Giant sharp magnetoelectric switching in multiferroic epitaxial
\( \text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3 \) on \( \text{BaTiO}_3 \)

**DIPLOMARBEIT**

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Abstract

Multiferroic materials, which are both ferromagnetic, ferroelectric and/or ferroelastic, have increasingly been studied over the past six years due to several promising advantages for applications. The application potential comes from the magnetoelectric (ME) effect, which means the magnetisation can be controlled by an applied electric field or vice versa. This can be applied in e.g. data storage, field sensors and actuators. However, no single phase material has been discovered yet that is both ferromagnetic and ferroelectric at room temperature. In fact, most known multiferroics are anti-ferromagnetic and possess low ordering temperatures. In addition, the ME coupling is often weak and requires large applied fields. Here I report on huge coupling effects in a multiferroic epitaxial heterostructure consisting ferromagnetic La$_{0.66}$Sr$_{0.33}$MnO$_3$ film and ferroelectric (piezoelectric and ferroelastic) BaTiO$_3$ substrate. Magnetic coupling due to induced strain at the phase transitions of the substrate were successfully investigated, showing large changes in magnetisation as function of temperature. Upon that, novel ME measurements were performed inside a vibrating sample magnetometer. By applying a small electric field (4-10 kV cm$^{-1}$) across the entire structure, we achieved sharp and persistent changes in film magnetisation of up to 65% near the BaTiO$_3$ structural phase transition at $\sim$ 200 K. This represents a giant magnetoelectric coupling ($\alpha = 2.3 \times 10^{-7}$ s m$^{-1}$) that arises from strain fields due to electrically driven switching of ferroelastic non-180° domains in the BTO, whose presence we confirmed using x-ray diffraction. The hereby produced in-plane piezoelectric strain modifies the overlying ferromagnetic LSMO by switching its strain, resulting in a switching of the magnetic anisotropy of the film. The coupling persists over a wide range of temperatures including room temperature. These results deliver a vital contribution towards applications and understanding strain coupled ME effects.
Acknowledgements

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<tr>
<td>$a$, $b$, $c$</td>
<td>Crystallographic axes</td>
</tr>
<tr>
<td>$a_f$</td>
<td>Lattice parameter $a$-axis film</td>
</tr>
<tr>
<td>$a_s$</td>
<td>Lattice parameter $a$-axis substrate</td>
</tr>
<tr>
<td>$A$</td>
<td>Ampere</td>
</tr>
<tr>
<td>$d$</td>
<td>Distance</td>
</tr>
<tr>
<td>$d_{film}$</td>
<td>Film thickness</td>
</tr>
<tr>
<td>$e$</td>
<td>Electric charge</td>
</tr>
<tr>
<td>$E$</td>
<td>Electric field</td>
</tr>
<tr>
<td>$F$</td>
<td>Free energy</td>
</tr>
<tr>
<td>$H$</td>
<td>Magnetic field (strength)</td>
</tr>
<tr>
<td>$H_C$</td>
<td>Coercive field</td>
</tr>
<tr>
<td>$I$</td>
<td>Intensity</td>
</tr>
<tr>
<td>$l$</td>
<td>Orbital angular momentum</td>
</tr>
<tr>
<td>$L$</td>
<td>Electron’s angular momentum</td>
</tr>
<tr>
<td>$m_e$</td>
<td>Mass electron</td>
</tr>
<tr>
<td>$m$</td>
<td>Magnetic (dipole) moment (absolute)</td>
</tr>
<tr>
<td>$m_o$</td>
<td>Orbital magnetic moment of electron</td>
</tr>
<tr>
<td>$m_s$</td>
<td>Spin magnetic moment of electron</td>
</tr>
<tr>
<td>$m_{tot}$</td>
<td>net magnetic moment</td>
</tr>
<tr>
<td>$M$</td>
<td>Magnetisation</td>
</tr>
<tr>
<td>$M_R$</td>
<td>Remanent magnetisation</td>
</tr>
<tr>
<td>$M_S$</td>
<td>Saturation magnetisation</td>
</tr>
<tr>
<td>$n$</td>
<td>Number</td>
</tr>
<tr>
<td>$n_s$</td>
<td>Nanosecond</td>
</tr>
<tr>
<td>$P,P_{Sp}$</td>
<td>(Spontaneous) polarisation</td>
</tr>
<tr>
<td>$P_R$</td>
<td>Remanent polarisation</td>
</tr>
<tr>
<td>$P_S$</td>
<td>Saturation polarisation</td>
</tr>
<tr>
<td>$r$</td>
<td>Radius</td>
</tr>
<tr>
<td>$S$</td>
<td>Spin quantum number</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
</tr>
<tr>
<td>$t_{dept}$</td>
<td>Deposition time</td>
</tr>
</tbody>
</table>
\[ T \] Temperature
\[ T_c \] Curie temperature
\[ T_{\text{subst}} \] Substrate temperature
\[ U \] Voltage
\[ \epsilon \] Relative dielectric permittivity
\[ \epsilon_m \] Lattice mismatch
\[ \epsilon_s \] Lattice strain
\[ \lambda \] Wavelength
\[ \mu_0 \] Permeability of free space (electromagnetism)
\[ \mu_B \] Bohr magneton
\[ \Theta \] Angle of incidence and angle of reflection (Bragg’s law)

**Units**

- atm Standard atmosphere
- \( C \) Coulomb
- \( ^\circ C \) Celsius degree
- \( \text{emu} \) Electromagnetic unit
- hr Hour
- Hz Herz
- J Joules
- K Kelvin
- nm Nanometer
- s second
- \( O_e \) Oersted
- \( Pa \) Pascal
- V Volts, Volume
- Å Angstroms
- \( \mu m \) Micrometer
## Abbreviations

<table>
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<tr>
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<th>Description</th>
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<tr>
<td>a.u.</td>
<td>Arbitrary units</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
</tr>
<tr>
<td>BTO</td>
<td>Barium titanate, $\text{BaTiO}_3$</td>
</tr>
<tr>
<td>CFC</td>
<td>Complementary ferroelectric-capacitor</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>CMR</td>
<td>Colossal magnetoresistance effect</td>
</tr>
<tr>
<td>et al.</td>
<td>et alii (and others)</td>
</tr>
<tr>
<td>FRAM</td>
<td>Ferroelectric random access memory</td>
</tr>
<tr>
<td>Ge</td>
<td>Germanium</td>
</tr>
<tr>
<td>i.e.</td>
<td>Id est (= that is)</td>
</tr>
<tr>
<td>KrF</td>
<td>Krypton fluoride</td>
</tr>
<tr>
<td>LN$_2$</td>
<td>Liquid nitrogen</td>
</tr>
<tr>
<td>LSMO</td>
<td>$\text{La}<em>{0.67}\text{Sr}</em>{0.33}\text{MnO}_3$</td>
</tr>
<tr>
<td>ME</td>
<td>Magnetoelectric</td>
</tr>
<tr>
<td>MRAM</td>
<td>Magnetoresistive random access memory</td>
</tr>
<tr>
<td>Nd:YAG</td>
<td>Neodymium-Yttrium-Aluminium-Garnet</td>
</tr>
<tr>
<td>NGO</td>
<td>NdGaO$_3$</td>
</tr>
<tr>
<td>O$_2$</td>
<td>Oxygen</td>
</tr>
<tr>
<td>PLD</td>
<td>Pulsed laser deposition</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning tunnelling microscope</td>
</tr>
<tr>
<td>STO</td>
<td>SrTiO$_3$</td>
</tr>
<tr>
<td>vs.</td>
<td>Versus</td>
</tr>
<tr>
<td>VSM</td>
<td>Vibrating sample magnetometer</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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Chapter 1

Introduction

Making the simple complicated is commonplace; making the complicated simple, awesomely simple, that’s creativity.
Charles Mingus (1922 - 1979)

The increasing demand in data storage and simultaneously the trend towards device miniaturisation has led to a rising activity in the area of novel devices based on ferroelectricity and ferromagnetism in the past six years. The coupling of the ferroelectric and ferromagnetic phenomena can be merged into the term “multiferroics” [1] and offers the potential to control the magnetisation order parameter via electric fields and vice versa.

