

*Growth and characterization of $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3/\text{BaTiO}_3$ multiferroic
bilayers deposited by pulsed laser deposition*

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Universidad del Valle
Facultad de Ciencias Naturales y Exactas
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Santiago de Cali
2017

*Crecimiento y caracterización de bicapas multiferroicas
 $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3/\text{BaTiO}_3$ depositadas por Ablación Laser*

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*Trabajo de Investigación presentado como requisito parcial
para optar por el título de Doctor en ciencias Física*

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Programa Académico de Doctorado en Ciencias Física
Santiago de Cali
2017

Dedicada a mi esposa, mi hijo y mi padre.....

Alba Rocío, Juan José y José Santos,.....

Agradecimientos

- Agradezco a Dios por haberme dado el don de ciencia, el conocimiento, pero sobre todo de la curiosidad todo este tiempo, además de la fuerza y la sabiduría para vencer los innumerables obstáculos que a lo largo de esta investigación se me presentaron, desde la fabricación de las muestras, el desarrollo de las medidas hasta el entendimiento de los resultados.
- Agradezco a mi esposa Alba Muñoz y a mi bebe Juan José, por entender todos los sacrificios que hemos tenido que realizar para terminar este trabajo, además de su apoyo en la realización del mismo. A mis padres por su apoyo incondicional, porque fueron quienes me dieron la fuerza y las ganas para salir adelante, a mis hermanos por haber estado junto a mí en todo momento. Agradezco a mis amigos y compañeros que estuvieron conmigo brindándome una palabra de aliento cuando más lo necesitaba o una explicación sobre un tema que para mí no fuese claro... ó simplemente de su compañía...
- Expreso mis más sinceros agradecimientos la Dra. María Elena Gómez y al Dr. Wilson Lopera Muñoz, por su dirección en este trabajo desde la elaboración de la propuesta, análisis de los resultados y la conclusión de esta investigación, además de su comprensión y paciencia durante el desarrollo de este trabajo. Al Dr. Gustavo Zambrano miembro del grupo de películas delgadas de la Universidad del Valle por sus aportes y sugerencias en esta investigación. Agradezco a Colciencias por darme la oportunidad de participar en el proyecto de investigación *“Study of structural and physical properties in oxide materials and interfaces as potential sensor and control systems”* bajo el número CI 7917, CC 10510, contrato 0002 de 2013 y de COLCIENCIAS-Univalle y *“Growth and characterization of an YBCO-BTO superconductor dielectric multilayer*

and its application as an optoelectronic device” con CI 71062-UNIVALLE. A la Universidad del Valle mediante la vicerrectoría de investigaciones en aprobar y fomentar la participación de estudiantes recién graduados en proyectos de investigación, ya que sin este tipo de proyectos muchos estudiantes no podríamos continuar vinculados a la investigación mientras finalizamos un programa de posgrado.

- Agradezco al Dr. Pedro Antonio Prieto Pulido, quien como docente del grupo de Películas Delgadas y director del Centro de Excelencia en Nuevos Materiales-CENM, sirvió de ejemplo para alcanzar los objetivos y las metas propuestas, además de que puso a nuestra disposición sus recursos de equipamiento y asesoría, sin los cuales no hubiera sido posible la culminación de esta investigación.
- De la misma manera, Agradezco a los profesores del Instituto de Nanociencias de Aragón en Zaragoza, España, Dr. José Ángel Pardo, Dr. Luis Morellón, Dr. Pedro Algarabel, Dr. Cesar Magen y Dr. Ricardo Ibarra, quienes colocaron a nuestra disposición su laboratorio y experiencia académica e investigativa en la discusión de los resultados para finalizar esta investigación.
- A mis amigos Lorena Marín y Luis Alfredo Rodríguez, pues sin su valiosa ayuda no me hubiese sido posible establecer la colaboración con el Instituto de Nanociencias de Aragón, además me acogieron en su hogar como si fuera un integrante de su familia, experiencia que me ayudo a formarme también como persona y quienes tuvieron conmigo la mayor de la disposición para entenderme, enseñarme y ayudarme con mi estadía en España y en todo lo necesario para terminar este trabajo. A mis compañeros de laboratorio Carlos William Sánchez, Julián Ángel, Jackeline Narváez, James Zapata, David Reyes, José Manuel Caicedo, Carlos Melo, Claribel Domínguez, Mario Quiñonez, Angelica Perez, Isabel Cristina Arango, John Schnaider Betancourth, Luisa Fernanda Suarez, Nora Martínez, y Carlos Arango, por su apoyo y colaboración incondicional durante todo este tiempo. Además por que todos siempre estuvieron dispuestos a compartir sus conocimientos y expectativas para contribuir a la culminación de esta investigación.

Este trabajo se realizó bajo el apoyo de:

- COLCIENCIAS-Univalle a través del proyecto titulado “*Study of structural and physical properties in oxide materials and interfaces as potential sensor and control systems*”, CI 7917, CC 10510, contrato 0002 de 2013, de la Universidad del Valle.
- Univalle a través del proyecto titulado “*Growth and characterization of an YBCO-BTO superconductor dielectric multilayer and its application as an optoelectronic device*” con CI 71062-UNIVALLE.
- El Instituto de Nanociencias de Aragón, Zaragoza, España.
- El Centro de Excelencia en Nuevos Materiales (CENM-UNIVALLE), Cali, Colombia.

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Resumen

El desarrollo de nuevos materiales multiferroicos permite la investigación de propiedades ferroeléctricas y magnéticas en una sola fase. Sin embargo, en el escenario básico la combinación de estas propiedades se rige por los efectos de carga (electrones e iones), mientras que las propiedades magnéticas son controladas por electrones. En los multiferroicos estos grados de libertad se acoplan fuertemente. Por ejemplo, las propiedades magnéticas se controlan a través del campo eléctrico o viceversa, lo cual abre una nueva ruta para explorar la posibilidad de estudiar diferentes fenómenos físicos (perovskitas mixtas con d^0 y d^n iones, pares de iones, ordenamiento de carga, inclinación del MnO_6 prácticamente rígido, espiral magnética, ferroelectricidad en estructuras magnéticas colineales, ...) y aplicaciones tecnológicas. Sin embargo, un obstáculo para el uso de este tipo de materiales es la temperatura de funcionamiento (combinación de estados), que generalmente se desacoplan y/o se presentan a bajas temperaturas. Para solucionar estos problemas, los híbridos multiferroicos compuestos por heteroestructuras ferromagnéticas/ferroeléctricas han sido ampliamente estudiados como una posible vía para diseñar heteroestructuras con acoplamiento magnetoeléctrico artificial. En sistemas acoplados por deformación (diferentes sustratos ó parámetros de red), se han demostrado correlaciones directas entre la dirección de polarización dentro de los dominios ferroeléctricos y la anisotropía magnética localmente inducida.

En esta investigación se fabricaron bicapas ferromagnéticas de $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ y ferroeléctricas de BaTiO_3 . En nuestro caso, tres sistemas fueron estudiados: (1) Bicapas de $\text{BTO}(100\text{ nm})/\text{LSMO}(25\text{ nm})$ depositadas sobre sustratos de LaAlO_3 - LAO , $(\text{LaAlO}_3)_{0.3}-(\text{Sr}_2\text{TaAlO}_6)_{0.7}$ - LSAT y SrTiO_3 - STO orientados en la dirección (001), para analizar la influencia de la tensión sobre las propiedades magnéticas de

LSMO, (2) Bicapas de BTO(100 nm)/LSMO(20, 25 y 40 nm) sobre sustratos de STO, para estudiar la influencia del espesor de la capa ferromagnética en el comportamiento magnético, y (3) bicapas de BTO(100 nm)/LSMO(25 nm) depositadas sobre STO con diferente orientación cristalina: (001), (110) y (111).

A partir de la caracterización estructural, el análisis de mapas del espacio recíproco reveló que mientras el LSMO crecía epitaxialmente tenso, la película de BTO liberó las tensiones de su estructura a través de la formación de dislocaciones en la interfaz LSMO-BTO. La microscopía electrónica de transmisión muestra que en la bicapa depositada sobre el (001)STO, la capa LSMO crece de forma epitaxial, en contraste con una relajación presentada en la capa de BTO, asociada a la diferencia en los parámetros red y como consecuencia las regiones tensionadas y relajadas se separan a través de la formación de dislocaciones.

Las mediciones magnéticas muestran un orden ferromagnético para todas las bicapas BTO/LSMO a temperatura ambiente con $M_S^{10K} \sim 600 \text{ emu/cm}^3$, $M_S^{300K} \sim 280\text{-}320 \text{ emu/cm}^3$ y una $T_C \sim 350 \text{ K}$ para todas las muestras, acorde con las propiedades de LSMO. Para todas las muestras encontramos una ligera disminución en las propiedades magnéticas (M_S , H_C and T_C) en las bicapas de BTO/LSMO en comparación con las películas de LSMO. Estas variaciones están asociadas a regiones tensas/relajadas inducidas por los sustratos utilizados, formación de dislocaciones cercanas a la interfaz BTO/LSMO y una reorganización en la dirección del crecimiento a través de la orientación del sustrato, entre otros. Además, este decrecimiento probablemente sugiere que en la interfaz, la polarización espontánea del BTO (hacia arriba ó hacia abajo) influye en las propiedades magnéticas del LSMO.

La magnetización de saturación y el campo coercitivo en las bicapas de BTO/LSMO depositadas en STO depende del espesor del LSMO (t_{LSMO}) y la orientación cristalina del STO, como es esperado en manganitas. El mecanismo magnético se estudió utilizando el modelo propuesto por Berger et al., en nuestro caso el exponente crítico β varía entre 0.20 - 0.30, lo cual indica que podrían estar asociados a los modelos 3D XY Model, YMnO₃ y punto tricrítico, que suelen estar relacionados con materiales multiferroicos. Además, las imágenes de TEM permiten verificar el desplazamiento del ión Ti en la celda unitaria, mostrando la polarización en escala nanométrica del BTO, lo cual posibilita un comportamiento multiferroico a temperatura ambiente.

En particular, se analizó la dependencia angular de la magnetización en el plano de las bicapas BTO/LSMO. El objetivo fue investigar la influencia del sistema ferroeléctrico (BTO) y el efecto de la tensión inducida por el sustrato sobre las propiedades magnéticas del sistema ferromagnético (LSMO). En este caso, se encontró un cambio en la anisotropía magnética de un ordenamiento biaxial (película LSMO) a uniaxial (bicapa BTO/LSMO) bajo un esfuerzo tensil (sustrato STO). Este cambio de anisotropía magnética no se observa en las películas LSMO bajo esfuerzos compresivos (en este caso películas LSMO y bicapas crecidas en sustratos LSAT y LAO). Atribuimos el cambio de la anisotropía magnética a un efecto de interfaz entre las películas LSMO y BTO como regiones tensionadas/relajadas cerca de la interfaz, formación de dislocaciones y diferentes regiones de polarización ferroeléctricas en el BTO cercanas a la interfaz (dominios a, b y c). Este fenómeno se produce sólo para las muestras depositadas en sustratos (001)STO, y fue corroborado en bicapas con diferentes espesores de LSMO, y en bicapas depositadas sobre STO con diferentes orientaciones cristalinas. Los resultados de este proyecto permiten explorar la posibilidad de sintonizar la anisotropía magnética de biaxial (película delgada de LSMO) a uniaxial (bicapas de BTO/LSMO) a través de la deformación inducida por sustrato, en particular (001) STO.

Las propiedades eléctricas muestran un orden ferroeléctrico para las bicapas BTO/LSMO depositadas sobre sustratos LAO, LSAT y STO a temperatura ambiente. La polarización de saturación y el campo coercitivo dependen del sustrato usado. Se obtuvo una reducción en las propiedades FE cuando se aplicaron ciclos consecutivos de histéresis ferroeléctrica, lo cual fue asociado con la migración de vacantes de oxígeno. Por lo tanto, la existencia de un ordenamiento FE/FM en nuestro sistema, abre la posibilidad de estudiar el efecto magnetoelectrico a temperatura ambiente.

Palabras clave: Multiferroicos, Acople magnetoelectrico, Películas delgadas, heteroestructuras, Ferroeléctricos.

Abstract

The development of some new multiferroic materials allow the research of ferroelectric and magnetic properties in a single phase. However, in the basic scenario the combination of this properties are governed by the charge effects (electrons and ions), while the magnetic properties are controlled by electron spins. In multiferroics these degrees of freedom are coupling strongly. For example, the magnetic properties are controlled via electric field or vice versa, open a new route to explore the possibility of study different physical phenomenon (mixed perovskites with d^0 and d^n ions, ion pairs, charge ordering, tilting of the practically rigid MnO_5 , magnetic spiral, ferroelectricity in collinear magnetic structures, ...) and technological applications. However, an obstacle for the use of this type of materials is the operation temperature (combination of states), which generally are decoupling and/or are presented to low temperatures. To solve these problem, hybrid multiferroics composed of ferromagnetic/ferroelectric heterostructures have been extensively studied as a possible route to design heterostructures with artificial magnetoelectric coupling. In strain-coupled systems (different substrates or different lattice mismatch), direct correlations between the polarization direction within ferroelectric domains and the locally-induced magnetic anisotropy have been demonstrated.

In this research, we have fabricated ferromagnetic $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ and ferroelectric BaTiO_3 bilayers. In our case, three systems were studied: (1) $\text{BTO}(100\text{ nm})/\text{LSMO}(25\text{ nm})$ bilayers deposited on (001)-oriented LaAlO_3 -LAO, $(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{TaAlO}_6)_{0.7}$ - LSAT and SrTiO_3 - STO substrates to analyze the strain influence on LSMO magnetic properties, (2) $\text{BTO}(100\text{ nm})/\text{LSMO}(20, 25\text{ and }40\text{ nm})$ on STO substrate, to study the influence of ferromagnetic layer thickness on magnetic behavior and (3) $\text{BTO}(100\text{ nm})/\text{LSMO}(25\text{ nm})$ bilayers grown on STO with different

crystal orientation: (001), (110) and (111). From the structural characterization, the reciprocal space maps analysis revealed that while the LSMO grew epitaxially strained, the BTO film grew relaxing its single-crystal structure through dislocations formed in the LSMO-BTO interface. Transmission Electron Microscopy show that in bilayer deposited on (001)STO substrate, the LSMO layer grown epitaxially strained, in contrast with a relaxation on BTO layer, associated to difference on lattice parameters and as consequence strained and unstrained regions are identify through dislocations formation.

The magnetic measurements shows a ferromagnetic order for all BTO/LSMO bilayers at room temperature with $M_S^{10K} \sim 600 \text{ emu/cm}^3$, $M_S^{300K} \sim 280\text{-}320 \text{ emu/cm}^3$ and a $T_C \sim 350 \text{ K}$ for all samples, which are according with the LSMO properties. A slight decrease on the magnetic properties (M_S , H_C and T_C) on BTO/LSMO bilayers in comparison with the LSMO films for all samples was found. These variations are associated to strained/relaxed regions induced by the substrates used, dislocations formation close to BTO/LSMO interface and a reorganization on growth direction through substrate orientation, among others. In addition, these decrease would suggest that the interface spontaneous BTO polarization (up or Down) probably influence the magnetic properties. The M_S and H_C on BTO/LSMO bilayer deposited on STO are dependent of t_{LSMO} and STO orientation, as is expected on manganites. The magnetic mechanism was studied using the Berger model, in our case the critical β exponent varies from 0.20 to 0.30, which are associated to 3D XY Model, YMnO_3 Model and tricritical point, which are usually related to multiferroic materials. Additionally, the microscope image allow verify the Ti ion displacement on unit cell, showing the microscopic polarization of BTO making possible a multiferroic behavior at room temperature.

In particular, the in-plane angular magnetization dependence in BTO/LSMO bilayers was analyzed. The objective was investigate the influence of the ferroelectric system (BTO) and the substrate-induced strain effect on the magnetic properties of the ferromagnetic system (LSMO). In this case, a change in the magnetic anisotropy from biaxial (LSMO film) to uniaxial ordering (BTO/LSMO bilayer) under tensile strain (STO substrate) was found. This magnetic anisotropy change is not observed in compressive strained LSMO films (LSMO films and bilayers grown on LSAT and

LAO substrates). We attribute the change of the magnetic anisotropy to an interfacial effect between LSMO and BTO films as strained/relaxed regions close to the BTO interface, dislocations formations and different BTO polarization regions close to interface (a, b and c-domains). This phenomenon occur only for samples deposited on (001)STO substrate oriented, and it was corroborated in bilayers with different LSMO layer thickness grown on STO, and bilayers deposited on different STO substrate orientations. The results of this project allows to explore the possibility to tuning the magnetic anisotropy from biaxial on LSMO film to uniaxial on BTO/LSMO bilayers through of strain induced by substrate, in particular (001)STO.

The electrical properties show a ferroelectric order for BTO/LSMO bilayer deposited on LAO, LSAT and STO substrates at room temperature. Saturation polarization and coercive field are dependent of substrate used. A reduction on FE properties was obtained when consecutive ferroelectric hysteresis loops was applied, which was associated to migration of oxygen vacancies. Then, the FE/FM ordering existence in our system, open the possibility to study the magnetoelectric effect at room temperature.

Keywords: Multiferroics, Magnetoelectric coupling, Thin film, heterostructures, Ferroelectrics.

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Chapter 1

Introduction

There are few materials which exhibit multiple functional properties and this class of materials are called multiferroics [1]. This term refers to materials that exhibit at least two of the following ferroic properties: ferroelectricity, ferromagnetism and recently ferroelasticity and ferrotoroidicity in the same phase [2]. Due to nontrivial coupling in the interphase between electric and magnetic domains (magnetoelectric effect) magnetic polarization can be controlled by applying an electric field, and the ferroelectric polarization likewise, can be controlled by means of a magnetic field (fig. 1.1).

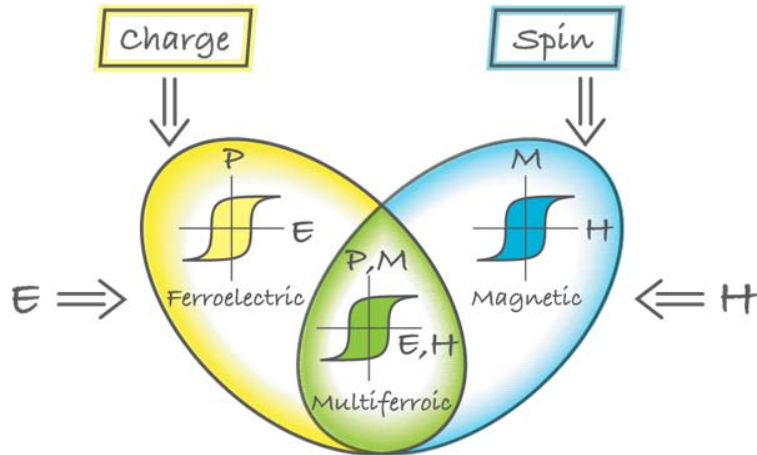


Figure 1.1: Sketch of possible combination of ferroelectric and ferromagnetic materials: Multiferroics materials [3].

Meanwhile, a perovskite single manganite (RMnO_3) [4–8] can be divided into two groups, according to its most stable crystalline structure. For $\text{R} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}$ the compounds crystallize in orthorhombic distorted perovskite structure (space group Pbnm), while for $\text{R} = \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$ and Lu , the compounds crystallize in a hexagonal structure energetically more favorable (space group $\text{P6}_3\text{cm}$). Both structures have a rich phase diagram ($H = 0$), illustrating the range of functions displayed by these compounds at some temperature range [9, 10].

There are few materials that exhibit multiferroic behavior at room temperature, as is the case of BiFeO_3 [11–13]. Nowadays, this material is the most widely studied multiferroic. This oxide has a perovskite distorted rhombohedral structure ($a=b=c=5.63 \text{ \AA}$, $\alpha=\beta=\gamma=59.4^\circ$) at room temperature, with space group R3c [14, 15] and antiferromagnetic and ferroelectric phases with relatively high Curie ($T_C \sim 1100\text{K}$) and Néel ($T_N \sim 673\text{K}$) temperature, respectively [16]. The symmetry allows the inclination of the antiferromagnetic sublattice which results in a macroscopic magnetization, known as weak ferromagnetism [17]. Overlying the antiferromagnetic spiral order spin structure exists in which the antiferromagnetic shaft rotates through the crystal with a period of $620 \text{ \AA}$ wavelength [18]. This spiral spin structure gives rise to the cancellation of any macroscopic magnetization and could occur hinders observation of linear magnetoelectric effect [19], although not quadratic [20]. However, the spiral structure can be suppressed by controlling the growth parameters of the material due to the occurrence of weak ferromagnetism and its effect can be observed as a linear magnetoelectric [21].

Therefore, it is necessary to find materials that can exhibit this behavior and to permit an additional alternative for memory devices and field sensors. For this reason, it is desirable to explore bilayers materials with well-defined independent properties and try to find out how these properties might interact [22], as displayed in fig. 1.2. For example different bilayers have been deposited by different methods, as in the case of the $\text{Pb}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3/\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ bilayers [24], $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3/\text{BaTiO}_3$ and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{BaTiO}_3$ [25], $\text{LSMO}/\text{BZT}/\text{LSMO}/\text{Si}$ [26], $\text{LSMO}/\text{PZT}/\text{LSMO}$ [27], $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3/\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ [28], $\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3 / \text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ [29], $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ [30], $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3 / \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ [31], BaTiO_3/Fe heterostructures types [32, 33] plus some composites as $\text{TbDyFe}_2/\text{Pb}$ -

$(\text{Zr,Ti})\text{O}_3$ / TbDyFe_2 or $(100-x)\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ / $(x)\text{BaTiO}_3$ [34].

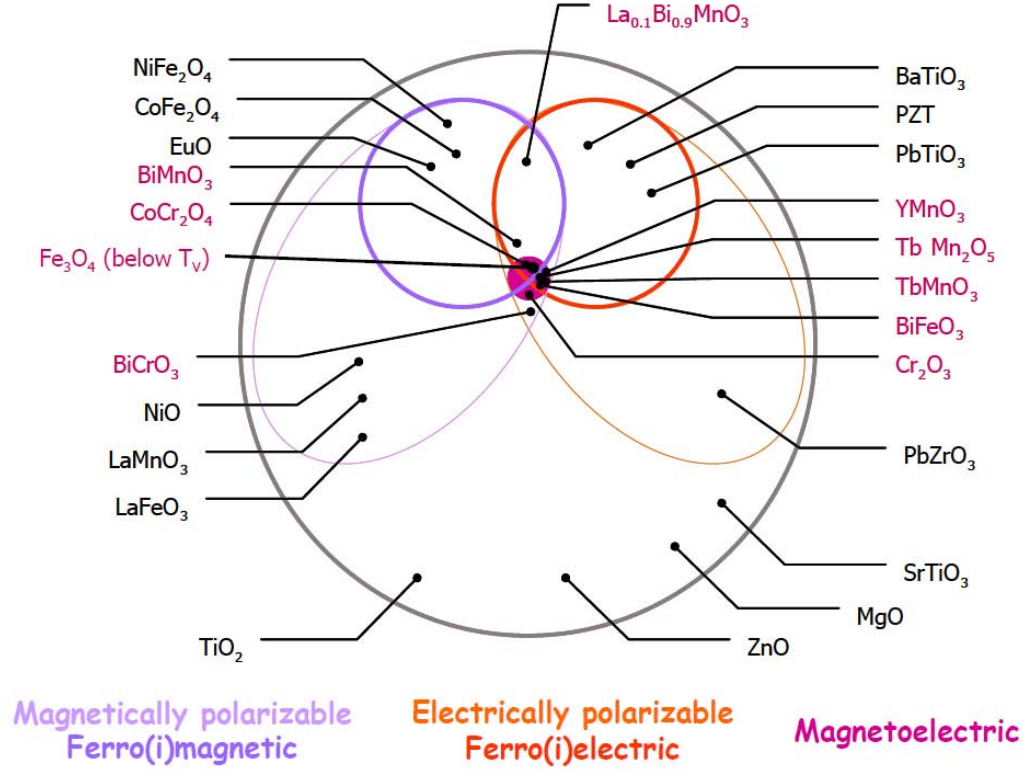


Figure 1.2: Sketch of categorization of insulating oxides according to their ferroelectric, ferromagnetic and magnetoelectric properties: Magnetically polarizable, Electrically polarizable and Magnetoelectric [22].

BaTiO_3 (BTO) differs substantially from other ferroelectric material because of its phase transitions at low temperature. The symmetry of the cubic phase is non-polar (space group $m\bar{3}m$) above the Curie temperature ($T_C \sim 393 \text{ K} \sim 120^\circ\text{C}$) and has a perovskite structure. Tetragonal phase (space group $4mm$) is stable between 393 K and 278 K (5°C) with a polar direction along the tetragonal c -axis, being the subject of extensive research, because it is structurally simple and stable at room temperature. BTO exhibits a transition to an orthorhombic structure for the temperature range between 278 K and 183 K (-90°C) while maintaining a spontaneous polarization, but now in the direction parallel to one of the original $[011]$ cubic direc-

tions. A third phase transition occurs, from orthorhombic to rhombohedral (space group 3m) below 183 K, having as a consequence a change in the polar axis along the [111] cubic direction [23]. Due to these phase transitions, BTO is a powerful material as candidate to build an ferroelectric/ferromagnetic -FE/FM structure that exhibit magnetoelectric effect at room temperature. BTO have a wide application in information storage devices such as capacitors and memory elements in Non Volatile Random Access memory (NVRAM). It is also expected major prospects in Micro Electro Mechanical systems (MEMS) [35] and electro-optical devices [36, 37].

$\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ (LSMO) system is a ferromagnetic material belonging to the perovskites family, appropriate for the coupling with a perovskite ferroelectric oxide such BTO. La^{3+} ions are replaced by Sr^{2+} and consequently for maintaining the charge neutrality, Mn^{3+} is replaced by Mn^{4+} ions, which allows increase of electrical conductivity [38]. Further, when the stoichiometric concentration of strontium ions is 1/3, LSMO exhibit both ferromagnetic/ paramagnetic and metal insulator transition at ~ 370 K [39, 40]. This material exhibits the phenomenon of giant magnetoresistance, where relatively low magnetic fields are sufficient to change its resistance at orders of magnitude [41–43].

In multiferroic heterostructures the magnetoelectric coupling between a ferroelectric material and a ferromagnetic film has been extensively studied during the last decade and various interaction mechanisms have been identified as promising routes towards exclusively electric-field controlled magnetism [44, 45]. Layered heterostructures consisting of magnetic films grown on FE substrates or FE - FM bilayer and multilayer structures, represent another attractive approach towards the design of artificial multiferroic heterostructures. Their strong sensitivity towards lattice strain makes manganites interesting candidates for the magnetic layer in multiferroic composites with large magnetoelectric effect. The strain induced in one component (either by magnetostriction in the magnet or by inverse piezoelectric effect in the ferroelectric) is mediated to the other and alters its polarization (be it electric or magnetic). For example, Lahtinen et al. [46–48], study the full pattern transfer from ferroelectric BTO substrates with alternating ferroelastic a_1 - a_2 domains in polycrystalline $\text{Co}_{60}\text{Fe}_{40}$ thin films. They concluded that the strain-induced uniaxial magnetoelastic anisotropy axis of this system rotates by 90° at domain boundaries

and this fully dominates the local magnetic properties, since the magnetocrystalline anisotropy of $\text{Co}_{60}\text{Fe}_{40}$ is negligibly small. However, this phenomenon has been not observed on BTO/LSMO bilayers deposited on SrTiO_3 (STO) substrates. One most studied example is the family of rare-earth manganites RAMnO_3 (R= rare earth metal, A=nontrivalent doping metal) which is well known for the colossal magnetoresistance (CMR) effect and further extraordinary sensitivities to external parameters including hydrostatic pressure and epitaxial strain in films. LSMO has the largest single electron bandwidth and the highest Curie temperature. These properties, together with the spin polarization, make LSMO an interesting material for application in spintronic devices.

Furthermore, LSMO is also used to investigate other materials, e.g. by spin-injection into cuprate superconductors, to probe spin polarization at the BTO/Fe interface. In this FM material, the tensile or compressive strain induced by the film-substrate lattice mismatch can induce in-plane or out of-plane easy magnetization directions, respectively. Strain in LSMO films deposited on STO (001) is in-plane tensile, in which has been observed in-plane biaxial magnetic anisotropy with the easy axis along (110) and hard one along (100) direction. For LSMO grown on STO (110), substrate induces a strain that is anisotropic in-plane (i.e., the two in-plane directions of strain are inequivalent). This causes an in-plane uniaxial magnetic anisotropy, with the easy axis of magnetization along the [001] crystallographic direction. For ferroelectric material, one of the fundamental problems in this area is the understanding of the microscopic origin of their electric polarization. Two basic mechanisms have been proposed in model studies. According to one of them, magnetic ordering results in the hybridization of electronic orbitals producing a polar charge distribution. The other, more conventional approach, views the displacements of ions from their centro-symmetric positions as the primary source of the polarization as BaTiO_3 . The competition between the biaxial (four-fold) and uniaxial (two-fold) anisotropy results in a magnetic reorientation, which depends on intrinsic parameters, as substrate step density, angle of deposition, or extrinsic ones, such as temperature range. Hence, breaking the symmetry of magnetic systems results in additional contributions to the magnetic anisotropy, which could alter both magnetization, easy and hard axes, and reversal processes.

1.1 Magnetism: a brief history and its importance

1.1.1 Fundamentals of Magnetism

A magnetic dipole is defined as either the magnetic moment, $\vec{m}$, of a bar magnet for small length or for a current loop in the limit of small area, both with finite moment. The magnetic field lines around a magnetic dipole are shown in fig. 1.3. The magnetic field lines leave the north pole and enter the south pole forming a closed path.

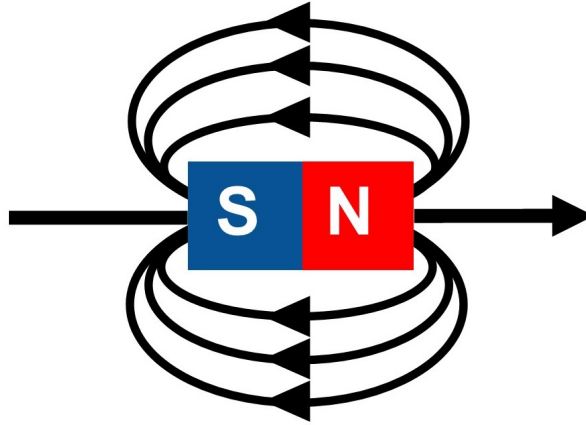


Figure 1.3: Magnetic field lines around a magnetic dipole. Adapted from [49].

1.1.2 Magnetic induction and magnetization

The response of a material so called magnetic induction $\vec{B}$, appear in presence of a magnetic field $\vec{H}$. The relationship between $\vec{B}$ and $\vec{H}$ is a physic property of the material. In some materials (even in free space), $\vec{B}$ is a linear function of $\vec{H}$, However, in general it is more complicated. The equation relating $\vec{B}$ and $\vec{H}$ is (using cgs units)

$$\vec{B} = \vec{H} + 4\pi\vec{M} \quad (1.1)$$

where $\vec{M}$ is the magnetization of the material. The magnetization is defined as the magnetic moment per unit volume,

$$\vec{M} = \frac{\vec{m}}{V} \left[\frac{emu}{cm^3} \right] \quad (1.2)$$

$\vec{M}$ is a property of the material, and depends on both the individual magnetic moments of the constituent ions, atoms, or molecules, and on how these dipole moments interact with each other. The cgs unit of magnetization is the emu/cm³. In free space, where $\vec{M} = 0$ ($\vec{B} = \vec{H}$), the unit of both magnetic induction and magnetic field are the same, that is, the Oersted.

In SI units the relationship between $\vec{B}$, $\vec{H}$, and $\vec{M}$ is

$$\vec{B} = \mu_o(\vec{M} + \vec{H}) \quad (1.3)$$

where μ_o is the permeability of free space. The units of $\vec{M}$ are obviously the same as those of $\vec{H}$ (A/m), and those of μ_o are weber/(A m), also known as henry/m. So the units of $\vec{B}$ are weber/m², or tesla (T); 1 gauss = 10⁻⁴ tesla [49].

Dependence of $\vec{B}$ or $\vec{M}$ of the applied magnetic field $\vec{H}$ for a ferromagnetic material is not linear and it exhibits hysteric behavior, fig. 1.4, called the magnetization loop. Characteristic magnitudes in magnetic hysteresis loops are the saturation magnetization (maximum magnetization), $\vec{B}_s$ or $\vec{M}_s$; coercive field (that needed in opposite direction to get zero magnetization), $\vec{H}_c$; remanent magnetization (that magnetization value of the material at $\vec{H}=0$), $\vec{B}_r$ or $\vec{M}_r$ depend on the type of material.

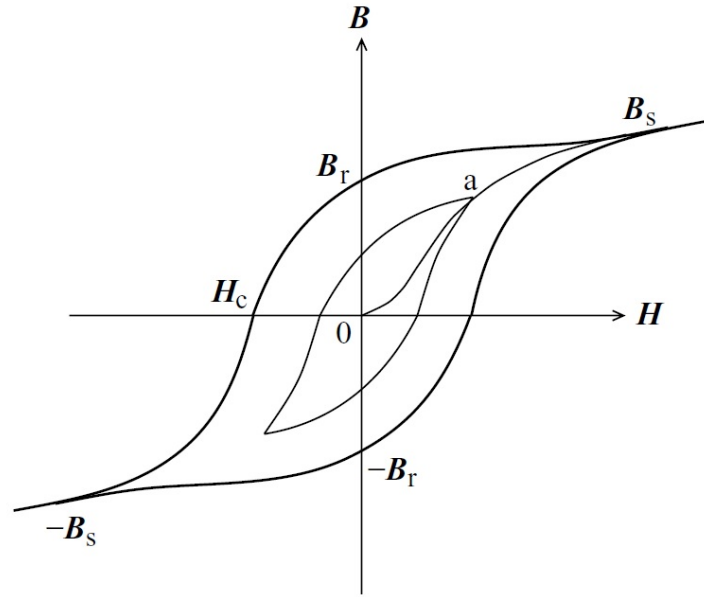


Figure 1.4: Isothermal hysteresis loop for ferroemagnetic material [49].

1.2 Magnetic anisotropy

The anisotropy occur when a physical property of a material is a function of direction. This term is associated with the dependence of the magnetic properties on the direction in which they are measured. The magnitude and type of magnetic anisotropy modify properties such as magnetization and hysteresis curves in magnetic materials. The magnetic anisotropy can have its origin in sample shape, crystal symmetry, stress, or directed atomic pair ordering [50].

The basic experiment for observing the manifestations of magnetic anisotropy must be determined in single crystals. Fig. 1.5 shows the easy axes of magnetization (that for which saturation magnetization is reached at low applied magnetic field) and hard axis (that for which the saturation magnetization is reached at high magnetic field) for Fe, Ni and Co. Fig. 1.5 also displays the magnetization versus applied field along the principal crystallographic axis, where we can identify the easy and hard axis for the classic ferromagnetic materials in the periodic table: Fe, Ni, Co [50].

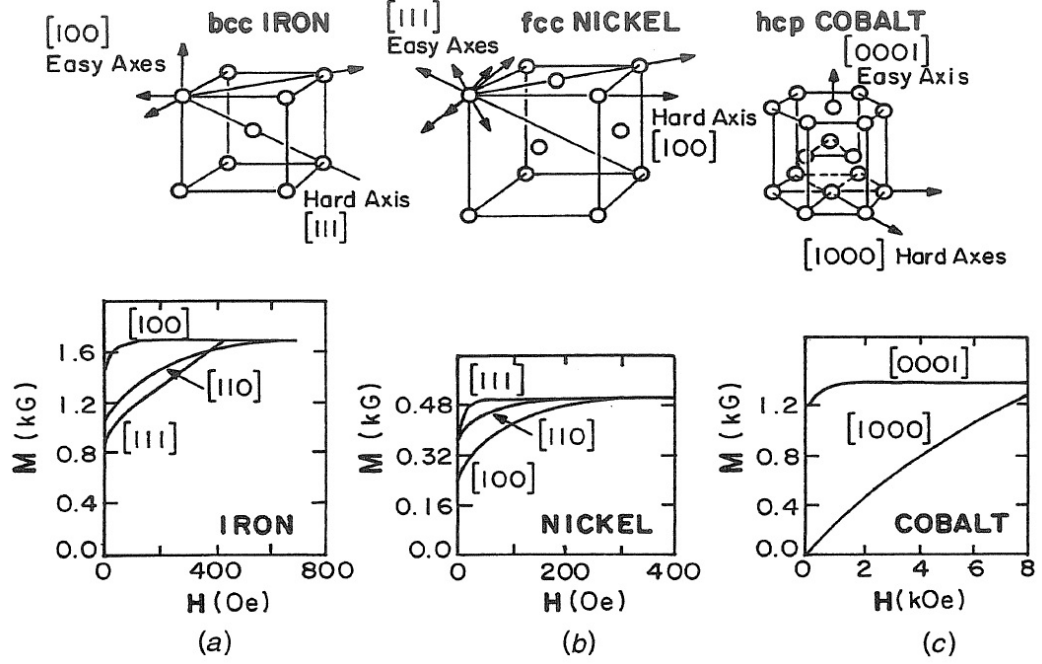


Figure 1.5: Crystal structure showing easy and hard magnetization directions as well as the magnetization versus applied field curves along the crystallographic axis (a) Fe, (b) Ni and (c) Co [50].

The magnitude of the strength of the magnetocrystalline anisotropy is called the anisotropy field H_a . This is the field needed to saturate the magnetization in the hard direction. The energy per unit volume needed to saturate a material in a particular direction is given by:

$$u_a = \int_0^{M_s} H(M) dM \xrightarrow{1st\ order} \frac{H_a M_s}{2} \quad [erg/cm^3] \quad (1.4)$$

$$u_a = \mu_o \int_0^{M_s} H(M) dM \xrightarrow{1st\ order} \mu_o \frac{H_a M_s}{2} \quad [J/m^3]$$

The first-order expressions above apply to magnetization curves linear in the field. Magnetic anisotropy energy density is the area between the magnetization curves in different crystallographic directions [50].

1.2.1 Magnetocrystalline anisotropy

The symmetry of the magnetocrystalline anisotropy is always the same as that of the crystal structure [49]. Therefore, an energy function allow describes exactly the equilibrium orientation of magnetization under field, stress, temperature, and others parameters fixed. The uniaxial crystal anisotropy energy density can be expressed as a power series:

$$u_a = \frac{U_o}{V_o} = \sum_n K_{un} \sin^{2n} \theta \quad (1.5)$$

If we take only the first three terms

$$u_a = K_{uo} + K_{u1} \sin^2 \theta + K_{u2} \sin^4 \theta \quad (1.6)$$

where K_{uo} is independent of the orientation of magnetization. In this case, $K_{u1} > 0$ implies an easy axis. Fig. 1.6 show cubic magnetic anisotropy energy surfaces. For an uniaxial material, the shape of energy surface for the first two terms in Eq. 1.6, when $K_{u1} > 0$, is an oblate spheroid as in fig. 1.6(c).

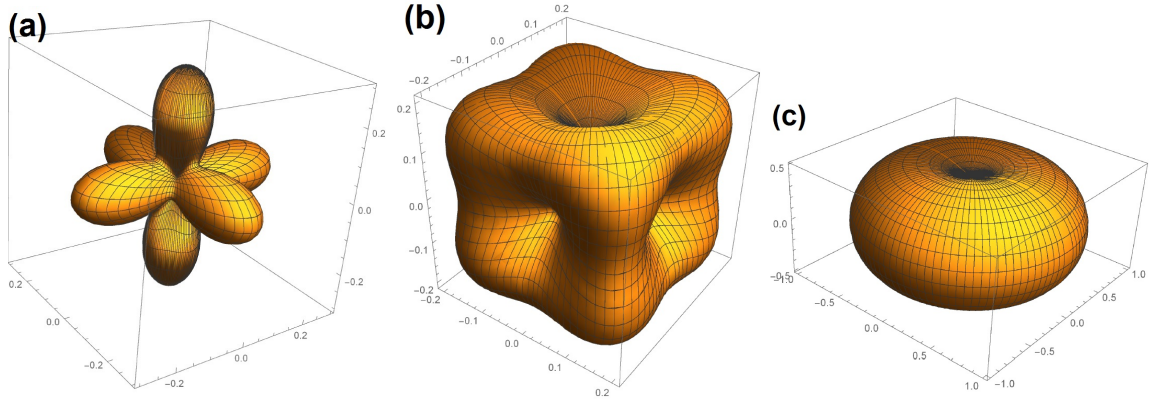


Figure 1.6: First-order anisotropy energy surfaces for iron (a), nickel (b), and cobalt (c). Adapted from [50].

When $\mathbf{H}_{applied}=0$, the magnetization tends to the lowest energy orientation along + z axis. The energy surface for a uniaxial material with $K_{u1} < 0$ is a prolate spheroid extended along the z axis and having minimum energy in the x–y plane.

In $\mathbf{H}_{\text{applied}}=0$, magnetization along any direction in the x–y plane is preferred to any magnetization orientation having a component out of this plane [50].

1.2.2 Cubic Anisotropy

The energy surfaces for cubic crystals are not as easy to imagine or construct as uniaxial ones. One could conceive an energy surface for Fe with (100) easy axes (see Fig. 1.6). For cubic crystals such as iron and nickel, the anisotropy energy can be expressed in terms of the direction cosines, α_1 , α_2 and α_3 of the magnetization vector with respect to the three cube edges.

The anisotropy of a cubic system may then be written as:

$$u_a = K_o + K_1(\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2) + K_2(\alpha_1^2\alpha_2^2\alpha_3^2) + K_3(\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2)^2 \dots (1.7)$$

1.2.3 Shape anisotropy

Fig. 1.7 sketches a magnetized ferromagnetic material by a magnetic field applied from right to left. The orientation of the magnetic moments of the material creates free poles on the surface. This effect is the origin of the demagnetization field inside magnetic materials in a direction contrary to the magnetization [49].

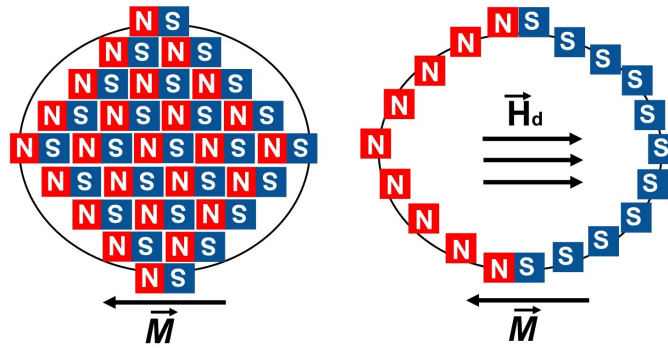


Figure 1.7: Sketch of the oriented magnetic dipoles in a magnetic material under an external magnetic field. Free dipoles on the surface and the demagnetization field. Adapted from [49].

If the sample is not spherical, then it will be easier to magnetize it along the long axis, as sketched in Fig. 1.8. This phenomenon is known as shape anisotropy. We see from the figure that the field inside the sample points from left to right – that is, in the opposite direction to the applied external field. This internal field tends to demagnetize the magnet, and so we call it the demagnetizing field, [49]. Intuitively, the value of H_d is bigger, Fig. 1.8(b), since there are much more free poles and those are closer [49].

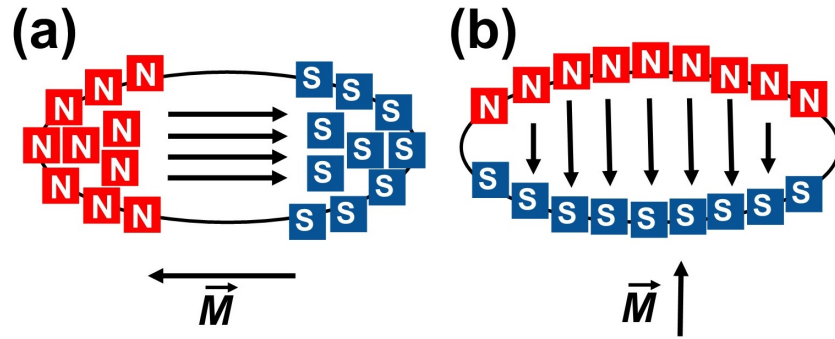


Figure 1.8: Scheme of the demagnetization field for an ellipsoid magnetized along the (a) longer and (b) smaller axis [49].

$\vec{H}_d$ is created by the magnetization of the sample. The magnitude H_d is directly proportional to the magnitude of the $\vec{M}$. Therefore, the demagnetizing field is

$$\vec{H}_d = N_d \vec{M} \quad (1.8)$$

where N_d is called the demagnetizing factor, and is determined by the shape of the sample. N_d is associated to the different shapes of samples. For elongated samples, N_d is smallest along the long axis and largest along the short axis. Thus, the anisotropy depend stronger as the aspect ratio increases, with $N_d \rightarrow 0$ as the distance between the poles $\rightarrow \infty$ [49].

