers become thicker. As opposed to the one broad PZT peak shown in 15 nm PZT, two PZT peaks (002) and (200) were present in at 30 nm PZT, which implied that the PZT lattice parameter in the same direction varied. This evidenced the emergence of polydomain structure of PZT.

Figure 31: Typical μ XRD spectra across a LSMO/PZT wedge sample. The LSMO and PZT peaks grow with increasing LSMO and PZT thickness.

3.2.5 Scanning Transmission Electron Microscopy (STEM)

Electron microscope

Optical microscopes use visible light and optical lens system to magnify the images. The image resolution is limited by the wavelength of electromagnetic waves, which are about 400 to 700 nm for visible light. After the discovery that electrons can behave like waves and have a shorter wavelength ($\sim 7 \text{ \AA}$ at 10^6 m/s) than visible light, electron microscopes were invented by using high speed electrons and electronic lenses (electromagnetic coils) to resolve even smaller images.

Electron microscopes are used in scanning electron microscopy (SEM), transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM). The electron

microscopes are set up similarly to an optical microscope.⁸⁷ Electrons are concentrated by electronic lenses to a small spot onto the sample. Scan coils are used in STEM to steer the electron beam from side to side. Electrons scattered into small angles with regards the central axis create the bright field image. The electrons that leave at large angles form the annular dark-field image. The byproducts of the imaging process include the electrons which lose measurable amount of energy and the x-rays generated from electron excitations in the sample. The microscope in TEM does not have the scan coils and the images are resulted from the transmitted electrons. The microscope in SEM has the scan coils like in STEM but the images are from the electrons bouncing off the sample surface. The respective resolution of SEM, TEM and STEM are 10 nm, 1 nm and sub-angstrom.⁸⁸

STEM images

Figure 32: An HAADF STEM image across the STO/LSMO/PZT region of the sample. (Reference 76. Reprinted from J. Zhou, V. Tra, S. Dong, R. Trappen, M. Marcus, C. Jenkins, C. Frye, E. Wolfe, R. White, S. Polisetty, J. Lin, J. LeBeau, Y. Chu and M. Holcomb, Appl. Phys. Lett., 107, 141603 (2015). with the permission of AIP Publishing.)

A probe-corrected FEI Titan 60-300 S/TEM equipped with a Super-X energy dispersive x-ray (EDX) spectrometer was used by Ryan White from James LeBeau group to image the cross sections cutting from one of the samples. A high-angle annular dark-field (HAADF) image is shown in Figure 32 (top left), which demonstrate good interface and sample quality. The EDX maps

of the cations (colored images) show abrupt element distributions, which indicate chemically sharp interfaces.

In this chapter, typical characterization results of the samples are included. The AFM images indicate a smooth sample surface; fluoresce mapping depicted uniform wedge shapes; XRD results were consistent with the epitaxial growth of the layers and verified the sample thickness; and, STEM images showed a sharp interface. These results collectively confirm the good quality of the samples, which means that the following investigations will give information on the intrinsic properties of these samples.

Chapter Four: Spectroscopy Results and Discussions

This chapter includes the spectroscopy results of the samples measured by synchrotron x-rays. Thickness dependent Mn valence results are explored from data analysis, experimental setup, theoretical modeling, to hypothesis testing. Depth dependent Mn valence has been established. Thickness dependent XMCD results are also included.

4.1 Valence estimation from x-ray absorption spectra

Mn is a transition metal with an electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$. The oxidation states of Mn are 7, 6, 4, 3, 2. The main peak of Mn *K*-edge XAS corresponds to the transition from 1s to 4p; the *L*-edges correspond to the transitions from 2p (L_2 , L_3) to 3d (e_g , t_{2g}). The electronic structures of the detected element in XAS shape the x-ray absorption fine structures. The oxidation states can be estimated through the features of the fine structures through several methods below:

- (1) Edge shift: As the oxidation state of the absorbing atom increases, the absorption edge frequently shifts to higher energy. This shift occurs because the nucleus is shielded by fewer electrons in a higher oxidized atom and more energy is needed to remove additional electrons. An example is shown in Figure 33, where the edge features increase linearly with the valence. Similarly, the energy differences between L_3 and L_2 peaks also serve as footprints for valence.

Figure 33: Energy positions of various absorption features vs. oxidation state in the vanadium *K*-edge XANES spectra of various vanadium oxides. (Reference 89. Reprinted figure with permission from J. Wong, F. W. Lytle, R. P. Messmer, and D. H. Maylotte, *Phys. Rev. B*, 30, 5596 (1984). Copyright (1984) by the American Physical Society.)

- (2) Linear combination of reference spectra: The linear combination method is based on the theory of linear combination of atomic orbitals. In the least squares linear combination method, a normalized unknown spectrum is fitted by several normalized reference spectra. These reference spectra are the spectra of the same element in different minerals and compounds. The equation used for the fitting procedure is

$$I = C_1 I_1 + C_2 I_2 + C_3 I_3 + \dots, \quad (4.1)$$

where I is the intensity of the unknown spectrum at a specific energy, I_1 , I_2 and I_3 are the intensity of the reference spectra at that same energy, and C_1 , C_2 and C_3 are the coefficients that give the best least square fit to the unknown spectrum. All coefficients should be positive and the sum of these coefficients equals one. Small residuals can often be obtained with two to six reference spectra but more spectra can be used.

The resulting valence value V for the unknown spectrum is

$$V = C_1 V_1 + C_2 V_2 + C_3 V_3 + \dots, \quad (4.2)$$

where V_1 , V_2 and V_3 are the valence values corresponding to the reference spectra. The linear combination method is a common method for valence analysis in XAS and was applied to the Mn K -edge absorption spectra.

- (3) L_3/L_2 peak ratios: The L_3/L_2 ratio method is frequently used in valence analysis in electron energy loss spectroscopy (EELS).^{90,91,92} EELS is a similar technique to XAS except that the incident beams are high energy electrons rather than x-rays. EELS and XAS are theoretically equivalent in the dipole approximation and look nearly identical experimentally. Figure 34 shows Mn L -edge spectra from both EELS⁹³ and XAS.⁹⁴ The two resemble each other except for the energy resolution, which is typically on the order of 1eV for EELS and less than 0.1eV for XAS. The ratio method was adopted in the valence analysis for the Mn L -edge absorption spectra, though linear combinations were also attempted for several samples and similar results were obtained.

Figure 34: Mn *L*-edge spectra from (a) EELS (Reproduced with permission from reference 93, © 1993, American Physical Society) and (b) XAS (Reference 94. Adapted with permission from The Journal of Physical Chemistry A, 107, 2839. Copyright (2003) American Chemical Society). EELS and XAS are equivalent in the dipole approximations, the process that dominates the signal.

The normalization procedure for each spectrum is taken from reference 95 and illustrated in Figure 35. The peak intensities are separated from the background through subtracting a linear pre-edge term and an arctangent term modeling the transitions to the unoccupied continuum states. The linear term (black line in Figure 35) is described by

$$f_{pre-edge}(E) = aE + b, \quad (4.3)$$

where a is the slope of the pre-edge, E is x-ray energy, b is the interception of the pre-edge.

The arctangent term (purple line in Figure 35) is determined by

$$f_{arctan}(E) = h_1 \cdot \left[\frac{\arctan(\pi \cdot (E - E_1))}{\pi} + \frac{1}{2} \right] + h_2 \cdot \left[\frac{\arctan(\pi \cdot (E - E_2))}{\pi} + \frac{1}{2} \right], \quad (4.4)$$

where h_1 and h_2 are the height difference between the minima immediately following the L_2 and L_3 energies, E_1 and E_2 are the transition energies launching the L_2 and L_3 peaks. E_1 and E_2 are identified by finding the first maximum of dI/dE in the peak regions. The integrated peak intensities are obtained by integrating the final curve under each peak. They are shown as the yellow area in Figure 35.

Figure 35: The integrated area for L_2 and L_3 peaks. The bottom black line is the background extended from the pre-edge. The pink models the contributions due to transitions from core electrons to continuum states. The yellow integrated area under L_2 and L_3 peaks are used for ratio calculation. (Figure based on our measurements at ALS)

This procedure of integrating the L_2 and L_3 peaks was applied to the Mn XAS L -edge spectra of Mn oxides from reference 94. The relationship between the Mn valence of these oxides and their L_3/L_2 ratio is shown in Figure 36 and was used to determine empirically the Mn valence of the LSMO samples. The best fit curve was found to be

$$V(r) = -1.35 \cdot \ln \left(\frac{r - 1.06}{8.50} \right), \quad (4.5)$$

where V is valence and r is L_3/L_2 ratio.

Figure 36: Mn valence vs L_3/L_2 ratio. A best fit is found and used for calculating Mn valences from L_3/L_2 ratio.

4.2 Thickness dependent x-ray absorption spectra

XAS was taken on multiple samples at different beamlines. Figure 37 shows three drastically different Mn spectra taken at beamline 6.3.1, ALS (setup in Figure 46) at three thicknesses of LSMO and PZT on sample 2 (LSMO wedge (0-3nm) / PZT wedge (0-300nm) / LSMO (5 nm) / STO). Mn valence values marked by the side of the spectra are estimated from the multiplet features on the peaks from the reference spectra in Figure 34. The Mn valence is most similar to +2 at $t_{\text{PZT}} \sim 45$ nm and larger than +2 at $t_{\text{PZT}} \sim 100$ nm at LSMO thickness $t_{\text{LSMO}} \sim 1.2$ nm. Along the LSMO thickness gradient and constant PZT thickness of 100 nm, Mn valence also increases with the increase of LSMO thickness. The quantitative analyses of Mn valence are discussed in the following sections.

Figure 37: Mn XAS spectra at three thicknesses of PZT and LSMO measured in TEY mode.

4.3 Dependence of Mn valence on PZT thickness

The dependence of Mn valence on PZT thickness was measured at Mn *K*-edge in FL mode at beamline 10.3.2 of the ALS.⁹⁶ The probe depth at *K*-edge FL mode is large and covers the interfacial region of the sample.

Experimental setup

The experimental setup for beamline 10.3.2 is shown in Figure 38. The current beam size can be as small as 1.7 μm (horizontal) $\times$ 1.6 μm (vertical) as listed on the official website (<https://sites.google.com/a/lbl.gov/microxas-lbl-gov/specifications>). The samples were measured with the incident x-rays coming in at a grazing angle. The typical spot size at the time of measurement is about 10 μm (horizontal) $\times$ 3 μm (vertical).

Figure 38: Experimental setup for XAS FL measurement. FWHM stands for full width at half-maximum. “demag.” stands for demagnification. The vertical and horizontal focusing mirrors (M3 & M4) along with the slits reduce the x-ray source size to the actual beam size on the sample. (Reference 96. Reproduced with permission of the International Union of Crystallography (<http://journals.iucr.org/>).)

Experimental results

The raw spectra were normalized before further analysis. A spectrum was energy aligned first. A linear fit to the pre-edge region was then extended and subtracted the same way as the black line in Figure 35. The post-edge of subtracted spectrum was divided by a linear fit to the post-edge. The obtained spectrum had its pre-edge at 0 and its post-edge wiggle around an intensity of one. The oscillating part of the spectrum was located in the extended region of XAS and is originated from the interference of the electrons scattering off the neighboring atoms around the absorption centers.

Eighteen Mn *K*-edge reference spectra⁹⁷ were used to fit the normalized spectra through the least square linear combination method. Because bulk LSMO is not cubic, its spectrum depends on the direction of measurement. Two reference spectra of bulk LSMO measured at two directions⁹⁷ were included as reference. Groups of 1 to 6 spectra were selected from the 18

reference spectra and linearly combined to fit each normalized spectrum. In total $\sum_{i=1}^6 C_{18}^i = 31179$ combinations were attempted. Fits with the smallest sum of squared residuals, i.e. best fit, were obtained for 1 to 6 combinations separately. Note that only fits with positive coefficients were considered. The fit with the smallest residuals among all gave the best valence estimation; the standard deviations among the legitimate best fits using 2 to 6 combinations were taken as the uncertainties of the estimate.