Ferromagnetic and ferroelectric materials nowadays play an essential role in modern technology, since both of the materials exhibit many interesting physical phenomenons which are applied in all kinds of devices such as MRAM and FRAM read heads, respectively. The most prominent features are without question their hysteresis behaviour and their spontaneous magnetisation and polarisation. Besides that, each material offers other properties like large values of permeability or dielectric constants. The different applications of ferromagnets such as permanent magnets, electric motors and magnetic data storage devices explains the importance of such materials. Similarly, the most significant applications of ferroelectric materials are data storage, capacitors, ferroelectric-based resonators and electro-optical devices.
1.1 Magnetoelectric multiferroics and magnetoelectric effect

A multiferroic in general, refers to a class of material in which at least two of the three "ferroic" properties, ferromagnetism, ferroelectricity or ferroelasticity occur simultaneously [1]. The combination of ferroelectricity and ferroelasticity is well known as the piezoelectric effect, used in application like electric cigarette lighters. The parallel coexistence of ferromagnetism and ferroelasticity is also well established and results in magnetostriction used i.e. in magnetostrictive actuators. The most fascinating but less known and also less existing coupling is between ferromagnetism and ferroelectricity, with or without ferroelasticity, resulting in a so called magnetoelectric (ME) effect. The interconnection between these two ferroics enables the coupling of the two order parameters magnetisation and electric polarisation, which allows an additional degree of freedom in device design. Possible new devices could arise like multiple state memory elements [3], that means data can be stored in the magnetic as well as in the electric polarisation. Further more, novel memory media which enables switching the magnetic polarisation by applying an electric field or vice versa can be expected in future. In the following sections, the background of magnetoelectric multiferroics and the magnetoelectric effect will be discussed, as well as previous work in this expanding area. Concluding, the objectives of this project will be set and described.

1.1 Magnetoelectric multiferroics and magnetoelectric effect

The above mentioned outlook, concerning the need of new data storage technologies hit the term multiferroics in the headline of many scientific magazines. Talking about multiferroics one has to distinguish between single phase multiferroics [1] and multiferroic composites.

Single phase ME multiferroics possess spontaneous magnetisation and electric polarisation in the same phase. The magnetic dipole in the material is caused by the exchange interaction of the electron spin, whereas the ferroelectric ordering arises by the redistribution of charge density in the crystal lattice. Extensive work was done by Nicola A. Hill in 2000 with the focus on the physics of single phase multiferroics [4, 5]. In these reviews, physical requirements for single phase multiferroics and reasons for their rare appearance were investigated. The precondition for ferroelectricity requires primarily a structural distortion from the symmetric
1.1 Magnetoelectric multiferroics and magnetoelectric effect

phase to an asymmetric phase. The asymmetric phase possesses a spontaneous polarisation as part of the unit cell contains more positive charge. Ferroelectricity features the alignment of the polarisations by means of an external electric field rather than the movement of conduction electrons. This illustrates the need of a ferroelectric material to be insulating. This demand often contradicts with the properties of ferromagnets which are commonly metals or semiconductors. The most significant challenge of creating a single phase multiferroics is the controversial electron configuration of ferroelectric and ferromagnetic materials. To anticipate the background chapter about the materials, ferroelectric crystals mainly have a general formula of $\text{ABO}_3$ with a $d^0$ electron configuration on the B cation, more precisely there is a vacant d orbital. In contrast, a ferromagnet requires occupied d shells to possess magnetic dipole moments. This d electron occupancy is therefore a very critical factor and considerably complicates the search of single phase multiferroics.

Nevertheless, few reports of “new” single phase multiferroics raise hope. Magnetoelectric effects in anti-ferromagnetic $\text{TbMn}_2\text{O}_5$ [6] and $\text{TbMnO}_3$ [7] have been studied, showing changes in electric polarisation caused by magnetic fields. Reversal or $90^\circ$ switching of polarisation ($P \leq 0.08\mu\text{C/cm}^2$) were achieved at temperature of about 30 K and 18 K. However, the polarisation is too low for useful applications and the temperature at which magnetoelectric coupling occurs is far below room temperature. In comparison, an other ferroelectric material, lead zirconate titanate (PTZ) used in F-RAMs, can exhibit electric polarisation of 80 $\mu\text{C/cm}^2$ at RT [8]. To date, a single phase multiferroic with robust electric and magnetic polarisation at ambient temperature has still not been discovered.

An alternative route and indeed promising way to obtain multiferroics is to synthesise them by combining ferroelectric and ferromagnetic materials in separate phases. This can be achieved by making epitaxial multilayer structures [9], composites [10, 11], laminates [12] or self assembled nanostructures [13] with ferroelectric and ferromagnetic constituents. There are several advantages compared to single phase multiferroics. Besides the ferroelectricity and ferromagnetism, more physical properties of the material can be tailored by the selection of different constituent phases to meet specific applications. Further more, it is more likely that the ME coupling effect in two phase multiferroics is remarkably higher that in the single phase ones, because the coupling mechanism is different
1.1 Magnetoelastic multiferroics and magnetoelectric effect

and takes place via strain. Multiferroic coupling has been achieved using lattice strain as a coupling medium in e.g. \( La_{0.67}Sr_{0.33}MnO_3 \) film on a BaTiO\(_3\) substrate \[9\]. Induced strain at the phase transitions of the ferroelectric substrate affects the magnetic anisotropy of the epitaxial grown \( La_{0.67}Sr_{0.33}MnO_3 \) film, resulting in huge change of magnetisation. Other geometries where strain-coupling has been studied in a two phase multiferroic include e.g. ferrimagnetic CoFe\(_3\)O\(_2\) pillars embedded in a BiFeO\(_3\) matrix, where the magnetisation was reversed by an electric field \[14\] at room temperature. This reversal is based on elastic strain-mediated coupling between the two ferroics, but the structure is difficult to fabricate and not easy to control.