There are an effective field acting inside the material, $\vec{H}_{eff}$, is smaller than $\vec{H}_{applied}$ by an amount equal to $\vec{H}_d$,

$$\vec{H}_{eff} = \vec{H}_{applied} - \vec{H}_d \quad (1.9)$$

In case of long axis, equivalent to N_d is small,

$$\vec{H}_{eff} = \vec{H}_{applied} - N_d \vec{M} \approx \vec{H}_{applied} \quad (1.10)$$

and most of the applied field magnetize the sample. In addition, along the short axis when N_d is large

$$\vec{H}_{eff} = \vec{H}_{applied} - N_d \vec{M} \ll \vec{H}_{applied} \quad (1.11)$$

and so most of the applied field goes into overcoming the demagnetizing field. As a consequence it is easier to magnetize the sample in a direction, the long axis [49].

1.3 The physics of manganites: from the structure to magnetic properties

1.3.1 $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$

Manganese oxides with perovskite-type $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ (R = rare earth, A = bivalent alkaline earth ion) (Fig 1.9), called manganite, are known for their structural, electrical and magnetic highly correlated properties. The phase diagrams of manganites strongly depend on the types of R and A ions; for our case $\text{R} = \text{La}$ ($\text{La}^{3+}=1.22$ Å) and $\text{A}=\text{Sr}$ ($\text{Sr}^{2+}=1.06$ Å) for the site A ; Mn ($\text{Mn}^{4+}=0.52$ Å and $\text{Mn}^{3+}=0.70$ Å) for the site B and oxygen ($\text{O}^{2-}=1.32$ Å). Mn is the smallest ion involved in the manganites, forming family $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ [51–55].

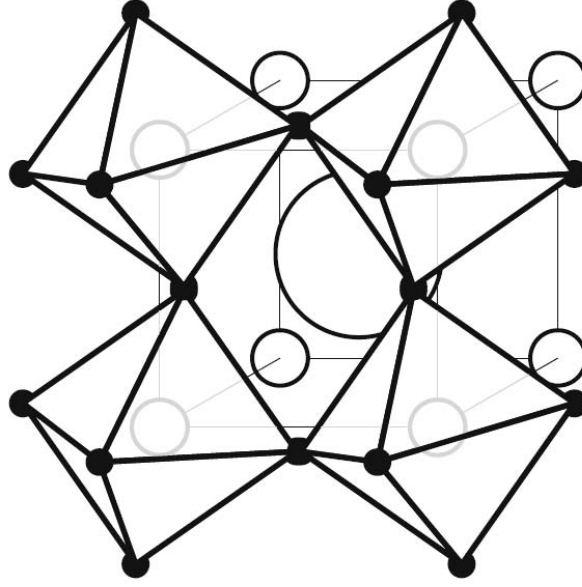
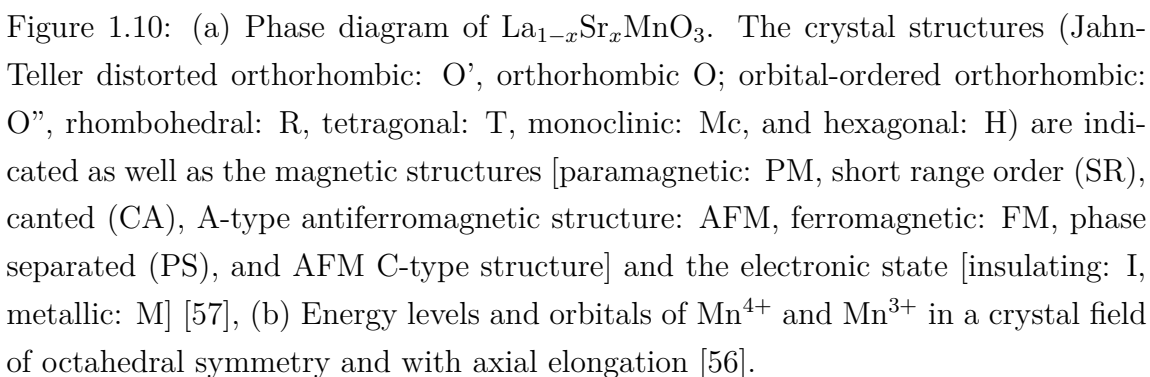


Figure 1.9: Typical perovskite structure structure with tetragonal distortion.

Curie temperature, T_C as a function of doping is relatively complex, and in the range $0.17 < x < 0.47$ the material exhibits the ferromagnetic phase (Fig 1.10), reaching $T_C \sim 370\text{K}$, which facilitates the application of this material in various devices [39]. In a crystal field of symmetry lower than cubic, the degeneracy of the e_g and t_{2g} levels is lifted, for an axial elongation of the oxygen octahedron. Although the energy of Mn^{4+} remains unchanged by such a distortion, and the energy of Mn^{3+} is lowered. Therefore, Mn^{3+} has a marked tendency to distort its octahedral environment in contrast to Mn^{4+} . This Jahn-Teller distortion is rather effective in the lightly doped manganites with a large concentration of Mn^{3+} ions; the Jahn-Teller distortions are not independent from one Mn^{3+} site to another (cooperative Jahn-Teller effect). This is illustrated by the structure of LaMnO_3 (Fig 1.10) in which the MnO_6 octahedra are strongly elongated within the ab plane in a regular way leading to a doubling of the unit cell. On increasing the Mn^{4+} content, the Jahn-Teller distortions are reduced and the stabilization of the $3z^2 - r^2$ e_g orbital becomes less effective. Nevertheless, in a large number of manganites, the e_g orbitals of the types, $3z^2 - r^2$ and $x^2 - y^2$ are not occupied by the e_g electrons of Mn^{3+} at random and an orbital order is achieved [56].



In our case, $x = 1/3$, the compound have ferromagnetic ordering with the highest T_C , around 370 K [39], near this transition temperature, the material presents a decrease in resistivity ρ with temperature, i.e changes from insulator (paramagnetic) to the metallic state (ferromagnetic) type (fig 1.11).

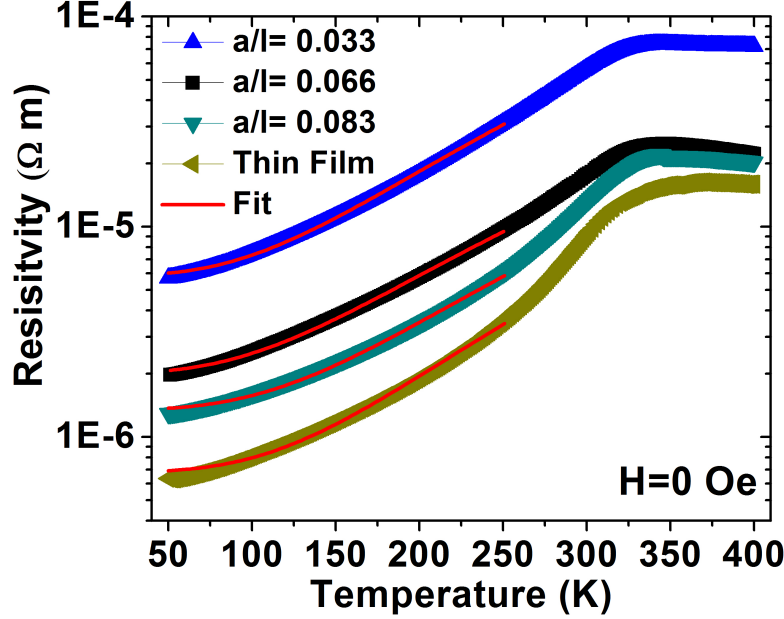


Figure 1.11: Temperature dependence of the resistivity for a $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ film and microwires with different a/l ratio (a =width and l =length) [58].

Due to the large magnetoresistance values reported at temperature near T_C , this remarkable change is known as colossal magnetoresistance (CMR) [17, 42, 59–61]. When a magnetic field is applied at temperature close to the ferromagnetic order one (T_C) it favors spin coupling and is a significant decrease in electrical resistivity, the favored alignment of the magnetic moments (fig 1.12), therefore, this material suffers the phenomenon known as magnetoresistance:

$$MR = \frac{\rho(H) - \rho_o(H = 0)}{\rho_o(H = 0)} \quad (1.12)$$

The basis of the understanding of “*spin polarization*” was presented by Zener in 1951 [62–64]. This phenomenon is produced, in principle, by a magnetic interaction between ions, known as “*double exchange*” which was proposed by Zener (fig 1.13) [62–64].

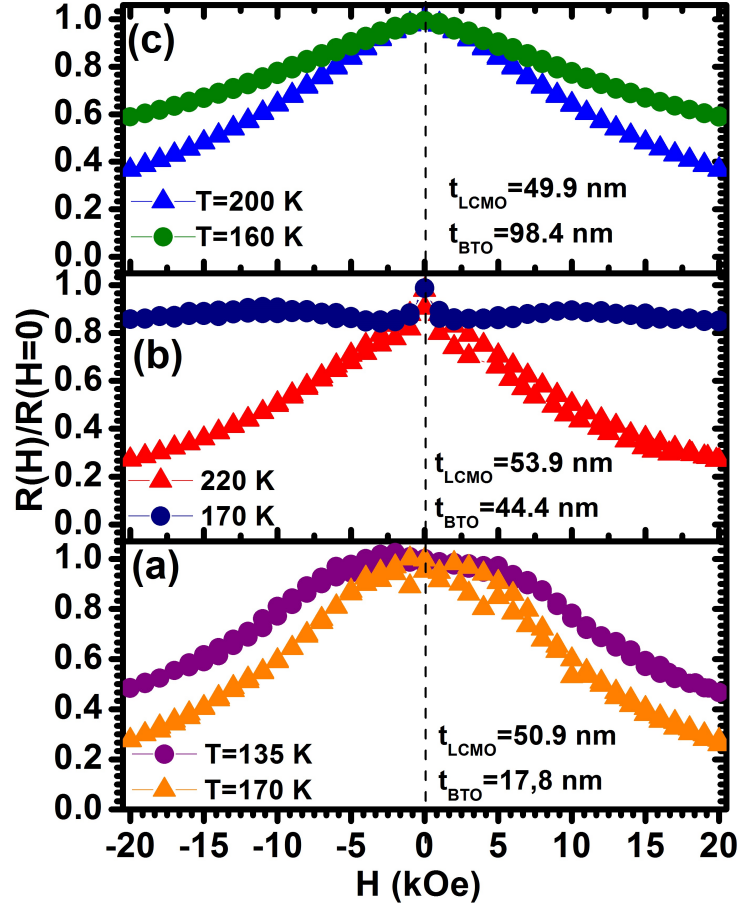


Figure 1.12: Isothermal MR LCMO as a function of magnetic field for sample with t_{BTO} (a) 17.8 nm, (b) 44.4 nm, and (c) 98.4 nm [65].

For the case of manganites, ferromagnetism occurs through this mechanism, which is based on the coexistence of ions Mn^{3+} and Mn^{4+} with electronic configurations $t_{2g}(3) e_g(1)$ and $t_{2g}(3) e_g(0)$ respectively [66, 67]. The t_{2g} electron energy is far from the conduction band, thus they do not contribute to the transport properties, however they have parallel spins ($S = 3/2$). Moreover, e_g electrons are in the conduction band, which are shared by O and Mn ions. In this energy band, e_g electron transfer occurs from Mn^{3+} ions to the O^{2-} and from O^{2-} to Mn^{4+} ions. Hopping of e_g electrons generates a coupling of $Mn^{3+}/Mn^{4+} - O^{2-} - Mn^{4+}/Mn^{3+}$ and due to the strong coupling between electrons $t_{2g} - e_g$, preserving the orientation of the spins at all sites of Mn and thus ferromagnetism arises (fig 1.14). Therefore, there

is a metallic ferromagnetic phase ($T < T_C$) in which the spins are fully polarized, allowing it use in spintronics based devices.

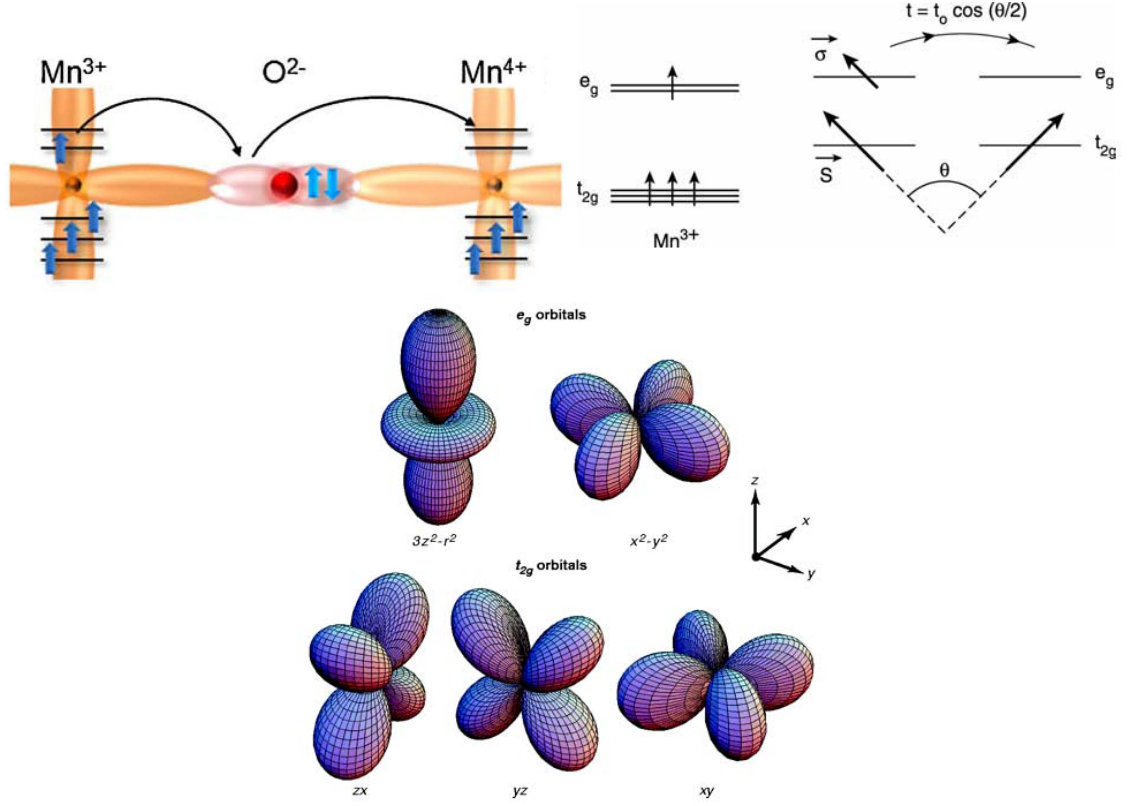


Figure 1.13: (a) Schematic view of the double exchange mechanism, (b) probability of the e_g electron transfer from Mn^{3+} to neighboring Mn^{4+} (c) e_g and t_{2g} orbitals [56, 68].

Theoretical studies have been performed [69], which show that only major bands are occupied at the Fermi level (for $x = 1/3$). Zener's work was continued by Anderson and Hasegawa [67], and they found that the transferring probability of the e_g electron from Mn^{3+} to neighboring Mn^{4+} is $t_0 \cos \theta/2$, θ being the angle between the Mn spins, in the case of strong Hund coupling (fig 1.13). The process of electron transfer lifts the degeneracy of the configurations $\text{Mn}^{3+}\text{-O-Mn}^{4+}$ and $\text{Mn}^{4+}\text{-O-Mn}^{3+}$ leading to two energy levels $E_{t=0} \pm t_0 \cos \theta/2$. The energy gain of the parallel spin configuration, $\theta = 0$, which maximizes t , with respect to the antiparallel one, $\theta = \pi$, reveals the ferromagnetic character of the double exchange interaction. However, the

double exchange angular dependence of $\cos \theta/2$ is quite different from $\cos \theta$ of the usual exchange interaction. Subsequently, de Gennes proposed spin-canted state and the possible state obtained when doping with electrons or holes antiferromagnetic materials [70].

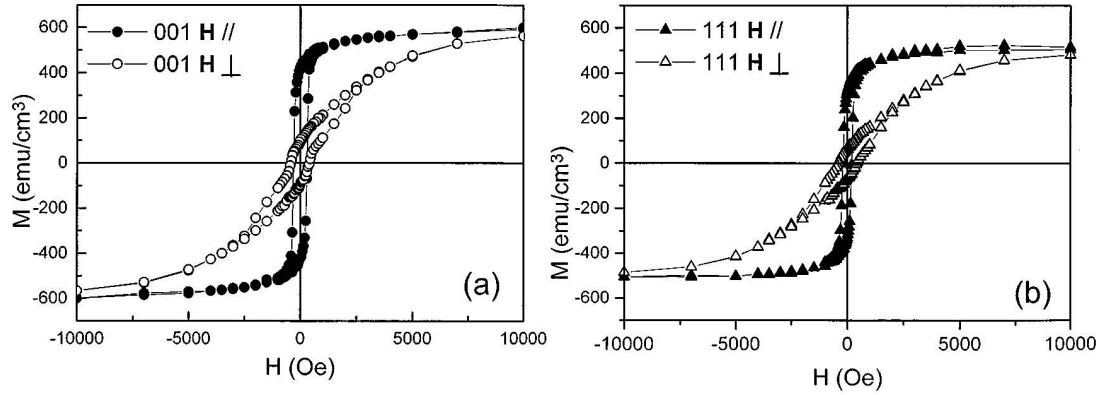


Figure 1.14: Magnetization $M(H)$ loops (at 10 K) for the (001) and (111) LSMO films; the $\perp$ and $//$ symbols indicate a measurement with H perpendicular and parallel to the film plane, respectively [71].

1.4 Ferroelectric materials

1.4.1 BaTiO_3

BaTiO_3 perovskite is widely studied due their potential applications in memory (*Dinamic Random Access Memory* - *DRAM*), capacitors and other devices because of their ferroelectric properties [8, 72]. This structure is common in ABO_3 compounds type, whose nature is representative of the CaTiO_3 mineral (fig. 1.15). The formal Valence ions are Ba^{2+} and Ti^{4+} , which exactly balance the oxygen one.

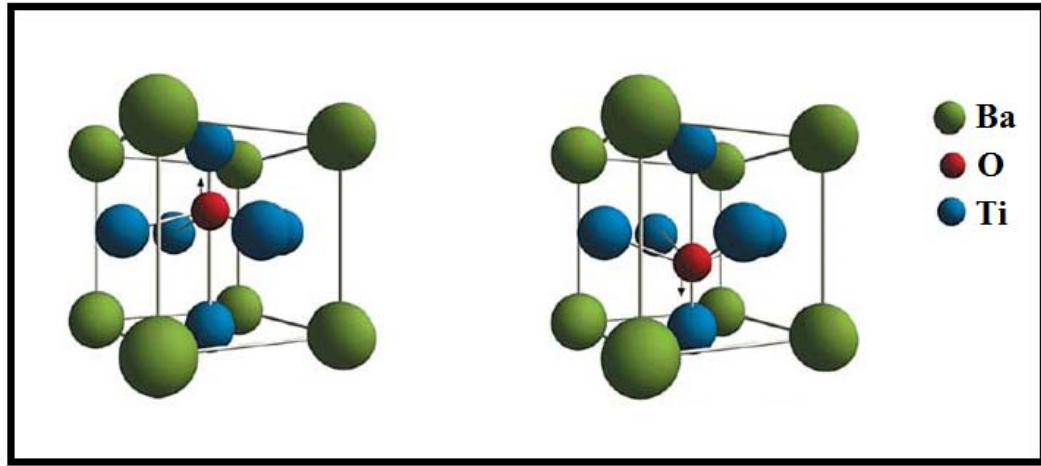


Figure 1.15: BaTiO_3 has a perovskite structure (ABO_3). The representations show the two stable states (up and down polarization) [73].

At high temperature, the material has a cubic paraelectric structure which transforms, by decreasing the temperature to a tetragonal ferroelectric structure (fig. 1.16). A second transformation to a ferroelectric phase with orthorhombic symmetry, which changes to rhombohedral at low temperature. Each transition is accompanied by small displacements, dominated by the Ti ion displacement relative to the array of octahedra and macroscopic stress in the structure, which produces variations in the dielectric constant. In the ferroelectric phase, the polar axis is aligned along directions $[001]$, $[011]$ and $[111]$, respectively, which correspond to the directions of the atomic displacements with respect to its position in the cubic reference structure. BTO thin films growth on substrates of rare earths (GdScO_3 and DyScO_3) by reactive molecular beam epitaxy (MBE) and by pulsed-laser deposition (PLD) demonstrated that T_C may be increased near 500°C and the remanent polarization can be increased almost 250 %, bought relating bulk samples [74] (fig. 1.17). It has also reported studies of the dependence of the lattice parameter with the thickness and temperature, by X-ray diffraction for samples with a thickness of 5 - 50 nm, and by electron microscopy (EM) and high resolution electron microscopy (HREM) for samples thickness of 2 nm in-plane ($//$) and out-of-plane ($\perp$) [75, 76].

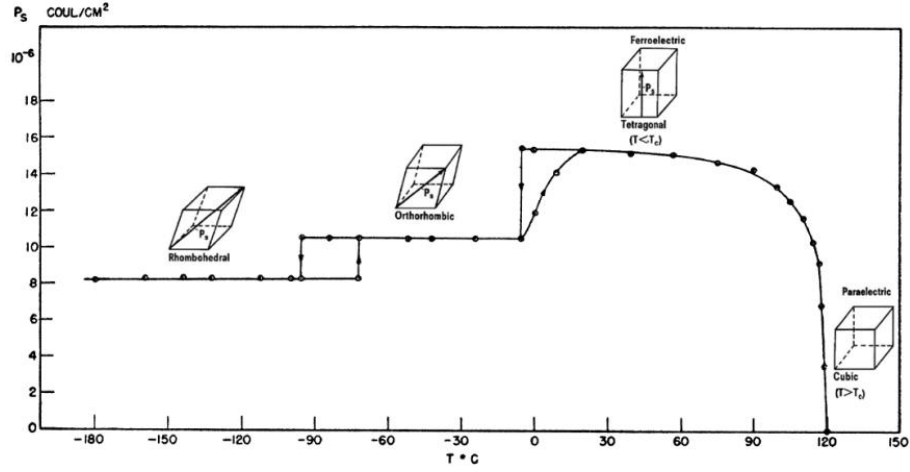


Figure 1.16: Dependence of spontaneous polarization with temperature. Four crystalline phases of BaTiO_3 are identified [23].

Spontaneous polarization measurements were made by Merz [23], using the modified Sawyer-Tower circuit for single domain crystals [77]. Additionally, they found higher polarization values $33 \mu\text{C}/\text{cm}^2$, $36 \mu\text{C}/\text{cm}^2$ and $27 \mu\text{C}/\text{cm}^2$ for rhombohedral, orthorhombic and tetragonal phase, respectively [23]. There are reasons to believe that the measured polarization in the rhombohedral phase can be smaller than the true value of intrinsic polarization, obtained by the first principles theory of $43 \mu\text{C}/\text{cm}^2$ [78]. Additionally, optical properties were found in the BaTiO_3 by Merz [23] using Chaulnes's method, showing a maximum refractive index for T_C , and the birefringence $\Delta\eta$ was measured by Forsbergh observing a sharp drop around the T_C [79]. Despite extensive investigation of the ferroelectric thin films [80, 81], the existence of a critical thickness, below which the phenomenon disappears, is a matter of debate. The influence of thickness in the electric polarization may be due to the interaction between various phenomena including surface effects related to dipole-dipole interactions [82] and the presence of a depolarizing field. Both effects depend strongly on the boundary conditions at the interface between the ferroelectric and the electrode materials used. Additional effects of tension produced by external stresses due to the substrate or system substrate / electrode also strongly affect the ferroelectric character of the material [83]. Depolarizing field effect increases when

the thickness of the samples decrease [82] and can lead to complete suppression of ferroelectricity and consequently a reduction in the unit cell tetragonality. Another way to reduce this high energy electrostatic at low thickness are the formation of domains with ferroelectric polarization pointing in opposite directions but also by electrical conduction within the film. This depolarising field arises from unbalanced loads which are formed on the surface of the film. A ferroelectric capacitor ideal shielding localized loads at the electrode/ferroelectric fully compensate surface charges related to the ferroelectric polarization.

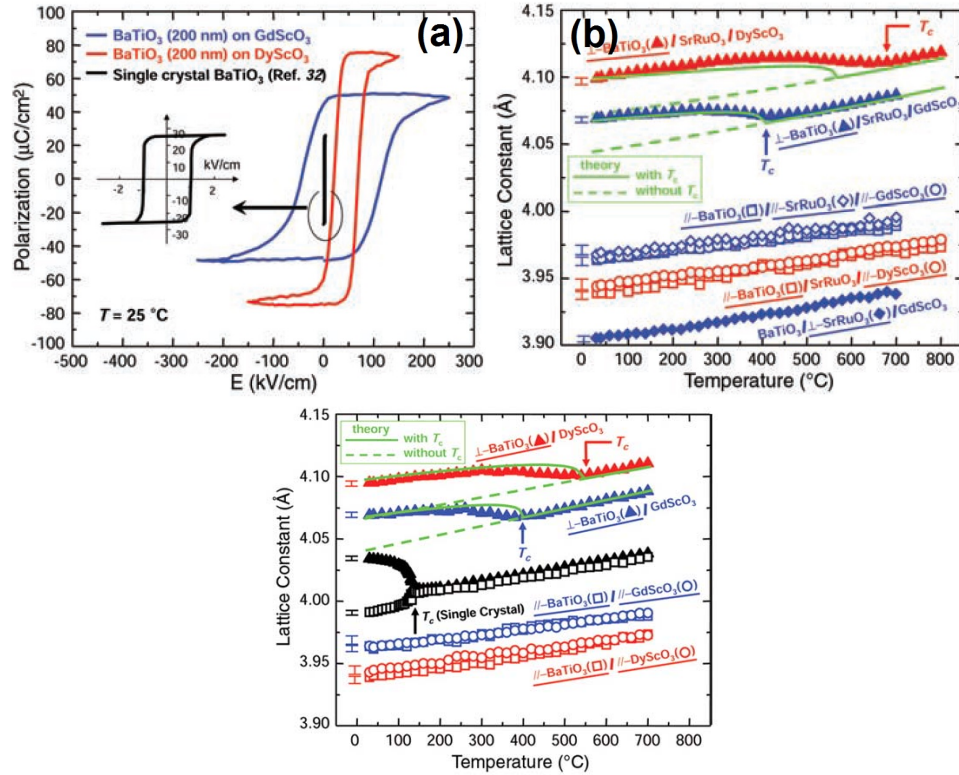


Figure 1.17: (a) Polarization-electric field hysteresis loops of BaTiO₃ thin film capacitors (2000 Å) grown by PLD with SrRuO₃ top and bottom electrodes. (b) Temperature dependence of the lattice parameters of strained capacitor structures [76]. (c) Temperature dependence of the lattice parameters of single-crystal BaTiO₃, and strained BaTiO₃ thin films grown by Molecular Beam Epitaxy on DyScO₃ substrates and GdScO₃ substrates. The in-plane (//) and out-of-plane (⊥) lattice constants of the BaTiO₃ thin films and underlying substrates are shown [76].

1.5 Hybrid multiferroic

The first attempts at engineering a magnetoelectric coupling in artificial multiferroic systems explored the elastic coupling between composites based on magnetic and ferroelectric particulate and phase segregated ceramics [84–88], where the epitaxial strain that develops at the structurally coherent interfaces is explored to attain a stronger elastic coupling between the ferroelectric and magnetic phases [89–91]. Ferromagnetic pattern formation via efficient coupling to ferroelectric domain structures has recently been demonstrated on Fe layer deposited on BTO substrates [46, 92].

The research on hybrid multiferroic systems has been allowed to study various phenomena as the change on magnetic properties due to ferroelectric orientation of polarization. Lahtinen et al. [47], found in Fe layer deposited on BTO substrates a change on Fe magnetic anisotropy, associated to the polarization direction of BTO (fig. 1.18). The Fe films exhibit biaxial magnetic anisotropy on top of *c* domains with out-of-plane polarization, whereas the in-plane lattice elongation of *a* domains induces uniaxial magnetoelastic anisotropy via inverse magnetostriction as is observed in fig. 1.18 to different polarization orientation. The strong modulation of magnetic anisotropy symmetry results in full imprinting of the *a*-*c* domain pattern in the Fe films.

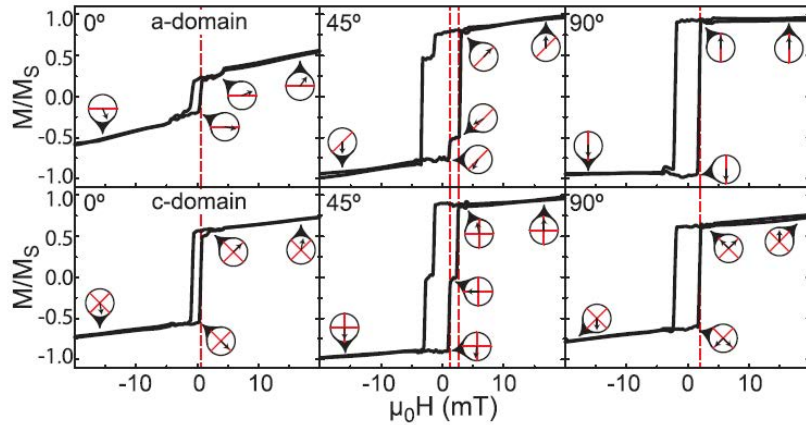


Figure 1.18: Magnetic hysteresis curves of single *a* (top row) and *c* (bottom row) domains measured at different magnetic field angles. The vertical red dashed lines illustrate simultaneous magnetic switching in the *a* and *c* domains [47].

The magnetoelastic anisotropy energy density (K_{me}) of Fe films on top of BaTiO₃ can be written as

$$K_{me} = B_1(e_{xx}\alpha_x^2 + e_{yy}\alpha_y^2) + B_2e_{xx}\alpha_x\alpha_y \quad (1.13)$$

Here, B_1 and B_2 are the magnetoelastic coupling coefficients, e_{xx} and e_{yy} are the strains along the cubic axes ([100] Fe and [010] Fe), e_{xy} is the shear strain along the diagonal [110] Fe direction, and α_x and α_y are the directional cosines with respect to [100] Fe and [010] Fe. The change in magnetoelastic anisotropy that this strain effect induces is given by the second term of Eq. 1.13. Using $B_2 = 7.83 \times 10^6$ J/m³, $e_{xy} = 1.0$ %, and $\alpha_x = \alpha_y = 1/\sqrt{2}$, this calculation yields $\Delta K_{me} = 3.9 \times 10^4$ J/m³. Since ΔK_{me} is positive, the [110] Fe direction is magnetically hard. Consequently, the uniaxial magnetic easy axis is oriented along the orthogonal [110] Fe direction, i.e., parallel to the magnetic domains and perpendicular to the BaTiO₃ ferroelectric polarization. The strength of the magnetoelastic anisotropy as determined from the slope and saturation field of hard-axis hysteresis curves is $K_{me} = 5 \pm 2 \times 10^4$ J/m³ [47].

Additionally, Y. Shirahata et al [93], study the switching of the symmetry of magnetic anisotropy in an epitaxial Fe layer on BaTiO₃ (fig. 1.19), in association with the interface lattice distortion occurred at the structural phase transition of BaTiO₃. The polar plot of the normalized remanent magnetization shows the fourfold symmetry with the magnetization easy axis along [100] of Fe at room temperature, while that at 230 K exhibits the twofold symmetry with the easy axis along [110]. Fig. 1.19 (a)-(c) show the in-plane magnetization curves of an Fe/BTO sample measured at room temperature, 230, and 150 K, in magnetic fields along [100] (black) and [010] (red) of the BTO substrate, where the magnetization M_s normalized by the corresponding saturation magnetization M_s , i.e., M/M_s [93]. It is obvious that the magnetization processes are distinct in the different phases of BTO and clearly depend on the direction of applied magnetic field. The results indicate that the interface lattice distortion induced by the structural phase transition of BTO at the Fe/BTO interface gives rise to the magnetoelastic coupling effect in the Fe layer. They clearly demonstrated the symmetry switching of the magnetic anisotropy in Fe/BaTiO₃ heterostructures, engineering the interface lattice distortion caused by the structural phase transition of BaTiO₃. The polar plots of the normalized rema-

nent magnetization have shown that the fourfold symmetry of the anisotropy in the tetragonal phase varies to the twofold symmetry in the orthorhombic phase [93].

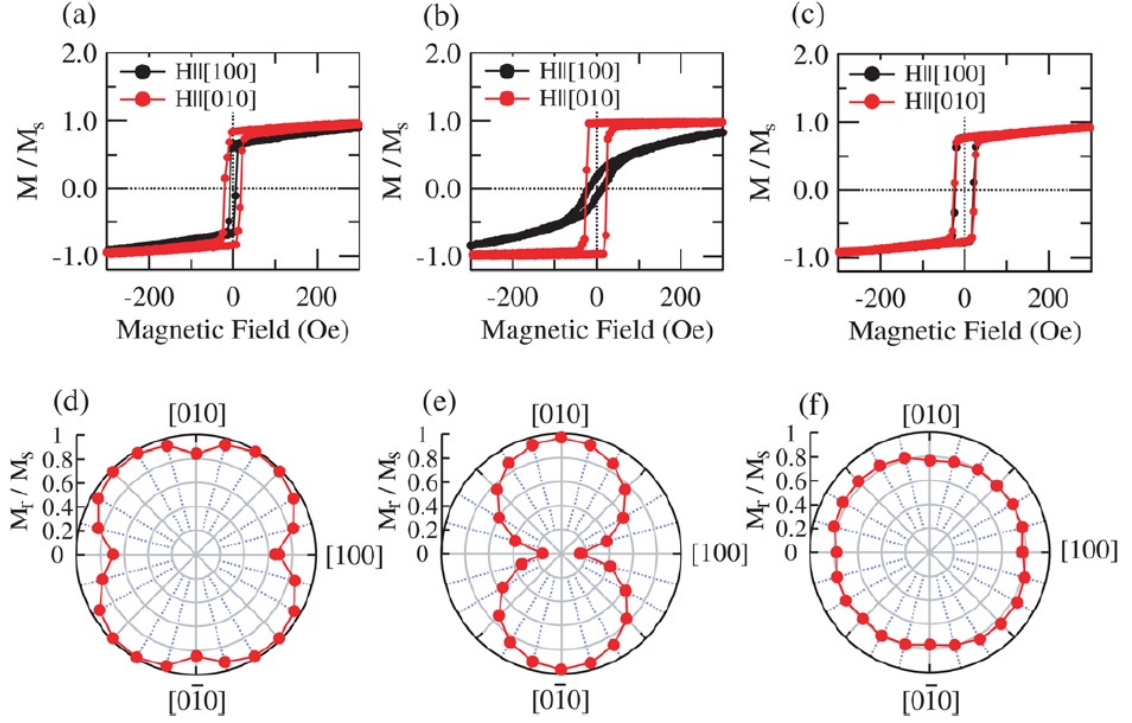


Figure 1.19: Normalized magnetization curves of an Fe/BaTiO₃ heterostructure for the field directions of [100] (black) and [010] (red) of BaTiO₃ substrate at (a) room temperature, (b) 230 K, and (c) 150 K. Polar plots of the normalized remanent magnetization (M_r/M_s) at (d) room temperature, (e) 230 K, and (f) 150 K[93].

1.6 Thesis objectives

1.6.1 General Objectives:

- Contribute to the research of new materials such ferroelectric and ferromagnetic bilayers to develop hybrid multiferroics.
- Growth and Characterization of BaTiO₃/La_{2/3}Sr_{1/3}MnO₃ bilayers thin films using the Pulsed Laser Deposition system in O₂ atmosphere.

- Deposit the bilayer on different substrates, and crystal orientation. To analyze the structural, magnetic and ferroelectric properties when this parameters are altered, and to interpret how they are related.

1.6.2 Specific Objectives:

- Find the optimal growth parameters of $\text{BaTiO}_3/\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ bilayers in ferromagnetic and ferroelectric phase on (001)- oriented LaAlO_3 , $(\text{LaAlO}_3)_{0.3}-(\text{Sr}_2\text{TaAlO}_6)_{0.7}$ and SrTiO_3 substrates in an atmosphere of O_2 .
- Characterization of the samples obtained by the technique X-ray diffraction (XRD) to determine the crystal structure, scanning electron microscopy (SEM), and by transmission electron microscopy (TEM) to determine surface morphology and structural properties. Electric and magnetic isothermal hysteresis for determining electrical properties using a physical property measurements system (PPMS) and a ferroelectric tester (RT66B), respectively.
- Dissemination of results.

1.7 Structure of this thesis

The study of multiferroic materials are a new field of investigation due to combine different physical properties in a single phase. However, the scenario is not simple, since the properties as ferromagnetism and ferroelectricity are present in different temperature ranges (moreover below room temperature). Therefore, the possibility of found magnetoelectric coupling to room temperature is reduced. For this reason, a simple solution is combine materials where a single phase is present, that is, a FM (FE) material with low coercive field and high saturation magnetization (saturation polarization). The structural properties as: lattice parameters, chemical structure among others are needed. In this cases, the principal goal is modify the FM properties by the presence of FE material or vice versa. In this thesis, we investigate the ferroelectric/ferromagnetic interaction in BTO/LSMO bilayers on different substrates (LAO, LSAT and STO on (001) direction) via Pulsed Laser Deposition. The proposal is analyze the influence of tensile or compressive strain induced through of

substrate. Additionally, the influence of LSMO layer on bilayers deposited on STO substrates was studied, to corroborate the possible influence LSMO relaxation strain in the system. For last, the influence of STO substrate orientation in BTO/LSMO bilayers was studied. The development of this investigation is described following:

In chapter 1, a brief introduction on multiferroics and hybrid multiferroics materials was displayed. We describe the nature problems of multiferroics materials and introduce the principal characteristic of LSMO and BTO, as candidates to build our system. Finally, different examples of changes on magnetic anisotropy associated to FE influence were described.

In chapter 2, we describe the principal techniques used to study our system. We explore the growth method used to prepare the samples and the different techniques to characterize the samples: structural, magnetic and ferroelectric properties. Therefore, the optimal quality of system will be analyzed and the correlation of different properties will be carried-out.

In chapter 3, we report the structural properties of BTO/LSMO bilayers. First, for samples deposited on LAO, LSAT and STO-(001) oriented. Second, for bilayers when the LSMO thickness is varied using (001)STO substrate. And finally, samples deposited on STO substrates with different orientations: (001), (110) and (111). In all cases, the LSMO layer have induced strain via substrate (tensile or compressive), while BTO layer is relaxed, adopting the bulk parameters. We focused on samples deposited on STO for Transmission Electron Microscopy, where dislocations and different strain/relaxation zones was observed.

In chapter 4, the magnetic properties of BTO/LSMO bilayers was discussed. All samples present a paramagnetic/ferromagnetic transition ~ 350 K and a saturation magnetization above 280 emu/cm^3 at room temperature. A slight difference on magnetic properties on bilayers in contrast with LSMO single layer was evidenced. Then, a in-plane magnetic anisotropy study was carried-out. These results display a change on magnetic anisotropy from biaxial in LSMO films to uniaxial only in bilayers deposited on STO(001) substrate. This change, was confirmed in bilayers different LSMO thickness. The anisotropy constants was calculated and the found values are according to literature.

In chapter 5, the FE properties was studied. In all samples, the isothermal

hysteresis loops at room temperature are consistent with FE materials. These properties display the following aspects: (1) BTO are the optimal FE material, reaching a saturation polarization $\sim 30 \mu\text{C}/\text{cm}^2$, (2) the LSMO layer can be used as bottom electrode and (3) the FE performance is according to fatigue test reported in literature. These results permit concluded a possible magnetoelectric effect due to optimal FE and FM properties was obtained.

Bibliography

- [1] H. Schmid et al., *Ferroelectrics*, **162**, 317 (1994).
- [2] B. Aken et al., *Nature*, **449**, 702, (2007).
- [3] D. Khomskii, *Physics*, **2**, 20 (2009).
- [4] T. Kimura et al., *Nature*, **426**, 55, (2003).
- [5] N. Hur et al., *Nature*, **429**, 392, (2004).
- [6] J. Wang et al., *Science*, **299**, 1719, (2003).
- [7] T. Kimura et al., *Phys. Rev. B* , **67**, 401(R), (2003).
- [8] M. Fiebig et al., *Nature*, **419**, 818, (2002).
- [9] M. Bibes et al., *Adv. in Phys.*, **60**, No. 1, 5, (2011).
- [10] T. Kimura et al., *Phys. Rev. B*, **68**, 1, (2003).
- [11] J. M. Caicedo et al., *J. Appl. Phys.*, **103**, 07E306, (2008).
- [12] J. Zapata et al., *IEEE transaction on magnetics*, **44**, 2895, (2008).
- [13] P. Ravindran et al., *Phys. Rev. B.*, **74**, 4412, (2006).
- [14] P. Fischer et al., *J. Phys. C: Solid State Phys.*, **13**, 1931, (1980).
- [15] I. Sosnowska et al., *J. Magn. Magn. Mater.*, **160**, 384, (1996).
- [16] J. R. Teague et al., *Solid State Commun.*, **8**, 1073, (1970).

-
- [17] A. M. Kadomtsevaa et al., Phase Transitions: A Multinational Journal, **79**, 1019, (2006).
 - [18] I. Sosnowska et al., J. Phys. C , **15**, 35, (1982).
 - [19] Y. F. Popov et al., JETP Lett., **57**, 69, (1993).
 - [20] M. Fiebig et al., J. Phys. D: Appl. Phys., **38**, 123, (2005).
 - [21] F. M. Bai et al., App. Phys. Lett., **86**, No 032511, 2511, (2005).
 - [22] H. Bea et al., J. Phys.: Condens. Matter., **20**, 434221, (2008).
 - [23] W. Merz, Phys. Rev., **76**, 1221, (1949).
 - [24] T. Wu et al., Phys. Rev. B, **73**, 4416, (2006).
 - [25] V. G. Prokhorov et al., Low Temp. Phys., **33**, 58, (2007).
 - [26] X. G. Tang et al., J. Appl. Phys., **100**, 114105, (2006).
 - [27] W. Wu et al., Appl. Phys. Lett., **85**, No. 21, (2004).
 - [28] S. Dussan et al., Appl. Phys. Lett., **96**, 072904 , (2010).
 - [29] C. A. F. Vaz et al., Phys. Rev. Lett., **104**, 127202, (2010).
 - [30] C. Thiele et al., Sens. Actuators A Phys., **129**, 180, (2006) .
 - [31] C. Zou et al., J. Appl. Phys., **111**, 07D718, (2012).
 - [32] C.-G. Duan et al., Phys. Rev. Lett., **97**, 7201, (2006).
 - [33] S. Sahoo et al., Phys. Rev. B, **76**, 2108, (2007).
 - [34] J. Ryu et al., Jpn. J. Appl. Phys., **40**, 4948, (2001).
 - [35] A. I. Kingon et al., Nature, **406**, 1032, (2000).
 - [36] A. Petraru et al., Appl. Phys. Lett., **81**, 1375, (2002).
 - [37] M. Zgonik et al., Phys. Rev. B, **50**, 5941, (1994).

-
- [38] J. Goodenough and J. Longon, *Magnetic and Other Properties of Oxides and Related Compounds*, Berlin: edited by K.-H. Hellwege and O. Madelung, Landolt-Bornstein, New Series, Group III, **4**, Pt. a (Springer-Verlag), (1970).
- [39] A. Urushibara et al., Phys. Rev. B, **51**, No. 20, 14103, (1995).
- [40] J. Z. Sun et al., Appl. Phys. Lett., **74**, No. 20, 3017, (1999).
- [41] N. V. Dai et al., J. Korean Phys. Soc., **53**, No. 5, 2427, (2008).
- [42] H. Y. Hwang et al., Phys. Rev. Lett., **77**, No 10, 2041, (1996).
- [43] A. Gupta et al., Phys. Rev. B, **54**, 15629, (1996).
- [44] J. Z. Sun et al., Annu. Rev. Mater. Sci., **28**, 45, (1998).
- [45] T. Venkatesan et al., Philos. Trans. R. Soc. London, Ser. A, **356**, 1661, (1998).
- [46] T. H. E. Lahtinen et al., Adv. Mater. **23**, 3187, (2011).
- [47] T. H. E. Lahtinen et al., Appl. Phys. Lett., **101**, 262405, (2012).
- [48] T. H. E. Lahtinen et al., Sci. Rep. **2**, 258 (2012).
- [49] N. Spaldin, *Magnetic Materials: Fundamentals and Device Applications*, Cambridge University Press, United Kingdom, (2003).
- [50] R. C. O'Handley, *Modern Magnetic Materials*, New York: Wiley, (2000).
- [51] R. Kusters et al., Physica B, **155**, 362, (1989).
- [52] K. Chabara et al., Appl. Phys. Lett., **63**, 1990, (1993).
- [53] R. Von Helmolt et al., Phys. Rev. Lett., **71**, 2331, (1993).
- [54] H. Ju et al., Appl. Phys. Lett., **65**, 2108, (1994).
- [55] M. McCormack et al., Appl. Phys. Lett., **64**, 3045, (1994).
- [56] A.- M. Haghiri-Gosnet et al., J. Phys. D: Appl. Phys. **36**, R127, (2003).