The Mn valence dependence of PZT thickness is shown in Figure 39. These data were measured at $t_{\text{LSMO}} \sim 0.4$ nm (blue triangles), 1.2 nm (black squares) and 3.2 nm (red dots) along the PZT thickness gradient on sample 2 (LSMO wedge (0-3nm) / PZT wedge (0-300nm) / LSMO (5 nm) / STO). The LSMO thickness t_{LSMO} are estimates from the fluorescence map as discussed in Chapter 3. While Mn valence is constant with respect to the PZT thickness for $t_{\text{PZT}} > 65$ nm, the Mn valence decreases with decreasing PZT thickness when t_{PZT} is smaller than 65 nm.

Figure 39: Mn valence vs. PZT thickness measured at Mn *K*-edge in XAS FL mode at three thicknesses of LSMO.

Hypothesis

To understand the Mn valence dependence on PZT thickness, it is crucial to figure out first how PZT itself changes with the thickness. When PZT becomes thicker, two things may happen:

1. The PZT in-plane lattice parameter may be larger. The in-plane lattice parameters for bulk STO, bulk LSMO and bulk PZT are 3.905, 3.885 and 3.935 Å (Table 1). In Figure 31, the change in the PZT (200) peak positions indicated this change in the PZT lattice parameter with thickness. Because both the STO substrate and the LSMO buffer layer have a smaller in-plane lattice parameter than that of PZT, ultrathin PZT will be strained by the LSMO buffer layer. When PZT grows thicker, PZT slowly relaxes towards its bulk lattice parameter. Because the lattice of top LSMO will match the PZT lattice at their interface, LSMO will also have a larger in-plane lattice at thicker PZT. This lattice parameter change could affect the bonding and electronic structures of LSMO and lead to Mn valence change.

This hypothesis is possible since the magnetization of LSMO is sensitive to strain, but PZT has the same lattice parameters for two opposite polarization states (e.g. up and down). If LSMO and PZT are coupled through strain alone, LSMO should be at the same state at two opposite PZT polarizations.

2. PZT domains may change. PZT is monodomain below a thickness of about 40 to 100 nm.⁵⁰ With the increase of PZT thickness, it transitions from monodomain pointing perpendicular to the sample surface to polydomain as shown by the presence of both PZT (200) and (002) peaks at thicker PZT in Figure 31. Given the similar strength of ferroelectric domains, monodomain structures have larger effective surface charge (illustrated in Figure 40) than polydomain structures. When PZT is adjacent to LSMO, screening charges are induced in LSMO to screen the

PZT polarization/surface charge. This screening charge attracts charge carriers to the LSMO interface and modifies the Mn valence.

The measured Mn valence at thin PZT in Figure 39 is smaller than those at thicker PZT, the domains in thin PZT should therefore be pointing upwards following this hypothesis. The polarization strength in single domain PZT, however, may gradually decrease as the PZT lattice relaxes from a highly strained state to a less strained state, during which Mn valence gradually increase. From $t_{PZT} = 65$ nm to 180 nm, PZT might have similar surface charge so that the Mn valence is nearly stable.

The second hypothesis is highly possible and is consistent with the prior work discussed in Chapter 1. Most efforts were made to test this second hypothesis, though several measurements were made and further investigations are needed to understand the effect of strain or other factors.

Figure 40: Comparison of effective surface charge in FE monodomain (left) and polydomain (right) structures. The arrows mark the ferroelectric domain directions which microscopically point from electron cloud centers to cation centers. Having mixed ferroelectric directions will reduce the net effective surface charge.

4.4 Hypothesis testing

4.4.1 Experimental testing

Thickness dependent PZT domain structures

In order to test the second hypothesis, I collaborated with graduate student Vu Thanh Tra at National Chiao Tung University for piezoresponse force microscopy (PFM) measurement along

the PZT wedge. The domain images obtained for 20 nm and 300 nm PZT are shown in Figure 41. Areas in the vicinity of the measured spots were poled beforehand in a distinct pattern for a comparison to the as-grown domain structures. Poling refers to a process where an external electric field is applied to a FE material. It can be done through the same set up as PFM but with higher voltage. Local domains of the poled FE material tend to align to the applied field direction. The poled pattern consists two center-sharing squares as delineated by black and blue boxes in Figure 41. An upwards electric field was applied to the area inside the blue box first. A downwards field was re-applied afterwards to the area inside the black box. The voltages used for poling were 6 V for $t_{PZT} = 20$ nm and 10 V for $t_{PZT} = 300$ nm, as more voltage is needed to switch the ferroelectric direction in a thicker film. Because FE domains tend to align with external fields, the domain directions of the poled areas are known. For example, the areas inside of the black boxes in Figure 41 are poled downwards and are darker than any other regions.

Figure 41: PFM images at two PZT thicknesses. PZT is single domain at 20 nm (left) and has multiple domains at 300 nm. (Reference 76. Reprinted from J. Zhou, V.Tra, S. Dong, R. Trappen, M. Marcus, C. Jenkins, C. Frye, E. Wolfe, R. White, S. Polisetty, J. Lin, J. LeBeau, Y. Chu and M. Holcomb, Appl. Phys. Lett., 107, 141603 (2015). with the permission of AIP Publishing.)

By comparing the contrast of the as-grown area outside the blue box to the contrast at known polarizations from the poled area, the as-grown domain structures are identified. The as-

grown domains for 20 nm PZT resemble those with upward polarization, which indicates a natural upward polarization direction at 20 nm PZT as expected. The image for the as-grown 300 nm PZT has both light and dark colors which reveal the existence of multiple domains. The appearance of dark spots in the upward-poled region is probably due to in-plane domains which was not completely poled to align to the external field.⁹⁸ These domain directions can also be determined by comparing in-plane and out-of-plane PFM measurements.

Poling effect on Mn valence

Mn valence was also measured at opposite PZT polarization states on sample 5 (PZT (0-80nm wedge)/LSMO (5-20nm wedge)/thin STO on a Si substrate). The PFM images of the sample are included in the Appendix, which show predominantly single domain structure. Three rows of eleven platinum electrodes with a diameter of 50 μm and thickness of 5 nm were grown on top of this thickness varying sample. The hysteresis response was measured at each electrode and the ones with reasonable hysteresis loops were selected for further study.

To clarify the desired and undesired features of a FE hysteresis loop, Figure 42 (a) - (d) illustrates the “polarization (P)” (surface charge measured by integrating the current) vs. E (applied electric field) responses for an ideal capacitor, a resistor, a lossy capacitor, and a FE material⁹⁹. The capacitor response is a line through the origin because the charge and the voltage is directly proportional with the slope being the capacitance. Note that the current and the voltage is out of phase for a capacitor but in phase for a resistor, for which the P-E response is a circle. A lossy capacitor can be described by a combination of a capacitor with some leakage as in a resistor. The response for a lossy capacitor is therefore a tilted open loop. An ideal FE hysteresis loop has non-zero interceptions on both x and y axes and saturation tails on both end of the loop (Figure 42 (d)). Figure 42 (e) is our measured hysteresis loop at about 80 nm PZT/20 nm LSMO. As compared to

the published squared shaped hysteresis loops for PZT by Vrejoiu, *et. al.*,^{100,101} leakage might be an issue for these samples. Impurities inside PZT might provide a short cut for electrons to run through the electrodes. The resulting response would have both features from a lossy capacitor and a FE hysteresis loop, like in our case here.

Figure 42: P-E response for (a) an ideal capacitor, (b) a resistor, (b) a lossy capacitor and (d) a FE material (Reference 99, © Queen's Printer and Controller of HMSO, UK, 1999. Reproduced with permission), along with (e) the P-E response of our sample at 80 nm PZT/20 nm LSMO.

External electric fields were applied to the selected electrodes and measured at beamline 10.3.2 of ALS (setup at section 4.3). The applied field was 2.4 V for 80 nm PZT and 1.2 V for 40 nm PZT. Poling at thinner PZT was not measured because thinner PZT appeared very leaky as observed through the lack of saturation in the hysteresis loops. The voltages were applied to the sample in both upwards and downwards directions. After each poling and before every x-ray absorption spectrum was taken, fluorescence intensity at the platinum L_3 peak (11663 eV) was scanned in the vicinity of the selected electrode to relocate the beam right on top of the electrode.

Figure 43: Mn valence change after PZT is poled upwards and downwards. The arrow by the side of the sample scheme represents the poling and polarization direction when PZT is poled upwards.

The poling effect on the Mn valences at $t_{\text{PZT}} \sim 80$ nm is shown in Figure 43 along with a schematic to help visualize the poling direction and a sample layout. The Mn valence is larger when PZT was poled upwards than downwards. This result is consistent with the second hypothesis and also excludes the possibility that PZT and LSMO are coupled only through strain, which should be similar (potentially even the same) for both upward and downward directions. When PZT had an upward polarization, the polarization pointed away from LSMO (marked by the arrow in the sample cartoon). As a result, the electrons were depleted in the PZT/LSMO interface in response to the PZT polarization which leads to a larger Mn valence. The electron redistribution due to PZT polarization is expected to be in the vicinity of the interface. As seen from the graph, the valence shift is smaller at thicker LSMO because of the increase of the unaffected LSMO regions at larger t_{LSMO} . This Mn valence change was also observed and reported for a single thickness on known similar magnetoelectric bilayers.¹⁰²

4.4.2 Theoretical modeling

Polar catastrophe

While PZT polarization would induce the change in Mn valence, polar discontinuity might also cause Mn valence to deviate from its nominal value. Polar discontinuity is the condition when one layer in a bilayer system exhibits polar planes (alternating non-neutral charges in atomic planes) and the other layer has charge neutral planes¹⁰³ (Figure 44). In the LSMO/PZT bilayer systems, LSMO is kept ultrathin, in which case LSMO is non-metallic and would have alternating polar planes of $(\text{La}^{3+}, \text{Sr}^{2+})\text{O}^{2-}$ or $\text{Mn}^{3.3+}\text{O}_2^{2-}$; PZT, on the other hand, has charge neutral atomic planes. Polar discontinuity therefore should be considered when modeling Mn valence behavior.

Figure 44: Charge rearrangement at LSMO/PZT interface. On the left of the sample cartoon, the interface has a similar charge arrangement as in the bulk which results in “polar catastrophe”; on the right, a charge rearrangement is suggested to solve the polar catastrophe. PZT polarization is not considered here. (Inspired by reference 107)

The termination layer at the polar interface is an important factor in determining the direction of the interfacial charge transfer. The LSMO layer has two possible terminations – the $(\text{La}, \text{Sr})\text{O}$ or MnO_2 plane – at the interface (Refers to Chapter 1 perovskite structures and Chapter 3 XRD measurements). Figure 44 illustrates the case when the termination plane is $(\text{La}, \text{Sr})\text{O}$. Because this is similar to the widely-studied n-type interface of $\text{LaAlO}_3/\text{STO}$,¹⁰⁴ $(\text{La}, \text{Sr})\text{O}$ termination has been labeled an n-type interface while MnO_2 is labeled as p-type in the simulation section below. The average plane charges per unit are listed on the sides of the lattice cartoon. The

charges for each individual atomic plane on the left are assumed to be the same as in the bulkⁱ. LSMO is a compound mixture of 70% $\text{La}^{3+}\text{Mn}^{3+}\text{O}_3^{2-}$ and 30% $\text{Sr}^{2+}\text{Mn}^{4+}\text{O}_3^{2-}$. The integer oxidation states of these elements¹⁰⁵ are listed in Table 6. A LSMO unit cell consists of an average number of 0.7 La^{3+} , 0.3 Sr^{2+} , one Mn, and three O^{2-} . The average charge per unit on a (La,Sr)O plane therefore is

$$0.7 \times (+3) + 0.3 \times (+2) + 1 \times (-2) = +0.7. \quad (4.6)$$

$$0.7 \text{ La}^{3+} \quad 0.3 \text{ Sr}^{2+} \quad 1 \text{ O}^{2-}$$

The average charge per unit on a MnO_2 plane is

$$0.7 \times (+3) + 0.3 \times (+4) + 2 \times (-2) = -0.7. \quad (4.7)$$

$$0.7 \text{ Mn}^{3+} \quad 0.3 \text{ Mn}^{4+} \quad 2 \text{ O}^{2-}$$

Using Gauss' law,¹⁰⁶ the electric field $\mathbf{E}$ between atomic planes would alternate between zero and a non-zero constant. The resulting potential $\mathbf{V}$ would accumulate over the layers and diverge at the surface for an infinite number of layers.¹⁰⁷ This situation, however, cannot occur in real materials as it would violate boundary conditions. This hypothesized scenario was popularly called “polar catastrophe”.¹⁰⁷