A theoretic analysis of the ME effect is described \[15, 16\] for a single phase multiferroic but considering with the free energy \( F \) in terms of an applied magnetic field \( H \) and an applied electric field \( E \) (see Equ. 1.1). The first and second term on the right hand side describes the contribution resulting from the electrical response to an electric field and the contribution resulting from the magnetic response to a magnetic field. The third term describes the linear magnetoelectric coupling and the fourth and fifth the quadratic coupling, with \( \alpha, \beta \) and \( \gamma \) for the coupling constants:

\[-F(E, H) = \frac{1}{2} \varepsilon_0 \varepsilon_{ij} E_i E_j + \frac{1}{2} \mu_0 \mu_{ij} H_i H_j + \alpha_{ij} E_i H_j + \frac{\beta_{ijk}}{2} E_i H_j H_k + \frac{\gamma_{ijk}}{2} H_i E_j E_k + \ldots \]

(1.1)

ME coupling is quantified either a change of magnetisation \( \Delta M \) per applied electric field change \( \Delta E \), or a change of electrical polarisation \( \Delta P \) per applied magnetic field change \( \Delta H \). The resulting linear ME coupling constant \( \alpha \) is defined either as \( \Delta P/\Delta H \) or \( \mu_0 \cdot \Delta M/\Delta E \) (\( \mu_0 \) is the permeability of free space) \[16, 17\].
1.2 Objectives

Multiferroic and magnetoelectric behaviour was investigated between the ferroelectric BaTiO$_3$ (BTO) and the ferromagnet La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO). LSMO thin films ($d_{\text{film}} \approx 20$–$80$ nm) were epitaxially grown by pulsed laser deposition on the BTO substrate. Atomic force microscopy and x-ray diffraction were used for structural characterisation. Magnetic properties were studied using a vibrating sample magnetometer. The first objective was to determine strain mediated coupling between the ferromagnetic and the ferroelectric BTO substrate (4 mm x 4 mm x 0.5 mm). Due to the induced strain at the structural transitions of BTO, changes in the magnetisation of the LSMO layer were analysed. Similar work was previously done by M.K. Lee et al. [9] reporting jumps in magnetisation of up to 70%.

The main objective was to expand upon this work and to analyse magnetoelectric effects as a function of an electric field and magnetisation in the LSMO-BTO system. The electric field generates mechanical stress in the crystal due to a rotation of ferroelectric domains. This way, strain can be induced at any temperature, not just at structural phase transitions. Thus, the magnetic order parameter could be controlled via an electric field. These experiments were performed by applying an electric field to the BTO in situ in a vibrating sample magnetometer and the changes in magnetisation could thus be measured directly. Such in situ measurements have not been performed before. Epitaxial heterostructures have hardly been investigated up to now, although they could permit precise ME studies and offer control of crystal orientations and interface roughness. Summarised, the purpose of my project was to determine relations between strain and magnetic anisotropy in the multiferroic epitaxial heterostructure consisting of a LSMO film on a BTO substrate. The corresponding strain which is transferred from the substrate to the film is induced by the ferroelectric phase transition according to ferroelastic effects and induced by strain from domain rotation according to piezoelectric effects.

The work in this thesis has been submitted to be published:
Chapter 2

Background Reviews

The subject of ferroic materials encompasses a large number of topics in material science for a long time. Ferroic crystals are those crystals which involve at least one phase transition which changes the directional symmetry of the crystal. The term ferroic materials is a general term covering ferroelectric, ferromagnetic and ferroelastic materials. This chapter covers the characteristics of ferroelectricity and ferromagnetism as well the properties of the used materials BaTiO$_3$ and La$_{0.67}$Sr$_{0.33}$MnO$_3$.

### 2.1 Basic principles of ferroelectricity and of BaTiO$_3$

This section will give a brief introduction into the field of ferroelectricity and ferroelectric materials with a detailed description of the used barium titanate (BaTiO$_3$, BTO). Furthermore, to understand the coupling between the ferroelectric and the ferromagnetic layer, one has to go into details about different phase transitions, ferroelectric domains and hysteresis behaviour. Two more effects which especially occur in BTO, ferroelasticity and piezoelectricity will be described briefly. Ferroelectricity was first mentioned in 1921 by J. Valasek [18] with investigations of Rochelle salt and in beginning of the 40’s, progressive studies were carried out in the field of ferroelectric materials. The discovery in 1941 of the so called ”prototype of ferroelectric ceramic”, barium titanate led to further interests in these materials and nowadays there is a broad group of crystalline ferroelectric materials.
2.1 Ferroelectricity and BaTiO$_3$

2.1.1 Ferroelectricity

The most prominent feature of ferroelectric materials is the spontaneous dipole moment, which can be switched diametrically by an external applied electrical field. The ability to switch the electric polarisation from one direction to another is useful for devises like ferroelectric random access memories (FRAM) [19] and complementary ferroelectric-capacitor (CFC) [20]. Furthermore, these materials exhibit additional interesting physical and technological properties such as large values of dielectric constants ($\epsilon_r = 10^3$ – $10^4$), piezoelectric constants and high electro-optic and pyroelectric coefficients. Applications of ferroelectric material can be found for example in high sensitive pyroelectric infrared detectors, piezoelectric sensors and in electro-optic modulators.

The spontaneous polarisation in ferroelectricity occurs since the centre of positive charge does not coincide with the centre of negative charge, due to small displacements of the ions. Many ferroelectrics are cubic and non-ferroelectric in their high temperature phases. Upon cooling, a phase transition occurs where the unit cell distorts and is no longer centro-symmetric (Fig. 2.1). The negative and positive ions are shifted with respect to each other and an electric dipole exist in the unit cell. This behaviour is observed below a certain temperature called the Curie temperature $T_C$ where the paraelectric phase converts into the ferroelectric phase. This temperature dependent appearance is called the pyroelectric effect. In a ferroelectric crystal, this dipole moment in addition can be switched by an electric field.

![Phase transition](image)

**Figure 2.1:** Example of a phase transition and the arising polarisation. The cubic unit cell (a) changes its crystal structure below the Curie temperature and due to the transition, the cell (b) exhibits a spontaneous polarisation $P_{Sp}$. 

7
2.1 Ferroelectricity and BaTiO$_3$

2.1.2 Perovskite structure and BaTiO$_3$

The ferroelectric component of the heterostructure, was a BaTiO$_3$ (BTO) substrate. Most of the ferroelectric crystals just as barium titanate have a perovskite structure. The group of perovskites, which are named by the mineral perovskite CaTiO$_3$ are linked together because of its specific lattice structure. An ideal cubic perovskite structure (Fig. 2.2a) has a general formula of ABO$_3$, where A represents a divalent or a trivalent cation and B is typically a tetravalent or a trivalent cation. The A ions occupy the corners of the cube, while the B ion sits in the body centre position inside an octahedron formed by the face centred oxygen ions. In the case of BTO, the crystal lattice consists of TiO$_6$ octahedron barium ions are on the edges. Fig. 2.2b shows the unit cell of BTO in the cubic state.

![Diagram](image)

**Figure 2.2:** (a) General cubic perovskite structure. The red A cations occupy the unit cell corner. The grey B cation is at the centre of an octahedron of the blue oxygen anions. (b) Occupation for BaTiO$_3$.

As mentioned above, the ferroelectricity depends on the temperature. Figure 2.3 shows the BTO structure as a function of temperature. BTO is cubic above 393 K, tetragonal above 290 K, orthorhombic above 190 K and rhombohedral at lower temperatures [21]. In the cubic state ($a = b = c = 3.99$ Å [21]) the material is paraelectric, more precisely, there is no spontaneous polarisation above the Curie temperature. Ferroelectricity occurs during cooling through $T_C$, in the case of BTO, $T_C$ is at 393 K (120°C) [22] where its structure changes from cubic to tetragonal. Thereby the $a$- and $b$-axis shorten and the $c$-axis is elongated. The elongation of approximately 1% of the $c$-axis, causes a displacement of the
2.1 Ferroelectricity and BaTiO$_3$

The room temperature tetragonal lattice parameter are 3.99 Å for the $a$- and $b$-axes and 4.03 Å for the $c$-axis [23]. Fig. 2.4a clarifies the deformation and shows the appearing spontaneous polarisation $P_{Sp}$ ($P_{Sp} \approx 25 \mu C/cm^2$ [24]) parallel to the elongated $c$-axis [001]. After the transition from cubic to tetragonal, the unit cell can take any of six crystallographically equivalent combinations of strain and polarisation (see Fig.2.4b).