-
- [57] J. Hemberger et al., Phys. Rev. B, **66**, 094410, (2002).
 - [58] I. C. Arango et al., J. Phys.: Conf. Ser., Accepted, (2017).
 - [59] Ll. Balcells et al., Phys. Rev. B **58**, R14697-R14700 (1998).
 - [60] J. Y. Gu et al., Appl. Phys. Lett. **72**, 1113, (1998).
 - [61] M. Viret et al., Europhys. Lett. **39** 545, (1997).
 - [62] C. Zener, Phys. Rev., **81**, 440, (1951).
 - [63] C. Zener, Phys. Rev., **82**, 403, (1951).
 - [64] C. Zener, Phys. Rev., **83**, 299, (1951).
 - [65] J. E. Ordoñez et al., J. Phys.: Conf. Ser., **480**, 1-4, (2014).
 - [66] K. Kubo et al., J. Phys. Soc. Jpn., **33**, 21, (1972).
 - [67] P. Anderson et al., Phys. Rev., **100**, 675, (1955).
 - [68] L.W. Martin et al., Mater. Sci. Eng., **68**, 89, (2010).
 - [69] W. Pickett et al., Phys. Rev. B, **53**, 1146, (1995).
 - [70] P. D. Gennes et al., Phys. Rev., **118**, 141, (1960).
 - [71] J. Fontcuberta et al., J. Appl. Phys. **85**, 4800, (1999).
 - [72] C. A. Paz de Araujo et al., Nature, **374**, 627, (1995).
 - [73] J. Schwarzkopf et al., Prog. Cryst. Growth Charact. Mater., **52**, 159 (2006).
 - [74] R. Kullmer et al., J. Appl. Phys. A, **65**, 273, (1997).
 - [75] V. Garcia et al., Nature, **460**, 81, (2009).
 - [76] K. Choi et al., Science, **306**, 1005, (2004).
 - [77] C. B. Sawyer et al., Phys. Rev., **35**, 269, (1930).

-
- [78] W. Zhong et al., Phys. Rev. Lett., **73**, 61, (1994).
 - [79] P. W. Forsbergh et al., Phys. Rev., **76**, 1187, (1949).
 - [80] M. Dawber et al., Rev. Mod. Phys., **77**, 1083, (2005).
 - [81] N. Setter et al., J. Appl. Phys., **100**, 051606, (2006).
 - [82] J. Junquera et al., Nature, **422**, 506, (2003).
 - [83] D. Schlom et al., Ann. Rev. Mater. Res., **37**, 589, (2007).
 - [84] J. van Suchtelen et al., Phil. Res. Rep., **27**, 28, (1972).
 - [85] J. van den Boomgaard et al., J. Mater. Sci. **9**, 1705, (1974).
 - [86] A. M. van Run et al., J. Mater. Sci. **9**, 1710, (1974).
 - [87] J. van den Boomgaard et al., Ferroelectrics **9**, 727, (1976).
 - [88] J. van den Boomgaard et al., J. Mater. Sci. **13**, 1538, (1978).
 - [89] W. Prellier et al., J. Phys.:Condens. Matter **17**, R803, (2005).
 - [90] C. A. F. Vaz et al., Adv. Mater. **22**, 2900, (2010).
 - [91] C. A. F. Vaz et al., J. Phys.: Condens. Matter., **24**, 333201, (2012).
 - [92] Y.-H. Chu et al., Nature Mater. **7**, 478, (2008).
 - [93] Y. Shirahata et al., Appl. Phys. Lett. **99**, 022501, (2011).

Chapter 2

Experimental method

In this chapter, we present a brief overview of the main experimental techniques employed in this thesis for the growth and characterization of thin films. A large part of the growth and characterization process has been performed using the instruments available at the Thin Films Group - GPD, the Instituto de Nanociencias de Aragón - INA and Institute of Material Science of Aragon - ICMA, Spain. A fruitful collaboration has been carried out with the Center Excellent of Novel Materials - CENM in Universidad del Valle on Cali-Colombia. These results have been obtained through different techniques, the most relevant being described in this chapter.

2.1 Pulsed Laser Deposition

Complex oxides motivated the growth of thin films by the technique of pulsed laser deposition (PLD) [1]. Subsequently, the oxides material were used for growth superconductors, semiconductors and dielectric materials [2], in addition to nanotubes [3] and quantum dots [4]. In fig. 2.1, the PLD scheme is described, which consists of focusing a high power laser pulse on the surface of the material to be evaporated (target), so that the energy per unit area at that point (for some nanoseconds) is so high that it allows the formation of a plume-shaped plasma; the ablation process provides the material flux for film growth (laser path is displayed on fig. 2.1 (a)). For multicomponent inorganic, PLD has proven remarkably effective at yielding epitaxial films. The ablation conditions are achieved by selecting an ultraviolet (UV)

laser wavelength, laser pulse repetition (frequency) and nanosecond pulse width that is strongly absorbed by a small volume of the target material.

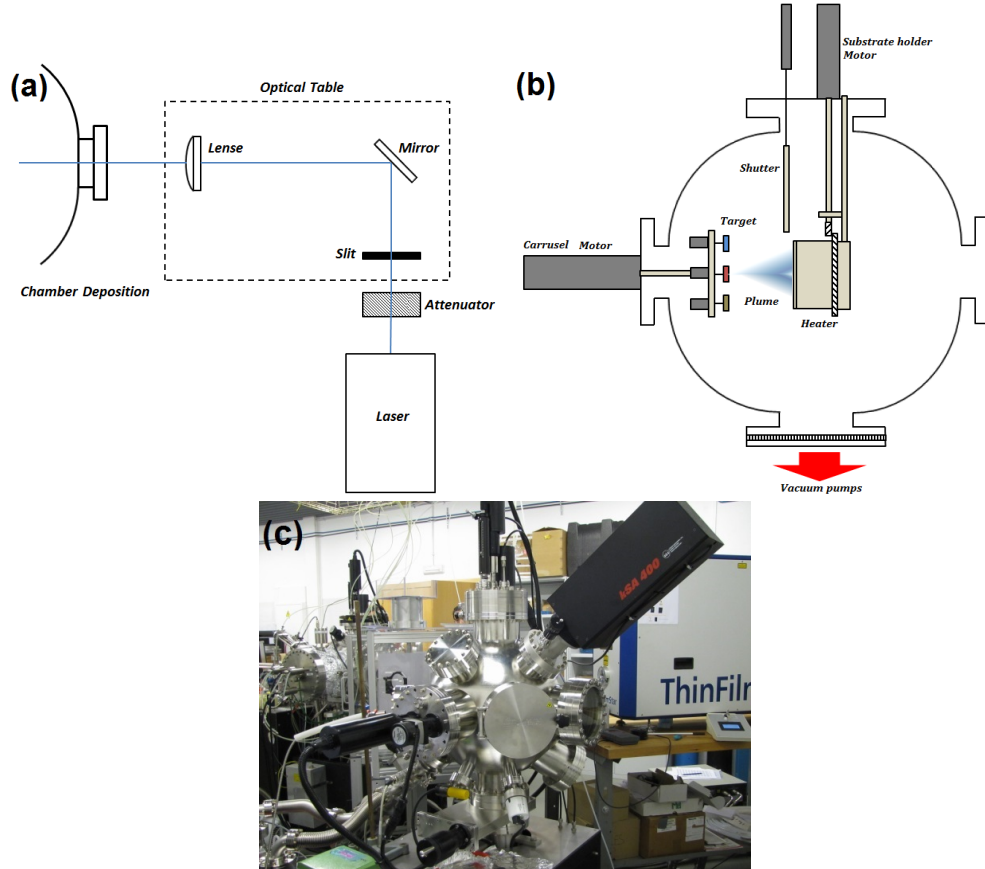


Figure 2.1: (a) Optical arrangement of the path traveled by the pulse emitted until reaching the deposition chamber, where it ejects the particles from the target (b) Diagram of the PLD system in Instituto de Nanociencias de Aragón (INA), and (c) PLD equipment photo.

The plume generated via ablation consists primarily of atomic, diatomic, and other low-mass species. In PLD, the thickness distribution from a stationary plume is quite nonuniform due to the highly forward-directed nature of the ablation plume. To first order, the distribution of material deposited from the ablation plume is symmetric with respect to the target surface normal and can be described in terms of a $\cos^n(\theta)$ distribution, where n can vary from ~ 4 -30. However, raster scanning of

the ablation beam over the target and/or rotating the substrate can produce uniform film coverage over large areas [5]. Thin films fabrication was done using a Pulsed Laser Deposition system localized on the Instituto de Nanociencias de Aragón (INA) in the University of Zaragoza (Spain) (Fig. 2.1), which consists of a KrF-laser ($\lambda=248$ nm), a deposition chamber equipped with two coupled vacuum pumps (Turbo Molecular - Membrane), an six targets carousel, which allows the deposition of several materials in-situ, a heater; which allows to control the temperature of the substrate until $\sim 1000^\circ\text{C}$, a removable substrate holder, and some pressure meters and other devices for the control of deposition parameters such as attenuators, windows and lenses, which enable the beam to be focused and collimated into the deposition chamber with the appropriate energy density.

In our case, the samples growth is carried out in reactive atmospheres, due to we want to deposit oxides, for which a controlled atmosphere of oxygen with a purity of 99.994 % and different substrates with perovskite structure was used. The Fig. 2.1 shows the optical arrangement of the path traveled by the emitted pulse. At the output of the laser, the laser energy is attenuated by an adjustable attenuator, collimated by an adjustable slit, then reflected in a flat mirror and focused by a convex flat lens, before entering the deposition chamber through a transparent infrared window. Later, the light-matter interaction occurs and the deposition of thin film is completed.

2.2 Structural Characterization

The structural and morphological characterization of the films is a fundamental part of this work, as will determine the quality of the films prepared by PLD. From this study, different issues such as the crystal structure and lattice parameter, chemical composition of the films, thickness, roughness and the interface structure with the substrate can be extracted. These can be achieved by means of different techniques, including X-ray diffraction (XRD), reflectivity (XRR) and transmission electron microscopy (TEM).

2.2.1 X ray diffraction-XRD

The interference for X-rays, is produced by the interaction radiation-matter. X-rays are electromagnetic radiation with photon energies in the range of 100 eV-100 keV. Due to the length X-rays is comparable with the size of the atoms, permit to scan the structural arrangement of atoms and molecules in different materials. X-rays interact with electrons in atoms in first instance. When Collide with the electrons, some photons of the incident beam will be deflected away from the direction in which originally traveled. If the wavelength of these scattered X-rays does not change, the process is called dispersion Elastic or Thompson dispersion. In crystals, the atoms are ordered in a periodic arrangement. Thus, the diffraction occurs when scattering in a certain direction is in phase with the scattered rays coming from others atomic planes, producing a constructive interference. For a given set of planes the condition for a diffraction (maximum intensity) is given by the Bragg law's:

$$n\lambda = 2d_{hkl}\sin\theta \quad (2.1)$$

Where λ is the wavelength of X-rays, d is the lattice interplanar distance of crystal and θ is the X-ray angle between the incident and the scattered ray (it is the angle we can measure) and n is a integer associated to the order of the diffracted beam. A diffraction pattern is obtained by measuring the intensity of scattered waves as a function of 2θ (scattering angle). When the Bragg condition is satisfied a maximum on intensity is obtained [6].

2.2.2 θ - 2θ scan

In this configuration the detector and sample holder are coupled with a goniometer so that the rotation of the detector and sample is in conjunction. The diffraction angle (2θ) is associated with the interplanar distance, allowing obtain information related to the out-of- plane lattice parameter (**c**), crystalline structure, stoichiometry and presence of other phases. In our films, θ - 2θ scan of 40° - 52° with a step of 0.005° and a time of 0.5 seconds per step was performed. The quality of peaks can be extracted from the full width at half maximum ($\text{FWHM}=\beta_{hkl}$) of a diffraction peak at the position θ , and the crystalline grain size D_{hkl} can be calculated using the Scherrer

formulae [6]:

$$D_{hkl} = \frac{\lambda}{\beta_{hkl} \cos \theta} \quad (2.2)$$

For strongly textured samples and diffraction patterns with few independent reflections, a rocking curve or so-called ω -scan is used. In this case, the detector is adjusted at the position $2\theta_o$ of the Bragg peak of our interest, while the sample is inclined by an angle θ in the neighborhood of the Bragg angle θ_o (fig. 2.2). In this case, the angles θ and 2θ are decoupled and the variation of the angle θ is known as ω [7, 8]. From this measurement, we can obtain information about the orientation distribution of the different (hkl) planes (mosaic spread) can be extracted. For FWHM lower values, the peak crystallographic orientation is better [7].

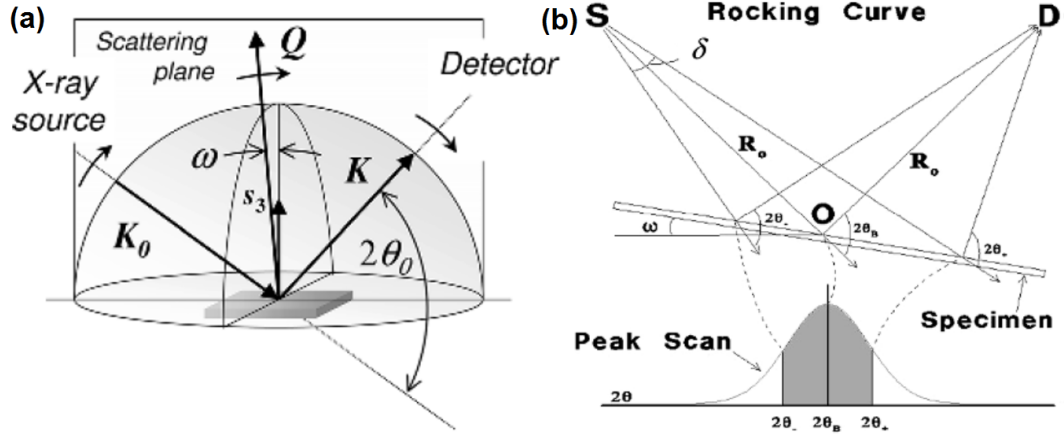


Figure 2.2: (a) Schematic representation of a rocking curve. The scattering angle $2\theta_o$ is fixed in the Bragg reflection, while the rocking angle ω is inclined around θ_o . (b) The slope of the sample allows to obtain a distribution around the Bragg peak, associated with the size of the crystallite [8].

2.2.3 Reciprocal Space Maps - RSM

RSM are the mapping from an area of interest in two directions of reciprocal space (Q_x and Q_z), which are obtained thorough of different θ - 2θ measurements with an ω offset between them (Fig. 2.3). In this configuration, if the reflections measured

are asymmetric, both out-of-plane (c) and in-plane (a) lattice parameters can be calculated [8].

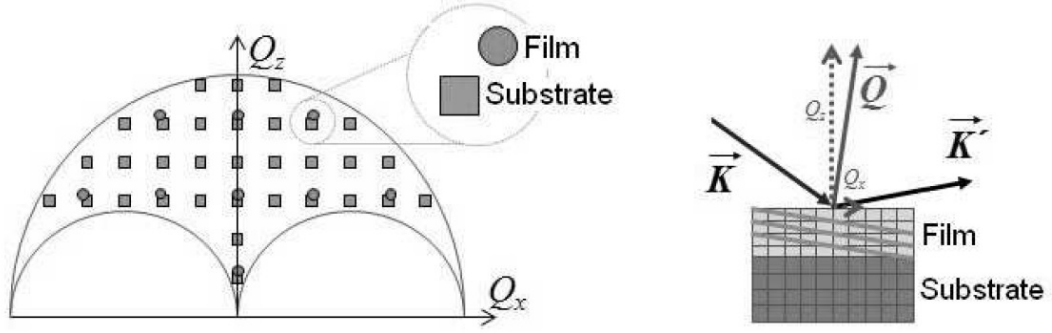


Figure 2.3: Schematic representation of a Reciprocal Space Map of a film and its substrate.

In fig. 2.3 the reflections between substrate and film is observed. From the comparison of the lattice parameters the epitaxial strain in the film can be found. The diffraction condition from asymmetric reflection associated to (hkl) plane satisfies the following relation [7]:

$$\vec{Q} = \vec{K}' - \vec{K} \quad (2.3)$$

$$|\vec{K}| = |\vec{K}'| = \frac{2\pi}{\lambda} \quad (2.4)$$

Then the lattice parameters can be calculated from Miller index:

$$a = \frac{2\pi\sqrt{h^2 + k^2 + l^2}}{Q_x} \quad c = \frac{2\pi\sqrt{h^2 + k^2 + l^2}}{Q_z} \quad (2.5)$$

2.2.4 X-ray Reflectivity

In this measurement the diffractometer is operated in the symmetric θ - 2θ configuration, but with much smaller θ angles in contrast with θ - 2θ diffraction. In this scenario, the interference of X-rays is reflected in the interfaces of consecutive layers which have different refraction index. For this reason, the gradients in composition

and also in mass density can be displayed. Different properties as film thickness (t_{film}), density (ρ) and roughness (σ) are determined with high accuracy from data direct analysis. In fig. 2.4, a reflectivity pattern is observed, where t_{film} are obtained from the period of interference fringes or so-called Kiessig's fringes at θ angles [8–10]:

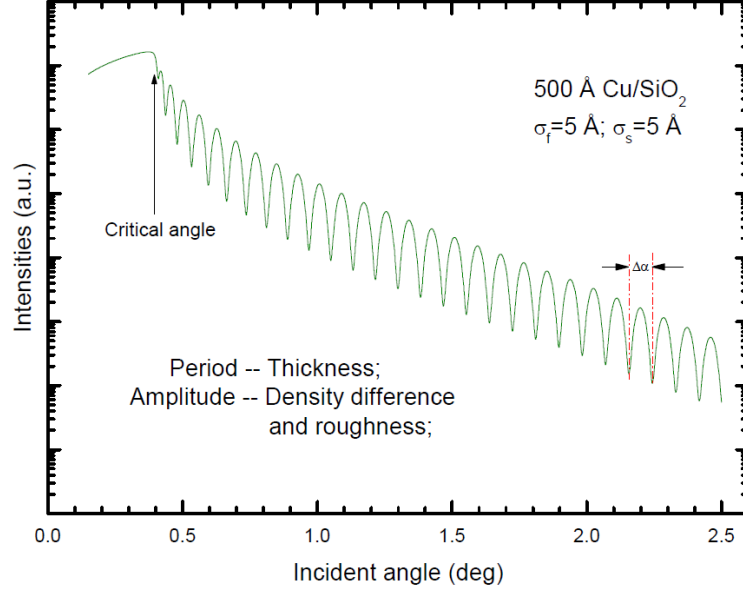


Figure 2.4: Reflectivity pattern for a Cu film onto SiO₂ substrate [10].

The critical angle (θ_c) is associated to the film density (black arrow in fig. 2.4) and the t_{film} are obtained from the modified Bragg's Law [8]:

$$\theta_m^2 = \theta_c^2 + \left(\frac{\lambda}{2t_{film}} \right)^2 m^2 \quad (2.6)$$

therefore, the slope S permit to found t_{film}

$$t_{film} = \frac{\lambda}{2\sqrt{S}} \quad (2.7)$$

Finally, large roughnesses or high thickness ($t_{film} \geq 100$ nm) produce a fast decrease in reflectivity intensity. In summary, this measurement allows identify t_{film} , ρ and σ for single layers, bilayer and multilayers.

In the case of our films, a Bruker D8 HRXRD diffractometer was used in at Instituto de Nanociencias de Aragón, INA. In Fig. 2.5, a photograph is observed,

where the X-ray source, the sample holder (Euler cradle), the monochromator and detector. This diffractometer has a high resolution monochromator with four crystal Ge (220) for selecting K_1 radiation of Cu source, providing a beam of X-rays with a wavelength $\lambda=1.54056 \text{ \AA}$.

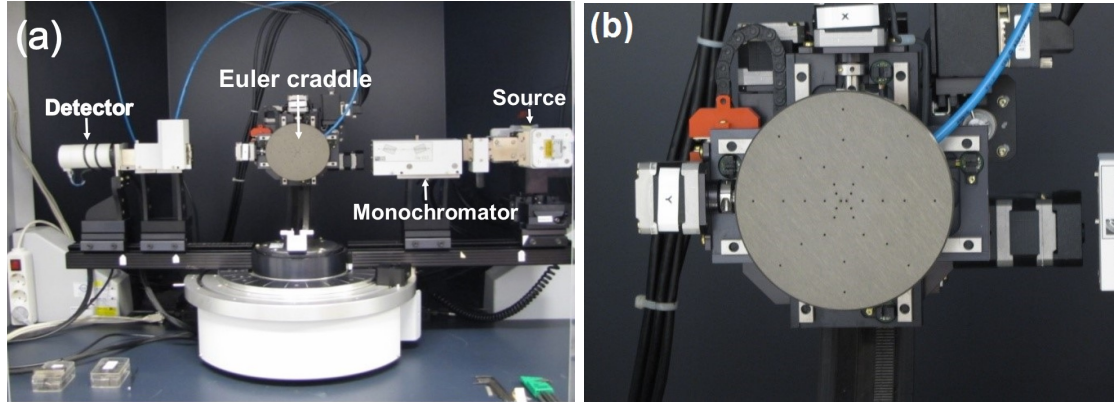


Figure 2.5: (a) Image HRXRD Bruker D8 Advance equipment in INA, (b) Detailed enlargement of the sample holder (Euler cradle), where the X positions are indicated, Y and Z, the latter out of the plane of the image.

For this case the calibration sample used corresponds to a thin film on (100) Si with a thickness of 500 nm, where the measured diffractogram were taken under the same conditions as the calibration sample. In our case we use the LEPTOS software, provided by the company in the diffractometer Bruker D8 with Bruker HRXRD to the INA, to facilitate the process of calculating the roughness parameters, density and thickness of the samples.

2.3 Transmission Electron Microscopy - TEM

In 1932, Ernst Ruska fabricate the first electronic microscope. From this investigation received the Nobel prize in 1986, with Gerd Bining and Heinrich Rohrer who developed the microscope of tunnel effect. Interestingly, the wavelength of electrons are much smaller than atoms. Thus, theoretically is possible to use them to see inside of atoms. A modern microscope, have physical aberration corrector and the new range

of electron gun of high brightness and great coherence (type XFEG or Cold FEG) can reach a spatial resolution of 0.7 Å, and a resolution in energy of 0.15 eV. In other words, a modern TEM be resolved with relative ease, atomic positions and chemical atomic maps to identify each of the constituent atoms of a lattice. The versatility of a TEM allow the development of many applications, from lattice images, defects and dislocations detection, magnetic images of nanostructures until 3D reconstructions. The image system, includes electromagnetic lenses and apertures, besides detectors, manager of magnifying and record the object image using some of the secondary signal beam emerging from the interaction of electrons sample (un-scattered electrons inelastically scattered electrons and elastic, backscattered electrons, X rays). All these components are integrated within a vacuum system so that the path of electrons is free of secondary interactions caused with small particles. Depending on the type of signal being recorded, or the way they scan the sample (beam parallel or convergent beam scanning), TEM can perform different imaging techniques. In High Resolution Transmission Electron Microscopy -HRTEM, the image is obtained by the interference of elastically scattered electrons in atomic columns on the crystal structure and electrons “not dispersed”. Some electrons passing through the sample without being “apparently” scattered. On the other hand, a few are scattered by atomic columns where are oriented parallel to the electron beam. The image formation (the points array in bright and dark contrasts) is attributed to the interference between the direct and the scattered beam following the pattern of the crystalline lattice[11, 12]. Scanning Transmission Electron Microscopy -STEM, in this technique the microscope uses a detector High Angle Annular Dark Field (HAADF) to collect the signal from the electromagnetic wave that scanning the sample (STEM). It permit study the crystalline structures formed by heavy elements, and deposited on a light support, or structures combining heavy and light elements, with considerable differences between their atomic number. The dispersion is collected it is proportional to the scattering cross section Rutherford, with a quadratic dependence on the atomic number Z (Z contrast image) [12, 13].

All the TEM images shown in this thesis have been obtained by Dr. C. Mágen, Dr. R. Gúzman and Dr. L. Rodríguez. For the structural characterization of samples a **FEI Titan 60-300 low base** was used (Fig. 2.6), belonging to the Advanced

Microscopy Laboratory (LMA) in the Instituto de Nanociencias de Aragón, INA. This microscope has a cannon XFEG type electron cannon latest generation of very high brightness, allowing you to shoot with highly coherent electrons. Furthermore, this microscope has a CETCOR aberration correction which corrects the aberrations present in the probe.



Figure 2.6: Titan Transmission Electron Microscope image at the Instituto de Nanociencias de Aragón in Zaragoza, Spain.

In order to perform cross-sectional images of the samples via TEM, is necessary manufacture a lamella (fig. 2.7). The process begin with a thin platinum layer (to protect the sample from the interaction with electrons or ions) deposited by Focused Electron Beam Induced Deposition - FEBID and Focused Ion Beam Induced Deposition - FIBID. In this techniques, the electrons or ions are used to dissociate a precursor material (organometallic) and create a selective deposition[14, 15]. Then, two Focused Ion Beam - FIB processes are performed. First, the material is removed to both sides of area covered with Pt, the trenches have dimensions of $18 \times 9 \times 4 \mu\text{m}^3$

(length x width x depth) with $\sim 1 \mu\text{m}$ of thickness. Second, the width is changed from 9 to $1 \mu\text{m}$, with $\sim 0.5 \mu\text{m}$ of thickness. After, the lamella is welded to a tip with Pt using FIBID and to release the lamella from the substrate by three cuts with FIB. When the lamella is placed on a copper holder (grid) by welding the free end with Pt by FIBID and releasing the nanomanipulator by FIB, a thinning is carried out which in our case between 10 - $5 \mu\text{m}$ to thicknesses of approximately 50 nm [15].

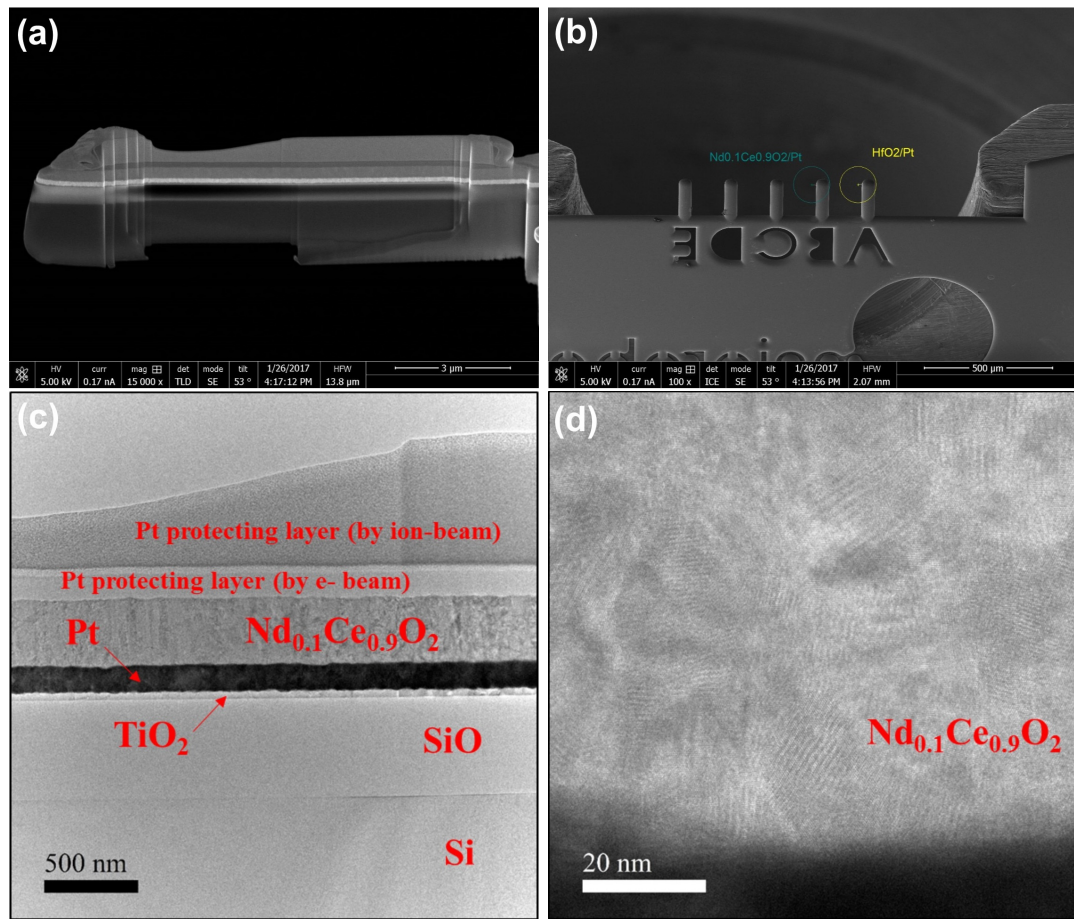


Figure 2.7: (a) Lamella fabricate from $\text{Nd}_{0.1}\text{Ce}_{0.9}\text{O}_2$ thin film, (b) $\text{Nd}_{0.1}\text{Ce}_{0.9}\text{O}_2$ lamella placed on a copper holder (grid), (c) low-magnification TEM images for the multilayered heterostructure and (d) High-magnification TEM image for $\text{Nd}_{0.1}\text{Ce}_{0.9}\text{O}_2$ layer.

2.4 Magnetic Measurements

For the magnetic measurements of the samples, we used a Superconducting Quantum Interference Device (SQUID) available on Magnetic Property Measurement System MPMS-5S DC SQUID from Quantum Design in the University of Zaragoza, Spain (Fig. 2.8(a)). SQUID is a sensitive technique for measuring magnetic properties. The device are based on two superconductors layers separated by thin insulating layers to fabricate two parallel Josephson junctions [16]. The superconductor state is obtained to low temperatures, therefore liquid helium (4.2 K) or liquid nitrogen (77 K) are necessary to operate. The electrical current density through of SQUID depends on the phase difference of the two superconducting wave functions. Thus, is used to convert magnetic flux obtained when the sample oscillate into ring in an electrical voltage. The system allows the study of magnetic materials between 1.7 K and 300 K and magnetic field from -50 kOe to 50 kOe.

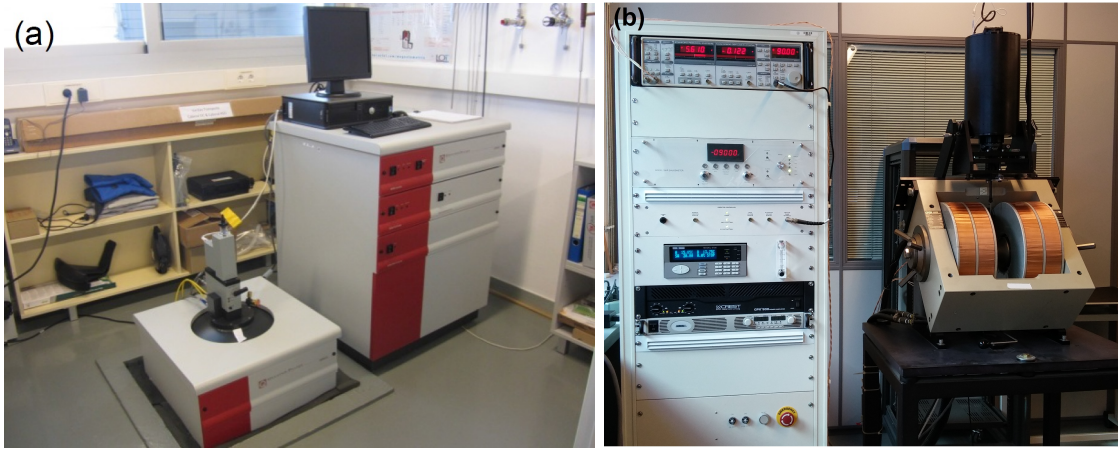


Figure 2.8: (a) Magnetometer photography used MPMS-5S DC SQUID Quantum Design at the University of Zaragoza-Spain, (b) VSM equipment from ADE Technologies at the Instituto de Nanociencias de Aragón, INA.

For magnetic anisotropy measures, we used a Vibrating Sample Magnetometer VSM equipment from ADE Technologies located at the Instituto de Nanociencias de Aragón, INA (Fig 2.8 (b)). VSM have a sensitivity of $\sim 10^{-6}$ emu in a wide temperature range. The sample is placed in a magnetic field generated by an water-cooled electromagnet (Not liquid He or N₂ are necessary) and moved up and down

at a frequency of 75 Hz perpendicularly to the magnetic field direction. It consists mainly of a linear motor for vibrating sample, a set of coils for detection, and the electronics necessary to drive the motor, transport and detect the response of the pickup coils, in addition to the implementation in software and control [17].

The measurement is basically performed by the oscillation of the sample near the detection coil by the voltage induced in the coil. The physical principle of operation of a vibrating sample magnetometer is a change in the magnetic flux which induces a voltage in the detection coil. The induced voltage is time dependent and is given by:

$$\begin{aligned} V_{ind} &= \frac{d\phi}{dt} \\ &= \left(\frac{d\phi}{dz} \right) \left(\frac{dz}{dt} \right), \end{aligned} \quad (2.8)$$

where ϕ is the magnetic flux in the detection coil, z is the vertical position of the sample relative to the coil, and t is time.

For a sample position sinusoidally oscillating voltage is based on the equation:

$$V_{ind} = 2\pi f C m A \sin(2\pi f t). \quad (2.9)$$

Where C is a coupling constant, m is the DC magnetic moment of the sample, A is the amplitude of oscillation, f is the frequency of oscillation [17].

2.5 Electric polarization

Ferroelectric measurements were carried out at room temperature on the capacitive structures. $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ layer was used as the lower electrode, while as a top electrode was deposited through a stainless steel mask gold circles of different diameters. For the deposition of the top electrodes, it was necessary to use the high vacuum evaporation equipment at the Universidad del Valle, which consists of an evaporator in a canoe, whose ends are connected to two copper electrodes, which can be applied between 1-100 amps of current through an electrical transformer. The thickness of the electrodes is controlled by varying the distance between the source and the film

evaporator. In Fig. 2.9 equipment for ferroelectric hysteresis measurements, consisting of a BX60M Olympus optical microscope, micromanipulators system, a pair of fasteners, a pair of microtips, ferroelectric system RT66B measures the observed Radiant Technology and a computer for data storage which is used the principle of the Sawyer-Tower circuit[18], the data acquisition system has the software Vision Radiant Technologies company [19]. Micromanipulators are composed of micrometer screws to move the nickel tips in three dimensions (X, Y, Z). The tips used was 7A model from The micromanipulator Inc with a length of 0.5 mm and a tip radius of 0.35 mm.

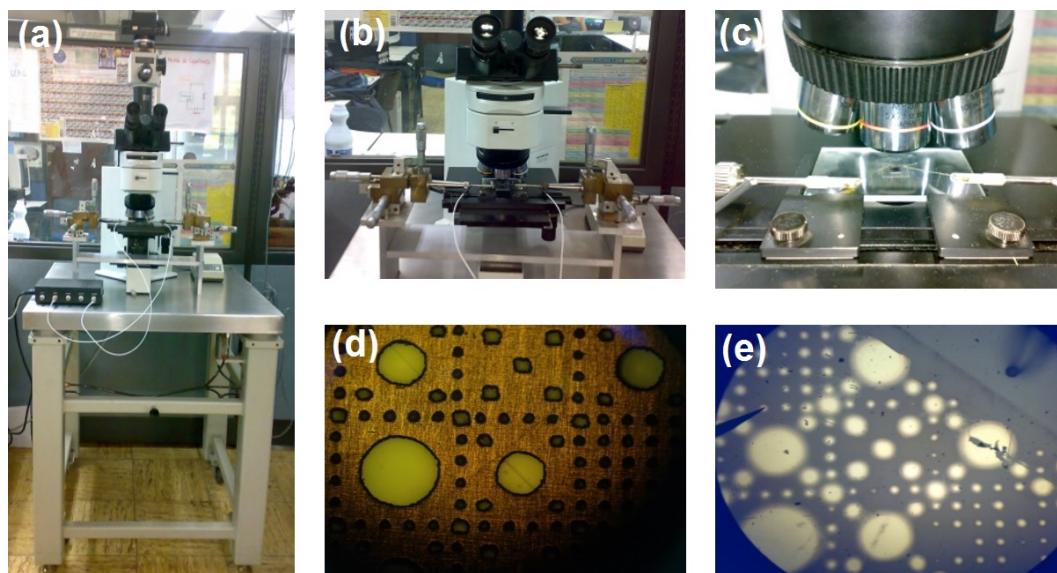


Figure 2.9: (a),(b) Ferroelectric equipment of Thin Films Group at the Universidad del Valle. (c) Expanding the micromanipulators that allow movement in three dimensions of the microneedles. (d) Stainless steel mask used in the manufacture of the micro Au, and (e) Optical microscopy micrograph of the capacitive structures, in which the microtips are observed contacting the capacitive structure.

Bibliography

- [1] X. Wu et al., Mater. Res. Soc. Symp. Proc., **191**, 129, (1990).
- [2] H. Smith et al., Appl. Opt., **4**, 147, (1965) .
- [3] Y. Zang et al., Appl. Phys. Lett., **73**, 3827, (1998).
- [4] T. J. Goodwin et al., Appl. Phys. Lett., **70**, 3122, (1997).
- [5] R. Eason, Pulsed Laser Deposition of Thin Films: Applications-Led Growth of Functional Materials, John Wiley and Sons, Inc., Publication (2007).
- [6] B. D. Cullity, Elements of X ray diffraction, Addison-Wesley, (1978).
- [7] U. Pietsch, V. Holy, T. Baumbach, High-Resolution X-Ray Scattering From Thin Films to Lateral Nanostructures, Springer Verlag, (2004).
- [8] M. Birkholz, Thin Film Analysis by X-Ray Scattering, Wiley-VCH Verlag GmbH Co. KGaA, Weinheim, (2006).
- [9] H. Kiessig, Schichten Ann. Phys., **10** (1931).
- [10] F. Huang et al., Research Notes, Center for Materials for Information Technology, The University of Alabama, (2005).
- [11] J. C. H. Spence, High-Resolution Electron Microscopy, Oxford University Press, (2008).
- [12] B. Fultz, Transmission Electron Microscopy and Diffractometry of Materials, Springer Berlin Heidelberg, (2008).

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- [13] S. J. Pennycook, Scanning Transmission Electron Microscopy, Springer New York, (2011).
 - [14] N. Yao, Focused ion beam systems: basics and applications, Cambridge University Press, (2007).
 - [15] L. Marín, Control de las propiedades eléctricas y magnéticas en nanoestructuras de manganitas de valencia mixta, Universidad de Zaragoza, (2014).
 - [16] B. D. Josephson, Phys. Rev. Lett., **1**, 251, (1962).
 - [17] Q. Design, PPMS VSM and ACT Option User's manual, San Diego: Quantum Desing, (2004).
 - [18] C. B. Sawyer and C. H. Tower, Phys. Rev., **35**, 269, (1930).
 - [19] Radiant technologies, User's Manual Radiant Precision Series with Vision Software, San Diego: Hardware Architecture and System Design, (2008).

Chapter 3

Growth and Structural characterization of $\text{BaTiO}_3/\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ bilayers

3.1 Growth bilayers

BTO/LSMO Bilayers were deposited on (001)-oriented SrTiO_3 (STO), $(\text{LaAlO}_3)_{0.3}-(\text{Sr}_2\text{TaAlO}_6)_{0.7}$ (LSAT) and LaAlO_3 (LAO) substrates of 0.5 x 0.5 cm by pulsed laser deposition (PLD). The deposition of bilayers was realized at 950 °C and an oxygen pressure of 3.0 and 400 mTorr BTO and LSMO, respectively. After deposition, the bilayers was cooled down at 700 Torr to obtain an optimal oxygen stoichiometry. The crystal structure of the film was analyzed by X-ray diffraction (XRD). Reciprocal space maps on (013) direction shows the high crystalline quality of the samples with a LSMO strained and a BTO relaxed on all substrates. The film thickness was determined by X-ray reflectivity (XRR). High angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) carried out in a probe aberration corrected FEI Titan 60-300 operated at 300 kV for verify the morphology of bilayers.

For deposition of LSMO, the Institute of Nanoscience of Aragón have a wide experience in the study about of optimal parameters for this system, while for BTO thin films we used (001)STO for analyzing the structural properties and identify the relevant parameters for the deposition as: oxygen pressure, laser energy, frequency,

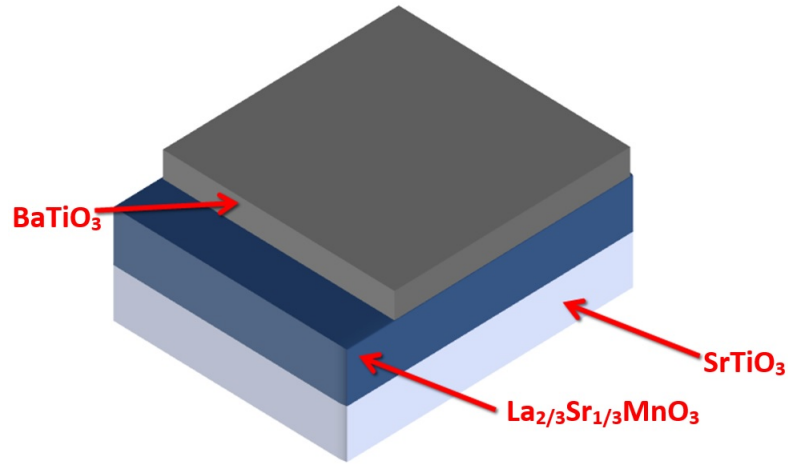


Figure 3.1: Configuration for $\text{BaTiO}_3/\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$, maintain fixed $t_{\text{LSMO}}=25$ nm and $t_{\text{BTO}}=100$ nm, using different substrates.

substrate temperature and annealing. In this way, we obtain the optimal parameters of deposition for each material. Next step is the fabrication of bilayers for multiferroic system in the configuration $\text{BaTiO}_3/\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ deposited on STO, LSAT and LAO (fig 3.1). In this configuration, the manganite will be employed as bottom electrode. The deposition parameters and sample nomenclature is consigned on Table 3.1.

Table 3.1: Deposition parameters and samples nomenclatures to BTO/LSMO bilayers deposited on different substrates.

Sample	N [Pulses]	Energy [mJ]	$T_{\text{substrate}}$ [°C]	Frequency [Hz]	Preassure [mTorr]	Annealing 700 Torr
LAO	2600-6000	70-50	950	10	400-3.0	30 - 60 min
LSAT	2600-6000	70-50	950	10	400-3.0	30 - 60 min
STO	2600-6000	70-50	950	10	400-3.0	30 - 60 min

3.2 Structural characterization

For the characterization and optimization of thin films of $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ we used (001) STO, (001) LSAT and (001) LAO substrates. In our system, the induced strains generate a wide range of possibilities respect to the change of properties of this oxides. Strontium titanate - STO is one of the most used substrates in growth oxides, due to is chemical and compositional stable with a lattice parameter of 3.905 Å. Strontium aluminium tantalate- LSAT has the perovskite crystal structure with a lattice parameter of 3.868 Å, is compatible for the growth of a wide range of perovskite oxides with a relatively low strain, and Lanthanum Aluminate - LAO have perovskite rhombohedral distorted crystal structure with a pseudocubic lattice parameter of 3.792 Å. For this reason we studied the influence of substrate on structural, magnetic and ferroelectric properties on this system.

3.2.1 θ - 2θ scans, XRR and RSM for LSMO and BTO single layer: texture, out-of-plane unit cell parameter and thickness.

First, LSMO and BTO singles layers have been prepared by PLD on single crystalline (001) oriented SrTiO_3 . Annealing process with high oxygen pressure is necessary in this layers to full the oxygen vacancies on LSMO and BTO to improve the ferromagnetic and ferroelectric properties on this materials. In fig. 3.2, θ - 2θ scans is present to LSMO and BTO films. All the peaks corresponds to diffraction from the STO substrate. For all possible (hkl) diffraction peaks, where h , k , l correspond to the Miller index, the appearance of only $(00l)$ peaks for films grown on (001) STO substrate ensures the alignment of STO, LSMO and BTO c-axis, respectively, and as consequence the texture on (001) direction is confirmed in these films. Symmetrical θ - 2θ scan around the (002)STO Bragg peak from the substrate shows the (002)LSMO reflection and Laue oscillations up to 6th order is present (fig. 3.2(a)). The Laue oscillations have its origin in the finite number of diffractive layers. The FWHM of the rocking curve centered at the (002)LSMO peak is 0.03° , which evidences the high crystalline of the LSMO films. While, the (002) Bragg peak from the STO substrate shows the oriented (002)BTO reflection. No other phases has been found

in the samples. The orthorhombic LSMO can be also approximately described by a cubic cell - pseudocubic. The lattice parameter of pseudocubic LSMO is $3.895 \text{ \AA}$, closes to the lattice parameter of STO substrate ($\text{STO}_{\text{cubic}}=3.905 \text{ \AA}$). The lattice mismatch is small, $f=(a_{\text{STO}}-a_{\text{LSMO}}/a_{\text{LSMO}})\times 100=+0.26 \%$. Thus epitaxial growth with cube-on-cube epitaxial relationships is expected. Due to the unitary cell of the LSMO film is smaller than that of the substrate ($c_{\text{LSMO}} < c_{\text{STO}}$), films will suffer a tensile epitaxial stress, and then before lattice relaxation, in-plane parameters will be tensile strained.