Table 6: Oxidation states of elements. (Reference 105)

<i>Elements</i>	<i>La</i>	<i>Sr</i>	<i>Mn</i>	<i>Pb</i>	<i>Zr</i>	<i>Ti</i>	<i>O</i>
<i>Oxidation states</i>	3	2	7, 6, 4, 3, 2	2, 4	4	4	-2 (common in compound), -1 (mainly in peroxides, such as H_2O_2)

The unphysical polar catastrophe scenario can be resolved by offsetting the electric field so that the average $\mathbf{E}$ equals zero. The resulting surface potential $\mathbf{V}$ will thus be finite. Minor

ⁱ Bulk refers to the region that is not at the phase boundaries such as interface and surface.

changes of charge arrangement at the interface are enough to offset $\mathbf{E}$. The physical mechanisms relieving this divergence of the potential are still controversial. Intermixing, oxygen vacancies and charge transfer at the interface have all been proposed.^{103, 108} However, considering the sharp interface seen in the STEM images (Chapter 3) and to stay focused on the polar discontinuity effect on Mn valence, only charge transfer is discussed. According to Janotti *et al.*, for the LaAlO₃/STO system, the LaO plane acts as a shallow donor¹⁰⁹ and transfers half of its charge to the neighboring planes above and below. Because the (Zr,Ti)O₂ plane below the (La,Sr)O plane has a higher energy for excess electrons,¹¹⁰ the (La,Sr)O plane may transfer all additional charges to the MnO₂ plane above leading to a different Mn valence at the interface. On the right hand side of the sketch of the lattice in Figure 44, the charge transfer directions are marked by the red arrows. The effect is equivalent to a charge transfer from the surface region to the interface region. Because of the charge transfer to the interfacial MnO₂ plane, Mn valence at the interface will deviate from its bulk valence.

Model Study

LSMO/PZT system was simulated through a two-orbital double-exchange model^{111,112} by Shuai Dong. The model Hamiltonian is formulated as¹¹²

$$H = -\sum_{\langle ij \rangle}^{\alpha\beta} t_{\alpha\beta}^{\vec{r}} (\Omega_{ij} c_{i\alpha}^{\dagger} c_{j\beta} + \text{H. c.}) + J_{AFM} \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j + \lambda \sum_i Q_{3i} \tau_{zi} + \sum_i V_i n_i, \quad (4.8)$$

where α/β are indices for two e_g orbitals, i/j denote the lattice sites, $t_{\alpha\beta}^{\vec{r}}$ are the components in the hopping amplitude tensor, $c_{i\alpha}^{\dagger}$ and $c_{j\beta}$ are annihilation and creation operators. The berry phase Ω_{ij} is

$$\cos \frac{\theta_i}{2} \cos \frac{\theta_j}{2} + \sin \frac{\theta_i}{2} \sin \frac{\theta_j}{2} e^{-i(\phi_i - \phi_j)} \quad (4.9)$$

in the infinite Hund coupling approximation, where θ and ϕ are the polar and azimuthal angles of the electron spins. Coefficient J_{AFM} has units of energy and coefficient λ is dimensionless. $\vec{S}_i$ and $\vec{S}_j$ are electron spins. Q_3 denotes the Q_3 mode of the Jahn-Teller distortions. τ_z is an orbital pseudospin operator. V_i is the Coulomb potential from the surrounding cations, electrons and oxygens. n_i is the local e_g electron density. Detailed discussions on each term can be found in Dr. Dong's article (reference 112).

This model Hamiltonian includes the known interactions discussed in Chapter 1 and has been reported as a realistic description for manganite compounds.¹¹³ The first term of the Hamiltonian describes the double-exchange hopping process. The second term is the antiferromagnetic super-exchange interaction. The third term is the electron-lattice interaction that lifts the energy degeneracy of the two e_g orbitals. The fourth term is the on-site Coulomb potential energy. The Hamiltonian is solved numerically on finite clusters and the ground state phases are determined by comparing the energies of candidate phases in the $J_{\text{AFM}}\text{-}V$ parameter space for several values of λQ_3 . The goal of this new method was to model FE field-effect transistor and target the strongly correlated electronic components that is challenging in *ab initio* simulations. This method has successfully predicted the phases that were predicted based upon density functional theory (DFT), and also suggested other possibilities that DFT failed to predict.¹¹²

A $4 \times 4 \times N$ (c direction) LSMO lattice was created to simulate the LSMO/PZT binary system. Twisted boundary conditions were adopted in the 4×4 a - b plane to reduce the artificial finite size effects via a 15×15 k -mesh. Open boundary conditions were applied along the c -axis

to distinguish the surface and interface. LSMO was simulated with a proper dielectric constant ($\epsilon_r \sim 45$) and an ideal ferromagnetic background.¹¹⁴ Both the FE polarization and polar interface were considered in the simulation. The effect of FE polarization was modeled through surface charges. PZT polarization can be as high as $100 \mu\text{C}/\text{cm}^2$,¹⁰⁰ which is equivalent to a surface charge Q of 1.0 electron charge per unit cell area (e/u.c. area). Because the film used in the PZT thickness dependence study has an upwards polarization (towards LSMO), the PZT polarization is also chosen as pointing towards LSMO in the simulation and the PZT surface charge Q is thus positive. Zero surface charge is present for comparison as well as neutral interfaces. The neutral interface is modeled as half p-type and half n-type interface. The number of the unit cells N in c directions is set as 10 in the current simulation, though other thicknesses were also explored and presented in the LSMO thickness dependence section.

Figure 45: (a) Plane resolved Mn valence in LSMO (4 nm)/PZT. Both effects of PZT polarization and polar interface are considered. Q is the PZT surface charge in the unit of electron charge per unit cell area (e/u.c. area). “Neutral” and “n-type” refer to neutral and n-type interface. Index i is the sequence number of the MnO_2 plane counted from the interface. (b) Plane resolved Mn valence under varied PZT surface charge Q .

Figure 45 (a) shows the resulting theoretical Mn valence of each MnO_2 plane under four combined conditions of surface charge and termination plane. The plane number i represents the

i^{th} MnO_2 plane counted from the interface. t_{2g} is always half filled for LSMO (Chapter 1). The e_g charge density determines the Mn valence. The bulk Mn valence 3.3 (70% Mn^{3+} and 30% Mn^{4+}) is marked in pink on the left axis. Both the n-type interface and upwards polarization direction lead to an infusion of electrons to the interfacial LSMO (interfacial Mn valence < 3.3). This may explain why the interface terminations determine the polarization directions of thin FE films in the research of Yu *et al.*¹¹⁵ The infused electrons greatly suppress Mn valence near the interface (small i). Farther away from the interface, the Mn valence gradually restores to 3.3 and is fully restored at around the 7th MnO_2 plane, which is about $7 \times 0.4 \text{ nm} = 2.8 \text{ nm}$ from the interface. Lu *et al.*¹¹⁶ recently measured the magnetization modulation length scale at a $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3/\text{BaTiO}_3$ interface and found it to extend 3 nm into $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$. Their magnetization length scale is consistent with our theoretical length scale of charge restoration. The correlation between Mn valence and LSMO magnetization was also studied in this dissertation and is included in section 4.2. The above observations also demonstrate that the effects from the polar interface are smaller than from the large PZT polarization. The simulated Mn valence at the surface ($i = 10$) is around +3.3 or larger. However, the surface is affected by the absence of apical oxygen coordination. The surface Mn valence would be smaller than in the bulk due to higher $3z^2-r^2$ orbital occupancy in surface Mn.¹¹⁷ Smaller Mn valence was observed both in the current experiment and in literature. Thus, both the surface and the interface valence should be different than the bulk valence value.

The effects of varied PZT surface charge were also modeled and shown in Figure 45 (b). The depth dependence of Mn valence exhibited in the large surface charge case ($Q = 1.0 \text{ e/u. c. area}$) in Figure 45 (a) is still true for smaller Q 's, though the deviation of Mn valence is smaller when the surface charge is smaller. This is consistent with the hypothesis that the Mn valence changes less for smaller PZT surface charge due to the emergence of in-plane domains at thicker

PZT. Note that the PZT thickness dependent Mn valence data included the LSMO buffer contribution because the measurements were in FL mode. For single domain PZT, PZT polarization would point towards the top LSMO layer and away from the bottom LSMO layer. One of the LSMO layers would be depleted with electrons while the other is infused with electrons according to the hypothesis. The effects on Mn valence, however, do not cancel out, probably because the change in Mn valence at the bottom interface was smaller than that at the top. The thickest part of the top LSMO layer was 3.2 nm while the bottom LSMO layer was around 5 nm, which were consistent with the fluorescence element mapping results. The screening electrons at the top interface was condensed to the thin top LSMO while the infused holes at the bottom interface spread out more. The Mn valence at the top interface therefore was changed more drastically than those at the bottom interface when PZT was single domain. The PZT polarization at the bottom interface should also vary less with changing PZT thickness than the top due to larger lattice relaxation at thicker PZT. The PZT lattice is strained by the substrate for the first several layers and gradually relaxed to its bulk lattice as PZT grows thicker. The interface between PZT and the bottom LSMO would therefore be relatively similar throughout the change of PZT thickness, while the top interface between LSMO and PZT are more thickness dependent. To conclude, the measured Mn valence in Figure 39 was influenced most by the Mn valence at the top LSMO/PZT interface and reflect the behavior of Mn valence at the top interface.

4.5 Dependence of Mn valence on LSMO thickness

PZT thickness dependence of Mn valence indicated that Mn valence was not uniform throughout the LSMO layer. Because the interfacial Mn valence is especially interesting for the understanding of coupling mechanism, Mn valence was measured in two modes with drastic different attenuation length—TEY mode at the Mn *L*-edge and FL mode at the Mn *K*-edge¹¹⁸—to

determine the depth dependence of Mn valence in LSMO and the interfacial Mn valence. The experimental details and results are summarized in this section. Discussions and in-depth interpretations are included in the next section.

Measurement in TEY mode

Figure 46: Setup scheme for beamline 6.3.1. (Reference 119. Reprinted from AIP Conf. Proc., 705, 454 (2004) with the permission of AIP Publishing.) This is a bending magnet beamline operating at an energy range of 200 to 2000 eV. It features a variable-line-spacing plane-grating monochromator, which scans the wavelength through rotating the grating. The light exits a fixed slit and is refocused on the reflectometer. The reflectometer is used to position the samples to within $4 \mu\text{m}$ with an angular position of 0.002° .

The Mn *L*-edge absorption spectra used for the quantitative valence analysis were taken in TEY mode at beamline 6.3.1 of ALS.¹¹⁹ The setup scheme for the beamline is shown in Figure 46. This beamline is built to provide soft x-ray measurement of XAS, XMCD and x-ray magnetic linear dichorism. An end station photo is displayed in Figure 47. The magnet can supply up to 2 T magnetic fields parallel to the x-ray propagation direction. The incident intensity is monitored by

an Au mesh which absorbs $\sim 20\%$ of incident x-rays and produces a reference photo current I_0 . Samples are transferred to the vacuum chamber from the top. Sample temperatures can be lowered to 15 K by a cryostat.

Figure 47: End station of beamline 6.3.1. X-rays coming from the right are monitored by the Au mesh and incident onto the sample inside the vacuum chamber in between the 2T magnet. (Courtesy of Elke Arenholz, Advanced Light Source, Lawrence Berkeley National Laboratory.)

The samples were positioned at a 30° grazing angle and kept at 80 K during the measurement. The strength of the external magnetic field was set at 1 T. Because LSMO is ferromagnetic, dichroic spectra are generated when the field direction is reversed (refer to Chapter 2 XMCD). To greatly reduce the effects from the small variations of incident x-rays, the magnetic field direction was reversed at every energy stop and the photo current from the sample was recorded under both magnetic directions. The average of the two dichroic spectra is the absorption spectra used for valence analysis. The difference of the two is the XMCD spectra, which is discussed in the XMCD result section in this chapter. The L_3/L_2 ratio (Chapter 4, 4.1.1) method was used to process the absorption spectra and calculate the valence. The reliability of valence

estimation was confirmed by comparing the features of the spectra to the reference spectra. Figure 48 (a) presents the LSMO thickness dependence data of Mn valence from sample 2 and 3. These two samples are identical except for the top LSMO thickness ranges. The data were obtained for a constant PZT thickness of 150 nm. The obtained Mn valence increased with increasing LSMO thickness. The raw spectra correspond to Mn valence 2.46 (sample 2 at 0.5 nm), 2.58 (sample 3 at 0.5 nm), and 2.94 (sample 3 at 10 nm) are shown in Figure 48 (b). They showed significant similarity to reference spectra with similar valence.