**Figure 2.3:** Variation of lattice parameters as a function of temperature in a BTO crystal. The letters R, O, T and C represent the rhombohedral, orthorhombic, tetragonal and cubic phase. The transition temperatures slightly vary depending on whether the materials is cooled or heated. (after [25])

At lower temperatures, two more phase transitions take place. At the transition from tetragonal to monoclinic, the $a$- and $c$-axis shorten till $b$ and $c$ have the same length. In addition, the angle between $b$ and $c$ decreases, resulting a turn in polarisation ($P_{Sp} \approx 0.21C/m^2$ [24]) in [110]-direction (Fig. 2.5). Fig. 2.3 also demonstrates the last transition from monoclinic to rhombohedral. At this state, all the axes have same lattice parameter and are not perpendicular to each other. The polarisation ($P_{Sp} \approx 0.19C/m^2$) [24] in the rhombohedral phase is in line with the diagonal of the cube [111] (Fig. 2.5). An explanation of these
phase transitions is described by the Landau theory [26]. The theory is a formal, consistent thermodynamic theory about the behaviour at phase transitions and can be used in the case of ferroelectric crystals.

**Figure 2.4:** (a) Deformation of the BTO structure from cubic to tetragonal below $T_C$. The displacement of the Ti ion causes a distortion of the original cubic unit cell and in addition causes a slight displacement of the oxygen anions. Due to this structural modification the centre of the positive charges and the negative charges are not at the centre of the unit cell. A permanent dipole moment arises. (b) Upon the cubic to tetragonal phase transition, the unit cell can take any of six equivalent combinations of strain and polarisation in the crystal. The arrow indicates the direction of polarisation.
2.1 Ferroelectricity and BaTiO$_3$

**Figure 2.5:** Spontaneous polarisation as a function of temperature in a BTO crystal. BTO undergoes numerous phase transitions as a function of temperature. Only the cubic phase is not ferroelectric, for the other phases the direction of spontaneous polarisation $P_{Sp}$ is indicated by the arrows in the unit cell. (after [23])

2.1.3 Ferroelectric domains

In ferroelectric materials, domains arise from energetic reasons. A big area with a polarisation in just one direction creates a huge electric field, which retains a large amount of energy. As every natural process has the goal to minimise its energy, this state is unfavourable for the crystal. Therefore, the material is trying to balance the energy by forming domains with different directions of polarisations. The domain structures of ferroelectric perovskite materials usually fall into two different types at room temperature, namely 90° and 180° domains [27]. The 90°-domain walls which occur by reason of minimising mechanical strain in the material are 90° turned unit cells in the lattice structure. Fig.2.6 shows the orientations of the polarisations of BTO in the tetragonal phase. In the rhombohedral and orthorhombic state, besides the 180° domains, different low energy domain walls (non-180° domains) arise, 107°-walls and 60°-, 90°-, 100°-walls, respectively.
2.1.4 Hysteresis in Ferroelectricity

As mentioned in the first subsection, ferroelectric materials have a permanent electric polarisation below the Curie temperature. This polarisation can be influenced in terms of their direction with an electric field and performs a hysteresis loop (Fig. 2.7). By applying a sufficiently large electric field, the polarisations in the domains align in the direction of the electric field. The maximum polarisation is called the saturation polarisation $P_S$ and is reached, since the crystal consist of a single domain, meaning all polarisations are completely aligned in the same direction of the electric field. After removing the field, a permanent or remanent polarisation $P_R$ maintains, but usually with a lower polarisation. An inverse directed field does not immediate change the direction of the polarisation. Not until reaching the critical point at $E_C$ (coercive field), the value of the polarisation is decreased to zero and by increasing the inverse field further, the polarisations switch into the opposite direction.

Figure 2.6: Ferroelectric domains ($90^\circ$ and $180^\circ$) in BTO in the tetragonal phase separated by $90^\circ$ and $180^\circ$ boundaries.
Figure 2.7: Ferroelectric hysteresis: The saturation polarisation ($P_S$) shows the maximum polarisation, since all domains are aligned. The remanent polarisation ($P_R$) is the polarisation remaining at zero electric field. Coercive field ($E_C$) is the field required to reduce the polarisation to zero.

2.1.5 Origin of crystal deformation and lattice strain in BTO

In ferroelectric perovskites such as barium titanate two more effects can be spotted, ferroelasticity and piezoelectricity. Ferroelasticity specifies the manipulation of the electric anisotropy due to mechanical stress or strain. Compressive or tensile stress inside the crystal leads to a non-180° domain switching. Fig.2.8 shows a ferroelastic structure in an unstressed state. An applied tensile strength leads to a crystal distortion and to a domain wall movement, associated with a change in lattice dimensions.

Piezoelectricity describes the coupling between a material’s mechanical and electrical behaviour (see Fig.2.9). In piezoelectric materials a mechanical deformation (stress) induces an electric charge (electric polarisation), this effect is called the piezoelectric effect. More interesting for our work is the inverse piezoelectric effect, also called piezostriction, when an electric field is applied to the
2.1 Ferroelectricity and BaTiO$_3$

crystal, resulting in deformations of the crystal lattice combined with changes of the strain state.

Figure 2.8: Ferroelastic 90°-domain wall motion as a consequence of anisotropic stress.
2.1 Ferroelectricity and BaTiO$_3$

Figure 2.9: Illustration of the piezoelectric effect and inverse piezoelectric effect (piezoelectric). a) A mechanical stress (F) induces electric charge (V). b) A applied voltage (U), corresponding an electric field (E) induces a crystal deformation.

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Example text
2.2 Basic principles of ferromagnetism and of La$_{0.67}$Sr$_{0.33}$MnO$_3$

A two phase magnetoelectric multiferroic consists of ferroelectric and ferromagnetic constituents. In our case, the thin film is the ferromagnetic part of the heterostructure. This section will give a brief introduction on ferromagnetism, including basic concepts of magnetism, ferromagnetic domains and hysteresis loop. Furthermore, the properties of the manganite perovskite La$_{0.67}$Sr$_{0.33}$MnO$_3$ will be given.

2.2.1 Magnetism in materials

In general, the magnetic nature of materials is determined by the magnetic moments of electrons, atoms and ions in the material. Prior the introduction of ferromagnetism, I define and explain the basics of magnetism. The following notes, which refer to David Jiles [28] and Nicola Spaldin [29], give a short description of the origins of atomic magnetic moments and the types of magnetic behaviour that arise from them. In a classical view, magnetic fields as well as magnetic moments are, according to the electromagnetic Maxwell’s theory, the consequence of electron movements and the corresponding magnetic dipole moments $m$. There are two contributions to the net magnetic moment, an orbital magnetic moment due to orbital angular momentum and a spin magnetic moment due to electron spin. The angular momentum of the electron can be determined from the concept of electrical charge in motion. Figure 2.10 shows an electron with the mass $m_e$ and the electric charge $e$ travelling in circular orbits around the nucleus with a distance $r$, inducing a magnetic moment $m_o$ (which is proportional to the atomic electron’s angular momentum $L$). Equation 2.1 was derived from classical theory and would allow any value for $L$.

\[
m_o = -\left(\frac{e}{2m_e}\right) \cdot L \tag{2.1}
\]
However, the possible values of angular momentum are quantised. After quantum mechanical treatments, we obtain [28]:

\[ m_o = -\mu_B \cdot l \]  