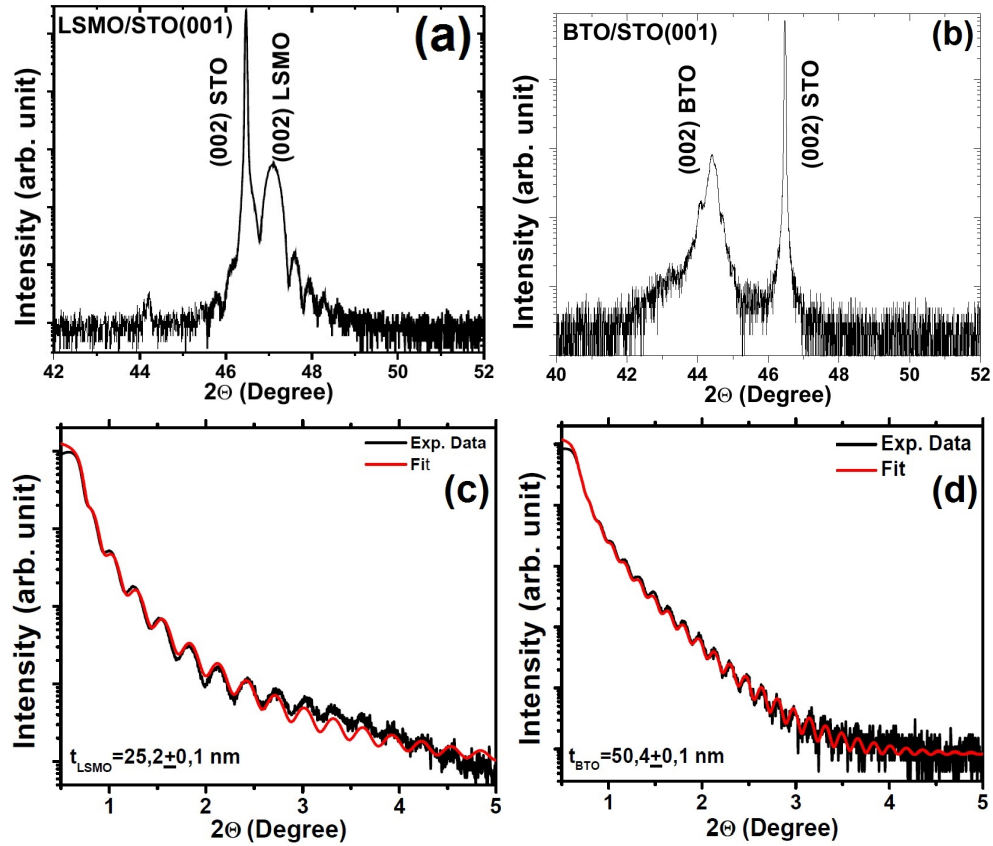


Figure 3.2: θ - 2θ scans at (002) peak for (a) $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3/\text{SrTiO}_3$ film and (b) $\text{BaTiO}_3/\text{SrTiO}_3$ film. XRR measurement for (c) LSMO and (d) BTO film. The red line corresponds to the numerical fit.

On the other hand, for tetragonal BTO, the in-plane lattice parameter is $3.992 \text{ \AA}$, and thus the lattice mismatch is -2.18% , indicating a compressive stress in the

film and as consequence a increasing on out plane parameter. The films are fully textured and there are no impurity crystalline phases within experimental resolution. In Fig. 3.2 (a) and (b), we observed that film peaks occur at higher angles than those expected for the bulk material, indicating smaller out-of-plane lattice distances than those of the bulk. This results from tensile strain imposed by the substrate on the basal plane of LSMO and BTO. Fig. 3.2 (c) and (d) show the low angle x-ray interference patterns for a 25-nm thick LSMO film and for a 50 nm- thick BTO film, respectively. We see in both patterns the chemically thickness oscillations. From the numerical analysis of the spacing between the Kiessig fringes, the film thickness was found to be $t_{LSMO}=25.2 \pm 0.1$ nm and $t_{BTO}=50.4 \pm 0.1$ nm, respectively. A value which is similar to the obtained from the Laue oscillations, indicating the crystalline coherence along the full thickness of the film.

The out-of-plane lattice parameter can be extracted from the LSMO(002) and BTO(002) peak position at the symmetrical θ - 2θ scans measurement (Fig. 3.2 (a) and (b)), obtaining:

$$c_{out-LSMO} = 3.850 \text{ \AA}; \quad c_{out-BTO} = 4.071 \text{ \AA}$$

In order to accurately obtain the in-plane unit cell parameters, Reciprocal Space Maps (RSM) were performed for analyzed both out-of-plane and in-plane lattice strains. The reflections to map, depends on the angular separation of film and substrate peak, additionally of the intensity of the asymmetric reflection. the reflections chosen was (103) direction for the samples deposited on (001) STO substrates. The lattice parameters obtained with both RSM and XRD are coherent. Due to the epitaxial growth, the LSMO in-plane lattice parameter is exactly the same as the STO lattice parameter. The LSMO out-of-plane value is lower than the bulk LSMO lattice parameter ($c_{LSMO-Bulk} = 3.877 \text{ \AA}$), suggesting that the film is tensile strained in the plane due to the slightly larger value of the STO lattice parameter with respect to the bulk LSMO value and, therefore, compressively strained in the out-of-plane direction. In Fig. 3.2, the BTO films are relaxed owing to the generation of misfit dislocations. We notice that for this film $c/a=1.015$ is higher than the tetragonal bulk value of BTO ($c/a=1.010$ Ref. [3]). From the RSM near the asymmetrical reflection (013) from the LSMO and (013) from the BTO, both a (in-plane) and c (out-of-plane) lattice parameters can be extracted (Eq. 2.5), as the scattering vector

is inversely proportional to the lattice parameters, we found the lattice parameters a , c , the c/a ratio and unitary cell volume, the values found was reported in the table 3.2. The values obtained is according with reported by different authors in literature [1–4].

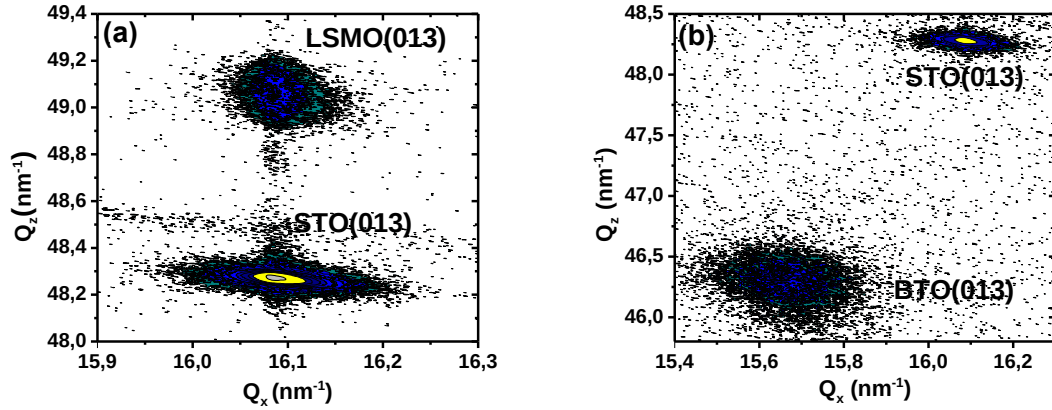


Figure 3.3: RSM near the asymmetrical reflections (a) (013)LSMO and (b) (013)BTO direction.

Table 3.2: Lattice parameters obtain from RSM for single layers growth on STO. To comparison different references has been included [1–4].

Sample	c [Å]	a [Å]	c/a	V [Å ³]
LSMO/STO	3.905	3.850	0.986	58.70
Ref. [1]	3.905	3.860	0.988	58.86
Ref. [2]	3.892	3.855	0.990	58.39
BTO/STO	4.011	4.071	1.015	65.45
Ref. [3]	4.009	4.048	1.010	65.15
Ref. [4]	3.994	4.038	1.011	64.41

From the numerical fit of the XRR data, the roughness (σ) between LSMO (BTO) film with the substrate and the density of material can be obtained (table 3.3). The film roughness is in the order of the nominal substrate roughness values, revealing the smoothness of the LSMO and BTO layer, and the film density is close to the

bulk value ($\rho_{LSMO}=6.40$ g/cm³ and $\rho_{BTO}=6.02$ g/cm³). Then, possible differences between film and bulk density could be explained as a film lattice distortion due to epitaxial strain with substrate. These structural properties on single films, allows to us identify the optimal deposition parameters to grown bilayers. Thus in the next section, we will study the structural properties on bilayers BTO/LSMO deposited on different substrates: LAO, LSAT and STO.

Table 3.3: Values obtained from the XRR numerical fit.

Material	Thickness (nm)	Roughness (nm)	Density (g/cm ³)
LSMO	50.4	0.08	6.61
BTO	25.2	0.72	5.84
STO	Substrate	0.10	5.11

3.3 BTO(100 nm)/LSMO(25 nm) bilayers growth on different substrates

In fig. 3.4, θ - 2θ scans around the (002) Bragg peak from the substrate performed on the bilayers show the appearance of the (002)LSMO and (002)BTO peaks for all substrates, a textured growth is observed and other phases not is identified.

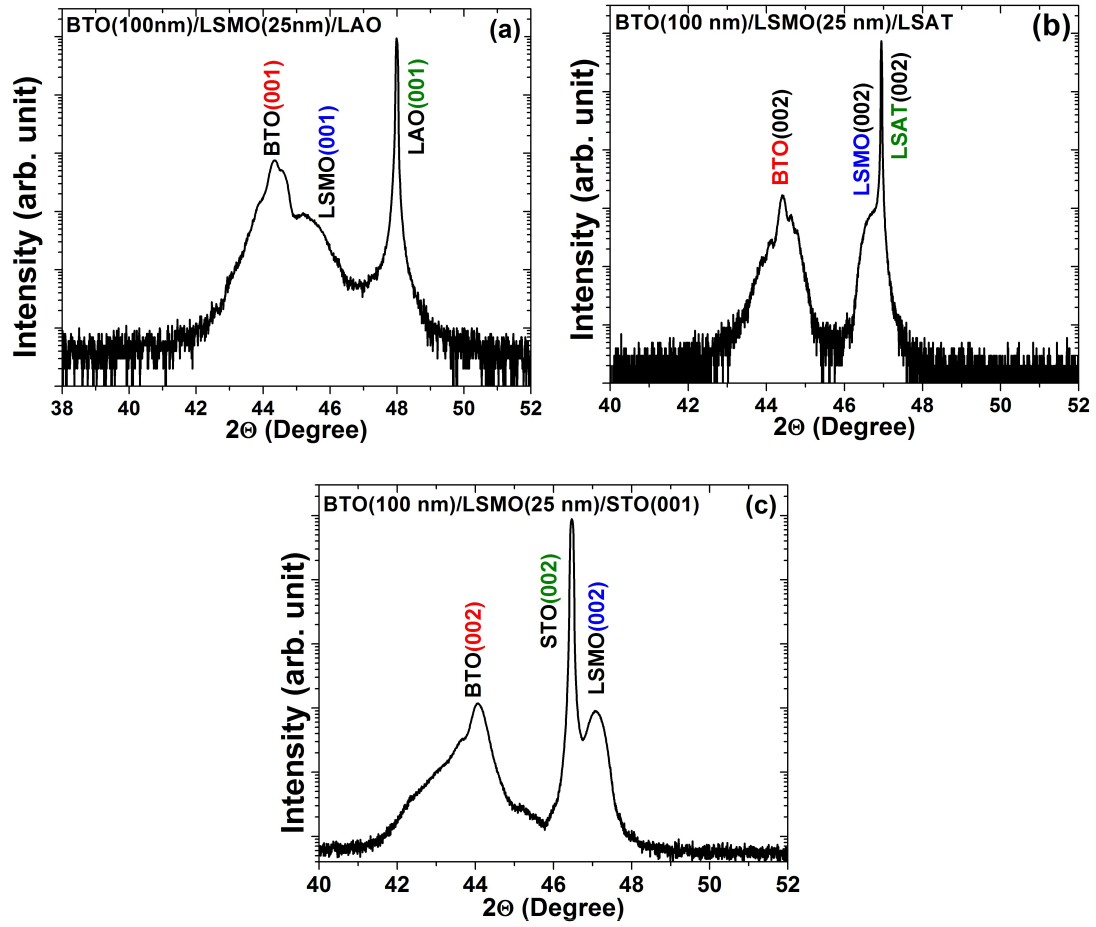


Figure 3.4: θ - 2θ scans at (002) peak for BTO/LSMO bilayers growth on (a) (001) LAO, (b) (001)LSAT and (c) (001)STO.

On LAO case, (002) BTO and LSMO peak is overlapping due to the difference on lattice parameter between LAO and layers. For LSAT case, (002) BTO and LSMO peaks shows a clear textured growth, with LSMO anchored to the substrate peak.

Finally, for STO the XRD shows a (002) BTO peak with almost two distributions: a broad peak on the base and a slight peak indicating various crystalline distributions associated to FE a, b and c-domains (Fig. 3.5) as was reported by Lahtinen et al. [5], in Fe/ $BaTiO_3$ structures, while LSMO is oriented on (002) direction. Shimizu et al., found this type of reflection on BTO/LSMO/STO bilayers [6], in these case an (002) peak asymmetrically broadens was identify, and suggested slow relaxation and a strain gradient [6–8]. The strain, caused by BTO/LSMO lattice mismatch, is an important factor affecting the FE properties of BTO. These strain can modify the phase diagram [9, 10], change the order of the transition [10], and shift transition temperatures. Strain gradients, on the other hand, are known to couple to the polarization via the flexoelectric effect [7, 11–14], and could, in theory, cause significant dielectric peak smearing in inhomogeneously strained films [15].

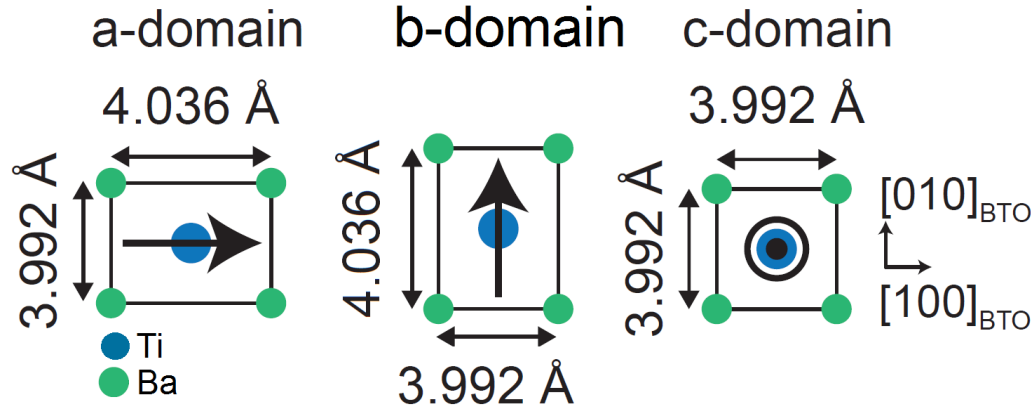


Figure 3.5: Schematic illustration of the domain configuration in the $BaTiO_3$ layer. Three configuration is identify: a-domain and b-domain where FE polarization is present in-plane substrate, while in c-domain the FE polarization is out-of-plane. The black narrow indicate FE polarization state. Adapted from [5].

The out-of-plane lattice parameter can be extracted from the (002)LSMO and (002)BTO peak position at the symmetrical XRD measurement (Fig. 3.4), the found values are reported in table 3.4.

Table 3.4: Lattice parameter obtaining from θ - 2θ measurements for BTO/LSMO bilayers on different substrates. To comparison different references has been included [17–20]

Sample	c-LSMO [Å]	c-BTO [Å]
LAO	3.792	4.079
Ref. [17, 18]	3.793	4.070
LSAT	3.890	4.102
Ref. [17, 19]	3.868	4.049
STO	3.855	4.108
Ref. [20]	3.870	4.167

The **c**-parameter value is lower than the LSMO bulk lattice parameter ($c_{LSMO-Bulk} = 3.889$ Å [16]) for LAO and STO, while for LSAT is very close to bulk parameter. The values obtained is according with reported by different authors in literature [17–20]. This differences on lattices parameter have as consequence deformations that distorts the octahedron formed by the oxygen and collective Jahn -Teller effect appears [21]. This mechanism is responsible for the transition metal-insulator, as well as the magnetic properties. For LSMO all samples have ferromagnetic properties, according to Konishi et al. [22], the physical properties of LSMO thin films are sensitive to tetragonal distortion, and $La_{1-x}Sr_xMnO_3$ bulk crystals with $x=0.4$ and $x=0.5$ exhibit ferromagnetic metallic FM properties. These properties of LSMO can be explained on the basis of a double-exchange mechanism [23], and LSMO thin films growth on LAO, LSAT and STO.

Fig. 3.7 displays RSMs taken around the pseudocubic (103) reflection for the LSMO bilayer grown on LAO, LSAT, and STO substrates. All maps exhibit three main irregular spots that correspond to the pseudocubic (103) reflection of the three crystals present in the heterostructures (BTO and LSMO films, and the substrate). In all cases, we note that the $\mathbf{Q}_x$ position of the (103) reflections of LSMO coincides with those of the substrates, while the $\mathbf{Q}_z$ position is different in each substrate. This behavior corroborates the expected fully strained epitaxial growth (cube on

cube) of the LSMO film where its in-plane lattice parameter is adapted to that of the substrate, and its out-of-plane lattice parameter is deformed accordingly [24, 25]. As we expected from the LSMO and substrate mismatches, RSMs demonstrate that LSAT and LAO substrates induce a compressive strain on the LSMO lattice, and STO induces a tensile strain. For the ferroelectric BTO layers the RSM show Q_x values different from the other reflections and an in-plane lattice parameter close to the bulk one. These results therefore reflect that the BTO lattice grows relaxed.

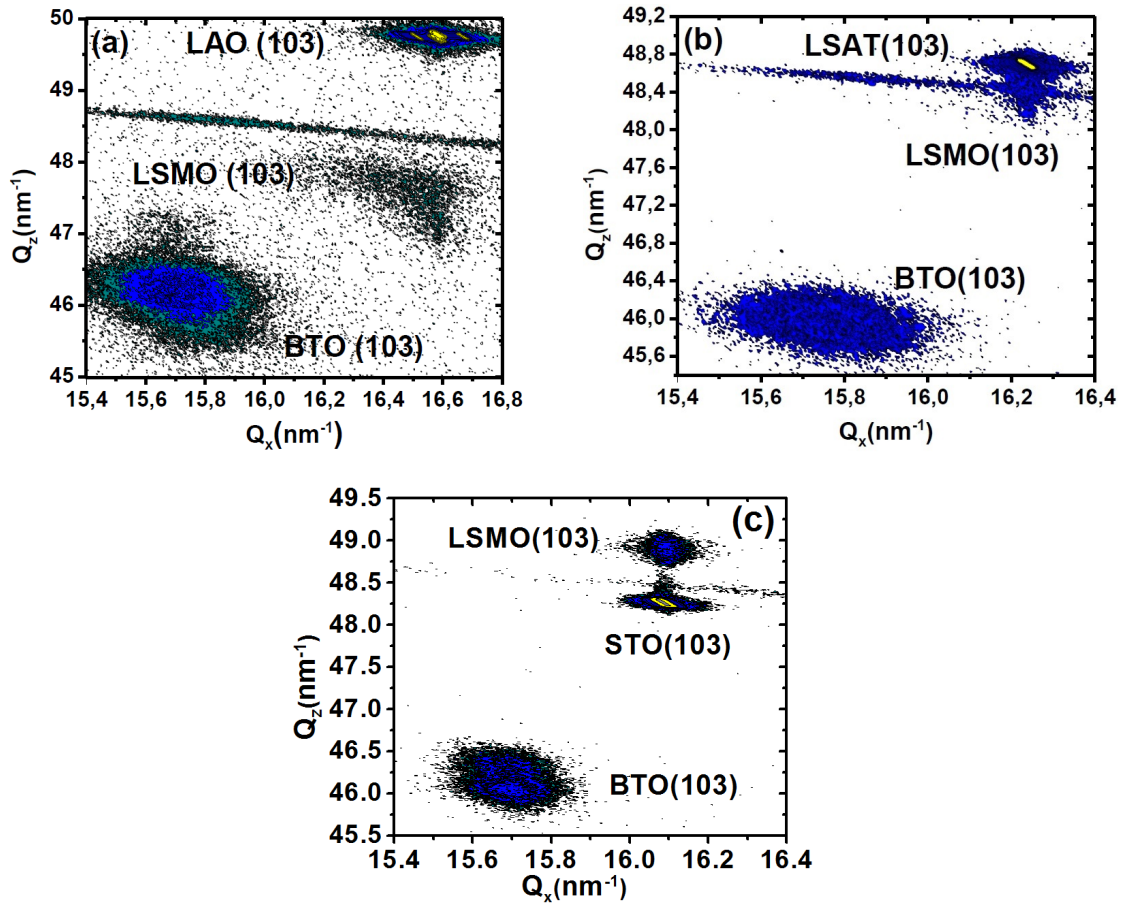


Figure 3.6: X-Ray RSM around the (103) reflection for the LSMO/BTO bilayers grown on (a) LAO, (b) LSAT, and (c) STO substrates.

Due to different compressive and tensile strain, associated to LAO, LSAT and LAO substrates, a distortion of the LSMO lattice occurs as sketched in Fig. 3.7.

The strain between the film and bulk in-plane and out-of-plane are defined by $f_a = 100 \times (a_{LSMO} - a_{substrate}) / a_{substrate}$ and $f_c = 100 \times (c_{film} - c_{bulk}) / c_{bulk}$. Positive values of f_a (f_c) correspond to tensile strains (the cell is elongated in the film plane and compressed in the out-plane direction), while negative values describe compressive strain (the cell is elongated out-of-plane and compressed in the film plane). The summary of all the calculated in-plane and out-plane for BTO/LSMO bilayers deposited on LAO, LSAT and STO are collected in Table 3.5.

Table 3.5: Lattice parameters for bilayers deposited on different substrates (bulk values $a_{LSMO}=3.889$ Å, $a_{BTO}=3.999$ Å and $c_{BTO}=4.033$ Å).

Substrate	Thickness [±1 nm]	a [Å]	c [Å]	c/a ratio	f_a in-plane	f_c out-of-plane
LAO	$t_{LSMO}=25$ nm	3.79 ± 0.02	3.96 ± 0.02	1.045	-2.55	+1.83
	$t_{BTO}=100$ nm	4.00 ± 0.04	4.09 ± 0.09	1.023	+0.03	+1.41
LSAT	$t_{LSMO}=25$ nm	3.87 ± 0.08	3.87 ± 0.01	1.000	-0.49	-0.49
	$t_{BTO}=100$ nm	4.00 ± 0.04	4.10 ± 0.02	1.025	+0.03	+1.66
STO	$t_{LSMO}=25$ nm	3.905 ± 0.01	3.855 ± 0.01	0.987	+0.41	-0.87
	$t_{BTO}=100$ nm	4.00 ± 0.03	4.09 ± 0.03	1.022	+0.03	+1.41

Due to the epitaxial growth, the LSMO in-plane lattice parameter is exactly the same as substrate. When LSMO thin films are grown on different substrates, which have a smaller lattice constant like LAO ($c_{LAO}=3.792$ Å), the LSMO thin films experience compressive strain in-plane causing the c axis to elongate ($c/a > 1$) as is observed on Fig. 3.7 (a). For our case $c/a_{LAO}=1.045$. This elongation are according with reported on similar bilayers deposited on LAO [26]. The properties of LSMO layer with grown on LSAT substrates are almost the same as those of the LSMO bulk crystals because the lattice constants of LSMO and LSAT (3.870 Å) are approximately the same (match LSMO-LSAT) and the structure is approximately cubic ($c/a=1$) as is observed on Fig. 3.7 (b), with $c/a_{LSAT}=1.000$, as was reported in similar structures [27–29]. And Finally, when LSMO layer is grown on STO, with a larger lattice constant than LSMO (3.905 Å), the LSMO thin films experience tensile strain in-plane, and the c axis is compressed ($c/a < 1$) as is observed on Fig. 3.7 (c) and has been found in this systems [30–34]. The lattice parameter fits exactly

with the substrate on a structure cube to cube. For the FE-BTO layers, their (103) reflections are completely mismatched of the others crystal phases (fig. 3.6), and their lattice parameters estimated by RSM are very close to that found in the BTO in bulk [35]. We can observe on the BTO reflexion a splitting around of the Q_z axis, for the compressive and tensile strain. Shimizu et al. [36], investigate for BTO films and in this case, 90° FE domain structures produce twin reflections with the same Q_x values near the $(400)_s$ reflection of the substrate due to the difference in the lattice parameters aligned on a- and c-axes. For LSAT substrate, the peaks overlaps in a single peak. This effect can be related with the strain gradient in side of the BTO layer. The BTO layers are relaxed for all substrates. This relaxations is associated to misfit dislocations, additional planes, vacancies and relaxation with thickness [18, 37]. In-plane and out-of-plane lattice parameters are found on values close to BTO bulk with $c/a > 1.020$ (Fig. 3.8(b)) as is traditional in this bilayers [17, 18, 26–32, 34, 37], indicating a tetragonal lattice (Fig. 3.7(a)) and the possibility for found ferroelectric properties on BTO ($c/a_{BTO}=1.010$ is considered like the limit for ferroelectricity to permit a tetragonal lattice)[35].

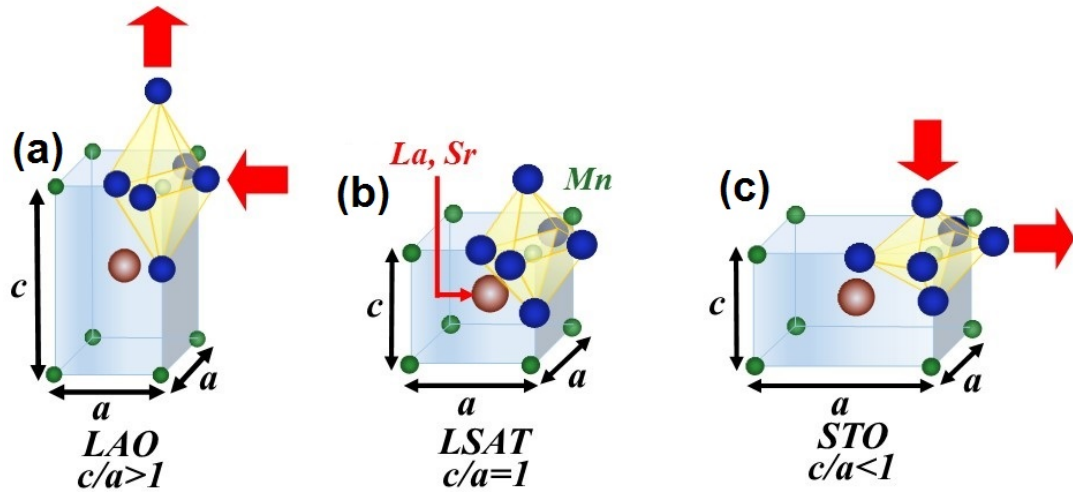


Figure 3.7: LSMO lattice strain induced by coupling with substrate, (a) LAO, (b) LSAT and (c) STO.

Now, we will study what occur to the manganite via strain. When LSMO layer are grown on LAO ($c_{LAO}=3.792 \text{ \AA}$), the LSMO experience compressive strain in-plane

$f=-2.03\%$, causing a tensile strain $f=+1.83\%$ out-of-plane and as consequence, the c axis is elongated with $c/a_{LAO}=1.039$, as is observed on fig. 3.7(a). This structural modification is similar to the cooperative Jahn-Teller-like distortion induced by the in-plane compressive strain, which in turn favors the stabilization of the e_g ($3z^2-r^2$) orbitals (Fig. 3.8). As a result, the disproportion in e_g orbital occupation induces a coupling between neighboring Mn cations that is ferromagnetic (FM) along the c -axis [38, 39].

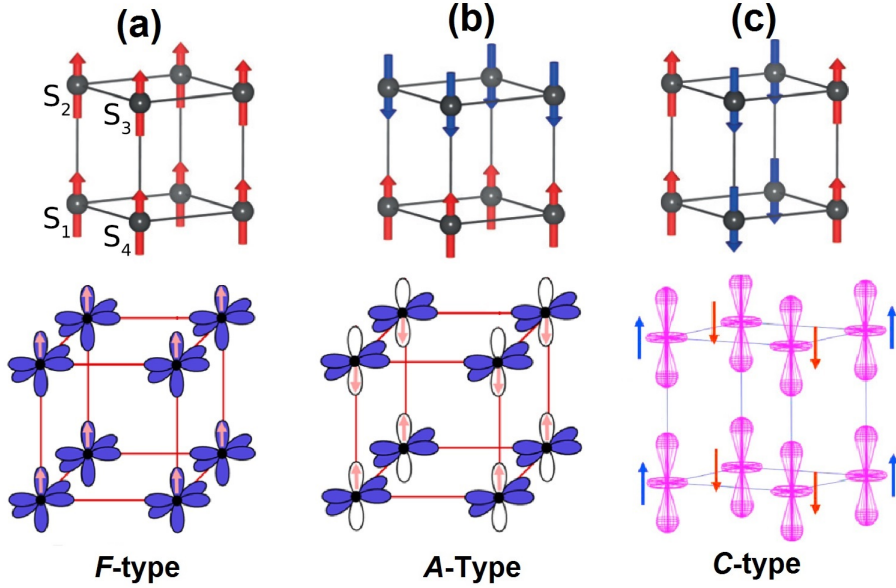


Figure 3.8: Schematic view of magnetic and orbital ordering (a) Ferromagnetic F-type ($c/a=1$ - LSAT), (b), Antiferromagnetic A-type ($c/a < 1$ - STO) and (c) Antiferromagnetic C-type ($c/a > 1$ - LAO). The arrows inside on atoms and orbitals indicate the spin direction of d electrons. Adapted from [40–42].

The properties of LSMO layer grown on LSAT substrates are similar to those of bulk LSMO because the in-plane mismatch between LSMO and LSAT ($3.870 \text{ \AA}$) is very small ($f_a = -0.49\%$), the film is weakly strained, see Fig. 3.7(b) and the structure is therefore approximately cubic ($c/a \sim 1$). When LSMO is grown on STO substrates ($3.905 \text{ \AA}$), the films experience tensile in-plane strain with $f_a = +0.41\%$, and the c axis is compressed, having a tetragonality factor of $c/a = 0.987$, see Fig. 3.7(c). Although in this case, the mismatch is approximately similar to

LSMO/LSAT but opposite (tensile strain), this remarks important changes on the magnetism properties of the LSMO associated to strain type (tensile or compressive). A tensile in-plane strain stabilizes the x^2-y^2 orbital levels occupation and favors A-type AF ordering, but in moderately strained LSMO is still FM [43, 44] and thus, a diminution on magnetic saturation is expected (Fig. 3.8).

3.4 BTO(100 nm)/LSMO(t_{LSMO}) bilayers growth on (001)STO with different LSMO thickness

BTO(100 nm)/LSMO(t_{LSMO}) bilayers was deposited on (001) STO substrates for study the influence of FM layer thickness on structural properties. Fig. 3.9 shows RSM for the BTO/LSMO bilayers, where we maintained fixed the BTO thickness, $t_{BTO} = 100$ nm, and varied the LSMO thickness, $t_{LSMO} = 20$ nm, (a), 25 nm (b) and 40 nm (c).

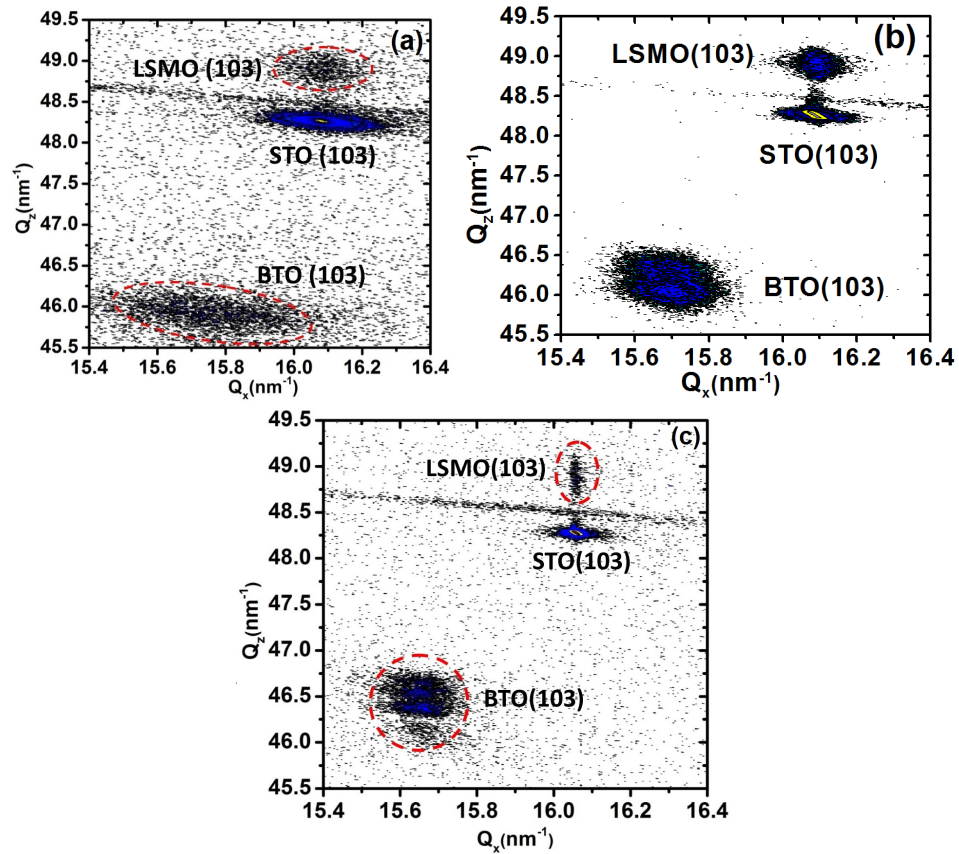


Figure 3.9: X-Ray Reciprocal Space Maps (RSMs) taken around the pseudocubic (103) reflection for the LSMO/BTO bilayers grown on STO with different LSMO thickness (a) 20 nm, (b) 25 nm, and (c) 40 nm.

All maps exhibit three main irregular spots that correspond to the (103) reflection

of the three crystal phases in the heterostructure: BTO film, LSMO film, STO substrate. In all cases, we note as the $\mathbf{Q}_x$ position of the (103) reflections of LSMO coincides with those for STO, while the $\mathbf{Q}_z$ position is different in each bilayer. In LSMO layer a biaxial deformation of lattice is found to preserve the volume of the LSMO unit cell [24, 25] for all bilayers. The summary of all the calculated in-plane and out-plane for BTO/LSMO bilayers deposited on STO are collected in Table 3.6 ($a_{LSMO}=3.889 \text{ \AA}$, $a_{BTO}=3.999 \text{ \AA}$ and $c_{BTO}=4.033 \text{ \AA}$).

Table 3.6: Lattice parameters for bilayers with different t_{LSMO} deposited on STO.

Bilayer	Thickness [$\pm 1 \text{ nm}$]	a [$\text{\AA}$]	c [$\text{\AA}$]	c/a ratio	f_a in-plane	f_c out-of-plane
1	$t_{LSMO}=20 \text{ nm}$	3.91 ± 0.01	3.85 ± 0.01	0.985	+0.53	-1.01
	$t_{BTO}=100 \text{ nm}$	4.00 ± 0.08	4.12 ± 0.09	1.032	+0.03	+2.15
2	$t_{LSMO}=25 \text{ nm}$	3.905 ± 0.009	3.855 ± 0.008	0.987	+0.41	-0.87
	$t_{BTO}=100 \text{ nm}$	4.00 ± 0.03	4.09 ± 0.03	1.022	+0.03	+1.41
3	$t_{LSMO}=45 \text{ nm}$	3.91 ± 0.01	3.87 ± 0.01	0.989	+0.53	-0.49
	$t_{BTO}=100 \text{ nm}$	4.00 ± 0.03	4.08 ± 0.03	1.020	+0.03	+1.17

According to the LSMO and STO mismatches, plots demonstrate that STO substrates induce a tensile strain on LSMO layer as is observed on fig. 3.7(c). Due to the epitaxial growth, the LSMO in-plane lattice parameter is exactly the same as substrate and the c axis is compressed ($c/a < 1$) as has been reported in the literature [30–34]. For the FE-BTO layers, their (103) reflections are completely mismatched of the others crystal phases for all samples (fig.3.9). Interestingly, the RSM pattern for the BTO is LSMO-thickness dependence. RSM for BTO spots exhibit from oval shape for $t_{LSMO} = 20$ and 25 nm and round for the $t_{LSMO} = 40 \text{ nm}$. Initially the spots have an oval shape around of $\mathbf{Q}_x$ position, as in the case of LSMO/BTO bilayers deposited by sputtering where BTO always is relaxed for different thickness [34]. This occurs for low LSMO thickness (20 and 25 nm), which may be associated with the way the ferroelectric layer is coupled to the LSMO. Due to the difference of lattice parameters between BTO and LSMO, dislocations, vacancies, grain boundaries are generated at the interface resulting in the formation of domains a, b, and c in the plane of the film [17, 18, 26–32, 34, 37], which allow stresses to relax even in regions close to the interface. For high LSMO thickness (45 nm) the spot of BTO

layer have a circular shape approximately, associated to a behavior similar to bulk. The BTO layers are relaxed for all LSMO thickness as has been found in previous investigations for LSMO/BTO bilayers deposited by sputtering [34]. In-plane and out-of-plane lattice parameters are found on values close to BTO bulk ($a_{BTO}=4.00$ Å) with $c/a > 1.020$, indicating a tetragonal lattice (Fig. 3.7(a)). Additionally, a diminution on $(c/a)_{BTO}$ value is observed with increase LSMO thickness, as is expected a relaxation on LSMO occur due to increase on thickness on this layer and lattice parameter is near to LSMO-bulk, allow a better coupling between both materials. Due to the BTO/LSMO bilayers are grown on STO substrates, in LSMO a tensile strain in-plane $\epsilon=+0.53$ % is observed in all bilayers, and c axis compression is generated ($c/a < 0.987$). Thus, a modification on shape of the lattice occur to preserve the lattice volume (Fig. 3.7 (c)). Tensile in-plane strain stabilizes the x^2-y^2 orbital levels, while the subsequent out-of-plane compression pushes up the z^2 orbital level, thus favoring electron occupancy of the x^2-y^2 orbitals and eventually leading to antiferromagnetic A-type orbital ordering [43, 44] and thus, a diminution on magnetic saturation is expected.

3.5 BTO(100 nm)/LSMO(25 nm) bilayers on different crystal orientation using $SrTiO_3$

Fig. 3.10 displays θ - 2θ scans around the (002) Bragg peak for BTO/LSMO bilayer grown on (a) (001) oriented STO, (b) (110) oriented STO, and (c) (111) oriented STO substrate. We identify the (002) Bragg peaks for the substrate, the BTO, and the LSMO layer. We also observe in all these x-ray spectra the Laue oscillations indicating a textured growth of the bilayer. No other phases has been found in the samples.

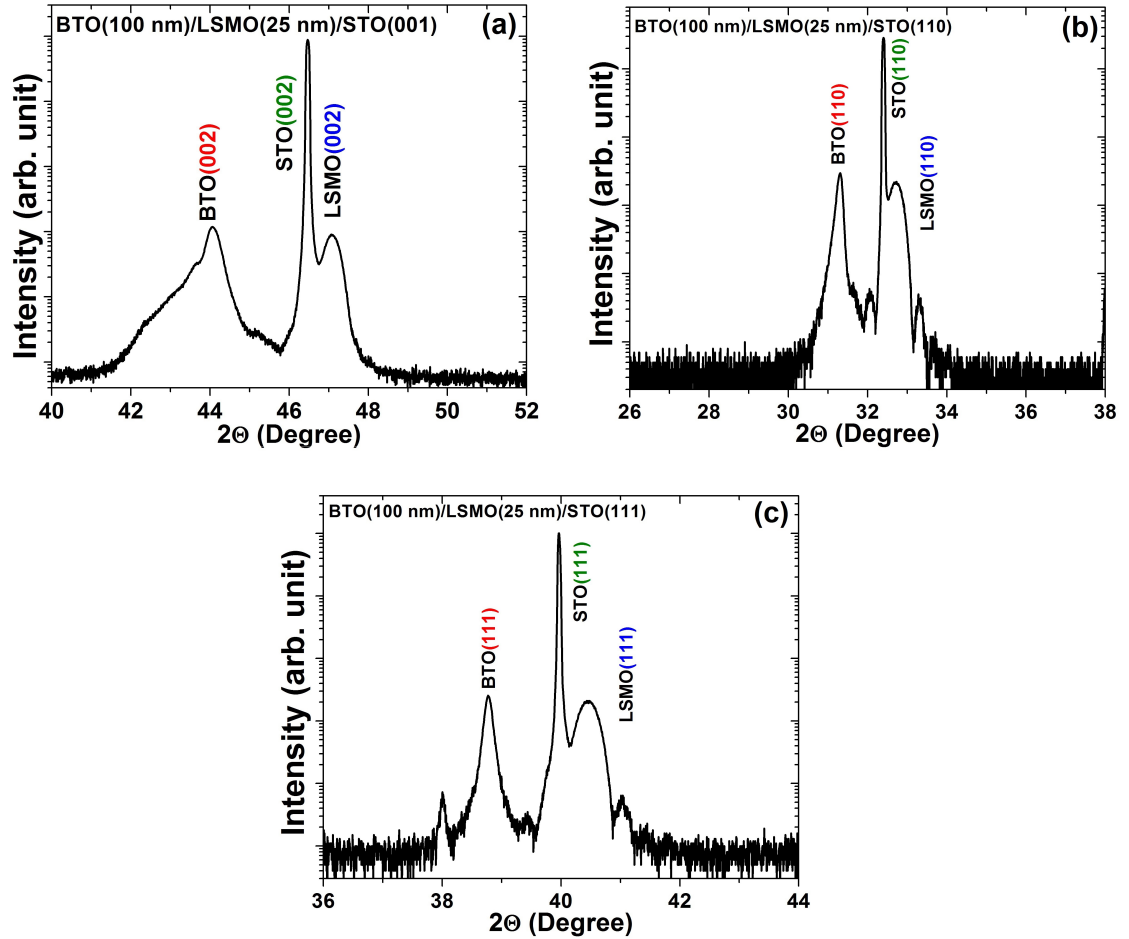


Figure 3.10: θ - 2θ scans of simultaneously BTO/LSMO for different substrates orientations, (a) (001) STO, (b) (110) and (c) (111) STO.

The FWHM of the (002) BTO Bragg peak is strongly dependent on the crystal orientation of the STO substrate. The peak is narrower for the bilayer deposited on (110) and (111), as is observed in fig. 3.10 (b) and (c), respectively, than for that grown on (100) oriented STO substrate (Fig. 3.10 (a)). Additional distributions on (110) and (111) BTO directions is not identified for this substrates, as occur for bilayer growth on (001)STO (probably due to dislocations and others mechanism of relaxation on this substrate). This results from the tensile and compressive strain imposed by the substrate on the basal plane of LSMO and BTO for (110) and (111) substrates [36]. The type and extent of the distortion of the cell is associated with the substrate orientation. The rhombohedral unit cell undergoes a biaxial tensile stress on STO(001) that imposes a tetragonal distortion on the unit cell. While, (110) and STO(111) substrates impose monoclinic and trigonal distortions of the unit cell, respectively. We would expect the out-of-plane distortion to differ as a function of orientation due to the anisotropic Young's moduli of LSMO films [45]. The out-of-plane lattice parameter and FWHM from XRD and rocking curves for BTO and LSMO layers, are summarized in Table 3.7. The lattice parameter found is according to values reported by Chopdekaret al. [45], and below to reported by Boschker et al. [46], where a in-plane tensile strain is observed for all orientations, which is associated to c-axis compression (Fig. 3.7) altering strongly the magnetic properties as has been reported for LSMO single layers [45–47] .

Table 3.7: Out-of-plane lattice parameters and FWHM for BTO/LSMO bilayers grown on STO substrates with different orientations.

Substrate	Layer Reflection	c [Å]	FWHM-Layer [deg]	FWHM-STO [deg]
(001)STO	(002)LSMO	3.86 ± 0.02	0.179°	0.170
	(002)BTO	4.09 ± 0.03	0.385°	
(110)STO	(220)LSMO	3.867 ± 0.008	0.113°	0.110
	(220)BTO	4.037 ± 0.008	0.266°	
(111)STO	(222)LSMO	3.858 ± 0.008	0.098°	0.120
	(222)BTO	4.018 ± 0.008	0.192°	

In Fig. 3.11, the BTO crystallographic orientations is observed for all substrates.