Figure 48: (a) Mn valence versus top LSMO thickness at 150 nm PZT measured in TEY mode. Sample scheme for the two samples is shown in the inset. The uncertainties were estimated by the standard deviations from repeated measurement results. (b) Raw spectra with similar valence to the reference spectra (Figure 34) are presented for comparison.

Measurement in FL mode

Mn *K*-edge XAS was also measured along $t_{PZT} = 150$ nm of sample 2 and 3 in FL mode at beamline 10.3.2 of the ALS. The experimental setup and procedures for data analysis were introduced in section 4.3. The detected Mn valence versus top LSMO thickness (sample scheme in the inset of Figure 48) is shown in Figure 49 (a). As discussed in Chapter 2, the attenuation length of the fluorescence x-rays is a few micrometers at the Mn *K*-edge (~ 6 keV), and thus the 5

nm LSMO buffer layers underneath the 150 nm PZT also contribute to the detected signal. The attenuation length of the TEY measurement, however, is determined predominately by the mean free path of the ejected electrons. Mn 3s electrons have a mean free path of about 1.2 nm at Mn *L*-edge energies,¹²⁰ which corresponds to a probe depth of about 5 nm. The buffer layers therefore do not contribute to the final result of the TEY measurement.

Figure 49: Mn valence versus top LSMO thickness at 150 nm PZT measured in FL mode. (a) Due to the buffer (5 nm LSMO) contributions, the detected Mn valence is boosted at thin LSMO. (b) After the buffer contributions were subtracted (Right), the apparent Mn valence at thin LSMO decreased.

The LSMO buffer layer contributions to the FL measurements were subtracted (buffer subtraction examples for both samples are included in Figure 75 in the appendix) to directly compare the FL and TEY results. The buffer XAS were measured at the flat borders before the start of the top LSMO wedges in FL mode. Noisy spectra at ultra-thin LSMO were dropped. Other subtracted spectra were normalized and fitted by the linear combination method. The accuracy of the fine structure from the best fits is shown in Figure 50 at two thicknesses of LSMO. Estimated from the linear combination fitting results, a new set of Mn valence for the top LSMO only is shown in Figure 49 (b). The uncertainties were estimated by the standard derivations among the

legitimate best fits using 2 to 6 combinations of reference spectra, which provides uncertainties among estimations at difference confident level. The obtained Mn valence in FL mode also increases with LSMO thickness. Even after the buffer subtraction, the overall Mn valence in FL mode is still higher than those in TEY mode due to the surface sensitive of TEY measurement and lower Mn valence at the LSMO surface¹²⁰ than in the bulk.

Figure 50: Fitting results at two thicknesses of LSMO. (Reference 76. Reprinted from J. Zhou, V.Tra, S. Dong, R. Trappen, M. Marcus, C. Jenkins, C. Frye, E. Wolfe, R. White, S. Polisetty, J. Lin, J. LeBeau, Y. Chu and M. Holcomb, Appl. Phys. Lett., 107, 141603 (2015). with the permission of AIP Publishing.)

4.6 Determining Mn valence at the interface

Mn valence from each MnO_2 plane can be estimated from the TEY and FL experimental results. The depth dependence of plane contributions in both techniques is discussed. A depth dependent Mn valence model is proposed for the films and fitted to the experimental data. The surface, interface and bulk Mn valence as well as the length scale over which surface and interface valence varies from the bulk are estimated based upon residual minimizing of the model.

Depth dependence contributions in TEY and FL measurements

In TEY (and even slightly in FL), the surface layer contributes much more strongly to the measurement of valence than the layers below it. These depth dependent contributions in TEY and FL measurements come from the attenuation of signals. The attenuation is from two parts: the attenuation of the incident x-rays and the attenuation of the outgoing electrons/fluorescence x-rays. Figure 51 illustrates the attenuation in both modes. X-rays attenuate at a rate of $e^{-s/\lambda}$ where s is the distance that x-rays traveled and λ is the attenuation length of x-rays at a specific energy in a specific material. Along the depth z (origin at the sample surface), the x-rays decay at a rate of $e^{-z/(\lambda \sin \theta)}$, where z is the depth, and θ is the angle between the x-ray propagation direction and the sample surface. A similar relationship also applies to the outgoing x-rays. Electrons, however, are driven out of the sample by an electric field perpendicular to the sample surface. The attenuation of electron yield with regards to depth x is e^{-x/λ_e} , where λ_e is the electron mean free path. Combining both the attenuations from the incident x-rays and outgoing electrons, the attenuation in TEY mode is $e^{-z/(\lambda_x \sin \theta_x)} e^{-z/\lambda_e} = e^{-z/L_t}$, where the attenuation length of incident x-rays and the incident angle are specified as λ_x and θ_x for TEY mode. L_t is the effective TEY attenuation length which satisfies

$$\frac{1}{L_t} = \frac{1}{\lambda_x \sin \theta_x} + \frac{1}{\lambda_e}, \quad (4.10)$$

Similarly, the effective FL attenuation length L_f is

$$\frac{1}{L_f} = \frac{1}{\lambda_i \sin \theta_i} + \frac{1}{\lambda_f \sin \theta_f}, \quad (4.11)$$

where the subscripts i and f stands for “incident” and “fluorescence”.

Figure 51: Attenuation in TEY and FL modes.

X-ray attenuation lengths λ_x , λ_i , and λ_f depend on the x-ray energy and the material traversed. For LSMO with a density of 6.6 g/cm^3 ,¹²¹ λ_x ($E = 640 \text{ eV}$; an L edge absorption energy) $= 0.2 \text{ }\mu\text{m}$, λ_i ($E = 6.5 \text{ keV}$; the K edge absorption energy) $= 3.9 \text{ }\mu\text{m}$, λ_f ($E = 5.9 \text{ keV}$; the fluorescence x-ray energy) $= 4.5 \text{ }\mu\text{m}$ as estimated by Hephaestus¹²², an XAS program. The angles are $\theta_x = 30^\circ$, $\theta_i + \theta_f = 90^\circ$, $\theta_i \sim 3^\circ$ in the measurements. If λ_e for LSMO is 1.2 nm ,¹²⁰ L_t is roughly 1.18 nm . L_f is roughly $0.2 \text{ }\mu\text{m}$.

Figure 52: Illustration for the weighted contribution of each MnO_2 plane to the total signal. MnO_2 planes lie in the center of each purple box (simplified LSMO lattice). Because of the exponential decay of signal with depth, the contribution of each plane decreases with increasing depth z . The total signal, which is the sum of signals from all contributing planes, increases with the sample thickness t . The thickness t varies in various measurement spots. The curvature of exponential decay curve differs in TEY and FL measurement, which are discussed in detail in the main text.

TEY and FL results can be calculated as a weighted sum of the Mn valence from each MnO₂ plane, which is illustrated in Figure 52. Non-LSMO layers do not contribute to the element specific signal because they do not contain any Mn. The weighted contribution of a MnO₂ plane at depth z from a LSMO film with thickness t could be estimated as the ratio of the signal from the lattice plane at z to the total signal from the sample (LSMO), i.e.

$$\frac{\int_{z-0.2}^{z+0.2} \exp\left(-\frac{x}{L}\right) dx}{\int_0^t \exp\left(-\frac{x}{L}\right) dx}, \quad (4.12)$$

where L is L_t for TEY mode and is L_f for FL mode. The number 0.2 comes from the unit cell lattice spacing of nearly 0.4 nm. The sizes of the samples are comparable to the TEY L_t . Thus, the TEY numerator drops drastically with increasing depth. The TEY denominator, which is the sum of all signals, increases less than 1% beyond a thickness of 5 nm for $L_t \sim 1.18$ nm.

These samples, however, are significantly thinner than the effective FL attenuation length L_f because $z \leq t \leq 10$ nm, $L_f \sim 0.2$ μm . Therefore,

$$\begin{aligned} \exp\left(-\frac{z}{L_f}\right) &\approx 1 - \left(\frac{z}{L_f}\right), \\ \int_{z-0.2}^{z+0.2} \exp\left(-\frac{x}{L_f}\right) dx &= -L_f \exp\left(-\frac{x}{L_f}\right) \Big|_{z-0.2}^{z+0.2} \approx 0.4. \end{aligned} \quad (4.13)$$

That is to say, the numerator of equation (4.10), or the contribution of a single MnO₂ plane, is a constant 0.4 (unitless) for thin films. The denominator of equation (4.10) — the contributions from all planes—increases almost proportionally to the thickness t for thin films. For a fixed thickness t , the denominator is a constant. Therefore all planes contribute approximately the same amount to the total signal in FL mode regardless of the depth in a thin film. Note that this is not true for thicker films.

It has been demonstrated above that TEY and FL modes have drastically different attenuation length scales. It is this difference that makes the depth dependence study possible.

Depth dependence of Mn valence

In addition to the depth dependence of the atomic layer contributions to TEY and FL measurements discussed in the last section, the Mn valence of the LSMO thin film vary with depth. The depth dependence of the Mn valence in LSMO thin films was simulated theoretically by Shuai Dong with varied LSMO thickness. His simulation results are shown in Figure 53 and were used to establish a reasonable valence model to fit the experimental data. The simulation details are discussed in section 4.4.2. The PZT surface charge was set at 0.8 e/u.c.area. On the x axis of Figure 53, the number 1 refers to the first MnO₂ plane at the interface, whereas 8 would be at the surface of an eight unit cell film. The total number of considered MnO₂ planes N varies from 1 to 8, as indicated by the figure legend. This figure suggests that the Mn valence of each individual plane is approximately the same for films thicker than 2 unit cells, and that the Mn valence has a nearly identical depth dependence at the given PZT surface charge. The Mn valence restores to the bulk Mn valence 3.3 at around $i = 6$, slightly shorter than the former simulation result with $Q = 1.0$ e/u.c.area. This difference in the length scale over which the valence is deviated from the bulk value indicates that the depth dependence of Mn valence rely on the strength of PZT polarization. The deviation of Mn valence from the bulk value $V_d(z)$ was modeled from the theoretical results and found to follow an exponential decay

$$V_d(z) = (V_{int} - V_{bulk})\exp(-\frac{t-z}{L_i}), \quad (4.14)$$

where V_{int} is the Mn valence in the closest MnO₂ plane to PZT, V_{bulk} is the Mn valence in the interior region of LSMO, L_i is the characteristic length over which the valence change drops 1/e between the interface and bulk values.

Figure 53: Depth dependent Mn valence. N is the total number of MnO_2 planes. i is the plane number counted from interface. Q is the PZT surface charge used for simulation.

While the above considers the valence deviation at the interface, the surface valence is also different than the bulk due to the absence of apical oxygen. An exponential dependence was chosen to model the surface valence deviations with depth. The depth dependence of the Mn valence after the inclusion of the two exponential terms at both the surface and interface is

$$V(z) = \frac{V_{bulk}}{2} [1 - \alpha e^{-z/L_s}] + \frac{V_{bulk}}{2} [1 - \beta e^{-(t-z)/L_i}], \quad (4.15)$$

where α and β are the parameters that satisfy the boundary conditions $V(z = 0) = V_{surf}$ and $V(z = t) = V_{int}$, V_{surf} is the Mn valence from the top MnO_2 plane, L_s is the characteristic length over which the valence changes $1/e$ in the surface region.

Mn valence determination

The measured Mn valence $\overline{V(t)}$ from a LSMO film with a thickness t is a weighted (equation (4.12)) average of depth dependence Mn valence $V(z)$ (equation (4.15)) from all contributing planes and can be expressed as

$$\overline{V(t)} = \frac{\sum_{i=0}^t V(z_i) \int_{z_i}^{z_{i+1}} \exp\left(-\frac{z}{L}\right) dz}{\int_0^t \exp\left(-\frac{z}{L}\right) dz}, \quad (4.16)$$

where i stands for the i th unit cell, z_i is the distance from the surface to the unit cell center, $V(z_i)$ is the Mn valence described in equation (4.15), L is L_t for TEY mode and is L_f for FL mode.