(2.2)

Where \( l \) is the orbital angular momentum quantum number and can only have integer values and \( \mu_B \) is the fundamental unit of magnetic moments, the Bohr magneton, with numerical value:

\[ \mu_B \approx 9.274 \cdot 10^{-24} \text{Am}^2 \]

Besides the contribution of orbital angular momentums of the electrons we also have to consider the spin of the electrons itself. Spin does not have a classical analogue and is a quantum mechanical result. In fact, we do not know the actual size of an electron but we know that it possesses mass, charge and an intrinsic momentum spin \( S \). A spinning charged object (Fig.2.10) can be viewed as a circulating current, it therefore has an associated magnetic moment \( m_s = 2\mu_B \cdot S \) \((S = \pm 1/2)\). The net magnetic moment of an atom is the vector sum of its orbital and spin magnetic moments \( m_{tot} = m_o + m_s \)

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ions, diamagnetism exists. The spin and the orbital magnetic moment counter-vail against each other, therefore the material appears to be non-magnetic. The presence of a magnetic field causes small changes in the electron orbits which result in a circulating current where none existed before. This means a weak magnetic moment is induced, which is negative in positive magnetic fields and much smaller than paramagnetism or ferromagnetism.

Paramagnetism refers to materials which become magnetised in a magnetic field but their magnetism disappears when the field is removed. Figure 2.11 shows the ordering of the magnetic dipoles in the paramagnetic state. The moments are spread randomly such that the resulting total moment is zero, which is due to weak coupling between the dipoles and due to thermal energy movements (Fig.2.11a). An applied magnetic field leads to a rotation of the moments, but only a small fraction is deflected into the field direction (Fig.2.11b). The aligned moments reorder them selves immediately after removing the filed, the total moment is zero again.

![Figure 2.11: Schematic of the alignment of atomic magnetic moments in a paramagnetic material: (a) shows the alignment in the absence of an external field and (b) shows the deflection of the moments when a field of moderate strength is applied [29]](image)

In a ferromagnetic material, there is a strong exchange between neighbouring magnetic moments (which is also quantum mechanical in origin), causing all atomic moments to align. This interaction causes the dipole moments to line up
with each other, even without an external applied field. A spontaneous magnetisation $M_{sp}$ arises.

**Figure 2.12:** Schematic of the alignment of atomic magnetic moments in a ferromagnetic material. The dipole moments are parallel aligned due to interactions between the individual atomic magnetic moments. A spontaneous polarisation or also called spontaneous magnetisation $M_{sp}$ arises [29].

Analogously to ferroelectricity, the magnetic polarisation is a function of temperature. At $T = 0$ K, it reaches its maximum value and is decreasing with rising temperature, till it finally disappears at $T = T_C$ (Curie temperature). The Curie temperature in ferromagnetism is defined as the temperature at which the transition to a magnetically ordered state occurs. Above $T = T_C$ the material is paramagnetic.

In a magnetic solid state material, the magnetisation $M$ is defined as the total magnetic moment per unit volume $M = \frac{m}{V}$. Also, since each magnetic moment is a vector, the existence of a non-zero $M$ requires some degree of alignment of the contributing dipoles. In this thesis the magnetisation $M$ is specified in Bohr magneton per volume of a LSMO unit cell ($\mu_B$/unit cell).
2.2 Ferromagnetism and La$_{0.67}$Sr$_{0.33}$MnO$_3$

2.2.2 Ferromagnetic domains

Despite the spontaneous magnetisation, without an applied magnetic field a ferromagnet shows no magnetisation. The reasons can be found by noticing the assembling of the single moments. The moments are analogically to ferroelectricity lined up in small regions called domains. The directions of magnetisation of the domains varies from one domain to the other, so that the material shows no significant magnetic effects to the outside world. The formation of these domains allows the material to minimise its magnetostatic energy (total magnetic energy). Fig.2.13 shows the domain formation in a ferromagnet to reduce the magnetostatic energy.

![Domain and Domain Wall](image)

**Figure 2.13:** Illustration of ferromagnetic domain formation to reduce the internal magnetostatic energy. Hence, the material shows no significant magnetic effects to the outside world. (after[29])

2.2.3 Hysteresis in ferromagnetism

An applied magnetic field induces domain movements and thus alignments of dipole moments. When a ferromagnetic material is magnetised in one direction, it will not relax back to zero magnetisation as in a paramagnetic material when the field is removed. It must be driven back to zero by a field in the opposite direction. By changing the direction of the magnetic field, the magnetisation of the material will trace a loop called a hysteresis loop. Figure 2.14 shows a schematic of hysteresis loop. From the unmagnetised state with randomly oriented moments (a), the magnetisation follows a curve to a maximum magnetised state $M_S$. At the point of the saturation magnetisation ($M_S$) the material is magnetised to saturation with completely aligned domains (b). When the field $H$ is decreased to zero after saturation, the material still retains a considerable degree of magnetisation which is called the remanent magnetisation $M_R$. A reverse
2.2 Ferromagnetism and La$_{0.67}$Sr$_{0.33}$MnO$_3$

Field is required to reduce $M$ to zero. At the coercive field $-H_C$, the moments are aligned randomly again and the magnetisation is zero (c). Increasing the reverse field further leads towards a saturation magnetisation $-M_S$ in the opposite direction (d).

![Hysteresis loop](image)

**Figure 2.14**: Hysteresis loop for a ferromagnetic material: $M_S$ is the saturation magnetisation, $M_R$ is the remanent magnetisation at $H = 0$, $H_C$ is the coercivity at $M = 0$.

2.2.4 Ferromagnetic La$_{0.67}$Sr$_{0.33}$MnO$_3$

The perovskite manganite La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO) is a ferromagnetic material which has been studied intensively in the last few years due to its remarkable properties which are suitable for many application. The bad metal LSMO has a pseudo-cubic crystal structure with a lattice parameter of 3.87 Å at room temperature and shows ferromagnetic behaviour below $T_C = 370K$ [30]. This high Curie temperature makes LSMO an attractive material for applications at room temperature, like magnetic storage applications [31]. LSMO is also best known for having a very large magnetoresistance, which means, it dramatically changes its electrical resistance in the presence of a magnetic field. This effect is also
2.2 Ferromagnetism and $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$

called the colossal magnetoresistance effect (CMR) and could be used for i.e. magnetic field sensing [31]. The perovskite structure of LSMO (Fig.2.15) consists of a small cation, manganese (Mn) in our case, surrounded by an octahedron of oxygen anions, with a large cation, lanthanum (La) or strontium (Sr), filling the space at the corners of the unit cell. Ferromagnetism in LSMO occurs due to a double-exchange mechanism proposed by Zener [32]. The exact composition of LSMO is $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$. $\text{Mn}^{3+}$ contains 4 unpaired electrons corresponding to a atomic magnetic moment $m = 4\mu_B$ and $\text{Mn}^{4+}$ contains 3 unpaired electrons corresponding to $m = 3\mu_B$. The exchange interaction, by means electron hopping from $\text{Mn}^{3+}$ to $\text{Mn}^{4+}$ by a Mn-O-Mn path, results in ferromagnetic ordering and metallic conductivity [33]. Thus, the total moment of one LSMO unit cell is $(2/3 \cdot 4 + 1/3 \cdot 3)\mu_B = 3.67\mu_B$.