For STO(001) a correspondence between BTO and LSMO around of (001) direction is expected (Fig. 3.11(a)). As consequence both materials allows obtain the four-fold symmetry reported for the LSMO/STO. This growth permit the FE domain formation in out-of-plane substrate direction to permit the P_{up} and P_{down} states (Fig. 3.11(d)). For STO(110) a two-fold symmetry is expected with a 180° of separation (Fig. 3.11(b)). For this reason the FE domain is in-plane of substrate (Fig. 3.11(e)). For last case, in STO(111) a three-fold symmetry is expected with a 120° of separation around of (111) plane (Fig. 3.11(c)). In this orientation, the FE domains are in-plane (111) (Fig. 3.11(f)). These results are according to reported by Zhang et al. [48], in BTO films deposited on STO (001), (110) and (111) where the ϕ scans measurements corroborated the symmetries for each substrate.

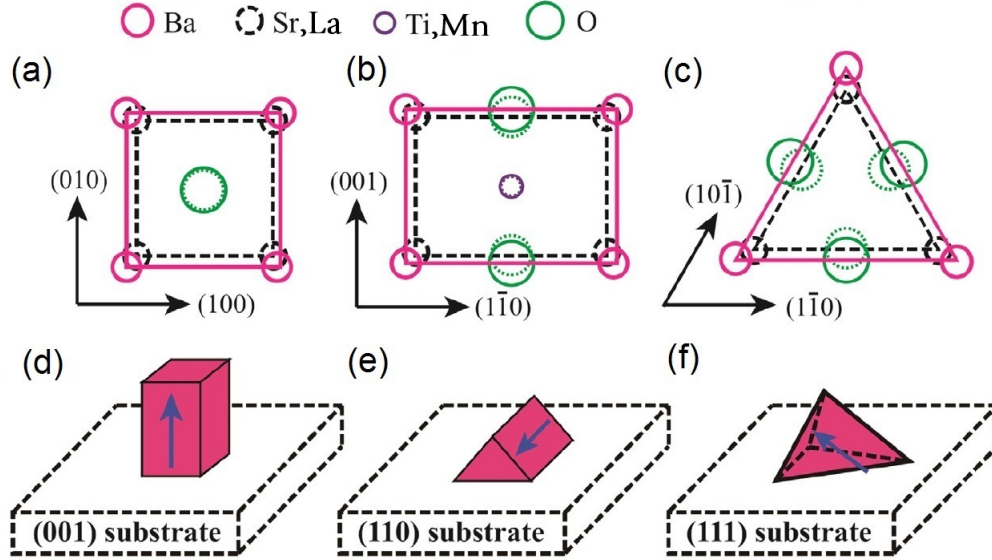


Figure 3.11: Schematic drawings of (a-c) the in-plane lattice matching relationships between BTO films and STO substrates, and (d-f) the out-of-plane epitaxial growth structures of BTO films in (001)-, (110)-, and (111)-BTO/STO heterostructures. The blue arrows in (d),(e),(f) represent the spontaneous polarization orientations. Adapted from [48].

Fig. 3.12 shows the normalized rocking curves, with the corresponding Pseudo-Voigt fit for the BTO/LSMO bilayers. Fig. 3.12(a) displays the rocking curves for (002) LSMO Bragg peak for bilayer grown on STO with orientation (001), (green

circles); (022) LSMO Bragg peak for bilayer grown on STO with orientation (110), (black squares); and (222) LSMO Bragg peak for bilayer grown on STO with orientation (111), (blue triangles). Fig. 3.12(b) displays the rocking curves for (002) BTO Bragg peak for bilayer grown on STO with orientation (001), (dark blue diamonds); (022) BTO Bragg peak for bilayer grown on STO with orientation (110), (purple pentagons); and (222) BTO Bragg peak for bilayer grown on STO with orientation (111), (wine triangles). FWHM analysis allows to us quantify the misorientation of out-of-plane crystal axis of the films.

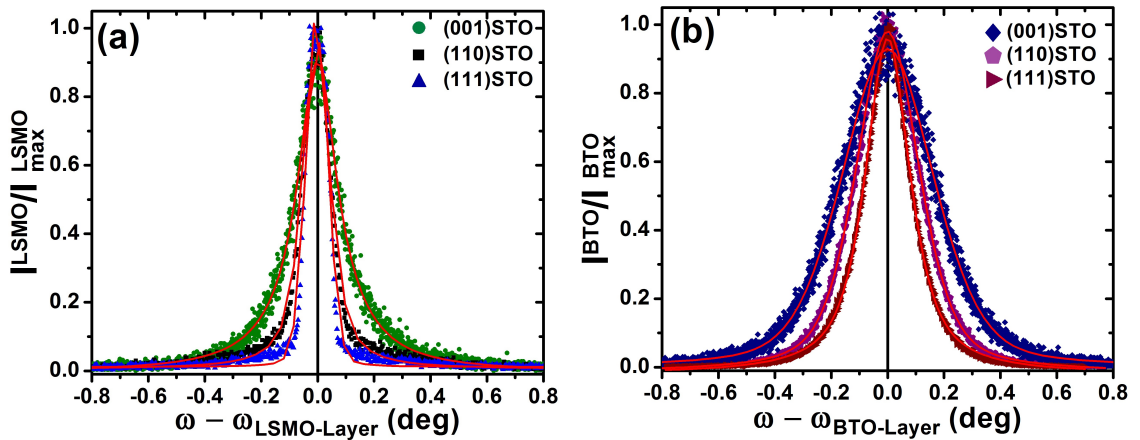


Figure 3.12: Normalized rocking curves for BTO/LSMO bilayers grown on oriented STO substrates (a) (002) LSMO Bragg peak on (001)-STO (green circles); (022) LSMO Bragg peak on (110)-STO (black squares); and (222) LSMO Bragg peak on (111)-STO (blue triangles). (b) (002) BTO Bragg peak on (001)-STO (dark blue diamonds); (022) BTO Bragg peak on (110)-STO (purple pentagons); and (222) BTO Bragg peak on (111)-STO (wine triangles). Solid lines correspond to pseudo-Voigt fits.

Table 3.7 summarized the FWHM for all samples extracted from the rocking curves in fig. 3.12. The FWHM of reflections peaks for the substrates are in the range of 0.10° to 0.17° due to instrumental limitations. For LSMO layer the FWHM values are near to those found for the substrate indicating high quality of the perpendicular textured growth of the LSMO film, in according with others reported in literature [47, 49, 50]. On the other hand, the FWHM values for the BTO layer is higher

than those for the LSMO layer. They exhibit dependence on the crystal orientation of the STO substrate being the highest value for sample grown on (001) oriented STO. We associate this high FWHM a different crystal distribution in the plane of the substrate accompanied by planar defect, as evidenced also in the XRD displayed in fig. 3.5 and fig. 3.10(a)). This values shows a high level of misorientation with respect to layer deposited on (110) and (111)STO substrate.

3.6 Transmission Electron Microscopy for BTO/LSMO bilayer on (001)STO substrate.

Fig. 3.13 shows HAADF-STEM micrographs for BTO/LSMO bilayer deposited on (001) STO substrate where we can observe both BTO/LSMO and LSMO/STO interfaces, image at the left. A High resolution STEM micrograph at the BTO/LSMO interface is shown at the right. Due to the Z-contrast effect, where the intensity recorded is inversely proportional to the square of the atomic weight, the more intense (brighter, whiter) points would correspond to the atomic positions of the elements with greater atomic number value. Thus, we can distinguish the Sr, Ba and La in the STO, BTO and LSMO layers respectively. In the image we observe the coupling between the substrate and the LSMO magnetic layer ($Z_{Sr} = 38$ and $Z_{La} = 57$) and the coupling between magnetic and the BTO ferroelectric layer ($Z_{Ba} = 56$).

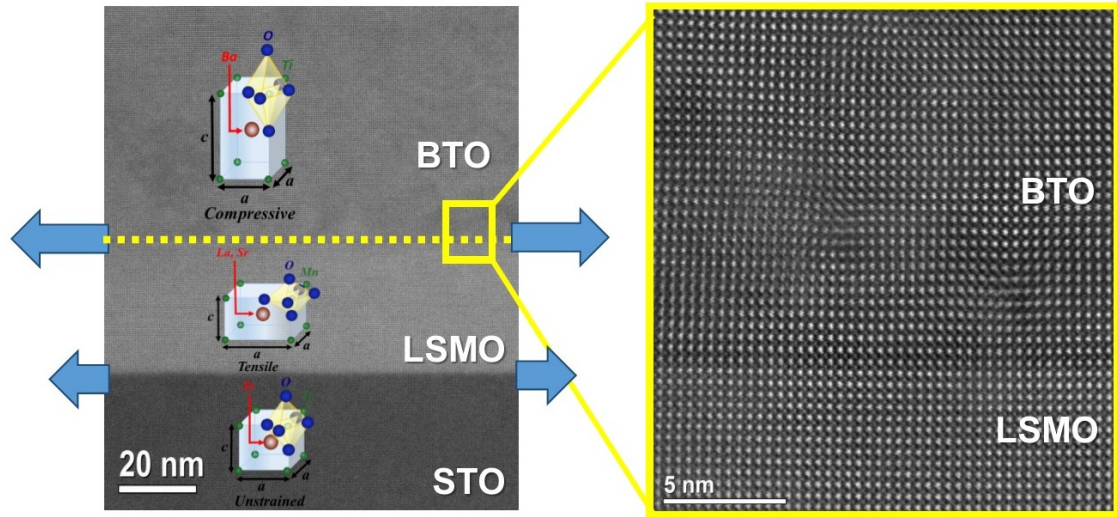


Figure 3.13: HAADF-STEM for BTO/LSMO bilayer deposited on (001) STO substrate. (Left) A Perovskite lattice diagram display the tensile distortion of the LSMO and compressive distortion on BTO. (Right) A zoom around BTO/LSMO interface is shown.

We sketch a perovskite lattice structure in each layer to display the tensile distortion

tion of the LSMO lattice to match with BTO layer and STO substrate. In the zoom of BTO/LSMO interface, the presence of dislocations, defects or imperfections in the sample was evidenced, due to lattice mismatch between BTO/LSMO as has been reported in this systems [18, 37], which could origin a, b, c-ferroelectric domains. This density of defects explains the broad peak of BTO that we found on the XRD on fig. 3.4(c).

Fig. 3.14 displays STEM-HAADF micrographs for the BTO layer (a), LSMO layer (c) and STO substrate (e). Filtered zoom for each layer are displayed in (b), (d) and (f), respectively.

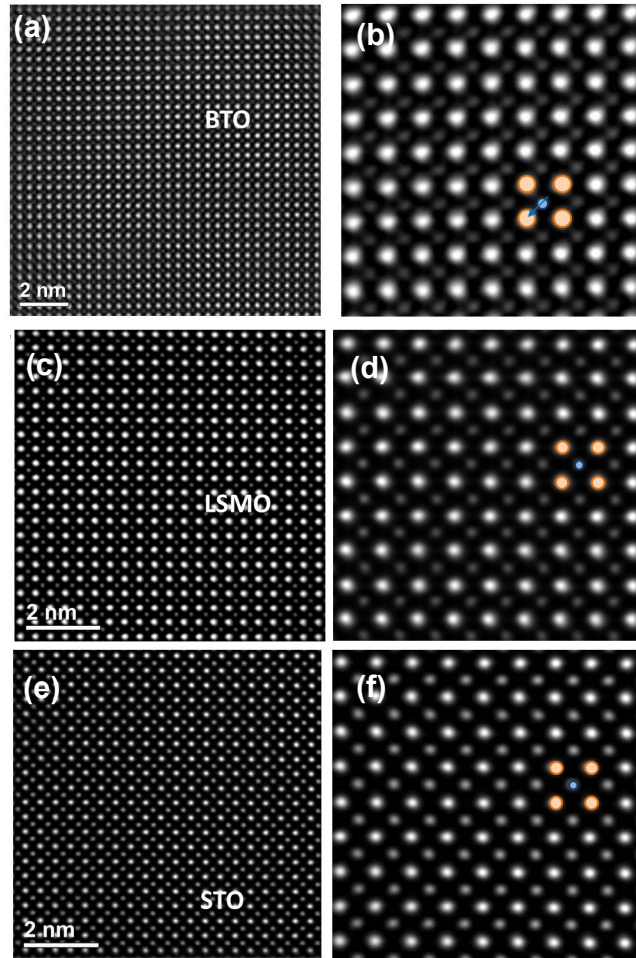


Figure 3.14: HAADF-STEM images for (a) BTO layer, (b) for LSMO layer, (c) for STO substrate. Filtered zoom of the BTO (d), LSMO (e) and STO (f).

In Fig. 3.14(b), using atomic resolution Ba atoms were identified and labeled with orange circles, while the Ti atoms with blue circles. In the image the Ti cation displacement along $[101]$ direction is observed and represented with a blue arrow. These displacements are the result of remanent polarization on BTO. This behavior contrast with the Ti displacement found for BTO(2.8 nm)/LSMO(20 nm)/STO(001) where HAADF-STEM reveals a control of Ti atom motion by gate voltage [30]. In case of LSMO and STO on fig. 3.14 (c)-(f), a perfectly aligned structure is visualized, in absence of dislocations, vacancies and other defects that can perturb the lattice as has been reported [20, 28, 33, 51].

For a local study of the lattice strain around the LSMO and STO interface, geometrical phase analysis (GPA) method is used. Thus, a Lamella to 90° (with respect to (001) direction) was cut to analyzed the lattice strain on bilayer. Fig. 3.15 displays a HAADF-STEM image (a), strain maps of the in-plane (ϵ_a) (b) and out-of-plane (ϵ_c) (c); the lattice parameters taken as reference the STO lattice.

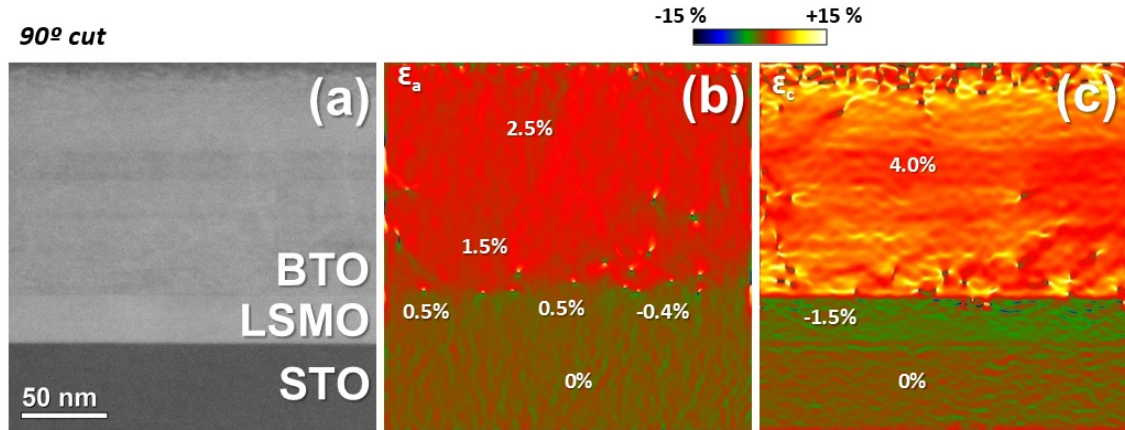


Figure 3.15: (a) HAADF-STEM image of the BTO/LSMO/STO system taken at an intermediate magnification. Strain maps obtained by GPA for the (b) in-plane (ϵ_a) and (c) out-of-plane (ϵ_c) deformation.

The field of view of the HAADF-STEM image cover the total thickness of the BTO/LSMO bilayer, thus, we can observed both interfaces LSMO/STO and BTO-/LSMO. It is worth nothing that the contrast variations observed in the STEM images reveal flat interfaces. Similar to that found in the RSMs patterns, the local

strain analysis also confirms the tensile strained growth of the LSMO film on STO substrates by adapting its in-plane lattice parameter to that of the substrate ($\epsilon_a = 0\%$), and the large deformation on the BTO film ($\epsilon_a > 1.5\%$ and $\epsilon_c > 4.0\%$) to recover the lattice parameter of the bulk BTO. In addition, the strain maps present several small helical-shaped spots with a strong color gradient caused by the presence of crystal defects. Most of them are concentrated close to the LSMO/BTO interface and they are induced by the large mismatch between BTO precursor and strained LSMO film, favoring the relaxation of the BTO lattice. The nanometer resolution of GPA also allows determining that ϵ_a for LSMO film is different to zero close to the LSMO-BTO interface. Locally we see how the strain can vary from -0.4 to +0.5 %. For single crystal LSMO grown on STO, it has been reported that the small mismatch between both phases favors that the film grows fully strained, keeping the same in-plane lattice parameter of the STO substrate along the total thickness in LSMO films with thicknesses up to 120 nm [1]. Thus, the local induced strain on the LSMO film is caused by the BTO film. In regions of the BTO/LSMO interface far to dislocation, where both LSMO and BTO lattice parameter are perfectly matched. The large mismatch between both systems can promote a strain effect than could affect both system.

Additionally, a lamella to 0° was cut for comparison of measurements. Fig. 3.16 displays a HAADF-STEM micrograph (a) for the BTO/LSMO bilayer grown on STO; (b) shows the strain maps obtained by GPA for the in-plane (ϵ_a), (b); and the out-of-plane (ϵ_c) deformation. We see that the strain at LSMO can vary from -0.4 to +0.5 % confirming the tensile strained growth of the LSMO film on STO substrates by adapting its in-plane lattice parameter to that of the substrate ($\epsilon_a = 0\%$). The out-of plane strain of the LSMO layer, Fig. 3.16, varies from -0.5% to -1.5%. We observe large deformation at the BTO film ($\epsilon_a > 1.0\%$ and $\epsilon_c > 6.7\%$ close to interface and decrease to +4.7 % near to surface) to recover the lattice parameter of the bulk BTO. Interestingly, like the other lamella, the strain maps present several helical-shaped spots with a strong color gradient caused by the presence of crystal defects. Most of them are concentrated close to the BTO/LSMO interface and they are induced by the large mismatch between BTO precursor and strained LSMO film, favoring the relaxation of the BTO lattice.

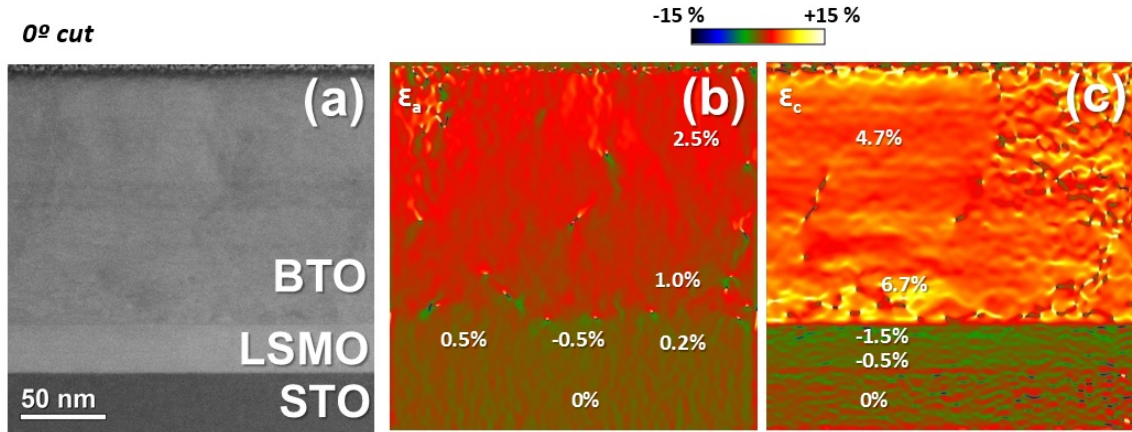


Figure 3.16: (a) HAADF-STEM image for the BTO/LSMO bilayer grown on STO. Strain maps obtained by GPA for the (b) in-plane (ϵ_a) and (c) out-of-plane (ϵ_c) deformation.

However, these defects are propagated in transversal direction around BTO layer, like mentioned a different mechanism as vacancies, defects and different BTO lattice orientations (a, b and c-domains visualized on XRD bilayer). This effect can affect the magnetic properties of LSMO, among the different changes are: crystalline field [56], perturbation of oxygen orbitals and change on anisotropy of magnetic material (as occur on $\text{Co}/\text{Gd}_2\text{O}_3$ interfaces) [58], accumulation or depletion of electrons on interface depending of polarization orientation; as was evidenced on local density of states (LDOS) on the interfacial LAMO unit cell assuming FM ordering [53]. Other effect is the charge transfer, as is evidenced on Fe/BaTiO_3 multilayers, where the calculated magnetic moment of the interface Fe atoms is notably enhanced up to about $2.64 \mu_B$ compared to the bulk moment of $2.20 \mu_B$. This enhancement is, however, not as significant as that for the $\text{Fe}(100)$ surface ($2.98 \mu_B$), indicating the involvement of bonding and charge transfer effects at the Fe/BaTiO_3 interface [54]. We can not forget the intrinsic interfacial phenomena, these processes take place as a consequence of a break in symmetry at the interface and that are confined to atoms that mediate such a transition. In this sense, the interface is treated as a new artificial material, due to the atoms and electrons at the interface not have bulk configuration due to the asymmetric environment, and therefore the physical properties can differ from bulk conditions [55]. An last case is the deformations and tilts/rotations of

BO_6 octahedra, associated to the strain on interface. Thus the magnetic and electric properties on LSMO can be influenced due to influence of different mismatch between BTO and LSMO. Due to the symmetry mismatch across the film-substrate or BTO/LSMO interfaces usually leads to Jahn-Teller type octahedral deformations [25], this implies that novel ferromagnetic properties can arise in the vicinity of the interface as the result of the deformation of oxygen octahedral surrounding cation and changes in M-O-M angles as was found for Borisevich et al. [57], on LSMO/BFO bilayers.

Fig. 3.17 displays strain maps obtained by the GPA analysis for the (a) Lamella cut to 0° and (b) Lamella cut to 90° . We observe a periodic distributions of misfit dislocations throughout the BTO layer. For lamella cut to 0° we analyzed regions with average of 5 dislocations on a region of 200 nm^2 approximately, while for lamella cut to 90° a average of 8 dislocations in the same area. In this case, additional dislocations on transversal direction of BTO layer is observed. This behavior was reported by Turner et al. [52], on BTO/LCMO multilayer. In this case, misfit dislocations is clearly present on BTO, and GPA show coherently strained as reported for LCMO layers in the case of $LCMO_{10}/BTO_5$ and $LCMO_{38}/BTO_{18}$ [52] and in PZT/ $La_{1.2}Sr_{1.8}Mn_2O_7$ system [56]. According to Speck and Pompe model [59], the effective misfit strain associated with a film grown on a substrate after some amount of relaxation is controlled by an effective substrate lattice parameter b^* :

$$b^* = b(T)(1 - \rho_i b_{edge,i}) \quad (3.1)$$

where b is the substrate lattice parameter and $\rho_i b_{edge,i}$ (i is either 0, 1, or 2) is the strain relief provided by the misfit dislocations at the film/substrate interface. In other words, b must be modified to account for the misfit dislocations and relaxation associated with the film growth [59].

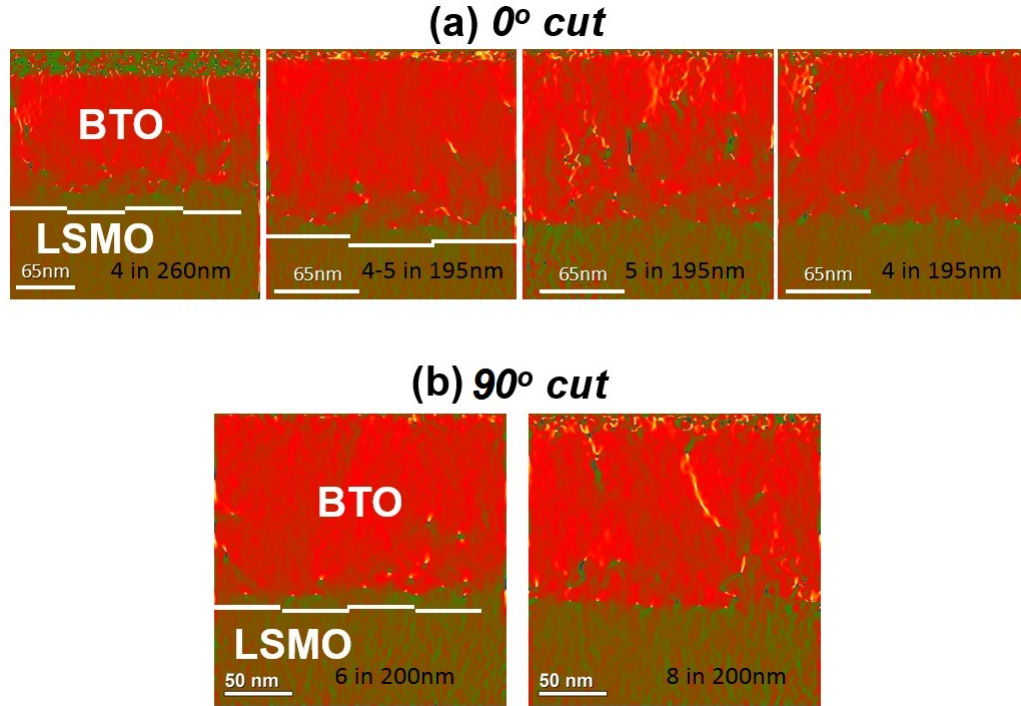


Figure 3.17: Strain maps obtained by GPA for the (a) Lamella cut to 0° and (b) Lamella cut to 90° .

Burton et al. [53], found by theoretical calculations that in $L_{1-x}A_xMO/BTO$ ($A=Ca, Sr$), metal-oxygen (M-O) displacements occur near the interface for the states with polarization pointing away from (squares) and toward (triangles) the interface as is observed on fig. 3.18 (a). The solid symbol are BO_2 displacements ($B=Mn$ or Ti) and the open symbol are A-O displacements ($A=La_{0.5}A_{0.5}$ or Ba). The displacements in the BTO are the typical soft-mode distortion that gives rise to FE polarization. Fig. 3.18 (b) show a scheme of electrically induced magnetic reconstruction at the LAMO/ BTO interface. It has been predicted a change of the Mn magnetic moments (small arrows) from FM to A-type antiferromagnetic (A_2) as the ferroelectric polarization (large arrows) of the BTO is reversed [53]. There are also substantial polar distortions near the interface in the LAMO (cation-anion separations of $\sim 0.1-0.2 \text{ \AA}$), and the sign and magnitude of these polar distortions depend on the polarization orientation, in essence constituting an ionic contribution to the screening of the bound ferroelectric polarization charges at the interface [53].

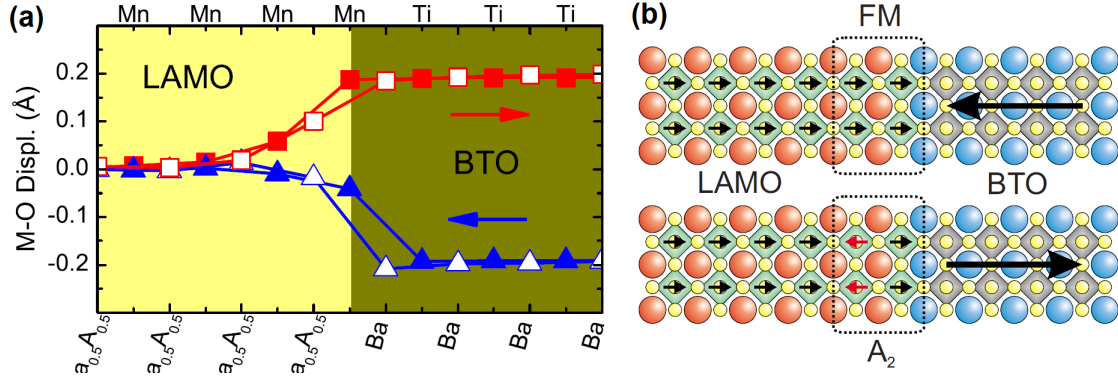


Figure 3.18: (a) Metal-oxygen (M-O) displacements near the LAMO/BTO interface for the states with polarization pointing away from (squares) and toward (triangles) the interface. The solid symbols are BO_2 displacements ($B=Mn$ or Ti) and the open symbols are A-O displacements ($A=La_{0.5}A_{0.5}$ or Ba). (b) Scheme of electrically induced magnetic reconstruction at the LAMO/BTO interface; the predicted change in order of the Mn magnetic moments (small arrows) from FM to A-type antiferromagnetic (A_2) as the ferroelectric polarization (large arrows) of the BTO is reversed [53].

Additionally, when they examine the magnetic ordering at the LAMO/BTO interface by performing self-consistent supercell calculations for different interfacial magnetic configurations, the most striking result is the different magnetic order at the interface favored for opposite polarization orientations of BTO. For polarization pointing into the interface, the FM configuration has minimum energy. For polarization pointing away from the interface, however, there is a transition to the A_2 configuration, corresponding to two unit cells of A-type AFM order at the interface [53], as shown schematically in Fig.3.18 (b). This change in net surface magnetization due to the transition from FM order to the A_2 state constitutes a large interfacial ME effect. In our case, there are a large possibility that this occur on BTO/LSMO interface, due to different configurations on FE domains (a, d and c orientations) as was evidenced on XRD and as consequence an alteration on magnetic properties is expected which will be analyzed on the next chapter.

Bibliography

- [1] Perna et al., J. Appl. Phys., **110**, 013919, (2011).
- [2] M. Ziese et al., J. Magn. Magn. Mater., **246**, 327, (2002).
- [3] Y. Yoshimura et al., Phys. Lett. A, **353**, 250, (2006).
- [4] Y. Yoneda et al., Jpn. J. Appl. Phys., **39**, 4839, (2000).
- [5] T. H. E. Lahtinen et al., Appl. Phys. Lett., **101**, 262405, (2012).
- [6] T. Shimizu et al., J. Phys.: Condens. Matter., **25**, 132001, (2013).
- [7] G. Catalan et al., Phys. Rev. B, **72**, 020102 (R) (2005).
- [8] T. Yamada et al., J. Appl. Phys., **109**, 091605, (2011).
- [9] O. Dieguez et al., Phys. Rev. B, **69**, 212101, (2004).
- [10] N. A. Pertsev et al., Phys. Rev. Lett., **80**, 1988, (1998).
- [11] Sh. M. Kogan et al., Sov. Phys. Solid State, **5**, 2069 (1964).
- [12] W. Ma et al., Appl. Phys. Lett., **79**, 4420, (2001).
- [13] W. Ma et al., Appl. Phys. Lett., **81**, 3440, (2002).
- [14] A. K. Tagantsev et al., Phys. Rev. B, **34**, 5883, (1986).
- [15] G. Catalan et al., J. Phys.: Condens. Matter., **16**, 2253, (2004).
- [16] C. Kwon et al., J. Magn. Magn. Mater., **172**, 229, (1997).

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- [17] T. X. Li, et al., J. Phys. D: Appl. Phys., **45**, 085002, (2012).
 - [18] V. G. Prokhorov et al., Low Temp. Phys., **33**, 1, (2007).
 - [19] G. Bouilly et al., Chem. Mater., **27**, 6354, (2015).
 - [20] Z. Yang et al., Solid State Commun., **150**, 1432, (2010).
 - [21] F. Rivadulla et al., Phys. Rev. B, **64**, 052403 (2001).
 - [22] Y. Konishi et al., J. Phys. Soc. Jpn., **68**, 3790, (1999).
 - [23] P. W. Anderson et al., Phys. Rev., **100**, 2, 675, (1955).
 - [24] A. Tebano et al., Phys. Rev. B, **74**, no. 245116, 1, (2006).
 - [25] A. Vailionis et al., Appl. Phys. Lett., **105**, 131906 (2014).
 - [26] T. X. Li et al., J. Alloys Compd., **592**, 266, (2014).
 - [27] T. X. Li et al., Thin Solid Films, **616**, 1, (2016).
 - [28] H. J. Mao et al., J. Appl. Phys., **116**, 053703, (2014).
 - [29] O. Vlasin et al., Sci. Rep., **5**, 15800, (2015).
 - [30] B. Cui et al., Adv. Funct. Mater., **26**, 753, (2016).
 - [31] H. Doganay et al., EPL, **109**, 67007, (2015).
 - [32] V. Kumar et al., Superlattices Microstruct., **98**, 54, (2016).
 - [33] R. Flaschmann et al., J. Appl. Cryst., **49**, 1693, (2016).
 - [34] J. E. Ordoñez et al., Rev. Mex. Fis., **62**, 543, (2016).
 - [35] W. Cao et al., Nat. Mater., **4**, 3, (2005).
 - [36] T. Shimizu et al., Appl. Phys. Express, **6**, 015803, (2013).
 - [37] Y. P. Lee et al., Phys. Rev. B, **73**, 224413, (2006).

- [38] C. Aruta et al., Phys. Rev. B, **80**, 1, (2009).
- [39] D. Pesquera et al., Phys. Rev. Appl., **34004**, 1, (2016).
- [40] E. Bousquet et al., J. Phys.: Condens. Matter **28** 123001, (2016) .
- [41] A. Shahee et al., Physica B **448** 290, (2014).
- [42] Y. Ding et al., Phys. Rev. Lett. **102**, 237201, (2009).
- [43] Z. Fang et al., Phys. Rev. Lett., **84**, 14, 3169, (2001).
- [44] I. C. Infante et al., Phys. Rev. B, **72**, 224415, (2007).
- [45] R. V. Chopdekar et al., Phys. Rev. B, **79**, 104417, (2009).
- [46] H. Boschker et al., J. Appl. Phys., **108**, 103906, (2010).
- [47] P. Perna et al., J. Appl. Phys., **110**, 013919, (2011).
- [48] W. Zhang et al., Ceram. Int., **42**, 4400, (2016).
- [49] P. Perna et al., J. Appl. Phys., **109**, 07B107, (2011).
- [50] J. Fontcuberta et al., J. Appl. Phys., **85**, No. 8, 15, (1999).
- [51] H. J. Mao et al., Chem. Phys., **17**, 10146, (2015).
- [52] S. Turner et al., Phys. Rev. B, **87**, 035418, 1, (2013).
- [53] J. D. Burton et al., Phys. Rev. B, **80**, 174406, 1, (2009).
- [54] C-G. Duan et al., Phys. Rev. Lett., **97**, 047201, (2006).
- [55] C. A. F. Vaz et al., J. Phys.: Condens. Matter., **27**, 123001, (2015).
- [56] T. Wu et al., Phys. Rev. B, **73**, 134416, (2006).
- [57] A.Y. Borisevich et al., Phys. Rev. Lett., **105**, 087204, (2010).
- [58] C. Bi et al., Phys. Rev. Lett., **113**, 267202, (2014).
- [59] J. S. Speck et al., J. Appl. Phys., **76**, 466, (1994).

Chapter 4

Magnetic properties

In this chapter, we present the results of the magnetic properties for the $\text{BaTiO}_3/\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ (BTO/LSMO) bilayers. We systematically realized Field Cooling (FC) and Zero Field Cooling (ZFC) temperature dependence of the magnetization, isothermal magnetization loops and magnetic anisotropy measurements for all samples. That is, bilayer grown on different substrates, LSMO thicknesses, and crystal orientation. The experimental details were described in Chapter 2. From this measurements the saturation magnetization (M_S), Curie temperature (T_C), magnetization dependence on in-plane crystal axes were calculated.

We perform the analysis of the influence growth parameters on the magnetic properties of the LSMO layer. The T_C was found using the model proposed by Berger et al. [1], used in this type of system in previous investigations [2–4], which also allows find the distribution width ΔT_C , of the ferromagnetic/paramagnetic transition temperature and critical β exponent, associated to the mechanism of magnetic interaction. Additionally, from hysteresis loops measured with magnetic field applied in-plane film, we evaluated the magnetic properties to low and high temperatures ($T=10$ K and 300 K). M_S and H_C was correlated with structural properties and strain state of samples, and the influence of the different growth parameters on magnetic properties.

In order to measure the anisotropy, we first saturate the film to ensure that the sample is initially in a single domain state. Then, the magnetization is measured as the field is lowered. We measured the magnetization at various angles that the

applied field makes with respect to the crystal axes in-plane of the film. In our case, the magnetic anisotropy of films is dominated by strain effects due to the lattice mismatch between the film and the substrates (LAO, LSAT and STO). Additionally, we studied the influence of different LSMO layer thickness for samples deposited on (001)STO and different orientations of STO substrates ((001), (110) and (111) directions).

4.1 BTO/LSMO bilayers on different substrates: (001)LAO, (001)LSAT and (001)STO.

In fig. 4.1(a), we show the magnetization dependence on temperature to ZFC and FC, for LSMO single layers ($t_{LSMO}=25$ nm) deposited on (001) oriented LAO, LSAT and STO substrates, where LSMO films were simultaneously grown. These curves permit to explore the FM transition on LSMO/STO and identify the structural transition of STO around 105 K, is very close to the literature value for the structural transition temperature T_S in SrTiO_3 [5–8]. Fig. 4.1(b) exhibit the hysteresis loop at 10 K for a LSMO film grown on (001) STO substrate. We took the hysteresis loops for LSMO film grown on LAO and LSAT substrates (not shown in the figure). In fig. 4.1(c) we plot the ZFC thermal demagnetization curves for 25 nm thick LSMO film grown on (001) LAO (blue squares), (001)LSAT (green triangles), and (001)STO (black squares). The fig. 4.1(d) is the derivative dM/dT of the curves shown in Fig. 4.1(c). For all samples we observe a FM behavior: transition temperature from paramagnetic to ferromagnetic response, increase of the magnetization with the decreasing of the temperature. The M_S obtained for these films were ~ 550 emu/cm³, 580 emu/cm³, and 600 emu/cm³ for LAO, LSAT and STO substrate at 10 K, respectively, which is in good agreement with values reported in literature on these substrates [7, 9–12] and STO with different capping layers [13].

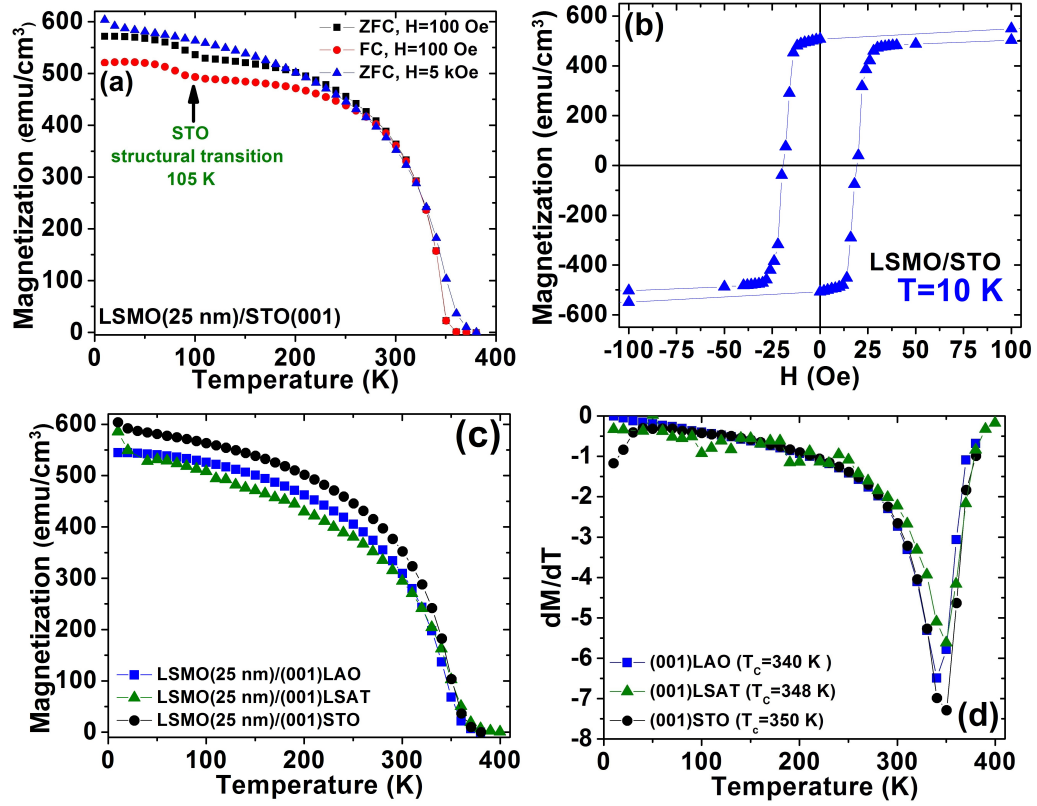


Figure 4.1: (a) Dependence of magnetization with temperature for LSMO(25 nm)/(001)STO. Applied magnetic field in heating cycle of 100 Oe; ZFC curves with $H_{app}=100$ Oe (black squares), $H_{app}=5$ kOe (blue triangles) while $H_{FC}=100$ Oe (red circles) (b) Isothermal hysteresis loop measured at 10 K for LSMO(25 nm) film deposited on STO. (c) Dependence of magnetization with temperature for LSMO (25nm)/(001) LAO (blue squares), LSMO (25nm)/(001)LSAT (green triangles) and LSMO (25nm)/(001)STO (black circles). (d) Derivate of normalized magnetization (dM_{norm}/dT).

Additionally, we observe an increase in T_C when the influence of substrate change from compressive (LAO) to tensile strain (STO), as was studied in previous section (fig. 3.7) and in accordance with those reported [7, 9–12, 14]. The deduction of the T_C from these measurements is obtained from the dependence of dM/dT with temperature, taking the value of temperature at the minimum of the curve (Fig. 4.1 (c)) and is similar to the found using the Berger model [1]. The extracted T_C values display

FM behavior with $\sim 300 \text{ emu/cm}^3$ at room temperature. T_C increase with strain in LSMO from 340 K on LAO (compressive strain), 348 K on LSAT (unstrained) and 350 K (tensile strain) as reported elsewhere [11, 14].

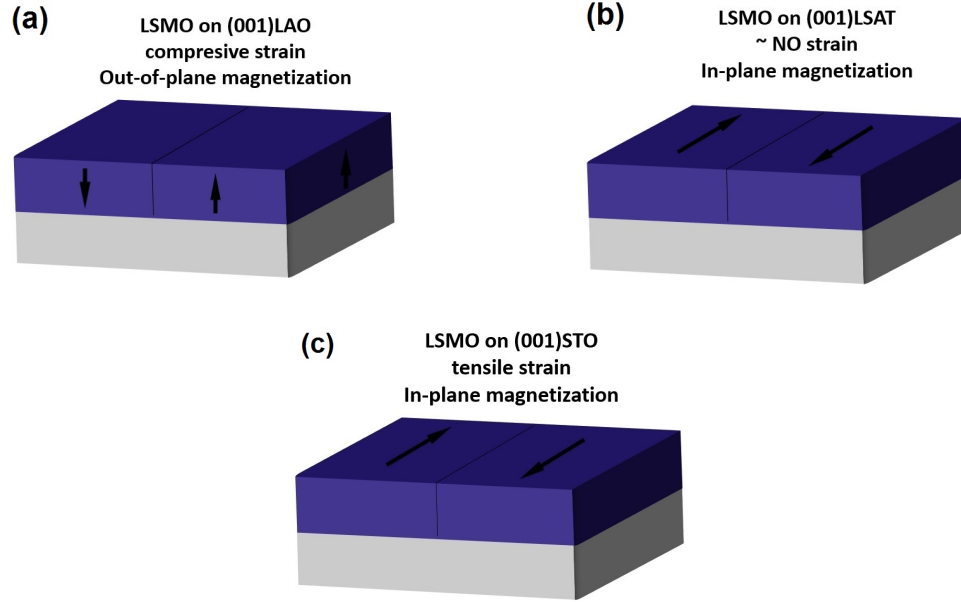


Figure 4.2: Strain influence on direction of magnetization: (a) Compressive strain (LAO), (b) unstrained (LSAT) and (c) tensile strain (STO).

In addition, it is well known that, in the case of LSMO films, the tensile and/or compressive strain induced by the film-substrate lattice mismatch can induce in-plane or out-of-plane easy magnetization directions, respectively, as sketched in Fig. 4.2. The stress degree induced by substrate, permits knowing the direction of magnetization. Then, for compressive strain the magnetization is out-of-plane as reported by Tsui et al. [15]. While, for unstrained and tensile strain, an in-plane biaxial magnetic anisotropy is generally observed, with the easy axis (EA) in-plane direction along (110), and the hard axis (HA) in-plane direction along (100) [10, 16–19].

In Fig. 4.3, we presented the thermal demagnetization curves after ZFC for LSMO(25 nm) film (black squares) and BTO(100 nm)/LSMO(25 nm) bilayer grown on (001)-oriented substrates (samples were grown simultaneously in the chamber). Fig. 4.3(a); $M(T)$ curves for film (black square) and bilayer (blue triangles) grown

on oriented (001)LAO, Fig. 4.3(b); $M(T)$ curves for film (black squares) and bilayer (yellow circles) grown on oriented (001)LSAT, and Fig. 4.3(c); $M(T)$ curves for film (black squares) and bilayer (green diamonds) grown on oriented (001)STO. We took the thermal demagnetization data applying a magnetic field of 5 kOe along the substrate surface. Red line correspond to fit of the curves according to Berger Model [1]. In Fig. 4.3(d) we present the hysteresis loops at 10 K for the LSMO film (square black) and for BTO/LSMO bilayer (blue triangles) grown on STO.