A global fitting program was written by Robbyn Trappen to fit equation (4.14) to the TEY and FL measurement results. L_f did not significantly affect the simulation results since $L_f \gg t_{LSMO}$ and thus was kept at 0.2 μm . Attenuation length L_t , interface and surface characteristic lengths L_i and L_s , and valence values V_{surf} , V_{bulk} , and V_{int} were all allowed to vary during the fitting. These values were determined by searching for the smallest sum of absolute values of residuals within the range of the experimental uncertainties. A residual is the difference between the fitting result and the experimental data. For the fitting results with the smallest absolute sums of residuals, L_s turns out to be larger than L_i . The attenuation length L_t was fitted to be approximately 2.5 u.c. = 1.0 nm, which is close to the 1.18 nm estimated in the previous section. The estimated valences are $V_{surf} \approx 2.0$, $V_{int} \approx 2.52$ and $V_{bulk} \approx 3.36$. The best fit results with the residuals are plotted in Figure 54 against the measured values (the plane-resolved fitting results for two LSMO thicknesses are shown in Figure 76 in the Appendix). The error bars (uncertainties) are on the experimental data. The uncertainties of the TEY experimental results (Figure 54 (a)) were estimated by the standard derivations among independent result of repeated spectrum at the same measuring spot. The uncertainties for the FL results (Figure 54 (b)) were the standard derivations among the best fit linear combinations with varied number of reference spectra. Smaller interfacial Mn valence than the bulk indicates a higher concentration of electron charges at the interface, which is consistent with the hypothesis that electrons are drawn to the interfacial LSMO to screen the PZT polarization. Polar discontinuity may also play a role, although it is challenging to separate its contribution from the screening effects. Because electrons are drawn to the interface from the bulk region, the bulk Mn valence is slightly larger than 3.3.

Figure 54: Global fitting results for Mn valence measured in (a) TEY and (b) FL modes.

The fitting results also show that the residuals are larger for $t_{\text{LSMO}} \leq 3$ nm, which may be due to the slightly different values for some parameters at ultrathin LSMO, such as the surface and interface valences. To screen the PZT polarization, higher charge densities were assumed to be present in ultrathin films than in thicker films, which led to smaller valences in ultrathin films than in thick films, as shown in Figure 53. The length scales and structure of ultrathin films might also differ from those of thick film. These could all contribute to the deviation of the fitting results to the experimental data at ultrathin LSMO.

4.7 X-ray magnetic circular dichroism (XMCD)

The magnetization of LSMO was linked to this Mn valence through XMCD studies. The Mn *L*-edges correspond to the transitions of $2p$ electrons to $3d$ states. Because the magnetic properties of transition metals originate from the unpaired spins of electrons in the $3d$ -orbitals, Mn *L*-edge XMCD is ideal for magnetic analysis. XAS spectra were taken at beamline 6.3.1 in TEY mode at a 30° grazing angle under two opposite 1 T magnetic fields. The difference spectra (i.e. XMCD) between the XAS under the two opposite magnetic fields were normalized by dividing the average of the two. These normalized results are shown with the corresponding LSMO

thicknesses in Figure 55. Each XMCD spectrum was originally located around zero but are shifted in Figure 55 for easy comparison. With the increase of LSMO thickness, larger intensity changes occurred in XMCD, indicating an increase of LSMO magnetization, which is consistent with former experimental results that the magnetization of LSMO is thickness dependent.¹²³ A 1.5 nm magnetic dead layer, typical in LSMO system,¹²⁴ was also observed. Taking the spread of the XMCD spectrum (i.e. maximum minus minimum) as the representative strength of magnetization, the correlation between Mn valence and LSMO magnetization were established and plotted in Figure 56. The strength of magnetization in LSMO increased as Mn valence increased.

Figure 55: Thickness dependent XMCD results.

Figure 56: Correlation between LSMO magnetization and Mn valence.

Sum rule

The XMCD sum-rules¹²⁵

$$m_{orb} = -\frac{4\int_{L_3+L_2}(\mu_+-\mu_-)d\omega}{3\int_{L_3+L_2}(\mu_++\mu_-)d\omega} (10 - n_{3d}), \quad (4.17)$$

$$m_{spin} = -\frac{6\int_{L_3}(\mu_+-\mu_-)d\omega - 4\int_{L_3+L_2}(\mu_+-\mu_-)d\omega}{\int_{L_3+L_2}(\mu_++\mu_-)d\omega} (10 - n_{3d}) \left(1 + \frac{7\langle T_z \rangle}{2\langle S_z \rangle}\right)^{-1} \quad (4.18)$$

were applied to quantitatively estimate both the orbital and spin magnetizations of LSMO in units of μ_B/atom . In the sum-rules, m_{orb} and m_{spin} are the orbital and spin magnetic moments in units of μ_B/atom , $\mu_+ - \mu_-$ is the difference of the two spectra taken under two opposite magnetic fields, $\mu_+ + \mu_-$ is the sum of the two. n_{3d} is the number of 3d electrons per cation. Because Mn valence equals to the total number of electrons lost to surrounding atoms, the number of 3d electrons are

$$n_{3d} = 5 - (V_{Mn} - 2) = 7 - V_{Mn}, \quad (4.19)$$

where V_{Mn} is the Mn valence. For nominal Mn valence 3.3, $n_{3d} = 3.7$. $\langle T_z \rangle$ is the expectation value of the magnetic dipole operator. $\langle S_z \rangle$ is half of m_{spin} in Hartree atomic units. The contribution of $7\langle T_z \rangle / 2\langle S_z \rangle$ is on the order of 10^{-3} ,¹²⁵ which can be neglected in the calculations.

After neglecting the contribution of the term $7\langle T_z \rangle / 2\langle S_z \rangle$, the sum rule equations become

$$m_{orb} = -\frac{4I_1}{3I_0} (3+V_{Mn}) \quad (4.20)$$

and

$$m_{spin} = -\frac{6I_2-4I_1}{I_0} (3+V_{Mn}), \quad (4.21)$$

where $I_0 = \int_{L_3+L_2} (\mu_+ + \mu_-) d\omega$, $I_1 = \int_{L_3+L_2} (\mu_+ - \mu_-) d\omega$, and $I_2 = \int_{L_3} (\mu_+ - \mu_-) d\omega$. The uncertainties of the orbit and spin magnetizations can be estimated from the propagations of the uncertainties from the integrals and the valences. The mathematical expressions are

$$\delta m_{orb} = |m_{orb}| \sqrt{\left(\frac{\delta I_0}{I_0}\right)^2 + \left(\frac{\delta I_1}{I_1}\right)^2 + \left(\frac{\delta V_{Mn}}{3+V_{Mn}}\right)^2} \quad (4.22)$$

and

$$\delta m_{spin} = |m_{spin}| \sqrt{\left(\frac{\delta I_0}{I_0}\right)^2 + \frac{(3\delta I_2)^2 + (2\delta I_1)^2}{(3I_2 - 2I_1)^2} + \left(\frac{\delta V_{Mn}}{3+V_{Mn}}\right)^2}. \quad (4.23)$$

Figure 57: Integrations of (a) XAS and (b) XMCD.

Figure 57 shows a representative graph for the integration of a XMCD and XAS spectrum measured at $t_{LSMO} = 10$ nm. The two XAS spectra taken at different magnetic fields were first normalized and flattened. A direct subtraction of the two produced the bottom XMCD spectrum. The step-like function from equation (4.4) was subtracted from the sum spectra and shown in black at the top figure. The dash-dot lines are the integrated results of XMCD and XAS. After taking into account the 30° incident angle and the degree of circular polarization (90%), the orbit and spin magnetic moment were estimated to be $0.036 \pm 0.007 \mu_B/\text{Mn}$ and $0.28 \pm 0.05 \mu_B/\text{Mn}$ for $t_{LSMO} = 10$ nm. Other orbital and spin moment values are plotted in Figure 58 against the Mn valence. Figure 58 shows that the spin moment is larger than the orbital moment at all Mn valences and is also larger for bigger Mn valence where less d electrons are present.

Figure 58: The orbital and spin magnetic moment versus Mn valence in LSMO. The uncertainties were estimated by the uncertainty propagation equations. The standard deviation among the results of repeated spectra were used as integral uncertainties.

In conclusion, this chapter includes the spectroscopic results of the LSMO/PZT heterostructures. The Mn x-ray absorption spectra were measured along both the LSMO and PZT wedge. The Mn valence was estimated from these absorption spectra and found to increase with both LSMO and PZT thickness. The dependence of the Mn valence on PZT thickness might due

to a change in effective net surface charge at the interface. This idea was tested experimentally by measuring the PZT domain structures at several PZT thicknesses and the Mn valence at two opposite PZT polarization states. PZT transitioned from monodomain to polydomain along the wedge direction. The carrier densities, which are affected by the PZT polarization/surface charge, change the Mn valence at the interface. As observed in the experiments (Figure 43), Mn valence shifted consistently to larger values when the PZT polarization direction pointed away from LSMO; when the polarization of PZT pointed towards LSMO, Mn valence shifted to smaller values, which exclude the possibility that LSMO and PZT might be coupled by strain alone. Theoretical modeling was also carried out to simulate the charge densities in Mn e_g orbitals under the influence of PZT surface charge, and additionally, the effect of polar interface. Both PZT surface charge and polar interface were found to influence the charge density of Mn e_g orbitals, which is potentially useful for device design. The dependence of Mn valence on LSMO thickness is possibly due to the varying Mn valence at the surface and interface. In order to determine the depth dependence of Mn valence, x-ray absorption spectra were taken at two measurement modes with drastic different attenuation length/probe depth. Through global fitting the valence results from both modes, the depth dependence and the interfacial Mn valence were determined. Last but not the least, the correlation between the Mn valence and LSMO magnetization was explored by measuring XMCD. Larger dichroism was found to associate with larger Mn valence states.

Chapter Five: Photoemission Electron Microscopy (PEEM) Results

This chapter includes the microscopic results of the samples from PEEM. Angular dependence of PZT domain images were determined. Domains of LSMO were compared to the uncompensated spin images taken with circular polarized x-rays at the Ti edge. The result suggested that the induced Ti spin magnetic moment in PZT oriented perpendicular to the LSMO domain directions.

5.1 Angular dependence of linear dichroism on polydomain PZT film

Growth of PZT

In order to understand the LSMO/PZT system, it is useful to measure each individual layer. PEEM imaging on FM materials such as LSMO is well established while PEEM imaging of FE materials has not been widely studied. For the purpose of studying PZT linear dichroism, a 225 nm polydomain PZT/ 15 nm $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (LSCO) heterostructure was grown by J. Karthik from Dr. Lane Martin's group. The heterostructure was grown by pulsed laser deposition (PLD) on a 5 mm by 5 mm LaAlO_3 (LAO) substrate with a KrF excimer laser ($\lambda = 248$ nm). The laser fluence was kept at about 1.5 J/cm^2 throughout the growth of the heterostructure. The laser repetition rate was 3 Hz for the bottom electrode LSCO and 2 Hz for the PZT. The oxygen atmosphere was at 100 mTorr for LSCO and at 200 mTorr for PZT. The substrate temperature was 650 °C for LSCO and 600 °C for PZT. The sample was cooled to room temperature at 5 °C/min with a 760 mTorr oxygen atmosphere after the growth. This high pressure reduces the presence and effect of oxygen vacancies.

Domain structures

Figure 59: (a) Illustration of the poled pattern along with its out-of-plane PFM image. On the top left is the top view of the sample in blue. The poled pattern is delineated in green. The squares are named A, B and C. A scratch is made in the vicinity for easy locating the measuring spots. Silver paint at the corner created a contact to the bottom electrode LSCO for poling PZT. (b) Out-of-plane and (c) in-plane PFM images of A. The purple region in (b) has a polarization pointing downwards. The yellow is the as-grown area where the polarization points up. The dark cross-hatched a domains in (c) distribute over the bright orange background of c domain. (Courtesy of Mikel Holcomb, West Virginia University.)