![Perovskite structure of LSMO](image)

**Figure 2.15: Perovskite structure of LSMO**

The direction of the magnetic moments and domains are dependent on the internal energy of the system. Magnetic moments in ferromagnetic materials are vectors and the exchange with neighbouring moments aligns the vectors in a particular direction. This direction depends on the crystal structure and is usually along a certain crystal axis. This behaviour is known as magnetocrystalline anisotropy. Magnetocrystalline anisotropy is the energy necessary to deflect the magnetic moment from its favourable direction, called the easy direction, into a different direction. In addition, induced lattice distortions can also affect changes in magnetic anisotropy, called stress anisotropy or inverse effect of magnetostriction. Studies showed that the lattice mismatch between an epitaxial LSMO film
and the substrate can impose a strain which affects the properties and even the direction of the magnetisation [34].
Chapter 3

Thin film growth

The studied thin films in this work were grown by pulsed laser deposition (PLD) in on-axis geometry. Growing thin films using laser interaction had its major breakthrough in 1987 when high-temperature superconducting films were successfully grown [35]. It was this pioneering work led by D. Dijkkamp that literally lifted PLD off the ground. PLD is an extremely simple and versatile technique for preparing a wide range of thin films and epitaxial multilayer structures. In paragraph 3.1 the backgrounds of PLD are specified as well as the critical settings and conditions of the growth process. Paragraph 3.2 then discusses the general aspects of epitaxy and the growth mechanism of epitaxial thin films. The thin film growth conditions used in this project are described in paragraph 3.3.

3.1 Pulsed laser deposition

The pulsed laser deposition method involves evaporation of a solid target in a high vacuum by means of short and high energy laser pulses [36]. The deposition process takes place in a stainless steel vacuum chamber. Figure 3.1 shows a schematic diagram of a laser ablation system with the main components including the laser beam source, a spinning target stage and a heatable substrate stage. Generally, the PLD process can be divided into four steps: the laser radiation interaction with the target, the dynamics of the ablated material, the deposition of the ablated material on the substrate and the nucleation and growth of a thin film on the substrate’s surface. Each step above is described in the following section and they are particularly important for the quality and characteristic of the thin
3.1 Pulsed laser deposition

film. During the film growth process, a pulsed laser beam is focused through a lens and a window onto a target. The lasers generally used for PLD are ArF, KrF, XeF excimer lasers and ND:YAG laser with pulse width of typically 30 ns pulses, pulse energy in the range of 0.01-1.2 J and a frequency of 1-20 Hz. The laser hits the target material with high intensity and thereby the target evaporates. The target material is mounted on a spinning holder, in order to achieve the maximum utilisation of the material. To enable the growth of multilayer films, multiple targets can be used during the deposition process. The ablation process takes place in a vacuum chamber and it is usually pumped down to a base pressure of around $10^{-5}$ Torr (13 mPa). In the case of oxide materials, the background gas will be oxygen and it is added just before the deposition.

![Figure 3.1: Schematic of a pulsed laser deposition system (after [37])](image)
3.2 Epitaxy and film nucleation

Before starting deposition, critical parameters are optimised to achieve high quality growth. The experimental conditions (substrate temperature, laser energy density, base pressure, background gas pressure and pulse frequency) directly influence the film properties such as adhesion, structure, thickness and physical properties [38]. The crystalline film growth is dependent on the surface properties of the substrate. Generally, before sticking to a stable position, the adatom will diffuse through several atomic layers and this diffusion ability is dependent on the surface temperature. High temperatures usually enable rapid and defect free film growth, whereas low temperatures may cause disordered or amorphous structures. The thickness of the thin film certainly is directly dependent on the deposition time, the laser fluency and the target-substrate distance. The physical properties of a oxide thin film, especially of the LSMO film are strongly dependent on the oxygen content [39]. The background oxygen pressure affects the lattice strain of the film, which in turn induces large changes in the magnitude of magnetisation accompanied by large changes in the Curie temperature. After deposition, a final, but necessary step is following. The annealing of oxide thin films in an oxygen atmosphere generally prevents the occurrence of oxygen deficiency, which could result in decreasing both $T_C$ and saturation magnetisation $M_S$ [40].

3.2 Epitaxy and film nucleation

The significance of epitaxial growth and the various growth mechanism are described in this section. Epitaxy deals with the formation of single crystal films on single crystal substrates and with the resulting specific crystallographic orientation between the film and the substrate. The crystal systems and their lattice parameters are decisive factors for the crystallographic orientation. Epitaxy can be divided into two types, homoepitaxy and heteroepitaxy. Homoeptaxy describes the case when both the film and the substrate are of the same material. In contrast, heteroepitaxy refers to the case when film and substrate are of different materials, such as a LSMO thin film on a BTO substrate. The crystallographic orientation between the film and the substrate can also be demonstrated by examining the lattice parameter of both materials. During deposition, the lattice parameter of the thin film unit cell is dependent on the lattice parameter of the
substante. Figure 3.2 illustrates the various types of epitaxy. In the case of homoepitaxial growth, both lattice parameters have the same value, therefore the unit cells of both materials have a perfect match. However, regarding heteroepitaxy, where the materials in general have different lattice parameters, there is a mismatch between film and substrate. The magnitude of the difference and film thickness is decisive if the film forms a strained or relaxed epitaxy. In the strained state, the film unit cell adapts the lattice parameter of the substrate, resulting in a displacement of the unit cell’s in-plane axis due to internal stress. If the stress energy becomes bigger, the film creates dislocations and is relaxed. In general, lattice strain in LSMO is gradually relaxed with increasing film thickness [41].

**Figure 3.2:** Schematic illustration of lattice matched, strained and relaxed epitaxy. (after [42])

The fundamental criterion for epitaxy refers to the lattice mismatch equation (Equ.3.1), with $\epsilon_m$ for the lattice mismatch and $a_f$ and $a_s$ for the lattice parameters of the film and the substrate. Overall, for high quality epitaxial thin films,
the lattice mismatch should be less then 10% [43]. A positive or negative strain means the film is stretched in plane or compressed in-plane, respectively.

\[ \epsilon_m = \frac{(a_f - a_s)}{a_s} \]  

(3.1)

To complement the brief introduction in PLD and epitaxial thin films, the basics of the growth mechanism will be mentioned here. In general, there are three conventional models of film nucleation and growth [44, 45] of epitaxial thin films as shown in Fig.3.3: three-dimensional growth of islands, two-dimensional growth of monolayers and formations of full monolayers which switches to three-dimensional islands after several layers. The surface energy of film and substrate plays a decisive role in which mode dominates. The three-dimensional growth of islands is called Vollmer-Weber. The Vollmer-Weber growth leads to different sized, three-dimensional islands, expanding by successive deposition. This mode appears since the attraction force between the adatoms is stronger than the force between the adatoms itself and substrate. In general, the adatoms are bounded weakly to the surface which leads to a high desorption rate. Contrary to the Vollmer-Weber effect, the adatoms can be energetically more favourable for the substrate. That means the forces between the hitting atoms and the substrate are higher than between the neighbouring atoms itself. Consequently, the adatoms form small two-dimensional islands which merge to monolayers. After the complete formation of a monolayer, new monolayers are formed on the same principle. This layers growth is also called Frank-Van-der-Merve mode. The influence of the substrate gets weaker by increasing layer quantity and therefore the binding energy between the adatoms and the substrate declines and continuously converge the binding energy between the adatoms. A combination of the above mentioned modes is the Stranski-Krastanov mode. After an incipient growth of a few cohesive monolayers based on the Frank-Van-der-Merve mode, it continuous with nucleation in form of small islands. This abrupt mode change is caused by strain between the different monolayers.
3.2 Epitaxy and film nucleation