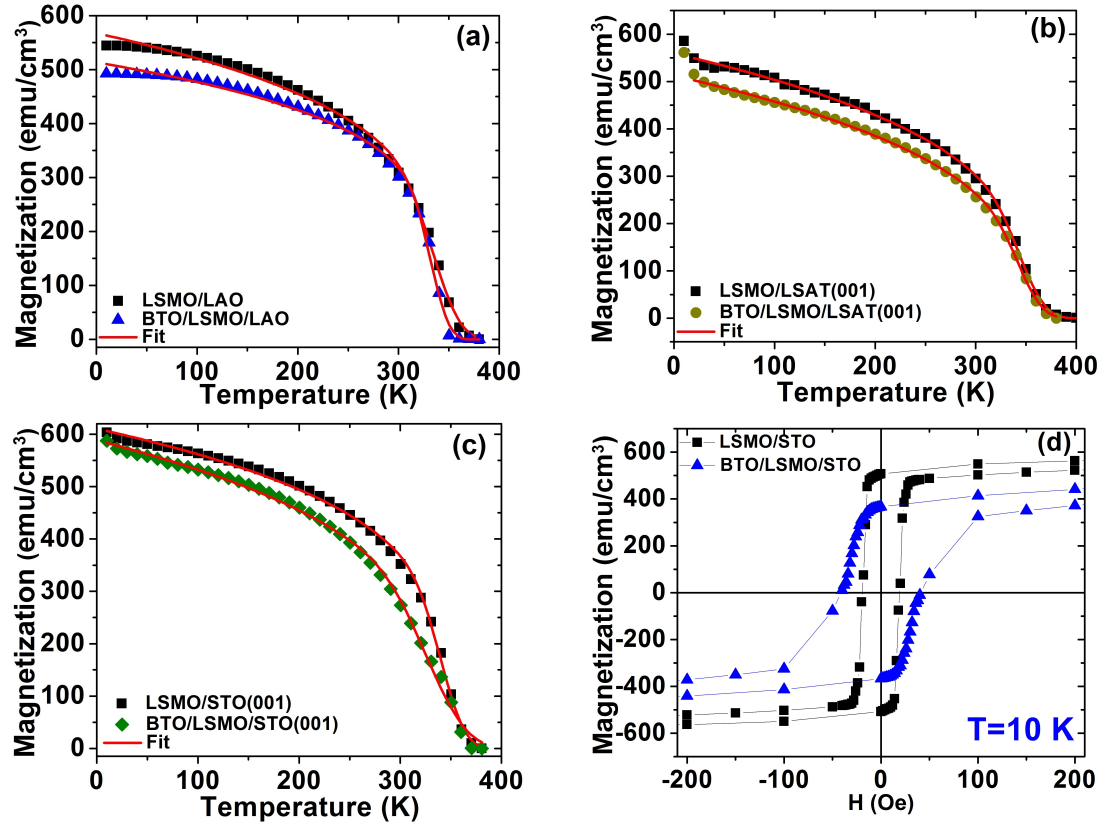


Figure 4.3: Dependence of magnetization with temperature for 25 nm thick LSMO film (black squares) and for BTO (100nm)/LSMO (25 nm) bilayer deposited on oriented (001): (a) LAO substrate (blue triangles); (b) LSAT substrate (yellow circles); (c) STO substrate (green diamonds). Solid red line is the fitting according to Berger Model [1]. (d) Isothermal hysteresis loops measured at 10 K for LSMO(25 nm)/STO (black squares) and BTO(100 nm)/LSMO(25 nm)/STO (blue triangles).

The curves $M(T)$ exhibit transition from a PM state at high temperatures ($T > 400$

K) to a FM behavior below the transition temperature ($T_C \sim 370\text{K}$). We fitted the experimental data according to Berger's model [1] (solid red line), from which we extracted the M_S , T_C , ΔT_C and β exponent, collected in Table 4.1. The quality of fitting between the model (solid red line) and experimental data (symbols) is observed in Fig. 4.3 for each case. We observed a slightly dependence of M_S , T_C , and β exponent with substrate for both LSMO film and BTO/LSMO bilayer, probably due to tensions and/or compressions at the interface [20–22].

Table 4.1: Summary of magnetic properties of ZFC magnetization for single layers and bilayers grown on LAO, LSAT and STO. T_C and ΔT_C are extracted from the Gaussian fit.

Sample	M_S [emu/cm ³]	T_C [K]	ΔT_C [K]	β
LSMO/LAO	550 ± 5	340 ± 1	41 ± 3	0.247 ± 0.009
BTO/LSMO/LAO	500 ± 4	335 ± 1	27 ± 2	0.207 ± 0.008
LSMO/LSAT	580 ± 5	348 ± 1	37 ± 2	0.313 ± 0.004
BTO/LSMO/LSAT	550 ± 4	337 ± 1	35 ± 1	0.336 ± 0.003
LSMO/STO	600 ± 6	350 ± 1	36 ± 1	0.244 ± 0.006
BTO/LSMO/STO	600 ± 6	350 ± 1	58 ± 4	0.283 ± 0.009

A slight difference between M_s and T_c from bilayer respect to LSMO films is found. BTO/LSMO bilayers display a FM behavior with a $M_s^{LAO} \sim 500 \text{ emu/cm}^3$, $M_s^{LSAT} \sim 550 \text{ emu/cm}^3$ and $M_s^{STO} \sim 600 \text{ emu/cm}^3$ at 10K; $T_C \sim 335, 348$ and 350 K for LAO, LSAT and STO, respectively, and β exponent varying between 0.207 to 0.336 in good agreement with literature. It has been reported that for high magnetic fields, as those we used in these measurements, β does not fluctuate considerably [26]. M_S is above of those reported by others authors in the same system [20–22], and similar for the opposite configuration LSMO(40 nm)/BTO/STO deposited by sputtering on previous work [4]. In LSMO(50 nm) film deposited on BTO substrates ($\sim 340 \text{ emu/cm}^3$) where the substrate structural transition was visualized [23], and with bilayers deposited on Si ($M_S \sim 380 \text{ emu/cm}^3$ and $T_C \sim 350 \text{ K}$) [24]. In Fig. 4.3(d), the isothermal hysteresis loops display a diminution on M_S and an increase for H_C on BTO/LSMO bilayer deposited in comparison with the LSMO film. Thus, the BTO layer also affects the magnetic properties of the LSMO film, as reported in

previous work[4], and predicted by Burton et al. [25], in LAMO/BTO ($A=\text{Ca, Sr}$) system, where the BTO polarization domains could induce in regions close to the BTO/LAMO interface (fig. 3.18(b)) antiferromagnetic domains in the LAMO layer, which could be responsible for the decrease of the magnetic properties (M_S and T_C) in comparison with the individual layers. In fig. 4.4, we plot the dependence of β exponent with the $(c/a)_{\text{LSMO}}$ ratio. β exponent exhibit a dependence with substrate, that is, a nearly relation between the lattice deformation and critical exponent is identified. For tensile (STO) and compressive (LAO) strain, the critical exponent is according to tricritical point; in our case, $\beta \sim 0.25$ (for LSMO film and BTO/LSMO bilayers), which have been reported for this type of manganites [26, 27].

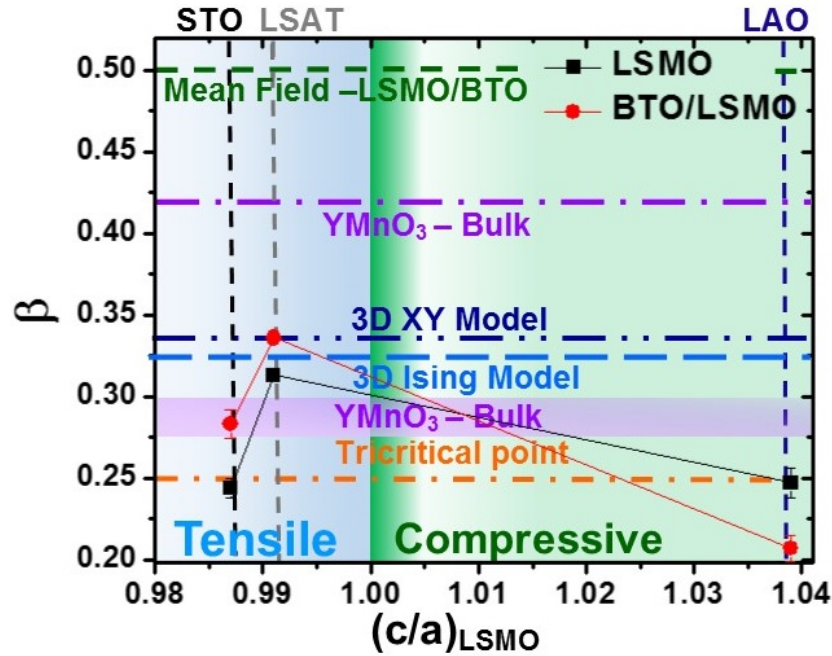


Figure 4.4: β exponent as a function of $(c/a)_{\text{LSMO}}$ ratio for LSMO(25 nm) films (black squares) and BTO(100 nm)/LSMO(25 nm) bilayers (red circles) deposited on different substrates: LAO, LSAT and STO. The dotted lines correspond to different values reported in the literature [26–34].

The critical exponents of a FM phase transition depend on the type of ordering and dimensionality, but, as was discussed by Huang, at a tricritical point, they are

universal: $\alpha = 0.5$, $\beta = 0.25$, $\gamma = 1$, and $\delta = 5$ [28, 29]. While, for films unstrained (LSAT), the critical exponent is near to 3D XY model and 3D Ising model for LSMO film and BTO/LSMO bilayer. Interestingly, these values are close to those reported in hexagonal multiferroic-magnetoelectric YMnO₃ ($\beta = 0.295 \pm 0.008$), is expected values for a 3D XY or Ising system [29–31]. Also, it has been reported for the same compound a value of $\beta = 0.271 \pm 0.003$ that is opposite to the results of other authors [32–34]. Whereas a $\beta = 0.421 \pm 0.006$ for LaMnO₃ has been reported experimentally [36, 37] and theoretically [35]. Additionally, in previous work for LSMO/BTO bilayers deposited by sputtering a mean field mechanism is identified on all samples with $\beta = 0.42$ to 0.54 [4].

From fig. 4.5(a), the isothermal hysteresis loops display a diminution on M_S and increase on H_C on BTO/LSMO bilayer deposited with respect to LSMO film deposited on STO at 300K. Additionally, a notable difference on magnetic properties is identified from substrate used (fig. 4.5(b)). We obtain the $M_S^{300K} \sim 160\text{--}250$ emu/cm³ for bilayers with a H_C in the range of 10 to 45 Oe for different substrates, observing that values is near to LSMO single layer [7, 9–12, 14]. In fig. 4.5(c)-(d), there are a strong dependence of M_S and H_C with the tensile or compressive strain associated to substrate used; as is expected on manganites [38]. A lattice deformation must be to occur to conserve the volume, and elongations of axis in-plane ($c/a < 1$) and out-of-plane ($c/a > 1$) take place as was studied on structural chapter (Fig. 3.7). Li et al. [39], shown for BTO/LSMO(50 nm)/LAO a $M_S \sim 300\text{--}380$ emu/cm³ when the LSMO thickness is the double that our case, and the oxygen pressure is varied. Additionally, the values found in our bilayers are in high percentage above of reported for bilayers deposited on BTO/LSMO(50–200 nm)/LSAT ~ 25 emu/cm³ and BTO/LSMO(400 nm)/LSAT ~ 80 emu/cm³ at 300 K [20–22]. This reduction on magnetic properties was associated to misfit dislocations at the interface between LSMO film and substrate due to the lattice mismatch in the first case, while in the last one, the a low oxygen content, which makes the double exchange interaction was weak [20–22]. On the other hand, bilayers deposited on different substrates as Si present a moderated magnetization $M_S \sim 170$ emu/cm³ [24]. Also, Flaschmann et al. [40], studied BTO/LSMO bilayers and BTO/LSMO multilayers deposited on STO, observing a strong diminution on M_S and obtaining a peak in the ZFC curves,

associated to transition (T_p) and a bifurcation between the ZFC and FC curves below the irreversibility temperature (T_F). This was associated to superparamagnetic (SPM) or super spin glass (SSG) type of behavior with blocked or frozen state of magnetic domains [40–42]. This blocked magnetic moment ($T_F \sim 50$ K) was reported previously on BTO(22.6 nm)/LCMO(49.8 nm)/STO bilayers indicating a granular magnetic behavior in LCMO layer [2, 43].

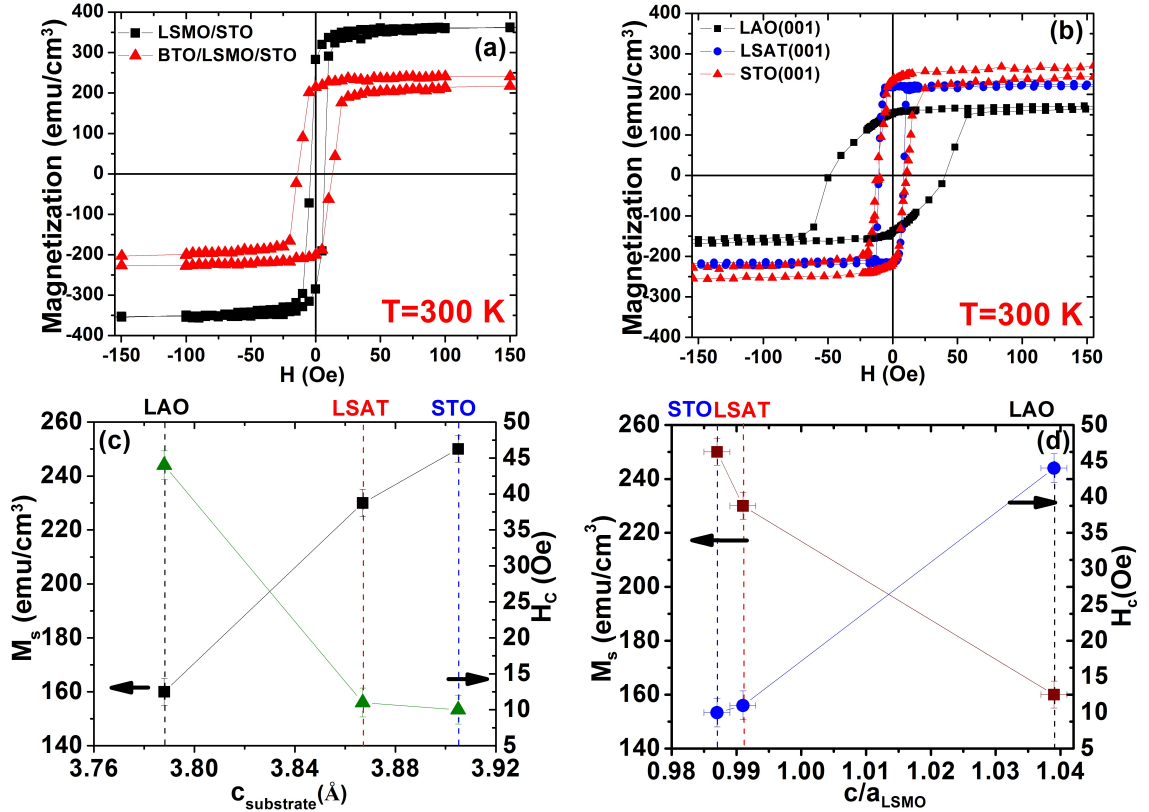


Figure 4.5: Isothermal hysteresis loops for (a) LSMO(25 nm) film (black squares) and BTO (100 nm)/LSMO(25 nm) bilayer (red triangles) deposited on STO at 300 K. (b) BTO/LSMO bilayers deposited on different substrates at 300 K: LAO (black squares), LSAT (blue circles) and STO (red triangles) denote measurements with H_{applied} in-plane substrate, respectively. Saturation magnetization as function of (c) substrate lattice parameter and (d) $(c/a)_{\text{LSMO}}$ ratio, for bilayers deposited on different substrates: LAO, LSAT and STO.

In BTO/LSMO superlattices, Murugavel et al. [44], observed that $T_C \sim 240$ K

which is lower than LSMO film, whose $T_C \sim 330$ K. The reduction was attributed to different mechanism to the spin canting at the interface, phase separation at the interface, and strain induced magnetic disorder in the film [44–48], as also low oxygen concentration, causing regions in the LSMO film which are separated by high Mn^{3+} containing non-magnetic clusters [49]. According to Shen et al., [42] in multilayer with ultrathin LSMO layers the magnetization also is greatly suppressed and it decreases with the increase of BTO thickness n in each period. Associated to the antiferromagnetic ground state under large tensile strain due to the change of Mn^{3+} -O- Mn^{4+} bond length and bond angle of LSMO under tensile strain like in this case [50–52]. They argue that a phase separation into FM-metal and AF-insulator in LSMO may occur especially in regions close to the LSMO/BTO interface, where there exists the strongest tensile strain, in addition, the coexistence of FM and AF phases in LSMO may result in a split in the ZFC/FC magnetization-temperature curves, as expected from the nucleation or depinning of reverse domains with increasing temperature [42]. In comparison, the opposite configuration LSMO(40 nm)/BTO/STO deposited by sputtering was studied on previous work, and we reported similar values at room temperature ($M_S^{300K} \sim 50$ emu/cm³ and $T_C \sim 300$ K), where the presence of the BTO layer affects the magnetic moment of the FM layer at the interface and this interaction depends on the thickness of the BTO layer. Probably, a magnetic contribution exists of the BTO induced by interfacial interactions at the interface, but also induced by crystalline strains originated during the growth process [4]. This phenomenon are similar to reported by Lee et al., in the same configuration [53]. Also, Chen et al [54], study the FE/ $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ interface with $x=0.5$ corresponding to accumulation state (Fig. 4.6(a)). Due to the presence of ferroelectric PbTiO_3 , strong polar distortions are induced at the interface layer of MnO_2 in the accumulation state (Fig. 4.6(b)). They argue that cation-oxygen vertical displacement in MnO_2 at the interface is $\delta = 0.2$ Å. Such a strong polar distortion (distinguished from the structural distortions of Pnma symmetry) is absent in bulk LSMO and is a direct consequence of the ferroelectric/manganite interface. In the analysis they identify three cases: when all the spins are FM coupled - F, if the spin is flipped in the first unit cell of manganite from the interface - A1 (probably our case, due to reduction on magnetic moment of bilayer).

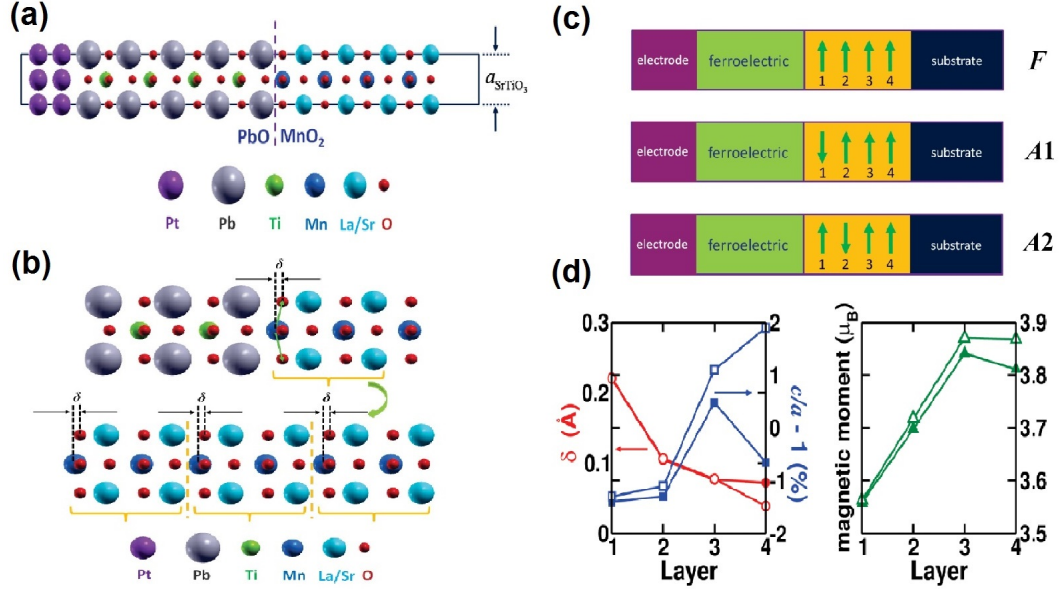


Figure 4.6: (a) Caption of Interface between FE - PbTiO_3 and $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. The dashed line is the FE/FM interface. The whole structure is coherently strained to the lattice constant of SrTiO_3 . (b) Strong polar distortion is induced at the interface layer of MnO_2 due to the presence of PbTiO_3 . (c) Different magnetic structures, F- FM configuration, A₁- Spin flips in the first unit cell, and A₂ Spin flips in the second unit cell. (d) The effects of SrTiO_3 substrate on structural and magnetic properties at the $\text{PbTiO}_3/\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ interface. Layer 1 is the interfacial layer of MnO_2 . Rumplings δ of each MnO_2 layer and c/a ratio of each oxygen octahedron that encloses Mn atoms. d-orbital magnetic moment of each Mn atom [54].

Finally, if the spin is flipped in the second unit cell of manganite - A2 (Fig. 4.6(c)). Additionally, they analyzed the inclusion of SrTiO_3 substrate in the simulation for test the effects on structural and magnetic properties on the $\text{PbTiO}_3/\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ interface. The principal focus was on two important quantities. One is the c/a ratio of each oxygen octahedron that encloses Mn atoms and the other is the rumpling δ of each MnO_2 layer. The structural and magnetic properties with or without substrate quickly converge as the interface is approached. The substrate effects, in general are generally very small and diminish at the interface (Fig. 4.6(d)) [55]. This charge-induced interfacial magnetic reconstructions driven by screening effects

has been demonstrated experimentally by different authors [55–59]. In our case on BTO/LSMO bilayer deposited on STO, we observed through STEM-HAADF images that in the FE layer, the Ti ion have a displacement on $[101]$ and as consequence a remanent polarization at nanoscale can be identify (Fig. 3.14). According to Chen et al. [55], using first principle, they proposed a mechanism based on the FE polarization of BTO at nanoscale. In this case they assume that BaO is the termination for FE layer and MnO_2 for FM layer. In the interface there are two possibles states for FE polarization: accumulation or depletion of holes (Fig. 4.7) and a non polarized state (paraelectric state-PE, $P=0$).

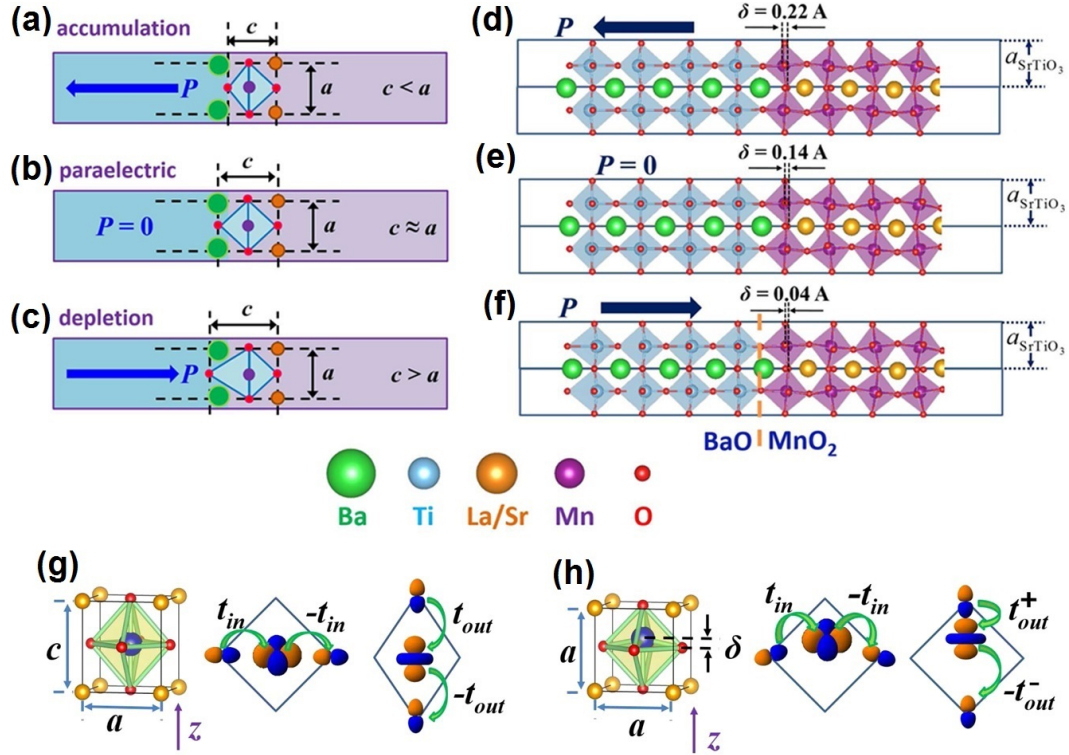


Figure 4.7: (a-c) Schematic of a BaTiO₃/LSMO interface. The interface is BaO/MnO₂. (a) Accumulation state; (b) paraelectric state; (c) depletion state. (d-f) Relaxed atomic structure of LSMO/BaTiO₃ interfaces from first-principles calculations. The in-plane (out-of-plane) Mn-O hopping is shown in schematics, denoted by t_{in} (t_{out}) [55].

For accumulation state (Fig. 4.7(a)), the interfacial BaO layer is polarized with

its O anion pushed toward the interfacial Mn and as consequence $c/a < 1$ (associated to in-plane deformation of lattice), where a stabilization of the in-plane $d_{x^2-y^2}$ occur as is consistent with crystal field theory. While for depletion state (Fig. 4.7(c)), the BaO layer oxygen is pushed away from the Mn, leading to $c > a$ and favoring $d_{3z^2-r^2}$ [55]. Additionally, the non-polarized state where the deformation not is expected; $c \sim a$ (Fig. 4.7(b)), and a spontaneous configuration on FM layer should occur. In fig. 4.7 (d-f) they estimate the displacement of oxygen atom, where δ is the displacement amplitude in each MnO_2 layer. For the FE states $\delta_{depletion}=0.04 \text{ \AA}$ and $\delta_{accumulation}=0.22 \text{ \AA}$. For paraelectric state, a $\delta_{PE}=0.14 \text{ \AA}$ (non FE state), associated to an asymmetric chemical environment with BaO layer on one side and FM layer on the other side. This situation is similar to our bilayers, where a local polarization was observed and FE influence of BTO on magnetic properties is expected. Thus, FE layer causes a perturbation of the orbitals associated to Mn-O bounding that govern the FM properties and as results a diminution on M_S and increase on H_C was obtained in the system. A final situation should be raised to the possible appearance of dead layer in LSMO near to the interface with insulating and non-ferromagnetic behavior (BTO/LSMO interface) as in the case of LCMO [60–65], BTO/LCMO bilayers [66], BTO/LSMO bilayers [66], LSMO/BTO bilayers on previous work [4], dielectric-FE/FM bilayers and multilayers [57, 67, 68]. This dead layer also have been studied at the electrode-ferroelectric interfaces and as result a decrease of dielectric constant is observed [69–71].

In order to verify the magnetic anisotropy (MA) for different substrates with (001)-orientation at room temperature, we measured the isothermal hysteresis loops along of different directions with the magnetic field applied in-plane of substrate as is observed in fig 4.8. Three different directions was selected, to analyze MA on LSMO layer and the possible influence of substrate and/or FE layer. To measure MA, first the film was saturate to ensure that the sample is initially in a single domain state. Later, the field is varied to completed the loops and the M_S and M_r was obtained directly from curve. This measurement is repeated for various angles with 15° step separation as indicated on fig. 4.8.

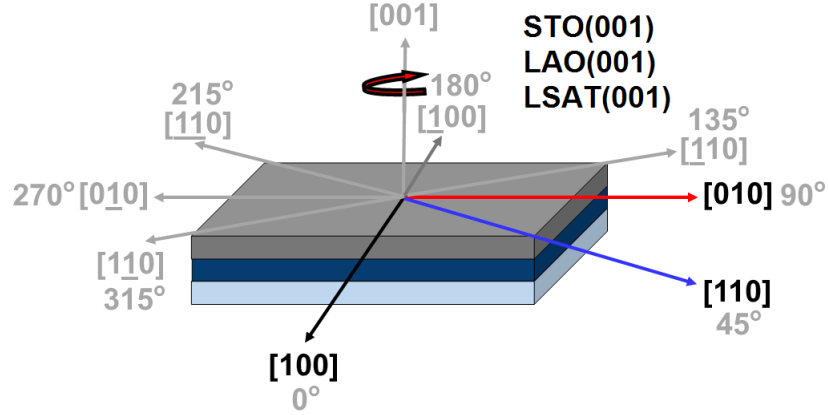


Figure 4.8: Sketch of the crystallographic directions with respect to bilayer plane. Three principal directions was selected for M-H loops: $[100]$ (black arrow), $[110]$ (blue arrow) and $[010]$ (red arrow).

In Fig. 4.9(a)-(b), a clear behavior of magnetic anisotropy on (001)-oriented substrates is observed at room temperature. For each case, the isothermal hysteresis loops was measured with magnetic field aligned in three directions: $[100]$ (black squares), $[110]$ (blue triangles) and $[010]$ (red circles). different magnetic fields are necessary to saturate the magnetization along of different directions. For bilayers deposited on LAO and LSAT; grown under compressive strain and unstrained, the in-plane hysteresis loops presents different shape for $[001]$ (black squares) and $[110]$ (blue triangles) directions. The remanent magnetization (M_r) is larger along $[110]$ that $[100]$ direction. Additionally, the M_s for $[100]$ direction is achieved to a magnetic field more highest in comparison with $[110]$ direction. On the other hand, for tensile strain, the bilayers deposited on STO, the in-plane hysteresis loops presents different shape for all directions. For bilayers deposited on LAO and LSAT, we observed two equivalent directions: $[100]$ (black squares) and $[010]$ (red circles) with a M_r lower than $[110]$ (blue triangles). Thus, this directions are hard axis (HA). These axis present a reduction of 22% and 25% on M_r in contrast with $[100]$, i.e. the easy axis (EA). In fig. 4.9, the $[010]$ direction also is plotted for each substrate to show the angular separation of EA and HA. For bilayer deposited on STO, the situation is different, due to for $[100]$ direction (HA) the M_r is 42% lower than along $[010]$ direction (EA). In all cases, the coercive field is different for all directions.

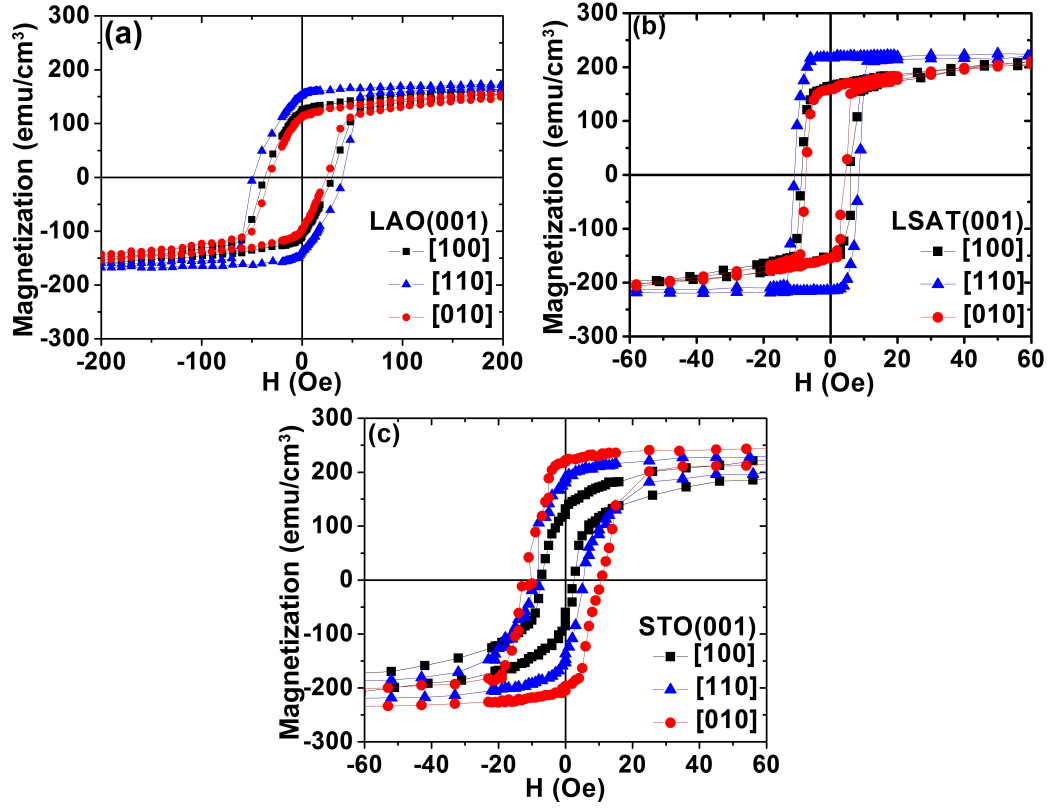


Figure 4.9: Isothermal hysteresis loops on BTO(100 nm)/LSMO(25 nm) on different substrates (a) LAO, (b) LSAT and (c) STO at 300 K. The magnetic field was aligned parallel to: [100] (black squares), [110] (blue triangles) and [010] (red circles) direction, respectively.

To corroborate the MA on LSMO the single layers and BTO/LSMO bilayers, an in-plane rotation with a 15° step was carried out (fig. 4.10). From these measurements we can identify the nature of MA on the LSMO layer. For this purpose, M_r/M_s polar plots for single films and bilayers have been presented in fig. 4.10. The experimental data was fitted using equation 1.11. The LSMO single layers have a biaxial MA (four-fold) for all (001)-oriented substrates. The in-plane MA clearly shows that LSMO single layers have EA on the [110] direction whereas the HA was found along the [001] direction (4.9(a)-(c)). In our LSMO single layers the MA is independent of the substrate material used (LAO, LSAT and STO), which indicates that this behavior is intrinsic to manganite. In the case of LSMO, the tensile or compressive

strain induced by the film-substrate lattice mismatch can induce in-plane or out-of-plane easy magnetization directions, respectively [15]. When LSMO is submitted to isotropic tensile strain (STO) the magnetocrystalline anisotropy are biaxial with EA aligned in $[110]$ direction [15, 17]. For compressive strain a biaxial behavior is expected, or a combination between biaxial-uniaxial MA has been found [74].

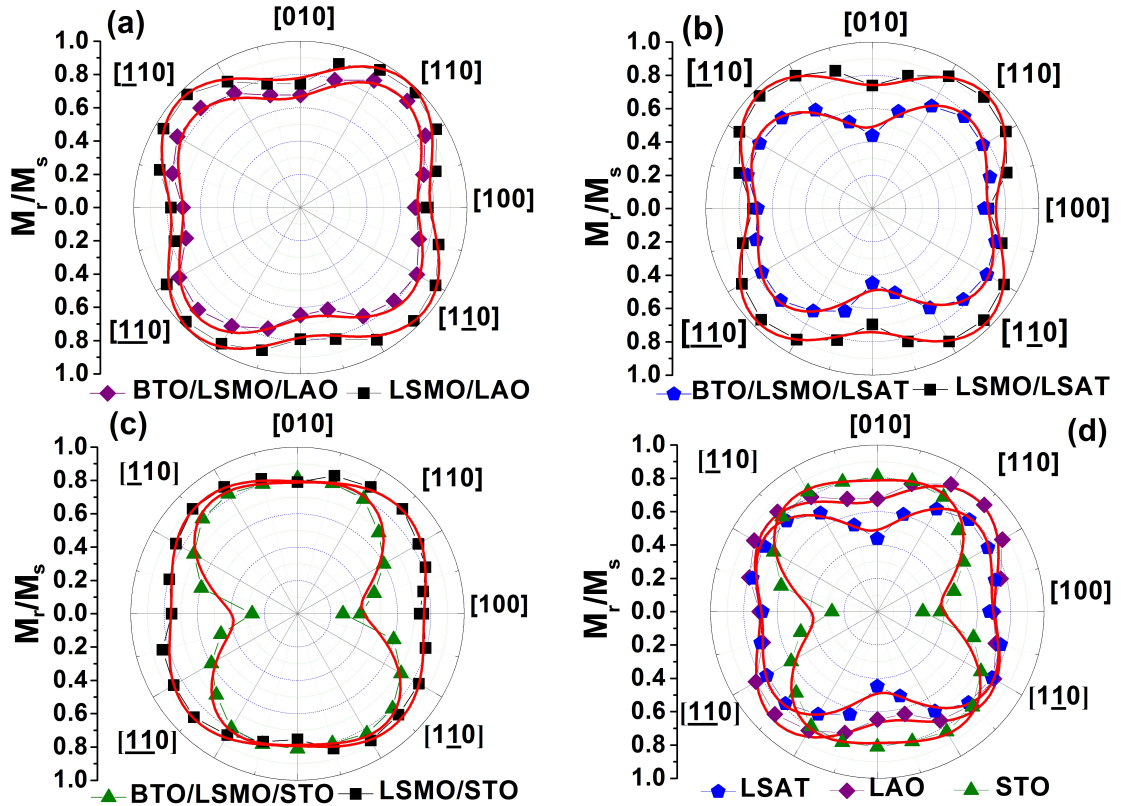


Figure 4.10: Polar plots display the M_r normalized to M_s for LSMO(25 nm) single films (black squares) and BTO(100 nm)/LSMO(25 nm) bilayers on different substrates (a) LAO (purple diamonds), (b) LSAT (blue pentagons), (c) STO (green triangles) at 300 K. (d) Polar plots for BTO(100nm)/LSMO(25nm) bilayers grown on LAO, LSAT and STO. The red continuous lines correspond to numerical fit.

Our results about biaxial MA are consistent with reported by different authors [10, 16, 17]. In this case, the magnetoelastic energy is isotropic in the plane of of films and therefore the MA is dominated by crystal structure effects [10, 17, 18, 72, 73]. However, uniaxial MA (two-fold) also has been reported in this material by others

authors, the mechanism are associated to different factors as crystal structure [74], strain (tensile or compressive) [19, 74, 75], symmetry breaking on substrate step-induced [55, 76–78], thickness [77, 79], and angle of deposition [80], or extrinsic such as temperature range [77, 79, 81]. For bilayers the results are very interesting. While samples grown on LAO and LSAT ($c/a \geq 1$) conserve the magnetic mechanism (biaxial MA); due to intrinsic properties of LSMO as in films case (fig. 4.9). In LSMO films deposited on LAO, there are a coexistence of stable FM and AF phases associated to thickness of layer and strain induced by the substrate. For our samples we expected orbital-state-mediated phase control of manganites using the epitaxial lattice strain from different substrate used. Additionally, in cubic crystal symmetry ($c/a_{LSAT}=1$) epitaxial magnetic thin films the competition between the biaxial (fourfold) and the additional uniaxial (twofold) anisotropies can result in a magnetic reorientation. This result has been associated to different causes: compressive strain of the LSMO layer induced by the substrate; magneto-crystalline anisotropy due to broken bonds and missing atoms at step edges; magneto-elastic anisotropy due the two-fold strain relaxation of the film at the step edges in a direction perpendicular to the steps, and other factors [15, 17, 19, 74, 75, 79]. On the other hand, the two-fold uniaxial anisotropy is found for the bilayer grown on STO, where $c/a < 1$, the MA changes from biaxial to uniaxial anisotropy. In the new scenario, the magnetic moments are easily aligned onto [010] direction-EA, while [100] direction is the HA (fig. 4.9(c)). We calculated k_u and k_1 , uniaxial and biaxial anisotropy constant, from isothermal hysteresis loop plotted in fig. 4.9, according to the method proposed by Boschker et al. [74]. The results obtained for samples LSMO films were $k_1=0.25$ kJ/m³, 0.28 kJ/m³ and 0.30 kJ/m³ for LAO, LSAT and STO substrate respectively, with a uniaxial contribution negligible. While in the bilayers case, the uniaxial contribution was -0.42 kJ/m³ for STO and 0.08 kJ/m³ for the others substrates.

To summary, in this section we demonstrate the influence related to elastic deformation on LSMO lattice deposited on different substrates. In all bilayers, the deformation was induced from tensile to compressive strain. Only, in bilayer deposited on STO the tensile strain induces a in-plane uniaxial anisotropy with EA [010] and HA [100]. The structural analysis demonstrate that tensile strain near to interface BTO/LSMO, deformations and dislocations are responsible of change on

MA. In this scenario, different strain/relaxed zones allow change on magnetic mechanism from biaxial to uniaxial MA. As consequence, a induced uniaxial MA can be modulated via substrate.

4.2 BTO(100 nm)/LSMO(t_{LSMO}) bilayers growth on (001)STO with different LSMO thickness

In Fig. 4.11 (a), we analyzed the magnetic properties with temperature of BTO(100 nm)/LSMO bilayers, deposited on STO (001) with different t_{LSMO} = 20 nm (black squares), 25 nm (green triangles) and 40 nm (blue circles) with H_{ZFC} = 5 kOe in-plane of substrate.

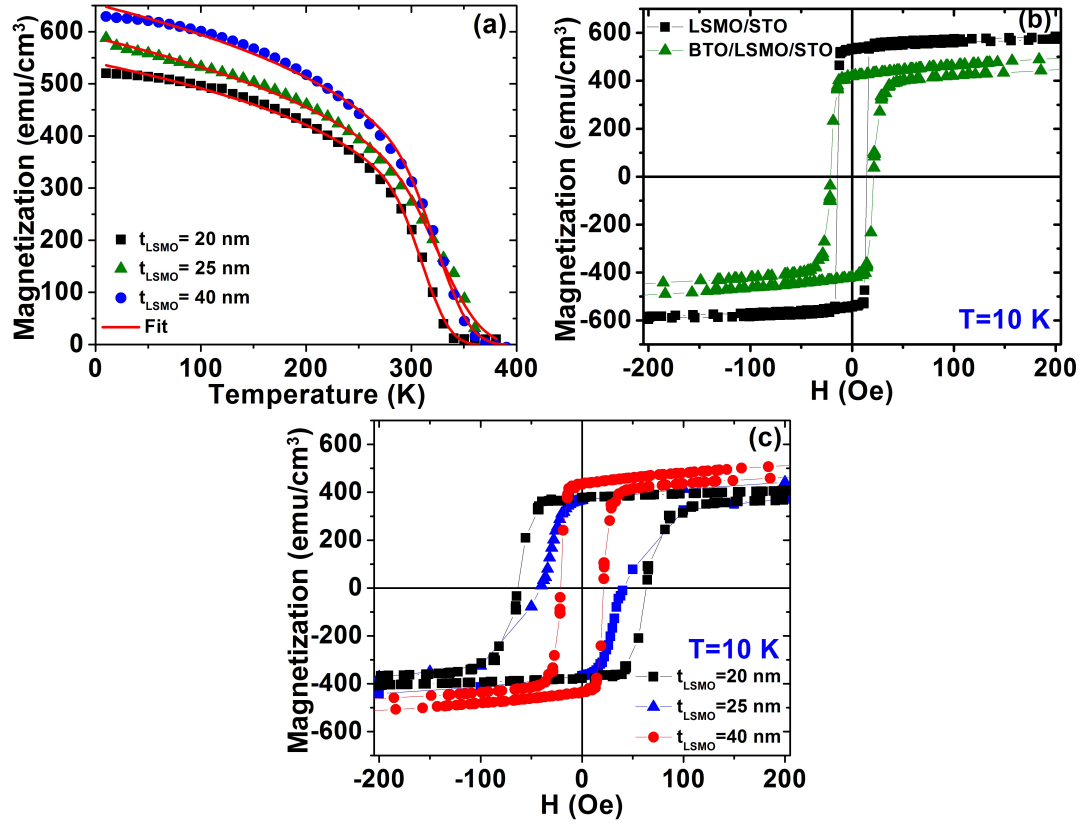


Figure 4.11: (a) Dependence of magnetization with temperature for BTO(100 nm)/LSMO bilayers deposited with different t_{LSMO} = 20 nm (black squares), 25 nm (green triangles) and 40 nm (blue circles) deposited on (001)STO. (b) Isothermal hysteresis loops for LSMO(40 nm)/STO (black squares) and BTO(100 nm)/LSMO(40 nm)/STO (green triangles) deposited on (001) STO at 10 K. (c) Isothermal hysteresis loops for BTO(100 nm)/LSMO bilayers with different t_{LSMO} = 20 nm (black squares), 25 nm (blue triangles) and 40 nm (red circles) deposited on (001)STO.

BTO/LSMO bilayers display a FM behavior with a $M_s^{20nm} \sim 510$ emu/cm³, $M_s^{25nm} \sim 580$ emu/cm³ and $M_s^{40nm} \sim 620$ emu/cm³ at 10 K. The highest value was found for bilayer with $t_{LSMO}=40$ nm (the samples were deposited with similar parameters, only change the magnetic material thickness). This results contrast with reported by others authors on BTO/LSMO bilayers and multilayers deposited on STO [2, 40, 43–48], where M_S and T_C are below of values reported in our samples. These increase on M_S are related to LSMO layer thickness, and results in the relaxation on strain of two interfaces (LSMO/STO and BTO/LSMO) and slight differences on lattice parameters as was found in XRD (Table 3.6). In our system FM-PM transitions were found using model proposed by Berger et al. [1] (solid red line). In this case, the bilayers present a $T_C \sim 350, 336$ and 352 K for $t_{LSMO}= 20, 25$ and 40 nm, respectively. The quality of fitting between the model (solid red line) and experimental data (symbols) is observed in Fig. 4.11 for each case. The T_C , ΔT_C and critical β exponent were estimated from the fit and collected in Table 4.2.