A pattern (Figure 59 (a)) consisting one single square and two concentric squares was written on PZT by J. Karthik to define the out of plane ferroelectric domain direction and to easily locate the investigation area. These squares were written by applying vertical electric fields on the PZT using the bottom electrode LSCO and a Cr/Pt coated cantilever. Dual-AC resonance tracking

(DART)¹²⁶ PFM was used to image the domains. An out-of-plane PFM image of the pattern is shown at the lower right corner of Figure 59 (a). The dark regions are the areas poled downwards. Similar square patterns were introduced and discussed in the Chapter 4 PFM measurement.

Figure 59 (b) and (c) shows the detailed out-of-plane and in-plane domain images of the singly poled square A. This square was created by applying a downward 22.5 V electric field. The purple color of the Figure 59 (b) denotes a vast majority of c domains pointing downwards. The surrounding as-grown area has an opposite contrast to the purple square, indicating an upward natural domain direction. The dark cross-hatched pattern in Figure 59 (c) are the in-plane a domains. They distribute over the bright background of c domains. This polydomain structure of PZT provides a good platform for angular dependence studies of PEEM images since each domain creates a different angle to the incident x-ray.

Linear dichroism of PZT

Ti L -edge XAS were taken at beamline 6.3.1 of ALS at room temperature. Linearly polarized x-rays were incident on the sample at 30° and 90°. The resulting spectra are plotted in Figure 60 in black and red. The difference of the two spectra is plotted in blue. Ti L -edges showed four distinct peaks due to the spin-orbit interaction and the crystal field interaction from the neighboring lattices.¹²⁷ A large dichroism effect was observed around the L_{3A} peak; PEEM images were therefore taken in the vicinity of the L_{3A} peak. As it will be discussed later, the PEEM intensity depends on the angle from the ferroelectric direction and the polarization of the incident x-rays. Therefore each PEEM image has a contrast between different domain directions and the contrast changes with the x-ray polarization angle.

Figure 60: Linear dichroism of PZT at the Ti L -edge. The x-ray absorption spectra at two incident angles are plotted in black and red. The difference spectrum between the two is plotted in blue, where the dichroism is the largest at around the L_{3A} peak.

PEEM images of PZT

PEEM images of the poled pattern of PZT were taken at beamline 11.0.1 of the ALS at the Ti L_{3A} edge ± 0.15 eV. The sample geometry is shown in Figure 61 (a). The linearly polarized x-rays were incident on the sample surface at a grazing angle of 30° . The x-ray polarization angle α was changed from 0° to 90° in steps of 10° . The double yellow arrows in the Figure 61 (a) is along $\alpha = 0^\circ$ and make a 60° angle to the sample surface. The double green arrows denotes $\alpha = 90^\circ$ and is parallel to the sample surface. Similar to the process for imaging antiferromagnetic domains,¹²⁸ the two images taken at Ti L_{3A} edge ± 0.15 eV, at which a large dichroism was observed in Figure 60, were aligned and divided to enhance the contrast. The final images from poled square A at $\alpha = 0^\circ, 40^\circ, 60^\circ$, and 90° are shown in Figure 61 (b) to (e). The x-ray propagation direction is marked in Figure 61 (e). The image contrast comes from the non-spherical electron density oriented in different directions, which reflect the domain structure of PZT. Because x-ray absorption is angular

dependent, different domains show different intensity depending on the projection of the ferroelectric direction onto the incident x-ray polarization axis. Figure 61 (b) shows both the a (a_1 and a_2) and c domains, which are delineated in black, red and blue. When the incident x-ray polarization changed from 0° to 90° , the image contrast reversed as expected for linear dichroism. The a domains went from bright to dark while the c domain changed from dark to bright. At 40° and 60° , one group of a domains is more visible than the other, illustrating the different angle dependences between the two in-plane domain types.

Figure 61: (a) Scheme for the orientation of incident x-rays and the polarization directions with regards the sample. (b)-(e) Divided PEEM images with enhanced contrast at different x-ray polarization (Reference 129. © IOP Publishing. Reproduced with permission. All rights reserved.).

The intensity changes of each type of domains with x-ray polarization angles were statistically summarized by Srinivas Polisetty¹²⁹ and presented in Figure 62 (a). The upwards and downwards triangles represent the intensities of two types of a domains with varied x-ray polarization. The c domain image intensities are represented by round circles. The image intensities of these domain types were identified by using image masks to separate contrast from different domain types. The average intensity within each individual mask was the domain image intensity. At $\alpha \sim 50^\circ$ and 60° , for example, the intensities of c domain images are close to one of the a domains, thus explain why one group of a domains was less observable than the other in PEEM images as shown Figure 61 (c) and (d). The angular dependence of all three domains were found to be described well by

$$I = (1 - \cos^2 \theta_F) \times \text{constant}, \quad (5.1)$$

where θ_F is the angle between the polarization of the incident x-rays and the ferroelectric domain direction. Based on the geometry of the setup shown in Figure 61 (a), the angle between the sample plane and the x-ray polarization plane is 60° . If the intersection between the sample plane and the x-ray polarization plane is named line l , polarization direction $\alpha = 0^\circ$ is perpendicular to l while $\alpha = 90^\circ$ is parallel l . The right sides of Figure 61 (b) to (e) PEEM image squares are also parallel to the intersection of the two planes. If the angle between the intersection and an in-plane domain direction is β , $\cos \theta_F$ can be expressed as

$$(\cos \theta_F)_\alpha = \sin \alpha \cos \beta + \frac{\cos \alpha \sin \beta}{2}, \quad (5.2)$$

where α is the x-ray polarization angle. The value of β is 135° for a_1 domains and 45° for a_2 domains. c domains point directly out of the plane of the sample. The angle between c domains and x-ray polarization plane is 30° . Thus, the angle between the c domains and the x-ray polarization angle α is

$$(\cos \theta_F)_c = \frac{\sqrt{3} \cos \alpha}{2}. \quad (5.3)$$

Figure 62 (b) plots the angular part of equation (5.1) against polarization angle α , which matches the general angular dependence of the experimental data. The red and black curves calculated from the equation, however, appear more separated than the correspondent experimental result. This discrepancy might due to the fact that the a domains are quite small. The masks used to identify the domain images might include more than one domain type.

Figure 62: (a) The experimental data and (b) the modeling results (angular part of equation (5.1)) of the domain intensities vs. the incident x-ray polarization α at Ti L -edge. (Reference 129. © IOP Publishing. Reproduced with permission. All rights reserved.)

The angular dependence of the domain images were further investigated and confirmed by rotating the sample by 45° . The other settings were kept the same as the above measurement: the incident x-rays was at a 30° grazing angle to the sample surface and the x-ray polarizations changed from 0° to 90° in steps of 10° . The orientations of the sample domains and x-rays, the PEEM images from the square A at $\alpha = 0^\circ$, 50° , and 90° , the angular dependence domain intensities and

the calculated results of the angular part from equation (5.1) are shown in Figure 63 (a) to (e). Equations (5.2) and (5.3) still apply to the a and c domains in the new orientation except that the value of β is 90° for a_1 domains and 0° for a_2 domains. Figure 63 (e) demonstrates excellent agreement between the experimental data and the cosine squared angular dependence of equation (5.1). At $\alpha = 0^\circ$, all three domains are clearly shown in the Figure 63 (b) PEEM image, which corresponds to the spread in domain intensities at $\alpha = 0^\circ$ in Figure 63 (e). Because the intensities for each domain direction were similar at around 40° to 50° (Figure 63 (e)), the PEEM image at $\alpha = 50^\circ$ (Figure 63 (c)) has a reduced contrast and appears blurry. At $\alpha = 90^\circ$, c domain intensities is the same as a_1 domains (Figure 63 (d) and (e)), whereas a_2 domains stand out. The written pattern square B and C (Figure 59 (a)) were also measured in both PEEM measurement and showed the same angular dependence of image intensities.

Figure 63: (a) Scheme for the orientation of incident x-rays and the polarization directions with regards the sample when the sample was rotated by 45° . (b)-(d) Divided PEEM images at $\alpha = 0^\circ$, 50° , and 90° . (e) Domain intensity vs. incident x-ray polarization α at Ti L -edge in the new setup. The top figure is the experimental data. The bottom figure is the angular dependence results from equation (5.1). (Reference 129. © IOP Publishing. Reproduced with permission. All rights reserved.)

The angular dependence of in-plane domain intensities demonstrates that the linearly polarized x-rays can be used to image the FE domains. It was previously suggested¹³⁰ that only the surface charges of FE materials are responsible for the image contrast of ferroelectric materials by PEEM. The surface charges modify spatially the strength of the external fields used to extract the electrons and thus produce electron yield variations across the sample surface. The surface charge from a_1 and a_2 domains in the PZT sample, however, should be equivalent and would follow the same angular dependence of x-ray polarization. The distinct angular dependence of a_1 and a_2 domains observed in PEEM images confirmed that the contrast of PEEM images may be affected by the surface charge but are determined by the non-spherical electron distributions in the FE sample. As a comparable technique to PFM, x-ray linear dichroism (XLD)-PEEM also has a unique advantage in imaging multiferroic systems. The charge and spin orders from the same site can be imaged at one setup. XLD-PEEM discussed in this section, XMCD-PEEM,^{131,132} and XMLD-PEEM^{133,134} can be applied subsequently without changing the setup by simply adjusting the x-ray energy and polarization, which has been used in imaging the LSMO-PZT layers and discussed in detail below.

5.2 PEEM imaging of the LSMO-PZT multiferroic systems

While circular dichroism is a common study of magnetism in LSMO and other magnetic materials, Ti rarely exhibits magnetic order. A pure ferroelectric layer as described above would not exhibit a change in the PEEM image contrast when switching between left and right circularly polarized light. This kind of switching has been observed and is analogous to the circular dichroism on the non-ferromagnetic element in exchange bias systems,¹³⁵ between a ferromagnetic and antiferromagnetic layer. This section will demonstrate the presence of uncompensated spins at the LSMO/PZT interface and their preferred orientation and thickness dependence. A magnetic dead

layer, below whose thickness LSMO is non-ferromagnetic, was also observed and accompanied by reduced number of uncompensated spins. This study of induced uncompensated spin at the interface may lead to a better understanding of the interfacial ME coupling effect.

PEEM imaging over the layers

PEEM can pick up layer specific information by tuning the x-ray energies to the elemental absorption edges unique to each layer, such as Mn *L*-edge for LSMO and Ti *L*-edge for PZT (Figure 64 (a)). By setting x-rays at proper polarizations (Figure 64 (b)), the magnetic (electric) domain structures of the layer produce a contrast in PEEM images. The correlations between the domains from the different layers therefore can be established because these PEEM images can be taken at exactly the same location (Figure 64 (c)).

Figure 64 shows an example of such usage of PEEM. The LSMO/PZT heterostructures were illuminated with right circularly polarized (RCP) x-rays at Mn *L*-edge, RCP x-rays at Ti *L*-edge, and linearly polarized x-rays at Mn *L*-edge, separately at two thicknesses of LSMO. The FM images for LSMO in Figure 64 (c) were obtained by dividing XMCD images recorded at the *L*₃ and *L*₂-edge energies; The FE contrast for PZT was obtained by dividing XLD images taken at the two *L*₂-edge peaks with linearly polarized x-rays. The middle images were obtained by division of the two images recorded at the Ti *L*_{3B} and *L*_{2B}-edge energies with RCP x-rays. The edge energy pairs chosen for division usually produced large opposite image contrast and the division of the images taken at the edge energy pairs further enhanced the image contrast.

Figure 64: (a) X-ray absorption spectra taken at Ti and Mn *L*-edge. Because PZT is buried underneath LSMO, the signal is a lot weaker than those from LSMO. (b) LSMO, PZT and the interface were imaged using x-rays at different polarizations. The contrast of PEEM images are produced by the dichroic absorption of x-rays at these polarizations. (c) Taken at the same location with varied x-ray settings, PEEM images show contrast from Mn XMCD, Ti XMCD and Ti XLD images, which can be used to study the correlation of each layer and the interface.