**Figure 3.3:** Schematic representation of the three growth modes.  
(a) Island growth (Vollmer-Weber).  
(b) Layer-by-layer growth (Frank-Van-der-Merve).  
(c) Layer-plus island growth (Stranski-Krastanov)
3.3 Bilayer LSMO on BTO

The films studied in the present work were deposited from a stoichiometric target of $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ by PLD technique on (100) $\text{BaTiO}_3$ substrates (4 mm x 4 mm x 0.5 mm). A KrF excimer laser was used with $\lambda$=248 nm and pulse width of 30 ns. Prior to loading the system, substrates were cleaned in a ultrasonic bath in acetone for 15 minutes. The cleaning process is important, because the growth of the first layer and consequently of the following layers and their properties are influenced by the substrate’s surface morphology. The samples were fixed on the heater using silver paint. The above mentioned variable parameters were changed to obtain high quality films and the expected results in magnetisation. After pumping down the chamber to $6 \times 10^{-5}$ Torr (8 mPa), the samples were heated at 750°C for 1 hr with an oxygen pressure of 0.1 Pa in the chamber. This procedure is necessary to improve surface quality and to remove contaminants like CO$_2$ and water. The target was cleaned by pre-ablating the surface with the laser beam, a shutter being used to shield the substrate from contamination. The background gas pressure (oxygen) was held constantly at 15 Pa during all deposition runs. The laser source was adjusted to a laser energy of 350 mJ, a repetition rate of 1 Hz and a target-substrate distance of 8 cm. As noted, the substrate temperature is critical for the film properties, so that the conditions were varied between 700°C and 800°C to achieve epitaxial growth. It is well established that the stress pattern in film depends on the film’s thickness, therefore the deposition time was varied between 0.25 and 1.0 hr, resulting in 20-80 nm thickness. We knew from past experiences, that these parameters result in a growth rate of around 1.4 nm/sec. The *in situ* annealing process is very crucial to the film properties. To obtain the best results, after the deposition, the samples were cooled to 700°C and annealed for 30 minutes in a oxygen pressure of around 0.5 atm (50 kPa). Cooling down to room temperature was carried out using a programmable heater with a cooling rate of 10°C per minute. However, Sample 1 was cooled to RT quickly.
Chapter 4

Structural and magnetic characterisation techniques and methods

This part will describe various characterisation techniques used in this work, including atomic force microscopy and x-ray diffraction for structural characterisation and vibrating sample magnetometry for magnetic characterisation.

4.1 Atomic Force Microscope

The atomic force microscope (AFM) was invented by Gerd Binning in 1986 [46] and it is a tool to determine direct images of solid state material surfaces as well as details about film smoothness and roughness. To obtain the topography images which could be down to 10 Å, the AFM uses the interaction between a small tip and the sample surface. The advantage of AFM is the fast and simple measurement with a high resolution. In contrast to the scanning tunnelling microscope (STM) there is no vacuum necessary and measurements can be carried out on every solid state material. Figure 4.1 shows the design of a standard AFM system. The sample is mounted on a piezoscanner fixed by a magnetic surface. The piezoscanner is responsible for the movements in the x, y and z directions. The tip is attached on a cantilever and it is generally made out of silicon or silicon nitride with a nominal radius of 5-10 nm. During the measurement, the tip rasterises a few hundred angstroms over the surface or even slightly touches
4.1 Atomic Force Microscope

An interaction force between the tip and the surface leads to a deflection of the cantilever. This deflection of the cantilever is detected optically. A laser beam is reflected on the tip surface and hits the photodetector which consists of a four-section split photodiode. Broadly, these photodiodes are able to detect displacements of the laser beam of 10 Å. Monitoring the difference between the top and lower diodes, the distance proportion between the tip and the detector and the length of the cantilever allows a quantification of movements in the scale of a few angstroms. The difference of the left and right diodes identify the deflection of the tip. These mechanical movements are transformed into electric signals. The use of appropriate software allows real topography images of the sample surface to be created.

![Diagram of atomic force microscope](image)

**Figure 4.1:** Simplified schema of an atomic force microscope. (after [47])

There are two basic modes of operation: the contact or the non-contact mode (tapping mode). Each mode uses different physical effects for their surface analysis. In the contact mode, the tip actually makes physical contact with the surface. Both electron clouds of the tip and the specimen overlap and electrostatic repulsive forces physically push them apart. The oscillations are transferred from the cantilever to the photodiode and an atomic scale resolution of the surface can be displayed. In the non-contacted mode (tapping mode), the tip is located tens to
hundreds of angstroms from the sample’s surface, and the van der Waals forces interact between tip and specimen, causing a weak attraction. Because it is difficult to detect small forces the cantilever is vibrating, typically at 100 to 400 kHz. Changes in vibrational amplitude or resonant frequency are easier to analyse. The advantages of this mode are the ability to measure soft or elastic materials and minimisation of both surface contamination and tip degradation. The characterisation of the LSMO surface was carried out with a Digital Instruments Nanoscope III (AFM) using the tapping mode.
4.2 X-ray diffraction

X-ray diffraction (XRD) [48] provides information about the crystalline orientation of the material and the lattice parameters. In addition XRD is able to determine thickness, density and roughness of thin films. The x-rays are generally produced by x-ray tubes with a typical photon energy of 0.1 keV-100 keV. In the structural analysis, only short wavelength x-rays in the range of 0.1 - several Å are used. This wavelength is comparable to the spacing between atoms. The theory of XRD is described by the Bragg’s law explained in Fig.4.2. X-ray beams, with wavelength $\lambda$ reach the crystal surface under an angle $\Theta$ and are scattered by crystal planes at an angle $\Theta$. The film consists of rows of crystal planes that are separated by a distance $d$ (out-of plane lattice parameter). The condition for constructive interference is that $|AB| + |BC|$ is an integral number $n$ of the wavelength. Since, $|AB| = |BC| = d \cdot \sin \Theta$, one obtains the Bragg’s law (4.1) which allows to calculate the value of the lattice parameters:

$$2d \sin \Theta = n\lambda \quad (4.1)$$

![Figure 4.2: Bragg diffraction of x-rays. Reflection of x-rays from two planes of atoms in a solid. (after [48])](image)

In this work, the lattice parameters and film crystallinity were studied using a four-cycle single crystal diffractometer (Philips X’Pert high resolution diffractometer, $\gamma=1.54$ Å) equipped with a Ge monochromator. During an experiment,
the intensity of the reflected beam was measured for a continuous range of angles \((\omega, \Theta)\). Different peaks of intensity were observed, corresponding to the different inter-planar distances present in the crystalline sample. This method is known as \(\omega - 2\Theta\)-scans.
4.3 Vibrating sample magnetometer

Due to the small material volumes and its small magnetic moments, the magnetic characterisation of thin films requires measuring equipment with good sensitivity and accuracy. The vibrating sample magnetometer (VSM) was first described by Foner [49] and is a suitable tool to measure the magnetic properties of materials as a function of temperature and magnetic field. Figure 4.3 shows a schematic drawing of a VSM. The magnetic sample is positioned with a non-magnetic sample holder between two large electromagnets, which create a homogeneous field \( H \). Directly next to the sample a set of pick-up coils is located and the magnetic centre of the sample coincide with the symmetric centre of the pick-up coils. The sample is made to vibrate with a vibration unit. Thus, the vibrating magnetic sample causes a flux change and generates an induction current in the pick up coils. The induction current is proportional to the magnetisation of the sample. The sample can be magnetised by a constant field up to 15 kOe with the large electromagnets. The generated field is controlled by the hall sensor. For temperature variations a cryostat can be inserted for cooling down to 4 K (using liquid helium) and a furnace allows to heat up to 500 K.