Table 4.2: Summary of magnetic properties of ZFC magnetization for single layers and bilayers with different t_{LSMO} deposited on STO(001). T_C and ΔT_C are extracted from the Gaussian fit.

Sample	M_S [emu/cm ³]	T_C [K]	ΔT_C [K]	β
LSMO(20 nm)/STO	500 ± 5	330 ± 1	36 ± 1	0.240 ± 0.006
BTO/LSMO(20 nm)/STO	480 ± 4	316 ± 1	39 ± 2	0.290 ± 0.005
LSMO(25 nm)/STO	580 ± 5	340 ± 1	37 ± 2	0.244 ± 0.005
BTO/LSMO(25 nm)/STO	550 ± 4	336 ± 1	58 ± 4	0.283 ± 0.005
LSMO(40 nm)/STO	610 ± 6	350 ± 1	38 ± 1	0.252 ± 0.006
BTO/LSMO(40 nm)/STO	580 ± 6	345 ± 1	48 ± 2	0.295 ± 0.006

In fig. 4.11(b) we observed that isothermal hysteresis loops have a slight difference between BTO/LSMO(40 nm)/STO bilayer respect to LSMO(40 nm)/STO. However, the values found are according to reported in literature for LSMO films [87, 88]. In addition, in Fig. 4.11(c), the isothermal hysteresis loops for BTO/LSMO bilayers with different t_{LSMO} , where a influence on M_S and H_C was observed. The M_S values are below of obtained for LSMO single layers (not shown) and as consequence, the BTO layer affects the magnetic properties of manganite layer as was

reported on previous work [2–4].

In fig. 4.12, from β exponent collected a dependence with t_{LSMO} is observed, that is, a nearly relation between the increase on thickness of magnetic layer and critical exponent is identified. For all thickness in LSMO single layer $\beta \sim 0.25$. Thus, the critical exponent is according to tricritical point; $\beta \sim 0.25$, which have been reported for this type of manganites [26, 27]. While, for BTO/LSMO bilayers, $\beta \sim 0.27$ to 0.30 . Interestingly, this values is near to reported by in hexagonal multiferroic-magnetoelectric $YMnO_3$ through of high-resolution powder neutron diffraction $\beta = 0.271 \pm 0.003$ [32] and using spin wave dispersions by inelastic neutron scattering, $\beta = 0.295 \pm 0.008$ [29–31]. This values is above for reported to previous work on LSMO/BTO bilayers (opposite configuration) where mean field mechanism is identified on all samples with $\beta = 0.42$ to 0.54 .

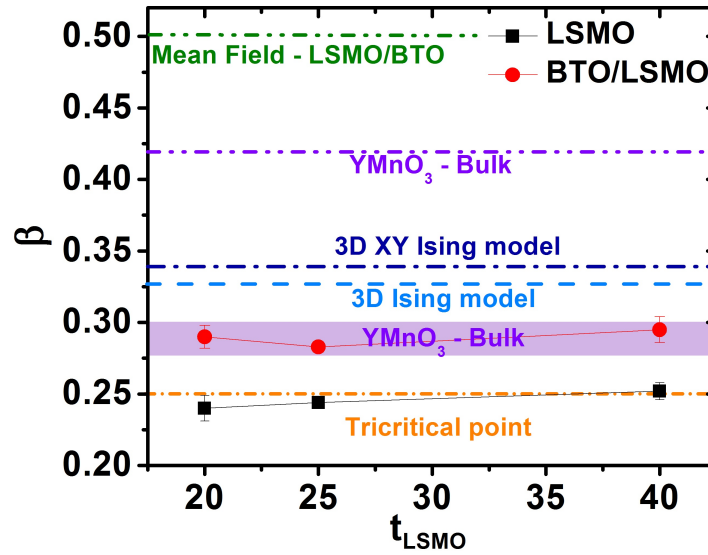


Figure 4.12: β exponent as a function of STO orientations for LSMO films (black squares) and BTO(100 nm)/LSMO(25 nm) bilayers (red circles) deposited on STO. $H_{ZFC} = 5$ kOe was applied in-plane of bilayer. The dotted lines correspond to different values reported in literature [26–34].

In fig. 4.13(a), we presented the isothermal hysteresis loops for BTO/LSMO(20, 25 and 40 nm) bilayers at 300 K. In the samples an increase on M_S and decrease on

H_C was found. For this case, we obtain the $M_S^{300K} \sim 250\text{--}280 \text{ emu/cm}^3$ for bilayers with a H_C in the range of 7 to 10 Oe for different t_{LSMO} . These values are near to reported for LSMO films [2, 4, 40, 43–48]. In fig. 4.13(b)–(c), there is a dependence of M_S and H_C with t_{LSMO} and (c/a) ratio; as is expected on manganites [38].

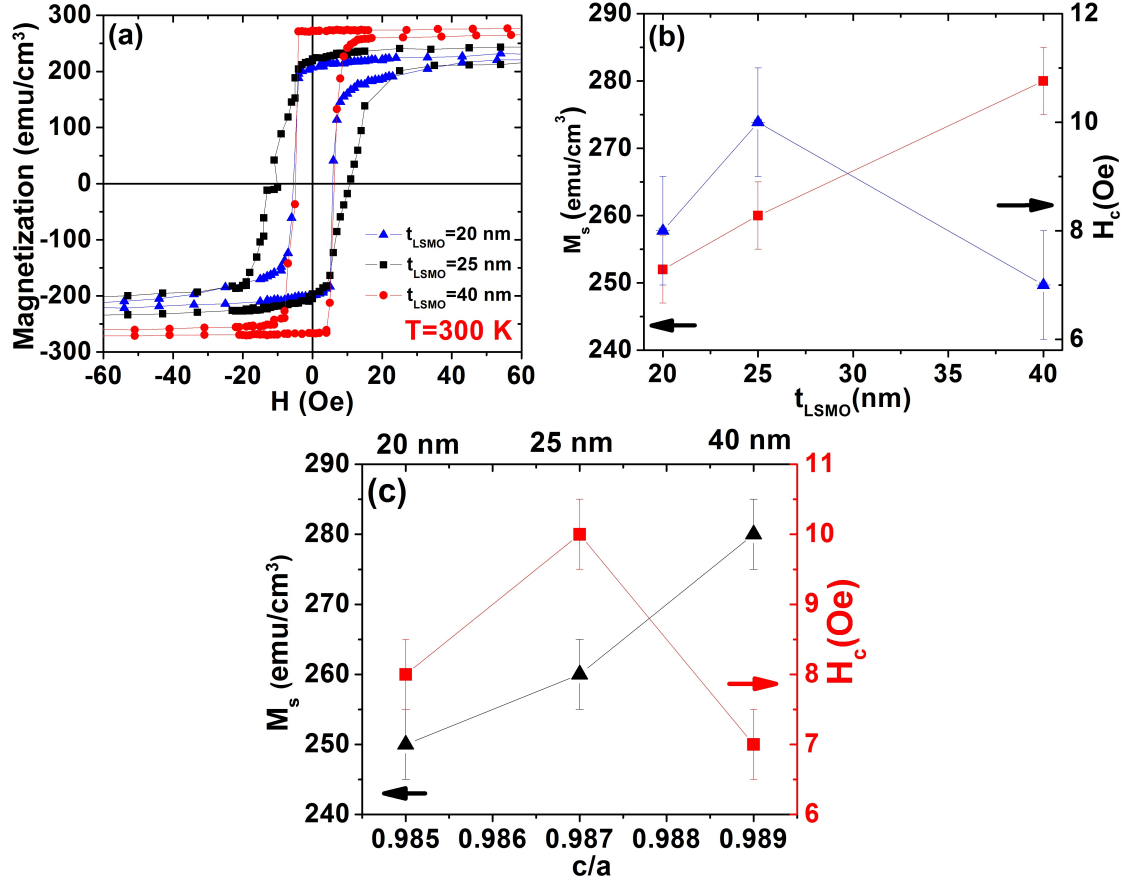


Figure 4.13: Isothermal hysteresis loops for (a) BTO(100 nm)/LSMO bilayers with different t_{LSMO} = 20 nm (blue triangles), 25 nm (black squares) and 40 nm (red circles) at 300 K. (b) Saturation magnetization (red squares) and coercive field (blue triangles) as function of (c) t_{LSMO} and (c) c/a ratio.

As was studied in previous section, the magnetic properties are strongly influenced by the FE layer, and as consequence different mechanism has been involved in this decrease: (a) Direction of polarization on BTO, which can form AF layers in regions close to the interface (Fig. 3.18(b)), and could be responsible for the

decrease of the magnetic properties in comparison with the individual layers [25]. RSMs display different configurations on FE domains (Fig. 3.5). (b) Accumulation state (Fig. 4.18(a)) associated to cation-oxygen vertical displacement in MnO_2 at the interface is $\delta = 0.2 \text{ \AA}$. (c) The non-polarized state where the deformation not is expected; $c \sim a$ (Fig. 4.7(b)), and a spontaneous configuration on FM layer should occur (FE a-domains). FE layer causes a perturbation of the orbitals associated to Mn-O bounding that govern the FM properties and as results a diminution on M_s and increase on H_C was obtained in the system. (d) A final situation should be raised to the possible appearance of dead layer in LSMO near to the interface with insulating and non-ferromagnetic behavior (BTO/LSMO interface) as in the case of LCMO [60–65], BTO/LCMO bilayers [66], BTO/LSMO bilayers [66], LSMO/BTO bilayers on previous work [4], dielectric-FE/FM bilayers and multilayers [57, 67, 68]. This dead layer also have been studied at the electrode-ferroelectric interfaces and as result a decrease of dielectric constant is observed [69–71].

In order to verify MA on bilayers with different t_{LSMO} at room temperature, we measured the isothermal hysteresis loops along of different directions with the magnetic field applied in-plane of substrate as is observed in fig 4.8. Three different directions was selected, to analyze MA on LSMO layer and the possible influence of t_{LSMO} and/or FE layer. The procedure used was described in the previous section. In Fig. 4.14(a)-(c), a clear behavior of MA on (001)-oriented substrates is observed at room temperature. For each case, the isothermal hysteresis loops was measured with magnetic field aligned in three directions: [100] (black squares), [110] (blue triangles) and [010] (red circles). Low magnetic fields are necessary to saturate the magnetization along [010] direction. The M_r is larger along [110] that [100] direction. Additionally, the M_s for [100] direction is achieved to a magnetic filed highest in comparison with [110] direction. For all bilayers we observed a equivalent direction with square loop: [010] (red circles) with a M_r highest than [100] (black squares), therefore this direction is EA. In [100] the M_r present a reduction of 71%, 43% and 80% for $t_{\text{LSMO}}=20, 25$ and 40 nm , respectively. In the fig. 4.14 the [110] direction is a intermediate direction and also is plotted for each bilayer to show the angular separation of EA and HA. Additionally, the coercive field is different for all

directions.

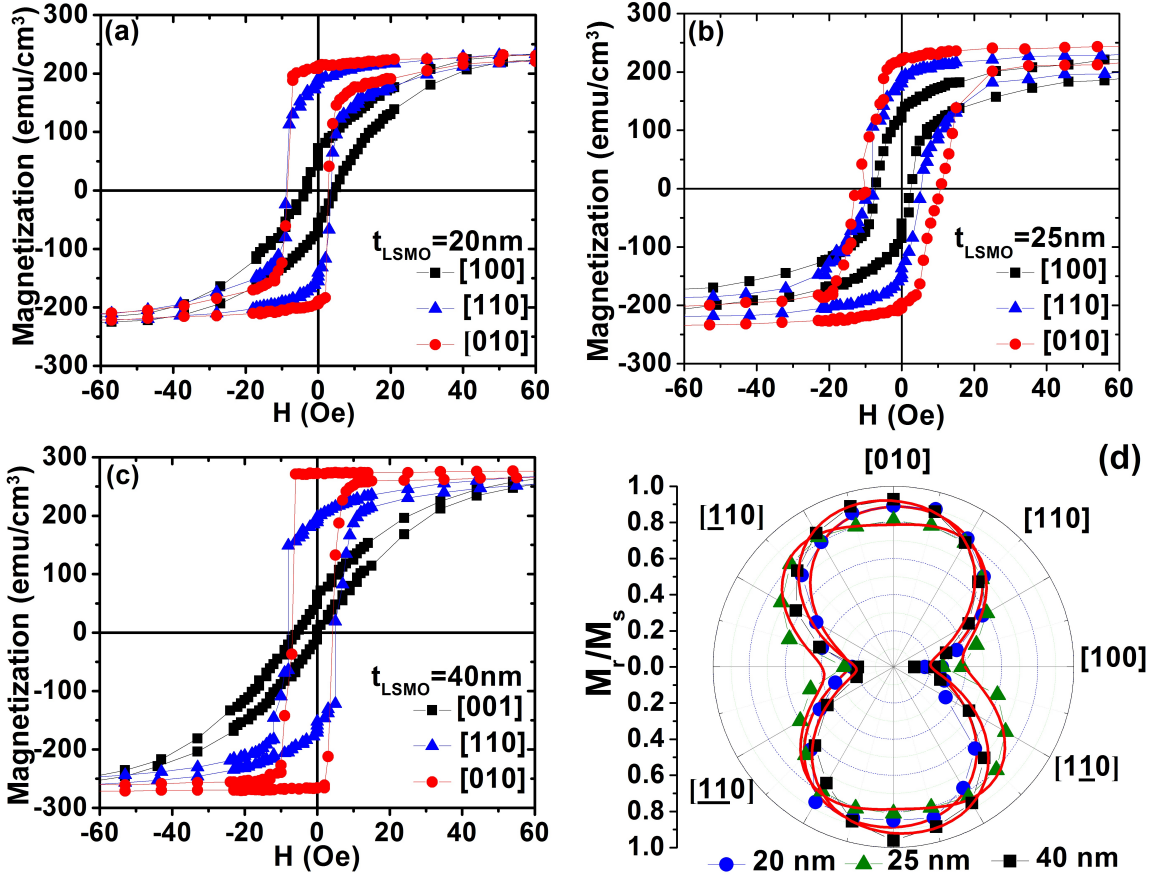


Figure 4.14: Isothermal hysteresis loops on BTO(100 nm)/LSMO/STO bilayer at 300 K, (a) $t_{\text{LSMO}} = 20 \text{ nm}$, (b) $t_{\text{LSMO}} = 25 \text{ nm}$ and (c) $t_{\text{LSMO}} = 40 \text{ nm}$. The magnetic field was aligned parallel to: [100] (black squares), [110] (blue triangles) and [010] (red circles) direction, respectively. (d) Polar plots display the M_r normalized to M_s for BTO(100nm)/LSMO(t_{LSMO}) bilayers with $t_{\text{LSMO}} = 20 \text{ nm}$ (blue circles), 25 nm (green triangles) and 40 nm (black squares) at 300 K. The continuous lines correspond to numerical fit.

To corroborate the MA on LSMO the single layers (not show) and BTO/LSMO bilayers, a in-plane rotation with a 15° step was carried out (fig. 4.8). From this measurements we can identify the nature of MA on LSMO layer. Thus, polar plots for bilayers have been presented in the fig. 4.14(d). The LSMO single layers have a biaxial MA (four-fold) for all t_{LSMO} (not show). The in-plane MA clearly show

that LSMO single layers has EA on [110] direction whereas the HA was found along of [001] direction (not show). Therefore, in our LSMO single layers the MA is independent of the thickness (relaxation imposed by STO substrate), which indicates that this behavior is intrinsic of manganite. However, for BTO/LSMO bilayer a change on magnetic anisotropy from biaxial to uniaxial mechanism was corroborated to samples deposited on (001)STO, where the substrate and BTO layer induce a tensile strain in LSMO.

We calculated k_u and k_1 from equation 1.11, uniaxial and biaxial anisotropy constant, from isothermal hysteresis loop plotted in fig. 4.14. The results obtained for samples deposited on STO display in average for LSMO films a $k_1=0.30$ kJ/m³ with a uniaxial contribution negligible. While in the bilayers case, the uniaxial contribution was -0.38 kJ/m³, -0.42 kJ/m³ and -0.55 kJ/m³ for $t_{LSMO}= 20, 25$ and 40 nm, respectively. These values are comparable with the biaxial contribution in LSMO film, but increase with t_{LSMO} . In bilayers, the LSMO thickness causes a slight relaxation of tensile strain on LSMO layer like was reported by Vailionis et al. [82]. Interestingly, we reported a possible to control the magnetic anisotropy of the LSMO system growing it on appropriate substrate. Our results also indicate that depositing the ferroelectric BTO material on top of an LSMO film makes possible to tune from biaxial anisotropy for a LSMO/STO single film to uniaxial anisotropy behavior for a BTO/LSMO bilayer grown on STO substrate, at room temperature. The magnetic anisotropy behavior of our samples could be due to the induced strains in the LSMO system originated from the lattice mismatch at LSMO/substrate interface but also at the BTO/LSMO interface. In our case, the magnetic anisotropy constants depend on the thickness of the LSMO layer, but the deposition of the ferroelectric BTO layer on top of LSMO influence dramatically these values. Other authors have reported similar behavior in FM/FE interfaces. Shirahata et al. [83], found switching of the symmetry of magnetic anisotropy in Fe- films deposited on FE-BTO substrate, due to interface lattice distortion occurred at different temperatures in regions where the structural phase transition occur. Lahtinen et al. [84], reported that biaxial magnetic anisotropy is associated with ferroelectric domains with out-of-plane polarization (c-domains), whereas the in-plane lattice elongation of a domains (a-domains) induces uniaxial magnetoelastic anisotropy via inverse magnetostriction.

You et al. [85], found in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{BiFeO}_3$ multiferroic system that uniaxial magnetic anisotropy is artificially induced in LSMO film with electrically patterned stripe domains. Recently, Peng et al. [86], investigated an elliptical $\text{Co}_{40}\text{Fe}_{40}\text{B}_{20}$ nanomagnet on top of a $\text{Pb}(\text{Zr,Ti})\text{O}_3$ thin film and computationally demonstrated a promising route to achieve voltage-driven in-plane 180° magnetization switching in a strain-mediated multiferroic heterostructures.

To summary, in this section we corroborate for different t_{LSMO} the influence related to (001)STO substrate on the change of MA. In all bilayers, we induced tensile strain via substrate. The tensile strain induces a in-plane uniaxial anisotropy with EA [010] and HA [100], independently of t_{LSMO} . The structural analysis demonstrate that tensile strain near to interface BTO/LSMO, deformations and dislocations are responsible of change on MA and slight variation on the lattice parameter of LSMO. For this substrate, different strain/relaxed zones allow change on magnetic mechanism from biaxial to uniaxial MA. As consequence, a induced uniaxial MA can be modulated via substrate in a wide range of LSMO thickness.

4.3 BTO/LSMO bilayers on different crystal orientation using SrTiO_3

In Fig. 4.15 (a), we analyzed the magnetic properties with temperature of BTO(100 nm)/LSMO(25 nm) bilayers, deposited on different substrates orientation: (001)STO (black squares), (110)STO (blue triangles) and (111)STO (green circles) with $H_{ZFC}=5$ kOe in-plane of substrate (samples were grown simultaneously in the chamber).

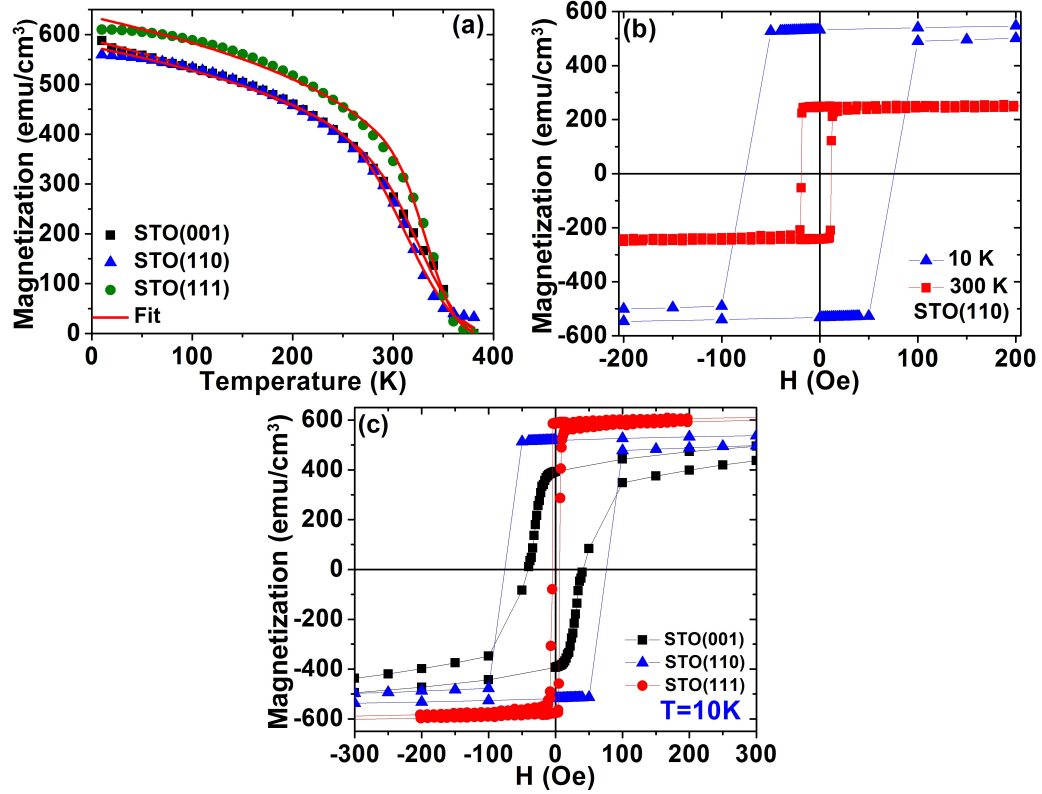


Figure 4.15: (a) Dependence of magnetization with temperature for BTO(100 nm)/LSMO(25 nm) bilayers deposited on different substrates orientation: STO (001) (black squares), STO(110) (blue triangles) and STO(111) (green circles), $H_{ZFC}=5$ kOe was applied in-plane of bilayer. (b) Isothermal hysteresis loops for BTO(100 nm)/LSMO(25 nm) deposited on STO(110) at 10 K and 300 K. (c) Isothermal hysteresis loops for BTO(100 nm)/LSMO(25 nm) bilayers deposited on STO substrates with different orientation at 10 K.

The samples display transition between a PM state at high temperatures ($T > 400$ K) to a FM behavior below of transition temperature $T_C \sim 350$ K, which was obtained according to the model proposed by Berger et al. [1]. BTO/LSMO bilayers display a FM behavior with a $M_s^{001} \sim 600$ emu/cm³, $M_s^{110} \sim 550$ emu/cm³ and $M_s^{111} \sim 610$ emu/cm³ at 10 K. The highest value was found to bilayer deposited on (111)STO (LSMO layer have the same thickness but different substrate orientations). This results contrast with found by Li et al. [91], in the same system where the $M_S \sim 300$ emu/cm³ for (110)STO substrate and $t_{LSMO} = 200$ nm. However, this differences on magnetic properties are associated to different strain states, due to different lattice parameters for different substrates orientations were found (Table 4.3). We observed that the magnetic behavior have a slight difference between M_s , H_c and T_c from bilayer respect to LSMO (not show) and are according to reported in literature for LSMO films [89, 90]. In Fig. 4.15(b), the isothermal hysteresis loops for BTO/LSMO bilayer deposited on (110)STO at 10 and 300 K, display the temperature influence on M_S and H_C . These values are below of obtained for LSMO films (not shown) and thus, the BTO layer affects the magnetic properties of LSMO like was reported on previous work [4]. In our system FM-PM transitions was found using model proposed by Berger et al. [1–4]. The $T_C \sim 350$, 336 and 352 K for (001)STO, (110)STO and (111)STO, respectively. The quality of fitting between the model (solid red line) and experimental data (symbols) is observed in Fig. 4.15 for each case. The T_C , ΔT_C and critical β exponent were estimated from the fit and collected in Table 4.3.

Table 4.3: Summary of magnetic properties of ZFC magnetization for single layers and bilayers grown on STO(001), STO(110) and STO(111). T_C and ΔT_C are extracted from the Gaussian fit.

Sample	M_S [emu/cm ³]	T_C [K]	ΔT_C [K]	β
LSMO/STO(001)	550 ± 5	350 ± 1	36 ± 1	0.244 ± 0.006
BTO/LSMO/STO(001)	500 ± 4	350 ± 1	58 ± 4	0.283 ± 0.005
LSMO/STO(110)	580 ± 5	340 ± 1	37 ± 2	0.231 ± 0.005
BTO/LSMO/STO(110)	550 ± 4	336 ± 1	42 ± 1	0.238 ± 0.005
LSMO/STO(111)	600 ± 6	350 ± 1	38 ± 1	0.262 ± 0.006
BTO/LSMO/STO(111)	600 ± 6	352 ± 1	52 ± 4	0.255 ± 0.006

In fig. 4.16, from β exponent collected from fits a dependence with substrate orientation is observed. For all directions the behavior is according to tricritical point; in our case, $\beta \sim 0.25$ for LSMO film and BTO/LSMO bilayers, which have been reported for this type of manganites [26, 27].

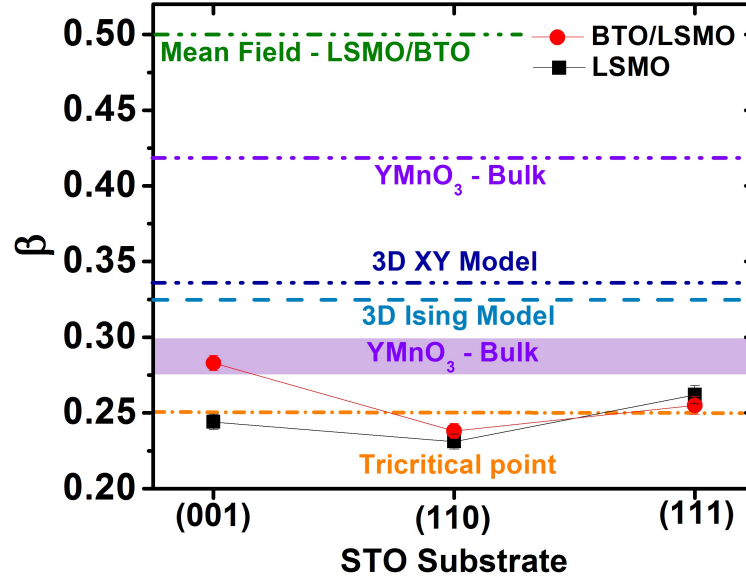


Figure 4.16: β exponent as a function of STO orientations for BTO(100 nm)/LSMO (25 nm) bilayers deposited on STO. $H_{ZFC}=5$ kOe was applied in-plane of bilayer. The dotted lines correspond to different values reported in literature [26–34].

The critical exponents of a FM phase transition depend on the type of ordering and dimensionality, but, as was discussed by Huang et al. [28, 29], at a tricritical point, they are universal. Interestingly, this values is near to reported by Gibbs et al. [32], through of high-resolution powder neutron diffraction on hexagonal multiferroic-magnetoelectric YMnO_3 where $\beta=0.271 \pm 0.003$ and as consequence an increasing of the polarization with raising temperature what is opposite to the results of other authors [33, 34]. This values also have been reported in multiferroic NdMnO_3 , associated to magnetoelastic coupling in a fluctuating regime with strong magnon-lattice hybridization [92, 93] and in BiFeO_3 where the material is strongly affected by structural fluctuations in a distorted environment with competing phases in the form of clusters [94]. These results, contrast with the reported values on previous work on

LSMO/BTO bilayers where mean field mechanism is identified on all samples with $\beta=0.42$ to 0.54 [4].

In fig. 4.17(a) the isothermal hysteresis loops for BTO/LSMO bilayers grown on different orientations at 300 K are presented. In this curves a slight differences on M_s is found. In fig. 4.17(b) we observed that the $M_s^{300K} \sim$ varies between 215 to 260 emu/cm^3 for bilayers with a H_C in the range of 10 to 24 Oe for different substrates orientations, these values are close to reported to LSMO films [61, 90, 95, 96, 98, 99].

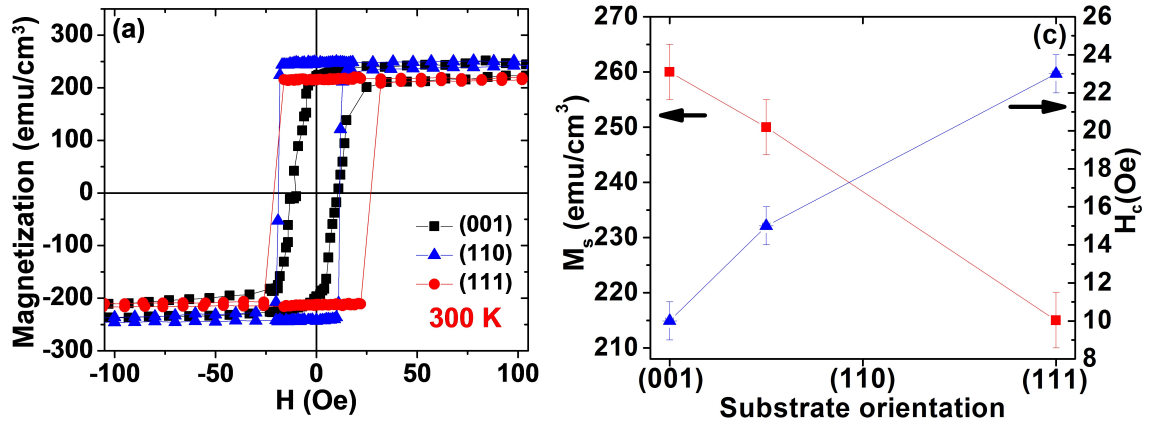


Figure 4.17: (a) Isothermal hysteresis loops for BTO(100 nm)/LSMO(25 nm) bilayer deposited on different substrates orientations at 300 K. STO(001) (black squares), STO(001) (blue triangles) and STO(111) (red circles) denote measurements with the field aligned with EA respectively. (b) Saturation magnetization and coercive field as function of substrate orientation.

This behavior shows that there are a strong dependence of M_s and H_C with the crystal orientation of substrate used. Interestingly, the XRD display that BTO grown on bilayer is better oriented for samples deposited on STO(110) and STO(111) (only c-domains in BTO was found) in comparison with STO(001) where different BTO domains-orientation is observed (Fig. 3.10), although all the substrates have the same lattice parameter value ($a_{STO}=3.905 \text{ \AA}$), differences were found in the LSMO lattice parameter deposited in the different orientations (Table 3.7), which can modify the magnetic and electric properties by action of tune the carrier density of LSMO channel [53, 55]. According to Cui et al., [103] a factor important is the oxygen vacancies migrate toward and away from the interface depending of the P_{up}

and P_{down} states, respectively (accumulation or depletion of holes as was visualized on fig. 4.7)[55, 109, 110]. The Ti-O-Mn bonding is based on the orbital hybridization between Ti, O, and Mn ions [111, 112], the P_{down} state (depletion) with less oxygen vacancies at the interface stabilize the bonding and orbital reconstruction, while the P_{up} state (accumulation) shows the opposite behavior. The influence of strain associated to double interface in LSMO (LSMO/STO and BTO/LSMO interface) as route for ME coupling are analyzed from following statements: (a) the FE layer act on LSMO by clamping effect of strain produced by polarization causing AF ordering near to interface; (b) in bilayer deposited on STO(001) the BTO a-domains are almost the same in P_{up} and P_{down} states as was studied by Cherifi et al., [108] in FeRh/BTO structures. In this case the application of a voltage converts the BTO from a mixed state with a- and c-type domains (with a 34%/66% c-to-a domain population ratio) to a largely homogeneous c-type configuration (98%/2% ratio) associated to the applied voltage generates an in-plane compressive strain on the FeRh via piezoelectric effect [108]. Additionally, in our case TEM image confirm the remanent polarization on BTO layer as is evidenced on fig. 3.14. Thus, a possible reconstruction of the orbitals on interface is expected, due to a Ti atom displacement occur. For our BTO/LSMO bilayer deposited on (001)STO the results are consistent with the work of Cui et al. [103], where the as-grown BTO exhibits a single domain with P_{up} . They proposed that the Ti atom (green atom) displacement on BTO induce the orbital reconstruction of Mn atom (blue atom) in the interface associated to different FE polarization direction (P_{up} and P_{down} states) as described in Fig. 4.18 (a). A overlapped out-of-plane orbital component of Mn- $d_{3z^2-r^2}$ and Ti- d_{xz} ($-d_{yz}$) in the lattice, hybridize into a bonding orbital with lower energy level than that of the originally occupied Mn- $d_{x^2-y^2}$ (Fig. 4.18(c)), strongly weakening the in-plane orbital occupancy [104, 105].

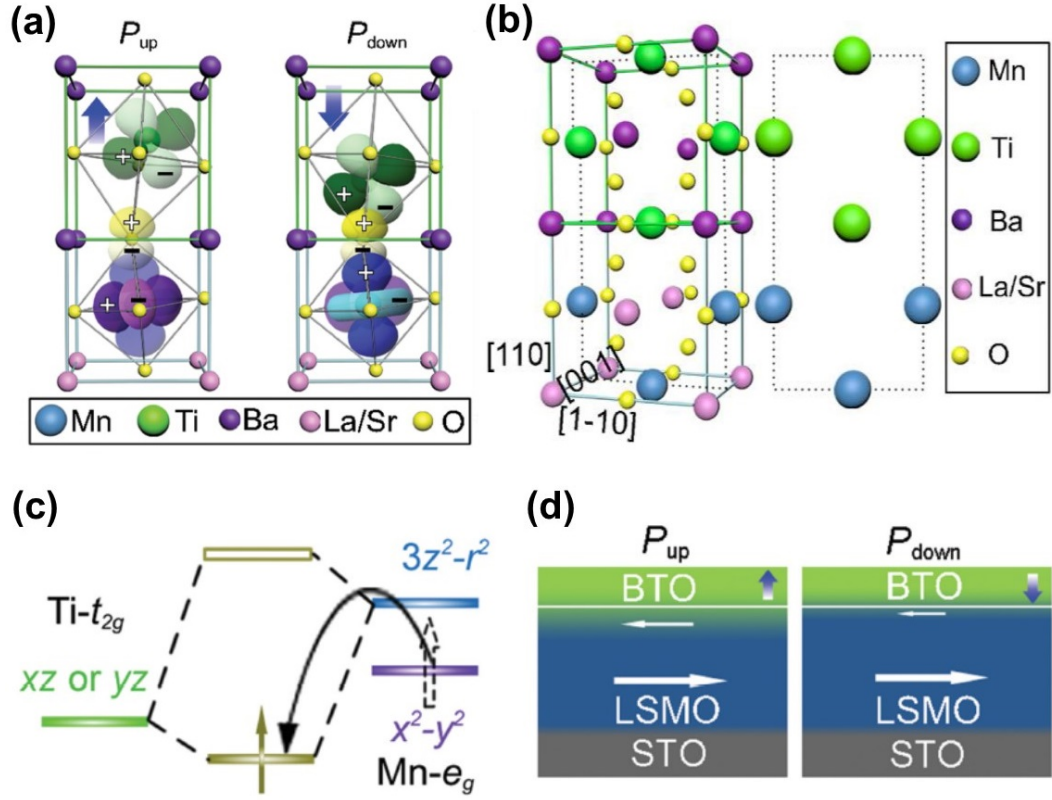


Figure 4.18: (a) Sketch for the interfacial orbital reconstruction under different polarization states. The favored orbitals are dense while the disfavored ones are washy. (b) Sketch for atomic arrangement of heterostructure on (110) STO and the cross-section view along (002) plane. (c) Schematic for the orbital hybridization between Ti, O, and Mn. (d) Schematic of the LSMO channel composed by interfacial and bulk layer under P_{up} and P_{down} , [103].

The P_{up} and P_{down} states suppress and enhance the interfacial orbital hybridization, accompanied by the intensified and weakened Mn- $d_{x^2-y^2}$ orbital occupancy, respectively. Interestingly, they found that the interfacial termination not change the effect of polarization as both the (La,Sr)O and BaO could supply O ions for the Ti-O-Mn bonding allows the interfacial orbital reconstruction. In addition, the LSMO layer was treated as two parallel channels of bulk and interface (Fig. 4.18 (d)). Altering the orbital occupancy at the interface, states of polarization (P_{up} and P_{down}) could be modulate the relative weight of the interfacial channel with

preferential Mn- $d_{x^2-y^2}$ occupancy [106, 107]. The interfacial layer behaves a spin arrangement antiparallel to the bulk one [106], and its modulation under electric field is bound to influence the magnetic and transport properties of LSMO as also was predicted by Burton et al. [53], and Chen et al. [55], in theoretical calculations and studied in previous section. For case of BTO/LSMO bilayer deposited on (110)STO a deep analysis is need. In the lattice the distribution of atoms along [110] direction is display in Fig. 4.18 (c) according to proposed by Cui et al. [103], the distance between Mn and Ti along the normal of substrate is enlarged without a connection between O. For this reason, FE polarization could not affect the orbital hybridization between Ti and Mn due to the absence of a key bridge of O ion. They found for dependence of resistance with temperature behavior that the orbital occupancy is stable in different polarization states. That is, no changes associated to P_{up} and P_{down} is observed, and as consequence, not change the magnetic and electric properties on bilayer is expected via this mechanism. However, for BTO/LSMO bilayer deposited on (111)STO the scenario is very complex and desert, due among others factors, to the geometry of substrate. The M_s , H_c and T_c is above of values reported by LSMO single layers according to literature [99, 101, 102, 113]. In case of bilayers deposited on (111)STO there are no work reported in the literature. Li et al. [21], reported the magnetic properties on BTO/LSMO bilayers deposited on LAO(111) where the $M_s^{10K} \sim 250 \text{ emu/cm}^3$ and $T_c \sim 270 \text{ K}$. The performance for this direction are below for found for (001) and (110)LAO. These results contrast with our case in STO, where the M_s and T_c found in STO(111) are above of found for other directions. In the case of STO(111) substrate, Hallsteinsen et al. [100], studied that the surface has a hexagonal symmetry where alternating layers of SrO_3^{4-} and Ti^{4+} , are each stacked in a "ABCABC..." manner as marked for the Ti^{4+} layers, with low-index in-plane directions [101] and [112] (Fig. 4.19). Thus, the connection between BTO and LSMO is very complex and uncertain.

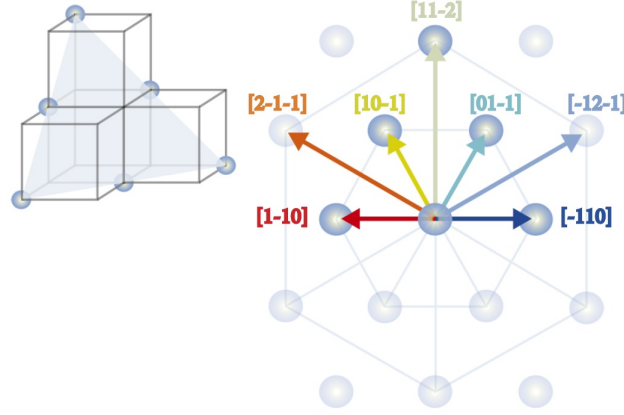


Figure 4.19: (a) Schematic of the atomic configuration of a (111)-oriented surface in a cubic perovskite, with indications of the in-plane low-index directions, i.e., $[1\bar{1}0]$ and $[1\bar{1}2]$ $[100]$.

In order to verify MA on bilayers with different t_{LSMO} at room temperature with different STO orientations, we measured the isothermal hysteresis loops along of different directions with the magnetic field applied in-plane of substrate as is observed in fig 4.20. Three different directions was selected, to analyze MA on LSMO layer and the possible influence of FE layer. The procedure used was described in the previous section. This measurement is repeated for various angles with 15° of separation as indicated on fig. 4.20.

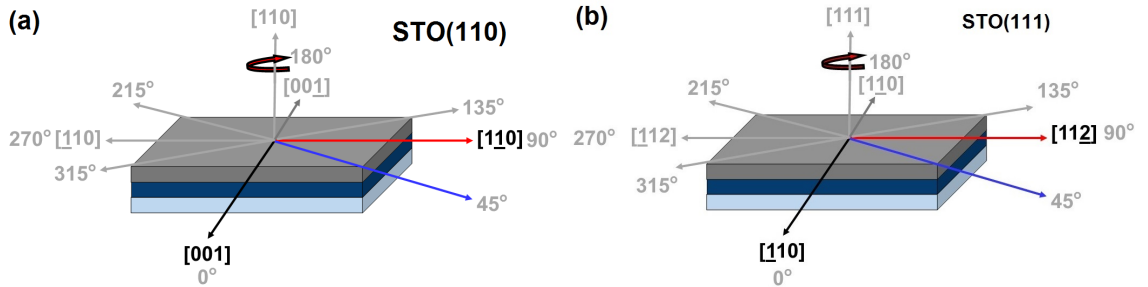


Figure 4.20: Sketch of the crystallographics directions with respect to bilayer plane on (a) (110)STO and (b) (111)STO substrate.

In Fig. 4.21(a), a clear behavior of MA on (001)STO substrate is observed at room temperature. The isothermal hysteresis loops was measured with magnetic

field aligned in three directions: $[100]$ (black squares), $[110]$ (blue triangles) and $[010]$ (red circles). The M_r is larger along $[110]$ than $[100]$ direction. Additionally, the M_s for $[100]$ direction is achieved to a magnetic field more highest in comparison with $[110]$ direction. The $[110]$ direction is an intermediated direction and also is plotted for each bilayer to show the angular separation of EA and HA. In $[100]$ the M_r presents a reduction of 43%.

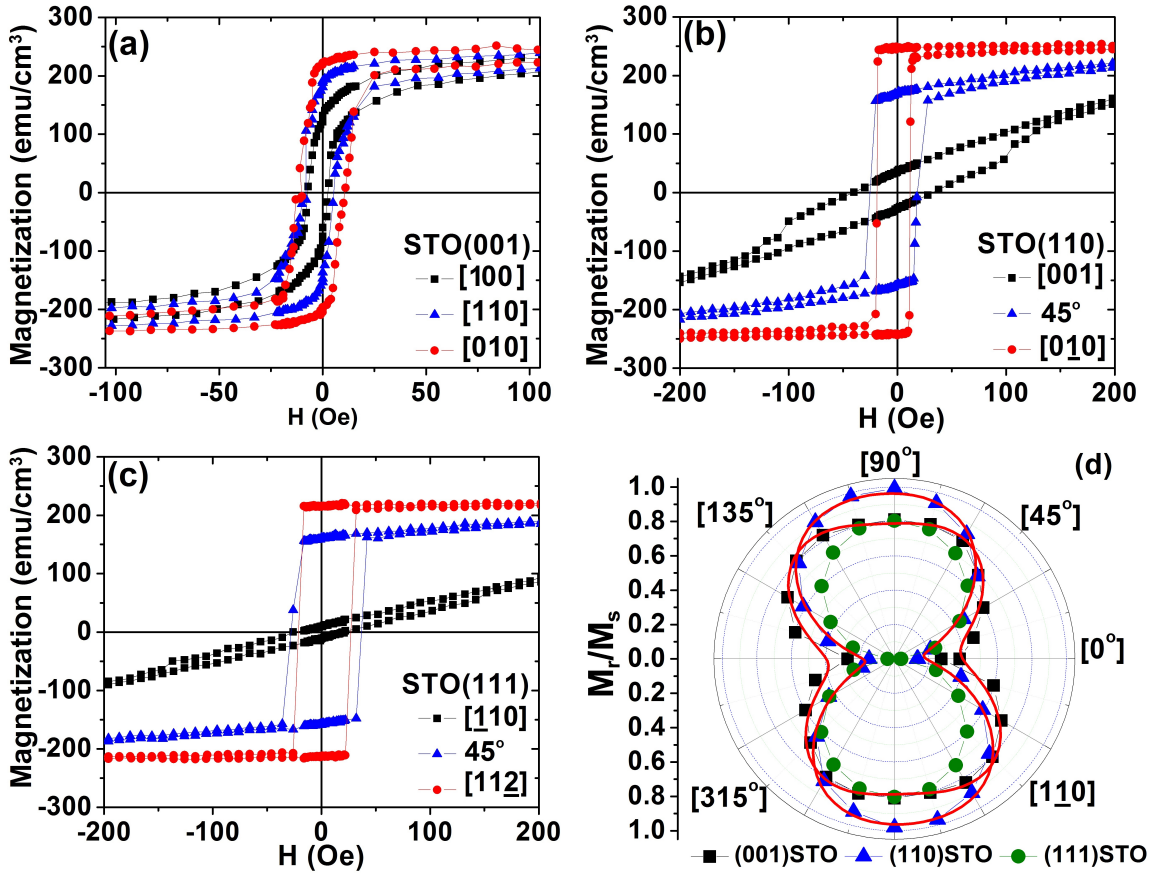


Figure 4.21: Isothermal hysteresis loops on BTO(100 nm)/LSMO/STO bilayer at 300 K, (a) STO(001), (b) STO(110) and (c) STO(111). Black squares, blue triangles and red circles denote measurements with the field aligned to 0° , 45° and 90° , respectively. (d) Polar plots display the remnant magnetization at 300 K for BTO(100nm)/LSMO(t_{LSMO}) bilayers on different substrate orientation (blue circles), 25 nm (green triangles) and 40 nm (black squares). The continuous lines correspond to numerical fit.