The XCD-PEEM image at Ti edge resembled both the XMCD-PEEM image of LSMO and the XLD-PEEM image for PZT for the 2 nm LSMO, as shown in Figure 64 (c). The resemblance

reduces when LSMO is thicker, probably because the magnetic domains are less sensitive to PZT domains when they are farther away from PZT. The contrast in middle images suggest that there might be induced spin structure in PZT. However, since any linearly polarized x-rays can be decomposed into the sum of a right circular and a left circular component, contrast originating from the projection of the linear dichroism in PZT needed to be eliminated first. The spins in Ti are normally compensated. When x-rays are switched between right and left circularly polarized (LCP) light, the compensated spins do not change contrast, but the induced uncompensated spins will reverse contrast. The induced uncompensated spin images can therefore be obtained by comparing the RCP and LCP images. Figure 65 compares the divided images taken with RCP (left) and LCP (middle) x-rays at Ti *L*-edge for the same region as $t_{Mn} = 4.4$ nm images in Figure 64 (c). Both divided images were normalized to the incident x-ray intensity I_0 . The difference image is the subtraction between the two normalized images. The contrast in the difference images suggests that PZT may develop uncompensated spins at the interface, which was confirmed through statistical analysis discussed in the next section. The division of XMCD-PEEM images with LCP x-rays at Mn *L*-edge is included in Appendix, along with the images taken after the heterostructure was exposed to the external magnetic field.

Figure 65: Normalized RCP (left), LCP (middle) and difference (right) images taken at Ti *L*- edge.

PEEM image process

Figure 66: Divided images obtained by dividing Mn L_3 images over Mn L_2 images with (a) RCP and (b) LCP x-rays; and divided images obtained by dividing Ti L_{3A} images over L_{3B} images with (c) RCP and (d) LCP x-rays. These images were taken at the same location and can be aligned by the two large dust particles, though other alignment techniques were also utilized. Based on the high Ti signal from the dust particles, there might be small Ti islands.

PEEM image contrast is a combined result from x-ray absorption, the work function of the material and the topographic features. Unlike any background intensity such as from surface roughness, the absorption contrast is energy dependent and can be enhanced by dividing the images taken at two energies with strong dichroism, which will be located around the absorption edges.¹³⁶ The images of the LSMO and PZT layers were taken at Mn and Ti L -edges at a grazing angle of 30° at beamline 11.0.1 of the ALS. The measurement temperature was set at 105 K, below the LSMO thin film magnetic critical temperature.¹³⁷ Based on selected energies where strong dichroism is observed, the magnetic domain images of LSMO were obtained by dividing the PEEM images taken at the Mn L_3 peaks by the images corresponding to the Mn L_2 peaks. Similarly, the induced spin structures of PZT were obtained by dividing the PEEM images of Ti taken at the L_{3B} peaks over the L_{2B} peaks. A set of the divided RCP and LCP images are shown in Figure 66. Due to the surface sensitivity of PEEM techniques, the image contrast of PZT buried underneath LSMO are relatively weak, causing a noisier image than observed for the top layer containing Mn. The contrast at the Ti edge is also dominated by Ti in the topmost atomic planes at the LSMO/PZT interface due to the fast decay of the number of electrons with depth. Note that the uncompensated

spin structure was obtained previously through the use of both RCP and LCP images. The uncompensated spin structure, however, can be observed directly from a single RCP or LCP divided image by orienting the x-rays in a direction that no contrast is produced from linear dichroism. As shown before in Figure 63 (c) for the linear dichroism signal from PZT domains, the contrast from each domain direction was similar at approximately $\alpha = 50^\circ$ for that specific geometry and only produced a gray background. A similar situation has been observed for the PEEM images of an exchange-bias system Co/NiO, where the contrast resembling the antiferromagnetic NiO domains disappeared in the XMCD-PEEM NiO image when the x-rays was set at 45° to the antiferromagnetic axis of NiO.¹³⁵ The RCP and LCP Ti images in Figure 66 of the current LSMO/PZT study did not show much contrast from PZT linearly dichroism. This could have happened because PZT has single domain structure and is also likely due to the x-ray orientation. For the condition that PZT has three domain directions which are perpendicular to each other, the angle of incident x-rays should be set at 54.8° to each domain directions to eliminate the linear dichroism contrast. The propagation direction of x-ray was 30° to the sample surface and 60° to the vertical domains, close to 54.8° .

Three types of image contrast—dark, bright and grey—are present in the images shown in Figure 66. Ferromagnetic domains appear the brightest when the magnetization direction is parallel to the circular x-ray polarization vector, and appears the darkest where the magnetic direction is antiparallel to the x-ray polarization vector. The same applies to the contrast from the induced spin in PZT. The contrast originating from ferromagnetic or spin structures would therefore switch from dark to bright (or bright to dark) when the x-ray polarization changes from RCP to LCP. The domains that are perpendicular to the x-ray polarization vector produced the grey contrast. Topographical features can also result in a change in background absorption intensity, but this

contrast will be invariant with change in x-ray polarization (and energy) and can be reduced by dividing the RCP and LCP images. Asymmetry images produced by dividing the difference over the average of RCP and LCP divided images, $(\text{Image}_{\text{LCP}} - \text{Image}_{\text{RCP}}) / (\text{Image}_{\text{LCP}} + \text{Image}_{\text{RCP}})$, can further reduce these background contrast and enhance the domain images. Note that each RCP and LCP image was obtained by averaging over hundreds of repeatedly taken images. Regions within PEEM images in Figure 66 are highlighted by blue and yellow ovals to facilitate the comparison of RCP and LCP image contrast. The reversed-contrast dots in Mn RCP and LCP images are from the domains that have the large projection along the x-ray polarization direction. The widths of these domains appear to be approximately 40 nm, consistent with the ultrathin nature of the LSMO film. The regions of the induced spins in PZT are even smaller. Careful and in depth statistics are needed to unravel the correlations between the LSMO domain structures and the induced spins in PZT.

Statistical analysis

PEEM was normally used as a visual tool to image the domain structures. However, Chih-Yeh Huang has done a statistical analysis on our images.¹³⁸ PEEM images at the Mn and Ti absorption *L*-edges were first aligned and processed to produce asymmetry images. Pixel by pixel comparisons were then carried out between the obtained Mn and Ti asymmetry images. Figure 67 shows the correlations between the pixel intensities from Mn and Ti asymmetry images of three LSMO thicknesses. The pixel intensities from Mn asymmetry images are represented by a_{Mn} while those from Ti asymmetry images are represented by a_{Ti} . The anisotropy shown in Figure 67 indicated that the Mn (Ti) asymmetry is the largest when the asymmetry of Ti (Mn) is small. This suggests that the induced Ti spins have a preference to align perpendicular to the Mn magnetization directions, since the contrast of images correspond to the domain directions with regards to the x-

rays. This perpendicular coupling is known as biquadratic coupling which is often observed in metallic systems.^{139,140} Due to the fact that ultrathin LSMO is not conducting, the biquadratic coupling might be caused by the Dzyaloshinskii-Moriya interaction¹⁴¹ at the interface between LSMO and PZT. Also note that the Mn asymmetry decreases with decreasing LSMO thickness due to the reducing magnetization with thickness.

Figure 67: Mn and Ti asymmetries shown in polar plot at three LSMO thicknesses. The anisotropy of the asymmetry polar plot suggests that the interfacial Ti spins prefer to orient perpendicular to the Mn ferromagnetic directions. (Reference 138. © IOP Publishing. Reproduced with permission. All rights reserved.)

In order to quantify the amount of contrast switching with circular light polarization, the correlation between LCP – RCP difference images and the original LCP (RCP) images were also explored for both Mn and Ti images. Specifically, it was important to verify our analysis methods on the Mn images before moving onto the weaker signal from the buried Ti interface. The absolute value of pixel intensities from LCP - RCP difference images were converted to a scale from 0 to

255 when imported into MatLab. Similarly, the pixel intensities of LCP images were also converted to the same scale. The choice of LCP images is equivalent to RCP images here, since the contrast due to spin in RCP images are the negatives in LCP images and the other factors influence equally to both RCP and LCP images. The same trends were observed if we switched the x-axis to the RCP image intensities. The correlation between the pixel intensities from a set of the difference and LCP images is illustrated as a scatterplot in Figure 68. The intensity 0 and 255 represent the darkest and brightest contrast respectively. These contrast correspond to the domains oriented along or opposite to the x-ray polarization direction in LCP images. Contrast valued around 127.5 are the grey contrast for LCP images and were produced by the domains perpendicular to x-ray direction. The maximum difference intensity of 255 along the y axis corresponds to the domain contrast switched from dark to bright or bright to dark when the incident changes from RCP to LCP. When the domain directions are perpendicular to x-ray polarization, the difference contrast should be zero (ignoring noise).

A linear fit was performed on the scatter plot of Figure 68. When the x-ray polarization changes from LCP to RCP, the electron spin projections along the x-ray propagation direction switch sign. Thus, if the LCP intensity is close to 0 (or 255), the RCP intensity should close to 255 (or 0), resulting in a difference of nearly 255. On the other hand, if the domain direction is perpendicular to the x-ray polarization, the intensity should be around 127.5 and will stay around 127.5 for the other circular polarization, the difference between LCP and RCP intensities will be close to zero. This behaviour results in a V-shape in the scatterplot. Since the $|LCP-RCP|$ pixel intensities range from 255 to 0 over the LCP intensity range of 127.5, the slope of the V should be ± 2 when noise is not considered. The red fitting line in Figure 68 produce a slope of ± 1.7 , close to the maximum of ± 2.0 .

Figure 68: Relationship between the changes in contrast to the original contrast for 5.2 nm LSMO when the x-rays change from LCP to RCP polarization. 100,000 random pixels were plotted. The average change was calculated over all pixel intensities and marked by blue dots. The red line is the best fit to average data. (Reference 138. © IOP Publishing. Reproduced with permission. All rights reserved.)

The contrast in LCP and RCP images originate from both the spins and the background. While the spins were responsible for the change in image contrast when the x-rays were switched from LCP to RCP, the background contribution stayed at similar intensity levels and would produce small $I_{|LCP-RCP|}$ values (zero values if the graphs are well normalized and no noise is involved) throughout the LCP pixel intensity ranges. The obtained slope in Figure 68 was the average of both spin and background contribution, which lead to a slope smaller than 2.0. Slope therefore is a way to tell the percentage of the spin contribution and the background, which is further explored in the thickness dependence study below. Because the correlation between the difference contrast and LCP image contrast produces a V shape in the scatter plot, we call this slope the “V fit slope”.

Figure 69: (a) Dependence of V fit slope on LSMO thickness. (b)-(g) The pixel correlations between difference images and LCP images at both the Mn and Ti *L*-edges for different LSMO thickness. (Courtesy of Mikel Holcomb, West Virginia University.)

The thickness dependence study of the V fit analyses were carried out for images taken at both Mn and Ti *L*-edges. The dependence of the V fit slope on LSMO thickness is plotted in Figure

69 (a) along with the individual $I_{|LCP-RCP|}$ vs I_{LCP} pixel correlation graphs shown in (b)-(d). Each pixel intensity from the LCP images corresponded to a range of pixel intensities difference between LCP and RCP images (for example, the scattered pixels in Figure 68). The median of the difference pixels were used in (b) to (d) to drop the low lying $I_{|LCP-RCP|}$ intensities from the background. Equation

$$y - y_0 = b(x - x_0) \quad (5.4)$$

was used to fit the data. Parameters y_0 , x_0 , and b were allowed to vary in this set of fits. As it is observed from the graph, the slope was smaller at thinner LSMO. Discussions below will address why the curves appear less V-like as the magnetic contribution decreases.

The origin of the smaller slope values are three fold: the “black spots”, the noise to signal level and most importantly, the stable but inhomogeneous absorption of x-rays from other sources.

(1) “Black spots” are unavoidable. Figure 66 shows the images with dark dust particles which were used as landmarks for image alignment. Regions sans these visually identifiable dust particles were chosen for statistical analysis. However, tiny spots where no Mn/Ti presents would also appear dark in the image. These dark spots are hard to eliminate and set the lower end of an image intensity. The higher end of an image intensity is limited by the threshold of the CCD camera. The black spot intensities stay low when the x-rays are switched from LCP to RCP. The inclusion of the dark spots in $I_{|LCP-RCP|}$ vs I_{LCP} graph brought down the difference intensity at the lower end of I_{LCP} and shift the “V shape” to the right. The intensity values for $I_{|LCP-RCP|}$ originated from the spins would be smaller than the possible maximum value 255. Therefore a slope smaller than 2 would result from the inclusion of dark spots.

(2) Noise broadens the image intensity range. The actual intensity change from spins (minus the noise) upon the switch of x-ray polarization is smaller than 255 due to the broadening

effect, which causes a smaller possible slope than 2. However, hundreds of repeated image were taken to reduce the noise and this effect should be greatly suppressed.