Fig. 4.21(b) display a MA on (110)STO substrate, hysteresis loops was measured with magnetic field aligned in three directions: $[100]$ (black squares), 45° (blue triangles) and $[1\bar{1}0]$ (red circles). The M_r is larger along $[1\bar{1}0]$ that $[001]$ direction. The 45° direction is a intermediated direction and also is plotted for each bilayer to show the angular separation of EA and HA. In $[001]$ the M_r present a reduction of 86%. In all cases, the coercive field is different for all directions. And finally, in fig. 4.21(c) display a MA on (111)STO substrate, hysteresis loops was measured with magnetic field aligned in three directions: $[1\bar{1}0]$ (black squares), 45° (blue triangles) and $[11\bar{2}]$ (red circles). The M_r is larger along $[11\bar{2}]$ that $[1\bar{1}0]$ direction. The 45° direction is a intermediated direction and also is plotted for each bilayer to show the angular separation of EA and HA. In $[1\bar{1}0]$ the M_r present a reduction of 95%. In all substrate orientation, the coercive field is different for all measurements directions. In (111)STO there are a hexagonal crystal symmetry, shown on fig. 4.19, as consequence the magnetic properties (M_s , H_C and MA) are different in comparison with others STO substrates with (001) and (110)-orientations. In fig. 4.21(d) the polar plots for bilayers have been presented. The LSMO single layers have a uniaxial MA (two-fold) for (110)STO and (111)STO substrate directions (not show), while the film grown on (001)STO the MA have a biaxial nature (as was studied on previous section). For bilayers, the in-plane MA clearly show that LSMO on bilayers has EA on $[010]$, $[0\bar{1}0]$ and $[11\bar{2}]$ direction for (001)STO, (110)STO and (111)STO, respectively. Whereas the HA was found along of $[001]$, $[110]$ and 0° direction, which is consistent with uniaxial MA. We calculated k_u and k_1 from equation 1.11, uniaxial and biaxial anisotropy constant, from isothermal hysteresis loop plotted in fig. 4.8. The results obtained for film deposited on (001)STO, a $k_1=0.30$ kJ/m³ with uniaxial contribution negligible was found. While in the bilayers case, the MA mechanism change from biaxial to uniaxial with -0.42 kJ/m³. For films and bilayers deposited on (110)STO and (111)STO substrates, a clear uniaxial MA was identified with 0.320 kJ/m³ and 0.340 kJ/m³, respectively.

These analysis, corroborated that the only in bilayer deposited on (001)STO the change on MA take place; as in the samples deposited on LSAT and LAO substrates, in different STO-oriented substrates, also the MA mechanism is conserved. This situation was to be expected, as we recall that in bilayer deposited on (110)STO

Cui et al. [103], proposed that the distance between Mn and Ti along the normal of substrate is enlarged without a connection between O (Fig. 4.18(c)). For this reason, FE polarization could not affect the orbital hybridization between Ti and Mn due to the absence of a key bridge of O ion. Then, there are not change the magnetic and electric properties on bilayer is expected via this mechanism. A similar situation was studied to (111)STO substrate by Hallsteinsen et al., [102] where the the substrate surface has a hexagonal symmetry (Fig. 4.19), with alternating layers of SrO_3^{4-} and Ti^{4+} , which are each stacked in a "ABCABC..." manner as marked for the Ti^{4+} layers (Fig. 4.22). Li et al.,[21] also studied BTO/LSMO bilayers deposited on LAO with different orientations. In these systems a ME coupling was studied through, ME voltage coefficient α_E , where the samples with (110) and (111)LAO orientation present weak electrical and magnetic properties and the most low coupling.

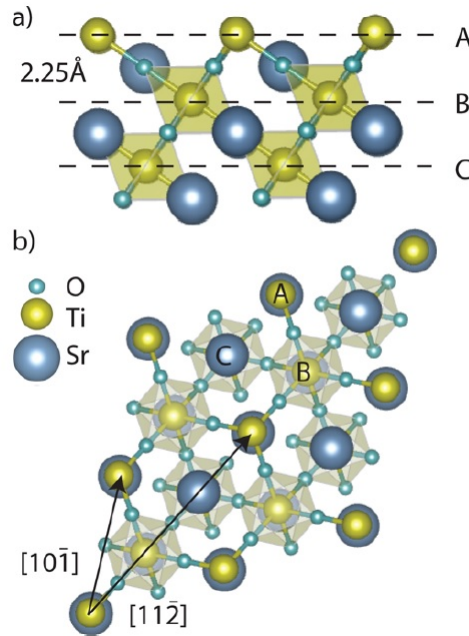


Figure 4.22: Schematic of an ideal cubic STO (111) Ti^{4+} terminated surface, with Ti in yellow, Sr in blue, and O in turquoise. The Ti^{4+} layers are indicated by dashed lines, and labeled A,B,C according to the "ABCABC..." stacking. (a) Cross-section view. The distance between two equivalent lattice planes is $d_{111} = a/\sqrt{3} = 2.25 \text{ \AA}$, where a is the cubic lattice constant of SrTiO_3 ($a = 3.905 \text{ \AA}$). (b) Top view. Arrows indicate the low-index in-plane crystallographic directions $[10\bar{1}]$ and $[11\bar{2}]$ [102].

To summary, in this section we corroborate that uniaxial anisotropy only is present on (001)STO when different STO-orientation substrates was used. In all bilayers an uniaxial anisotropy with EA [010] and HA [100] was reported, independently of crystal orientation of STO. The structural analysis demonstrate that tensile strain is induced in all cases. For all bilayers an slight variation on the lattice parameter of LSMO, but the orientations of LSMO is different and magnetic properties are influenced. On bilayer deposited on (001)STO, different strain/relaxed zones allow change on magnetic mechanism from biaxial to uniaxial MA. Thus, a induced uniaxial MA can be modulated via substrate orientation.

Bibliography

- [1] G. Campillo et al., J. Mag. Mag. Mat., **237**, 61, (2001).
- [2] J. E. Ordoñez et al., IEEE Trans. Magn., **49**, No. 8, (2013).
- [3] J. E. Ordoñez et al., J. Phys.: Conf. Ser., **480**, 1-4, (2014).
- [4] J. E. Ordoñez et al., Rev. Mex. Fis., **62**, 543-548, (2016).
- [5] L. Cao et al., Phys. Status Solidi a, **181**, 387, (2000).
- [6] V. K. Vlasko-Vlasov et al., Phys. Rev. Lett., **84**, 2239, (2000).
- [7] A-M -Gosnet, et al J. Phys. D: Appl. Phys., **36**, R127-R150, (2003).
- [8] M. Ziese et al., New J. Phys., **10**, 063024, (2008).
- [9] H Boschker, J. Phys. D: Appl. Phys., **44**, 205001, (2011).
- [10] P. Lecoeur, et al, J. Appl. Phys., **82** (8), 3934, (1997).
- [11] M. Ziese et al, J. Magn. Magn. Mater., **246**, 327-334, (2002).
- [12] V. S. Kumar et al, AIP Advances, **3**, 052127, (2013).
- [13] S. Valencia et al, J. Appl. Phys., **109**, 07D718, (2011).
- [14] M. Spankova et al., Vacuum, **126**, 24-28, (2016).
- [15] F. Tsui et al., Appl. Phys. Lett., **76**, 17, 2421, (2000).
- [16] Y. Suzuki et al., Appl. Phys. Lett., **71**, (1), 7, 140, (1997).

-
- [17] K. Steenbeck, et al, Appl. Phys. Lett., **75** (12), 1778, (1999).
 - [18] L.M. Berndt, et al, Appl. Phys. Lett., **77** (18), 2903-2905, (2000).
 - [19] M. Ziese, et al, J. Mag. Mag. Mat., **246**, 327-334, (2002).
 - [20] T. X. Li, et al, J. Phys. D: Appl. Phys., **45** 085002, (2012).
 - [21] T. X. Li, et al, J. Alloys Compd., **560**, 167-170, (2013).
 - [22] H. Lu et al, Appl. Phys. Lett., **100**, 232904, (2012).
 - [23] M. K. Lee et al., Appl. Phys. Lett., **77**, No. 22, 27, (2000).
 - [24] S. Singamaneni et al., J. Appl. Phys. **116**, 224104, (2014).
 - [25] J. D. Burton et al, Phys. Rev. B **80**, 174406, 1-6, (2009).
 - [26] J. Pino et al., J. Phys.: Conf. Ser. **466**, 01202, (2013).
 - [27] D. Kim et al, Phys. Rev. Letters **89**, 22, (2002).
 - [28] K. Huang, Statistical Mechanics, Wiley, New York, 2nd ed., Chap. 17.6, 432-438, (1987).
 - [29] M. F. Collins, Magnetic critical scattering (Oxford University Press, Oxford, 1989).
 - [30] T. Chatterji, Pramana-J.Phys., **71** , 847, (2008).
 - [31] T. Chatterji et al., Phys. Rev. B, **76**, 144406, (2007).
 - [32] A. S. Gibbs et al., Phys. Rev. B, **83**, 094111, (2011).
 - [33] J. Kim et al., Appl. Phys. Lett., **97**, 092902, (2010).
 - [34] J. M. Wesselinowa et al., J. Appl. Phys., **102**, 043911, (2007).
 - [35] J.M. Wesselinowa et al, Bulg. J. Phys., **38**, 420-425, (2011).
 - [36] M. Poirier et al, Phys. Rev. B, **76**, 174426, (2007).

-
- [37] E. Alves et al, CERN / INTC 2005 **016**, INTC-P132 Addl, (2005).
 - [38] G. A. Ovsyannikov et al, J. Exp. Theor. Phys., **108**, No. 1, 48-55, (2009).
 - [39] T. Li et al., Physica B, **475**, 32-34, (2015).
 - [40] R. Flaschmann et al., J. Appl. Cryst., **49**, 1693-1703, (2016).
 - [41] P. Mukherjee et al., Phys. Rev. B, **91**, 104419, (2015).
 - [42] X. Shen et al., J. Appl. Phys., **112**, 123919, (2012).
 - [43] A. Alberca et al., Phys. Rev. B, **86**, 144416, (2012).
 - [44] P. Murugavel et al., J. Appl. Phys. **100**, 023520, (2006).
 - [45] M. Fath et al., Science, **285**, 1540, (1999).
 - [46] K. Dorr et al., J. Appl. Phys., **89**, 6973, (2001).
 - [47] A. Biswas et al., Phys. Rev. B, **61**, 9665, (2000).
 - [48] M.-H. Jo et al., Appl. Phys. Lett., **75**, 3689, (1999).
 - [49] H. Doganay et al., EPL, **109**, 67007, (2015).
 - [50] G. Colizzi et al., Phys. Rev. B, **78**, 235122, (2008).
 - [51] M. J. Calderon et al., Phys. Rev. B, **60**, 6698, (1999).
 - [52] S. Y. Yang et al., J. Magn. Magn. Mater., **268**, 326, (2004).
 - [53] Y. P. Lee, Phys. Rev. B, **73**, 224413, (2006).
 - [54] H. Chen et al., Phys. Rev. B, **86**, 024433, (2012).
 - [55] J. Chen et al., Phys. Rev. Lett., **68**, 1212, (1992).
 - [56] C. A. F. Vaz et al., Phys. Rev. Lett., **104**, 127202 (2010).
 - [57] P. M. Leufke et al., Phys. Rev. B, **87**, 094416, (2013).

- [58] D. Yi et al., Phys. Rev. Lett., **111**, 127601, (2013).
- [59] X. Ma et al., Appl. Phys. Lett., **104**, 132905, (2014).
- [60] J. Z. Sun et al., Appl. Phys. Lett., **74**, 3017, (1999).
- [61] I. C. Infante et al., J. Appl. Phys., **103**, 07E302, (2008).
- [62] S. Liang et al., Appl. Phys. Lett., **95**, 182509, (2009).
- [63] W. W. Gao et al., J. Appl. Phys., **117**, 17C733, (2015).
- [64] A. Belenchuk et al., Appl. Phys. Lett., **109**, 232405, (2016).
- [65] W. Luo et al., Phys. Rev. Lett. **101**, 247204, (2008).
- [66] V. G. Prokhorov et al., Low Temp. Phys. **33**, 1, (2007).
- [67] R. Peng et al., Appl. Phys. Lett., **104**, 081606, (2014).
- [68] F. Song et al., Surf. Interface Anal., **45**, 1144-1147, (2013).
- [69] X. L. Li et al., Appl. Phys. Lett., **87**, 222905, (2005).
- [70] C. B. Parker et al., Appl. Phys. Lett., **81**, 340, (2002).
- [71] C. Zhou et al., J. Appl. Phys., **82**, 3081, (1997).
- [72] T. K. Nath et al., Appl. Phys. Lett., **74**, 1615, (1999).
- [73] Y. Konishi et al., Mater. Sci. Eng. B, **56**, 158, (1999).
- [74] Boschker et al., J. Mag. Mag. Mat., **323**, 2632-2638, (2011).
- [75] C. Kwon et al., J. Mag. Mag. Mat., **172**, 229-236, (1997).
- [76] P. Perna et al., J. Appl. Phys., **110**, 013919, (2011).
- [77] R. K. Kawakami et al., Phys. Rev. Lett., **77**, 2570, (1996).
- [78] A. Stupakiewicz et al., Phys. Rev. B, **80**, 094423, (2009).

-
- [79] M. Mathews et al., Appl. Phys. Lett., **87**, 242507, (2005).
- [80] S. van Dijken et al., Phys. Rev. B, **63**, 104431, (2001).
- [81] M. Mathews et al., Phys. Rev. B, **80**, 064408, (2009).
- [82] A. Vailionis et al., Appl. Phys. Lett., **105**, No. 131906, 1-5, 2014.
- [83] Y. Shirahata et al., Appl. Phys. Lett., **99**, No. 22501, 2012-2015, (2014).
- [84] T. H. E. Lahtinen et al., Appl. Phys. Lett., **101**, No. 262405, 1-5, (2012).
- [85] L. You et al., Phys. Rev. B, **88**, No. 184426, 1-9, (2013).
- [86] R. Peng et al., Sci. Rep., **6**, no. 27561, 1-9, (2016).
- [87] I. C. Infante et al., Phys. Rev. B, **76**, 224415, (2007).
- [88] A. M. Haghiri-Gosnet et al., J. Appl. Phys., **88**, No. 7 (2000).
- [89] J. Fontcuberta et al., J. Appl. Phys., **85**, No. 8, (1999).
- [90] R. V. Chopdekar et al., Phys. Rev. B **79**, 104417, (2009).
- [91] T. Li et al., J. Alloys Compd., **560**,167-170 (2013).
- [92] N. E. Massa et al., J. Phys.: Condens. Matter, **25**, 395601 (2013).
- [93] P. Dai et al., Phys. Rev. B, **61**, 9553, (2000).
- [94] N. E. Massa et al., J. Appl. Phys., **108**, 084114, (2010).
- [95] H. Boschker et al., J. Appl. Phys., **108**, 103906, (2010).
- [96] H. Boschker et al., Phys. Rev. B, **79**, 214425, (2009).
- [97] I. C. Infante et al., Phys. Rev. B, **76**, 224415, (2007).
- [98] C.L. Prajapatetal et al., Physica B, **448**, 100-102, (2014).
- [99] V. Flovik et al., J. Magn. Magn. Mater. **420**, 280-284, (2016).

-
- [100] I. Hallsteinsen et al., APL Materials **3**, 062501, (2015).
 - [101] I. Hallsteinsen et al., J. Appl. Phys. **113**, 183512, (2013).
 - [102] I. Hallsteinsen et al., Cryst. Growth Des., **16**, 2357-2362, (2016).
 - [103] B. Cui et al., Adv. Mater. , **27**, 6651-6656, (2015).
 - [104] J. G. Barriocanal et al., Nat. Commun., **1**, 82 (2010).
 - [105] J. M. D. Coey et al., MRS BULLETIN, **38**, 1040-1047, (2013).
 - [106] N. M. Nemes et al., Adv. Mater., **26**, 7516, (2014).
 - [107] F. Y. Bruno et al., Phys. Rev. Lett., **106**, 147205, (2011).
 - [108] R. O. Cherifi et al., Nat. Mater., **13**, 345 (2014).
 - [109] S. X. Wu et al., Phys. Rev. X, **3**, 041027, (2013).
 - [110] H. J. Mao et al., Phys. Chem. Chem. Phys., **17**, 10146, (2015).
 - [111] B. M. Wang et al., Nature Commun **4**, 2778, (2013).
 - [112] Y. Liu et al., APL Materials **4**, 046105, (2016).
 - [113] C. L. Prajapat et al., Physica B **448**, 100-102, (2014).

Chapter 5

Ferroelectric properties

In this chapter, we present the results of the ferroelectric properties for the $\text{BaTiO}_3/\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ (BTO/LSMO) bilayers. In our case, isothermal ferroelectric loops at room temperature was measures for all samples. The saturation polarization (P_S) and coercive field (E_C) were the variables to be studied. In Fig. 5.1 the BTO/LSMO configuration is displayed. In this arrangement, LSMO layer was used as bottom electrode, while multiple Au discs was deposited as top electrode on BTO surface, by means of an evaporation process using a shadow mask with holes of different diameters. (the diameter of the electrodes varies between 4 sizes).

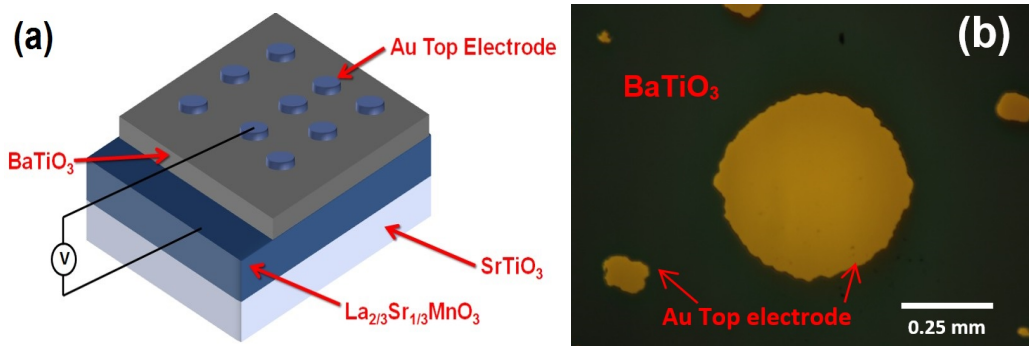


Figure 5.1: (a) $\text{Au}(25 \text{ nm})/\text{BTO}/\text{LSMO}$ capacitive configuration for FE measurements. (b) Image taken from optical microscope for BTO film ($t_{\text{BTO}}=100 \text{ nm}$) and Au electrodes ($t_{\text{Au}}=50 \text{ nm}$). Different Au electrodes deposited on the surface of the BTO layer.

First, we placing a microtip onto Au electrode and the other onto LSMO layer, and as consequence a capacitive structure is established with a dielectric material (BTO) in the center (fig. 5.1(a)). Second, using a RT66B equipment, a potential difference is applied between both electrodes, to subsequently measure the response of the material. For the different thicknesses, a maximum voltage of 8.0 V was applied, using an electrode of equal size (diameter of approximately 135 μm). According to RSM and TEM images, the tetragonality of the samples ($\mathbf{a} = \mathbf{b} \neq \mathbf{c}$, $(c/a)_{\text{BTO}} > 1.010$) was verified. Therefore, we expected a ferroelectric behavior, since the phenomenon of ferroelectricity takes place in materials with symmetry non-centrosymmetric, and tetragonality is this indispensable requirement.

5.1 BTO/LSMO bilayers on different substrates: (001)LAO, (001)LSAT and (001)STO.

Fig. 5.2(a) shows different ferroelectric hysteresis loops for the BTO/LSMO bilayers grown on (001)-oriented substrates: LAO (black squares), LSAT (blue circles) and STO (green triangles). We extract values for saturation polarization of $P_S \sim 17 \mu\text{C}/\text{cm}^2$, $20 \mu\text{C}/\text{cm}^2$ and $24 \mu\text{C}/\text{cm}^2$ for LAO, LSAT and STO, respectively. While, the coercive electric field of E_C varies from 60 to 85 kV/cm. P_S in bilayers are close to reported by bulk [1, 2] and close to reported by others authors in the same configuration ($\sim 30 \mu\text{C}/\text{cm}^2$); where coercive fields are approximately similar, using STO and others substrates [3–7], and reported in previously for BTO/LCMO bilayers [8]. In the curves an imprint shift $\sim 16\text{--}90$ kV/cm is observed. These phenomenon has been studied widely on literature [9], especially in capacitive structures with electrodes of different materials [10], films with strain effects and/or oxygen loss at the interface [11], electrons and vacancies trapped on the interface [12], charge compensation [12] and defect-dipole [12, 13]. The gap on hysteresis loop at 0 V (boundary 3th-4th quadrant) is associated with a depolarization phenomenon (loss polarization) [9].

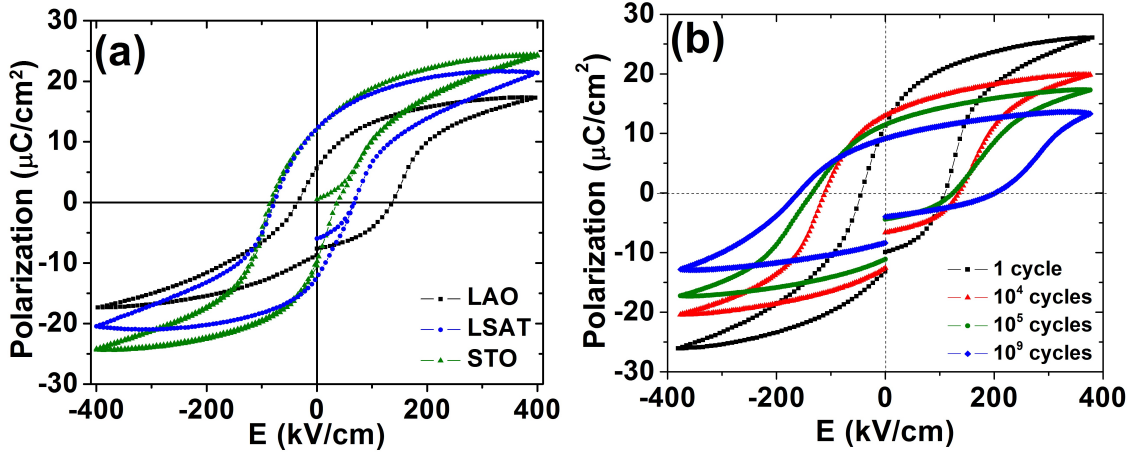


Figure 5.2: (a) Ferroelectric hysteresis loops for BTO/LSMO bilayer deposited on different substrates: LAO (black squares), LSAT (blue circles) and STO (red triangles) at 300 K. (b) PâĂŞE hysteresis loops at room temperature for BTO/LSMO deposited on STO: 1 cycle (black squares), 10^4 cycles (red triangles), 10^6 cycles (green circles) and 10^9 cycles (blue diamonds).

The anomalous behavior observed on bilayer deposited on LAO, is consistent for a ferroelectric material with leakage (capacitive structure with problems), dielectric linear loss [14] or a non-ferroelectric layer in the film represented as a series capacitor connected to the ferroelectric layer (leakage currents are represented by a resistive element) [15, 16]. Fig. 5.2(b) display the ferroelectric hysteresis loops for BTO/LSMO bilayer deposited on (001)STO for different cycles. Initially, a typical behavior of a ferroelectric material is observed after 1 cycle. However, when the material are submitted to repeated cycles of hysteresis in the range between 10^4 to 10^6 , P_S decreases about 45% of initial value and E_C increase from 75 to 185 kV/cm . This type of ferroelectric behavior is characteristic of the ferroelectric layer using as inferior electrode a manganite and is associated to the formation of FE dead layer, where oxygen vacancies and/or defects (dislocations observed on TEM images in chapter 3) migrate to FE-metal interface by electric field action and as consequence a screening the applied voltage is obtained [8, 17–20].

In fig. 5.3, normalized ferroelectric fatigue measurements from 1 to 10^6 cycles for BTO/LSMO bilayers grown on different substrates at room temperature are

presented. Normalized polarization decreases with the cycles for all samples, reaching the minimum value for bilayer deposited on STO (around 40% of initial value). The behavior was fitting using the theoretical model proposed by Yoo and Desu [21], according to the relation $P = P_o(An+1)^{-m}$, where A is a pilling constant and m is decay exponent. The values calculated are reported in Table 5.1.

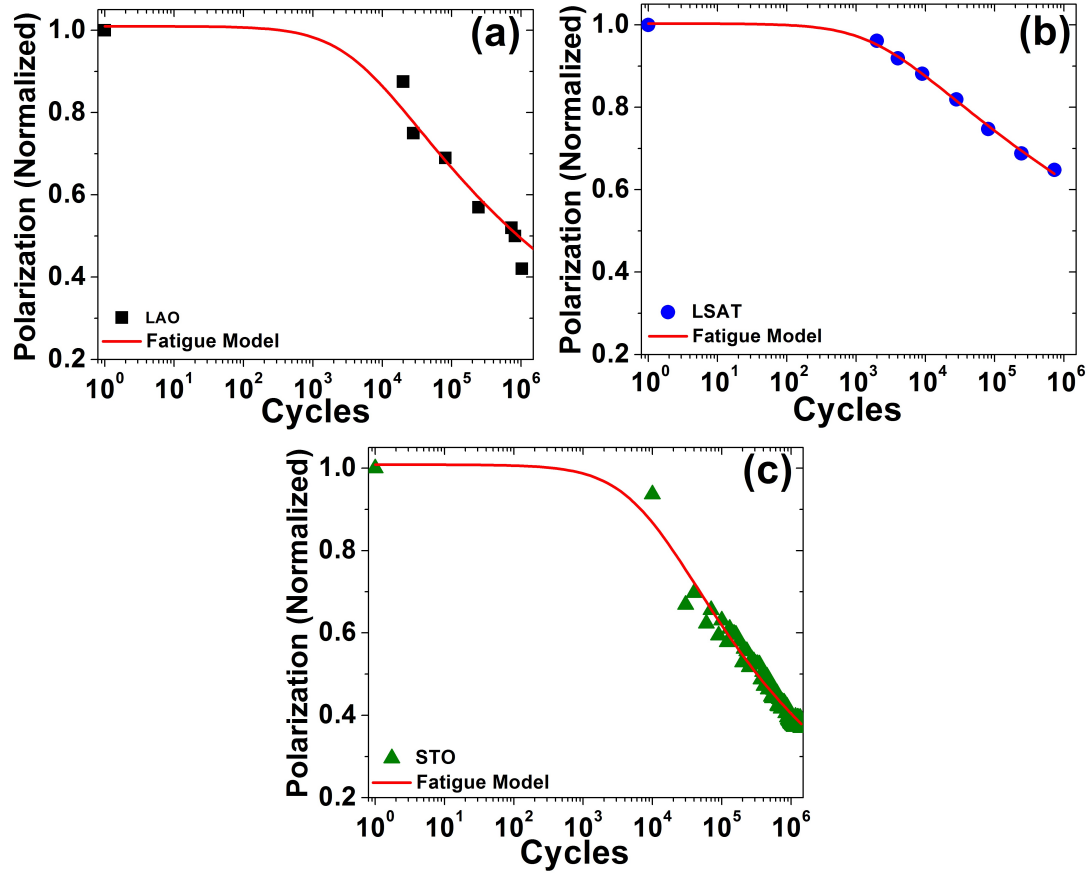


Figure 5.3: Normalized ferroelectric fatigue measurements for BTO/LSMO bilayer deposited on different substrates: (a) LAO, (b) LSAT and (c) STO at 300 K. The hysteresis cycles are in range from 1 to 10^6 cycles.

Table 5.1: Summary of parameters obtained from ferroelectric fatigue model. A , m and χ^2 are extracted from binomial fit.

Sample	A (10^{-4})	m	χ^2
(001)LAO	2.1 ± 0.1	0.12 ± 0.02	4.5×10^{-6}
(001)LSAT	4.9 ± 0.2	0.08 ± 0.01	7.2×10^{-6}
(001)STO	1.3 ± 0.2	0.17 ± 0.02	3.2×10^{-6}

In this scenario when we working to low frequencies, the oxygen vacancies will start to migrate in solid, and the trapped charges will gradually respond with the increase of applied voltage. The rearrangement of the oxygen vacancies affects the FE domains, the switching process are blocked and then a decrease in the polarization occur. Recovery can occur if the amount of the charged defects acting as pinning centers for the ferroelectric domains is reduced [22–24].

To summary, in this section we corroborate the FE properties on BTO layer, using LSMO layer as bottom electrode. In all bilayers a clear hysteresis loops was obtained, where P_S and E_C are dependent of substrate used. In bilayer deposited on (001)STO, the highest reduction on P_S was found. which are associated to presence of dislocations as reveals TEM image. Additionally, different strain/relaxed zones was reported as responsible of change on magnetic mechanism from biaxial to uniaxial MA. Therefore, moreover of the influence of FE layer on ferromagnetic properties for the LSMO studied in the previous chapter, we verify the ferroelectric nature of the BTO. As consequence, the existence of FE/FM hybrid with magnetoelectric properties are possible in our system.

Bibliography

- [1] H. H. Wieder et al., Phys. Rev., **99**, 1161, (1955).
- [2] Z. Shen et al., J. Mater. Chem., **22**, 23547, (2012).
- [3] T. X. Li et al., J. Phys. D Appl. Phys., **45**, no. 85002, 1, (2012).
- [4] O. Vlasin et al., Nature, **5**, 1, (2015).
- [5] W. Cao, Nat. Mater., **4**, 3, (2005).
- [6] T. Li et al., J. Alloys Compd., **560**, 167, (2013).
- [7] T. Li et al., Appl. Surf. Sci., **258**, no. 10, 4558, (2012).
- [8] J. E. Ordoñez et al., J. Phys. Conf. Ser., **614**, no. 12009, 1, (2015).
- [9] N. Inoue et al., IEEE transactions electron devices, **48**, no. 10, 2266, (2001).
- [10] J. J. Lee et al., Ferroelectr. Lett., **20**, 27, (1995).
- [11] W. Wu et al., Appl. Phys. Lett., **85**, no. 21, 5013, (2004).
- [12] G. E. Pike et al., Appl. Phys. Lett., **66**, 484, (1995).
- [13] V. C. Lo et al., J. Appl. Phys., **92**, pp. 6778, (2002).
- [14] M. Jimi et al., Thin Solid Films , **486**, 158, (2005).
- [15] S. L. Miller et al., J. Appl. Phys., **68**, 6463, (1990).
- [16] R. Bouregba et al., J. Appl. Phys., **93**, 522, (2003).

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- [17] S. Dussan et al., Appl. Phys. Lett., **96**, 072904 , (2010).
 - [18] C. A. F. Vaz et. al, Phys. Rev. Lett., **104**, 127202, (2010).
 - [19] C. Thiele et al., Sensors and Actuators A, **129**, 180, (2006).
 - [20] H. Lu et al., Appl. Phys. Lett., **100**, 232904, (2012).
 - [21] I. K. Yoo et al., Phys, stat. Sol., **133**, 565, (1992).
 - [22] J. F. Scott et al., Appl. Phys. Lett. **76**, 3801, (2000).
 - [23] L. Pintilie et al., Appl. Phys. Lett. **88**, (2006).
 - [24] J. Osorio et al., Rev. Colomb. de física, **36**, no 1, 31, (2004).

Chapter 6

Conclusions

- The $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ and BaTiO_3 deposition parameters were optimized using the pulsed laser deposition (PLD) technique: substrate temperature 950°C , laser frequency 10Hz , Laser energy 70 and 50 mJ, and pressure 400 and 3.0 mTorr, respectively. From these parameters three systems were studied: (1) BTO(100 nm)/LSMO(25 nm) bilayers were deposited on (001)-oriented LAO, LSAT and STO substrates to analyze the strain influence on LSMO magnetic properties, (2) BTO(100 nm)/LSMO(20, 25 and 40 nm) on STO substrate, to study the influence of ferromagnetic layer thickness on magnetic behavior and (3) BTO(100 nm)/LSMO(25 nm) bilayers grown on STO with different crystal orientation: (001), (110) and (111).
- X-ray diffraction techniques allows to found the (hkl) reflections associated to the substrate orientations. Using RSMs we observed that LSMO layer grown strained, while the BTO layer is relaxed for all samples on LAO, LSAT and STO substrates. The appearance of Laue oscillations in bilayers deposited on (110)STO and (111)STO substrates evidenced that exist a well-oriented alignment. TEM measurements reveals that the LSMO layer grown epitaxially strained and a relaxation on BTO layer, associated to difference on lattice parameters. Additionally, a periodic dislocations formation close to BTO/LSMO interface is observed.
- From different magnetic measurements a typical LSMO-ferromagnetic behav-

ior is observed. $T_C \sim 350$ K for all samples and $M_S^{10K} \sim 600$ emu/cm³ which are according with LSMO properties. We found a slight decrease on the magnetic properties (M_S , H_C and T_C) on BTO/LSMO bilayers in comparison with the LSMO films for all samples. These variations are associated to strained/relaxed regions induced by the substrates used, dislocations formation close to BTO/LSMO interface and a reorganization on growth direction through substrate orientation, among others. Also, these decrease would suggest that the interface spontaneous BTO polarization (up or Down) probably influence the magnetic properties. The M_S and H_C on BTO/LSMO bilayer deposited on STO are dependent of t_{LSMO} and STO orientation, as is expected on manganites. Using the Berger model, we found that the critical β exponent varies from 0.20 to 0.30, associated to magnetic mechanism: 3D XY Model, YMnO₃ Model and Tricritical point, which are usually related to multiferroic materials.

- The magnetic anisotropy in BTO/LSMO bilayers was studied at room temperature. We found a change on MA for bilayers deposited on STO that only occur under tensile strain, i.e. on (001)STO substrate. This phenomenon was corroborated change the strain substrate nature (LAO and LSAT) and the LSMO thickness. The change in magnetic anisotropy, was associated to strained/relaxed regions close to the BTO interface, dislocations formations and different BTO polarization regions close to interface.
- The ferroelectric properties for BTO(100 nm)/LSMO(25) bilayers deposited on LAO, LSAT and STO have been demonstrated. From ferroelectric fatigue test the bilayers display a reduction on saturation polarization due to migration of oxygen vacancies typical of ferroelectric materials, which are according to Yoo and Desu model.
- The result of the research of this thesis allows to explore the possibility to tuning the magnetic anisotropy from biaxial on LSMO film to uniaxial on BTO/LSMO bilayers through of strain induced by substrate, in particular (001)STO. In addition, the FE properties confirmation allows study potentially the magnetoelectric properties at room temperature.

Chapter 7

List of publications and Events

7.1 List of publications

From this thesis 9 articles has been published in journals that belong to Scopus Citation Index:

1. J. E. Ordoñez, J. Narváez, M.E. Gómez, and W. Lopera, *Angular dependence of the magnetoelectric coefficient on multiferroic BiFeO₃ thin film*, Revista Mexicana de Física S **58** (2) 97-100, (2012).
2. J. E. Ordoñez, M. E. Gómez, W. Lopera, and P. Prieto, *Ferroelectric/Ferromagnetic Bilayers Based on Oxide Materials by Pulsed-Laser Deposition*, IEEE TRANSACTIONS ON MAGNETICS, **49**, No. 8, (2013).
3. J. E. Ordoñez, M. E. Gómez, W. Lopera and P. Prieto, *Enhanced electric and magnetic properties in LCMO/BTO bilayer deposited by Pulsed Laser Deposition*, Journal of Physics: Conference Series **480**, 012031, (2014).
4. C. Domínguez, J. E. Ordoñez, M. E. Gómez, W. Lopera, *Study of exchange bias effect in bilayers based on La_{2/3}Ca_{1/3}MnO₃ and BiFeO₃*, Journal of Physics: Conference Series **480**, 012029, (2014).
5. J. E. Ordoñez, P. Prieto, M. E. Gómez, and W. Lopera, *Structural characterization on BaTiO₃/La_{2/3}Ca_{1/3}MnO₃ bilayers deposited on Nb:SrTiO₃*, MOMENTO Revista de Física, No. 48E, (2014).

6. J. E. Ordoñez, M. E. Gómez, W. Lopera, and P. Prieto, *Detailed Study of Structural and Ferroelectric Properties in $\text{BaTiO}_3/\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ Bilayers Deposited by Pulsed Laser Deposition*, Journal of Physics: Conference Series **614**, 012009, (2015).
7. J. E. Ordoñez, M. E. Gómez and W. Lopera, *Influence of ferroelectric layer on artificial multiferroic LSMO/BTO bilayers deposited by DC and RF sputtering*, Revista Mexicana de Física **62**, 543-548, (2016).
8. I. C. Arango, J. E. Ordoñez, C. Domínguez, C. Arango, M. E. Gómez, *Detailed study of the magnetic behaviour at low scale in $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$* , Journal of Physics: Conference Series, Accepted, August (2017).
9. C. Domínguez, J. E. Ordoñez, M. E. Gómez, W. Lopera, *Interfacial coupling in multiferroic BiFeO_3 and ferromagnetic $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ thin films*, Journal of Physics: Conference Series, Accepted, August (2017).

Additionally, 4 articles has been submitted to publication in different journals:

1. L. E. González, J. E. Ordoñez, G. Zambrano, and N. Porras-Montenegro, *$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}/\text{BaTiO}_3$ 1D superconducting photonic crystal with tunable broadband response in the visible region*, Physica B, submitted, September (2017).
2. J. E. Ordoñez, L. Marín, L. A. Rodríguez, P. A. Algarabel, J. A. Pardo, R. Guzmán, L. Morellon, C. Magén, E. Snoeck, M. E. Gómez, M. R. Ibarra, *Interfacial strain effect on magnetic anisotropy in artificial multiferroic $\text{BaTiO}_3/\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ system*, Journal of the American Chemical Society - ACS, Submitted, September (2017).
3. J. E. Ordoñez, I. C. Arango, L. Suarez, M. F. Quiñonez, M. E. Gómez, W. Lopera, *Resistive Switching Behavior in pure Orthorhombic HfO_2 Thin Films Grown in Oxygen Atmosphere*, Thin Solid Films, submitted, August, (2017).
4. L. Suarez, J. E. Ordoñez, S. Sulekar, M. Mehr, L. A. Rodríguez, E. Snoeck, M. E. Gómez, W. Lopera, and J. C. Nino, *Structural, morphological, and electrical*

properties of Nd doped CeO₂ thin films deposited by RF magnetron sputtering, Thin Solid Films, submitted, August, (2017).

7.2 Events assistance

From results obtained in this investigation, we participate in different congress, events and magnetism and magnetic materials school:

International events

1. *Magnetic behavior of La_{2/3}Ca_{1/3}MnO₃/BaTiO₃ bilayers*, APS Marchmeeting 2013, March 18-22, 2013. Baltimore Convention Center, Baltimore, USA.
2. *Improvement of electrical and magnetic properties in LCMO/BTO bilayer deposited by Pulsed Laser Deposition*, April 8-12, 2013. Facultad de Leyes, Universidad de Buenos Aires, Buenos Aires Argentina, X Latin American Workshop on magnetism and Magnetic Materials 2013.
3. *TEM strain mapping of epitaxial BaTiO₃/La_{2/3}Ca_{1/3}MnO₃ bilayer thin film*. September 24-28 2013, 12th Interamerican Microscopy Congress (CIASEM 2013), Cartagena de Indias, Bolivar, Colombia.
4. *Electrical and magnetic properties in LCMO/BTO bilayer deposited by Pulsed Laser Deposition*, September 30- October 04, 2013. 21st Latin American Symposium on Solid State Physics (SLAFES), Villa de Leiva, Boyaca, Colombia.
5. *Electric and magnetic properties on La_{2/3}Ca_{1/3}MnO₃/BaTiO₃ bilayers*, March 03-07, 2014. APS March meeting 2014, Denver, Colorado, USA.
6. *Electric properties on La_{2/3}Ca_{1/3}MnO₃/BaTiO₃ bilayers*, August 10-15, 2014. IEEE Summer School 2014, Centro Brasileiro De Pesquisas Físicas, Río de Janeiro, Brazil.
7. *Growth and characterization of hybrid multiferroic La_{2/3}Sr_{1/3}MnO₃/BaTiO₃ Bilayers deposited by Sputtering and La_{2/3}Sr_{1/3}MnO₃ from bulk to nanostructure*,

September 15-19, 2014. Workshop on Oxide Materials: Novel Multifunctional Properties, Universidad del Valle, Cali, Colombia.

8. *Influence of $BaTiO_3$ thickness on magnetic properties of $BaTiO_3/La_{2/3}Sr_{1/3}MnO_3$ Bilayers deposited by Sputtering*, May 04-04, 2015. The 3rd International Meeting of Researchers in Materials and Plasma Technology, Bucaramanga, Colombia.
9. *Magnetic and electrical properties on hybrid multiferroic bilayers deposited by sputtering technique at high oxygen pressures and pulsed laser deposition and Growth and characterization of hybrid multiferroic $La_{2/3}Sr_{1/3}MnO_3/BaTiO_3$ bi-layers deposited by sputtering DC and RF*, August 16-20, 2015. XIV International Materials Research Congress 2015, CasaMagna and J.W. Marriott Hotels Cancun, Mexico.
10. *Magnetic and electrical properties on hybrid multiferroic $BaTiO_3/La_{2/3}Sr_{1/3}MnO_3$ Bilayers deposited by Sputtering*, March 2-6, 2015. APS March Meeting 2015, San Antonio, Texas
11. *Superficial strain effect on magnetic anisotropy of $BaTiO_3/La_{2/3}Sr_{1/3}MnO_3$ bi-layers*, July 5-10, 2015. 20th International Conference on Magnetism, Palau de Congressos de Catalunya and Hotel Rey Juan Carlos I, Barcelona, Spain.
12. *Analysis of magnetic anisotropy on $BaTiO_3/La_{2/3}Sr_{1/3}MnO_3$ bilayers*, March 14-18, 2016. APS March Meeting 2016, Baltimore, Maryland, USA.
13. *Detailed study of the magnetic behaviour at low scale in $La_{2/3}Sr_{1/3}MnO_3$ and Interfacial coupling in multiferroic $BiFeO_3$ and ferromagnetic $La_{2/3}Sr_{1/3}MnO_3$ thin films*, May 23-26, 2017. 4th IMRMPT International Meeting of Researchers in Materials and Technology Plasma, Estelar Santamar Hotel and Convention Centre, Santa Marta, Colombia.

National events

1. *Optimization of deposition parameters for ferromagnetic $La_{2/3}Ca_{1/3}-MnO_3$ / ferroelectric $BaTiO_3$ bilayers*, September 10-14, 2012. 3er Congreso Nacional de Ingeniería Física, Universidad EAFIT, Medellín, Colombia.

2. *Influencia del espesor en los exponentes críticos en películas delgadas de $\text{La}_{2/3}\text{Ca}_{1/3}\text{-MnO}_3$ depositadas por PLD and $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ manganite from bulk to nanostructure*, September 22-26, 2014. IV Congreso Nacional de Ingeniería Física, Universidad del Cauca, Popayan, Colombia.
3. *Efecto de las tensiones en la anisotropía magnética de bicapas $\text{BaTiO}_3/\text{La}_{2/3}\text{Sr}_{1/3}\text{-MnO}_3$, Estudio de las propiedades físicas en bicapas del tipo $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3/\text{BiFeO}_3$ crecidas por la técnica de sputtering, Estudio de propiedades magnéticas y de transporte en películas delgadas de $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ and Estudio de la influencia de las interfaces en las propiedades físicas de tricapas ferro/antiferro/ferromagnéticas del sistema $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$* , September 29- October 02, 2015. XXVI Congreso Nacional de Física, Universidad Nacional de Colombia, sede Manizalez, Colombia.
4. *Crecimiento y estudio de bicapas basadas en BiFeO_3 y $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$, Propiedades morfológicas y eléctricas en películas delgadas de HfO_2 depositadas por RF and Estudio de las propiedades magnéticas en bicapas de $\text{BaTiO}_3/\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ depositadas sobre STO con diferentes orientaciones*. September 26-30, 2016. 5to Congreso de Ingeniería Física, Universidad EAFIT, Medellín, Colombia.

Magnetism school

1. *Exploring nanomagnetism and its applications*, April 15-19 2013. Centro Atómico Constituyentes, Atomic Energy Commission in Buenos Aires, Argentina.
2. *IEEE Summer School 2014*, August 10-15, 2014. Centro Brasileiro De Pesquisas Físicas, Río de Janeiro, Brazil.
3. *6th Spanish Workshop in Nanolithography*, October 28-30, 2014. Instituto de Nanociencias de Aragón, Zaragoza, Spain.
4. *La red nanoandes y la sexta escuela internacional nanoandes de nanociencias*, November 7-12, 2016. Universidad del Valle, Cali, Colombia.