(3) Background contribution such as the inhomogeneous x-ray absorption due to factors other than the spins plays a major role for the drastic slope change. PZT is a known FE material. LSMO might be antiferromagnetic when it is ultrathin. The ferroelectric or antiferromagnetic domains without uncompensated spins, as well as the surface features, do not switch contrast when the x-ray polarization is changed from LCP to RCP. The contrast from ferroelectric/antiferromagnetic structures only cancels out when the x-rays were incident at a specific angle.¹³⁵ As we wanted to image the ferroelectric domains as well, our images were purposely not taken at that specific angle to allow cancellation. The V fit slopes of the images therefore indicated the percentage of the signals of ferromagnetic domain structure of LSMO or the uncompensated spin in PZT from the background FE or antiferromagnetic contribution and we can single out only the changes between the images to focus on the spin contribution. Based on the thickness dependent result of the V fit slope in Figure 69 (a), the LSMO magnetization reduces with smaller LSMO thickness. This is consistent with the XMCD results discussed in Chapter 5. The V fit slope for uncompensated Ti spin images produced a similar trend, which showed that the strength of induced spin in PZT depends on LSMO thickness and/or the strength of LSMO magnetization. As LSMO approaches its dead layer thickness,ⁱⁱ less spins are induced in PZT.

Future image analysis

The above statistical image analysis is rarely utilized in PEEM imaging literature, but is extremely important for images with small signals. Since the contrasts in these images were from

ⁱⁱ The thickness limit under which the sample is no longer magnetic.

different sources, alternative treatment and additional methods can be taken to separate the spin contributions from the surface, FE or the plausible antiferromagnetic background. Below is a proposed recipe to refine the analysis procedures and to aim for a better understanding of these multilayer systems.

(1) As it was mentioned in the last section, the RCP and LCP images are normalized by setting the lowest intensities at 0 and the highest at 255. This procedure may not best represent the data, because the image intensities range from dark spots to the CCD camera threshold, both of which are not sample specific. The fluctuations in the incident x-ray flux could further misalign the intensities of the two images. The subtractions between RCP and LCP images will therefore benefit from a normalization procedure which is based on the sample characters.

The grey contrast in the Mn images were from the spins perpendicular to the incident light for both RCP and LCP cases. They do not change contrast with the incident polarization change and are also the most frequent pixels in the images. We can normalize RCP and LCP images by setting the grey pixels at the same value 127.5 through centering the RCP and LCP pixel frequency histograms. The full widths of the histograms at half maximum (FWHM) should also be adjusted to be the same. The lower tails which belong to the “black spots” are cut out as well as the ones close to the threshold limit of the camera, as these are artifacts of the surface and not really due to material properties being studied here. The pixel values in the two images can be adjusted in the same way that each histogram is treated.

An alternative method is to select a group of dust particles in the images. The pixel intensities of both images will be shifted and adjusted such that the absolute intensities and relative intensities of these dust particles are the same in both images. This method can be applied to align the intensities of the images taken at the pre-edge and at the absorption peak.

- (2) After the careful alignment in procedure (1), we can obtain the surface contributions from the images taken at the pre-edges, denoted Image (Surf).
- (3) All spin irrelevant contributions such as the FE or antiferromagnetic background and the surfaces can be obtained by averaging the RCP and LCP images. We denote the resulting image as Image (Ave).
- (4) The spin contributions are obtained by subtracting Image (Ave) from Image (RCP) or Image (LCP) images. The subtracted image pairs should be negative images of each other.
- (5) Subtracting Image (Surf) from Image (Ave), the FE or antiferromagnetic background images are obtained.
- (6) The pixel by pixel comparison among these images may provide new insight about the coupling effect.

To summarize, this chapter includes the microscopy results of a thick PZT sample and a wedge LSMO/PZT sample, though other samples were also measured with similar results. The thick PZT has a polydomain structure, which exhibited three FE domain directions. The angular dependence of the PZT domain image contrast was established by shining linearly polarized x-rays at two different orientation to the sample surface. The FE domain image contrast was found to depend on the angle between the domain directions and the incident x-rays for all sets of data. Left and right circular polarized x-rays at both Ti and Mn *L*-edge energies were used to image the LSMO/PZT sample along the LSMO wedge at a constant PZT thickness. Uncompensated spin were observed in Ti images. Statistical results showed that these uncompensated spin preferred the perpendicular orientation to the LSMO domain directions. The V shape method indicated that the LSMO magnetization and the density of uncompensated spins decreased with the decrease of LSMO thickness. The uncompensated spin might serve as a probe for the interface ME coupling

effect. The V shape method used to quantify contrast switching may potentially be applied on other image analysis where the contrast have multiple origins.

Chapter Six: Conclusions

This chapter summarizes most of the important results discussed in this dissertation and includes ideas about possible future investigation directions besides ideas already mentioned in former chapters such as the strain dependence on thickness.

6.1 Research summery

This dissertation research was focused on the studies of LSMO/PZT heterostructures through synchrotron, theoretical and other characterization techniques. It is the start of an on-going research project aiming to understand the interfacial ME coupling mechanism and to provide insight to the science community on the realization of applicable ME coupled media. While single ME materials are interesting, they are rare and pose great technique difficulties in enhancing the coupling effects at room temperature. The interface between two layers provide a feasible alternative and can open up indefinite possibilities in creating the desired material properties, but the detailed physics at these strongly correlated interfaces needs to be unraveled.

Characterization techniques include AFM, fluoresce mapping, XRD and STEM were performed on the heterostructures. The samples in general are smooth, epitaxially grown, and have clear wedge shapes. The interface was sharp as indicated by the STEM measurement on a wedged sample.

Both PZT and LSMO have been intensively studied in the past research. PZT is a strong FE material. LSMO is the result of an interplay among the lattice, charge and spin. Mn valence was used as an indicator of the state of LSMO in the current research similar to checking the color

of light to estimate its wavelength, and was quantitatively determined from the valence sensitive x-ray absorption spectra. The interaction between PZT and LSMO was studied through the dependence of Mn valence on PZT thickness. Mn valence was found to increase with PZT thickness under $t_{\text{PZT}} = 65$ nm and stabilized around bulk LSMO values when PZT was thicker. With the increase of PZT thickness, PZT transitioned from single domain to polydomain structure. The charge carrier density of LSMO near the interface would be tuned by the PZT polarization states/surface charge and influence the Mn valence, leading to a PZT thickness dependent valence state. This is consistent with the charge modulated ME coupling mechanism and was further tested by measuring the Mn valence at two opposite polarization states of PZT. Mn valence showed consistent response to the directions of PZT polarization states: when the FE polarization points toward LSMO, Mn valence shifted to a smaller value; when the polarization points away, Mn valence shifted to a larger value. This observation eliminates the possibility that the ME interface is coupled through strain alone and suggests that charge modulation is indispensable in the coupling mechanism.

The interfacial Mn valence was determined by measuring the valence at two modes with drastically different probe depth. The depth dependence Mn valence was determined through fitting both valence results and the interfacial Mn valence in the sample was found to be smaller than the bulk. The smaller interfacial Mn valence is probably due to the fact that PZT consists predominately upwards c domains at the measurement spots, and also, the polar interface as suggested by the theoretical modeling.

The correlation between the Mn valence and LSMO magnetization was explored by measuring dichroic effect in LSMO through XMCD. Larger dichroism was found to associate with larger Mn valence states. Individual contributions from spin and orbit were estimated. The orbital

magnetization contributed more to the total magnetization while the contribution from spin magnetization was slightly smaller at large Mn valence state.

The coupling between LSMO and PZT were imaged by PEEM. X-ray can selectively image one layer by tuning the energy at the absorption edge of an element unique to that layer. Image contrast due to the electronic spin and density are generated by imaging the sample with proper x-ray polarization and energy where a large dichroism happens. The LSMO domain images was compared to the induced PZT spin structure measured at the same spots. The induced spin was found to align preferably perpendicular to the LSMO domain directions. Both the LSMO magnetization and the amount of induced uncompensated spin in PZT decreases with the decrease of the LSMO thickness. A universal angular dependence of PZT domain image contrast were also determined through study the three types of PZT domains at two x-ray incident orientation. For materials that have both uncompensated spins and linear dichroism, the images taken with circularly polarized x-rays is an overlay of both effects. Angular dependence of linear dichroism can be used to decide the incident angle that minimizes the linear dichroism contribution.

6.2 Future investigation directions

The Mn valence was found to shift after poling the PZT polarization in two opposite directions in Chapter 4. The in-plane lattice parameters of PZT should stay the same theoretically. The LSMO lattice is therefore unlikely to be strained by the PZT lattice. However, LSMO may still undergo a structural rearrangement upon the switch of PZT polarization because the charge density is modified with the polarization change. LSMO structural change after the poling of PZT, or the general correlations between LSMO structure and PZT polarizations, would deepen the

understanding of the interfacial ME coupling effects. The nearest neighbor symmetry and distances can be measured by EXAFS. When combined with μ XRD, the LSMO crystal structure could potentially be constructed. XRD and PFM can be used to quantify the PZT domain types.

While off site poling was measured, onsite poling may produce results not obtainable in off-site poling measurements. The evolution of physical properties with the continuously changing PZT polarizations may benefit device designs such as the “writing” and “reading” of the logic bits (i.e. the domain information).

Investigation of LSMO surface treatment is potentially useful for improving magnetic properties. Annealing LSMO/PZT heterostructures in the oxygen atmosphere was found to enhance the LSMO magnetization (Figure 70). Investigations on possible treatment to the sample surface may be useful to build an ultrathin LSMO/PZT heterostructures and hence increase the ratios of the interface region.

Figure 70: XMCD of LSMO/PZT heterostructure before and after annealing.

Domain correlations across the PZT/LSMO heterostructures can be further studied. The orientation of LSMO FM domain directions and PZT FE domain directions are interesting for

understanding the interfacial ME coupling effects and can be studied with PEEM using circularly and linearly polarized x-rays. Ultrathin LSMO is found to be non-ferromagnetic and has been suggested to be anti-ferromagnetic. The domain correlation between ultrathin antiferromagnetic LSMO and FE PZT may uncover the existence or non-existence of ME coupling effects in this region. It is highly possible PZT may trigger LSMO to transit between FM and antiferromagnetic states through field effect and generate a strong ME coupling effect.

While a few research directions have been suggested above as the extension of the current dissertation research, a lot more questions are worth researching and answering, such as the layer sequence of the heterostructures, selection of electrodes, ways to measure ME coupling coefficient, and LSMO's effect on PZT. It is an on-going effort for the understanding of the ME effects, and to design a new generation of devices.

Appendix

Figure 71: RHEED image of substrate STO.

Figure 72: AFM images of substrate STO (left, treated and taken by Robbyn Trappen) and two thicknesses (middle and right) of a PZT/LSMO wedge.

Figure 73: Micro-fluorescence map of Mn, shows thicker LSMO on the bottom of the sample. The dark line in the center of the sample is a scratch for location reference.

Thin area

Thick area

Figure 74: PFM images on Sample 5 (0-80nm PZT wedge/5-20nm LSMO wedge/ STO on Si). The squares were poled up and down separately. The outmost as-grown region show homogenous contrast indicating the film is single domain.

Figure 75: Buffer subtraction for two FL spectra measured at (a) 1.6 nm LSMO of sample 2 and (b) 10 nm LSMO of sample 3. The buffer was measured at the beginning of the wedge for sample 2, which may include a thin layer of top LSMO and lead to an over-estimation of the valence of the top LSMO. The valence for the two buffers were included in Figure 49 (a) as the two data spots at 0 and 0.4 nm LSMO.

Figure 76: Mn valence on each MnO_2 plane from the best globe fitting results by Robbyn Trappen for a 5 unit cell (u.c.) and 10 u. c. LSMO. The plane number is counted from the surface. The surface and interface of the LSMO has been highlighted in green and blue in the figure. Note that the best fit result for bulk Mn valence was 3.36. The Mn valence inside these ultrathin films was smaller than 3.36, as expected from the depth dependence Mn valence formula (4.13).

Figure 77: Divided Mn RCP and LCP images for (a) as grown LSMO/PZT heterostructure and (b) the LSMO/PZT heterostructure exposed to external magnetic field.

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