![Schematic diagram of a vibrating sample magnetometer](image)

*Figure 4.3: Schematic diagram of a vibrating sample magnetometer. (after [50])*
4.3 Vibrating sample magnetometer

Coupling between BTO and LSMO as a function of temperature
In this work a Princeton vibrating sample magnetometer was used to measure magnetisation $M$ as a function of temperature $T$, as a function of magnetic field $H$ and as function of electric field $E$. Prior to the measurement, the silver paint at the undersurface of the samples was partially removed with sandpaper. Pure silver paint is not magnetic, but after heating up to high temperatures during the film growth, it reacts with iron from the heater block. This composition in turn is ferromagnetic and might influence the measurements. A thin layer of silicon grease was used to glue the specimen to the sample holder. Cooling was performed with liquid helium in the cryostat. In the first instance liquid nitrogen was used, but the temperature control was unstable. Liquid helium was more suitable for our requirements. The magnetic field was applied along the [100] direction of the LSMO film. Magnetic properties of Sample 1 and 2 were analysed from 77 K to 400 K in a 1000 Oe field. Due to the fact of multiple domain appearance, the measurement techniques had to be improved. Henceforth, the samples were heated up to 470 K and then cooled down to 70 K in $H = 8000$ Oe. The prior alignment of the magnetic dipoles in strong magnetic field ($H = 8000$ Oe) from 470 K to 70 K is a critical factor for our approach. This process allows the formation of a single domain in the LSMO film, which is easier to obtain when cooling down from above $T_C$. A multi-domain structure might average out the change in anisotropy, leading to no measurable changes in magnetisation. In addition, the field during measuring was decreased to 20 Oe due to the fact that high fields prevent deflections of the magnetic anisotropy.

Magnetoelectric coupling between BTO and LSMO
Investigations of magnetoelectric effects were carried out by applying an electric field to the substrate and simultaneously tracking the magnetic properties of the film. Measurements of magnetisation as a function of an in situ applied $E$-field with in a VSM are not common and therefore required a special design of the sample holder (made by J.L Prieto). Figure 4.4 shows this home-made sample holder. The specimen was connected with conducting silver paint to a voltage supply. The pre-alignment procedure of the magnetic moments was the same as mentioned above. The electric field (4–10 kV cm$^{-1}$) was applied at various
temperatures (70-300 K) perpendicular between the film surface and the substrate underside (along [001]). During measurement, the temperature was kept constantly and the field was slowly increased at 20 s till observing the magnetic response and then removed after a certain time. After each measurement, the samples were treated with the same heating and cooling process as described before.

Figure 4.4: VSM sample holder for in situ applied electric field.
Chapter 5

Results structural characterisation

In this chapter I present the results of the structural analysis using x-ray diffraction and atomic force microscopy. Several La$_{0.67}$Sr$_{0.33}$MnO$_3$ thin films were grown on the BaTiO$_3$ substrate to obtain a film with low roughness, epitaxial and crystalline growth and high magnetic properties. As already mentioned in Chapter 3 (Thin film growth), the deposition conditions like substrate temperature ($T_{\text{subst}}$) and deposition time ($t_{\text{dep}}$), had to be optimised. Well known parameter values for laser energy, O$_2$ pressure, repetition rate and annealing process were used and kept constant during all depositions (see Table 5.1). A list with the growth conditions and resulting thicknesses for all LSMO films is given in Table 5.2. The particular thickness ($d_{\text{film}}$) for every film was calculated using the known value for the deposition rate (1.4 nm/sec), which was also proved with XRD analysis (not shown here).

<table>
<thead>
<tr>
<th>Laser energy</th>
<th>O$_2$ pressure</th>
<th>Repetition rate</th>
<th>Annealing &amp; Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>350 mJ</td>
<td>15 Pa</td>
<td>1 Hz</td>
<td>cooling to 700°C (5° per min.); annealing at 700°C (30 min.); cooling to RT (10° per min.)</td>
</tr>
</tbody>
</table>

*Table 5.1: Constant deposition conditions*
5.1 Results x-ray diffraction

The lattice constants were obtained at room temperature from \( \omega - 2\Theta \) scans of the LSMO films on BTO substrates around the (002) reflection as shown in Fig.5.1. The reflections at 44.86° and 45.38° are both reflections from the BTO substrate and correspond to the (002) and (020)/(200) reflections. This has been confirmed by a XRD scan of a blank substrate (shown in Fig.7.4). The presence of both reflections indicate that there are two types of domains in the substrate, one with the \( c \)-axis out of plane (corresponding to the (002) reflection) and one with the \( c \)-axis in-plane (corresponding to the (020)/(200) reflection). This means there are 90° domains present in the substrate.

Table 5.2 lists the lattice parameter obtained for both BTO reflections and the out-of-plane lattice parameter of the LSMO film. The values obtained for BTO are very close to the bulk lattice parameters (3.99 Å and 4.03 Å). The lattice parameter of the LSMO film decreased slightly with decreasing film thickness. Sample 1 & 2 had a thickness of approximately 80 nm and the lattice parameter was within experimental error equal to the bulk value (3.87 Å). Decreasing the film thickness to 20 nm (Sample 6) resulted in a lower out-of-plane lattice parameter. We related this to epitaxial strain. The out-of-plane lattice parameter of the LSMO films are close to the bulk value of 3.87 Å indicating a large degree of relaxation, which is expected as the lattice mismatch (Table 5.3) between the

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate temperature ( (T_{\text{subst}} / {^\circ}\text{C}) )</th>
<th>Deposition time ( (t_{\text{dep}}/\text{hr}) )</th>
<th>Film thickness ( (d_{\text{film}} / \text{nm}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>750</td>
<td>1.0</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>700</td>
<td>1.0</td>
<td>80</td>
</tr>
<tr>
<td>3, 7, 8, 9</td>
<td>775</td>
<td>0.5</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>800</td>
<td>0.5</td>
<td>40</td>
</tr>
<tr>
<td>5</td>
<td>775</td>
<td>0.25</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>775</td>
<td>0.33</td>
<td>30</td>
</tr>
</tbody>
</table>

*Table 5.2: List of deposition conditions for all LSMO films*
### 5.1 Results x-ray diffraction

<table>
<thead>
<tr>
<th>Sample</th>
<th>BTO $a,b$ (Å)</th>
<th>BTO $c$ (Å)</th>
<th>LSMO $c$ (Å)</th>
<th>$a_{\text{BTO}} - a_{\text{LSMO}}$ (%)</th>
<th>$c_{\text{BTO}} - c_{\text{LSMO}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>3.992</td>
<td>4.036</td>
<td>3.881</td>
<td>-2.87</td>
<td>-3.83</td>
</tr>
<tr>
<td>Sample 3</td>
<td>3.991</td>
<td>4.036</td>
<td>3.859</td>
<td>-3.31</td>
<td>-4.37</td>
</tr>
<tr>
<td>Sample 4</td>
<td>3.992</td>
<td>4.036</td>
<td>3.839</td>
<td>-3.84</td>
<td>-4.87</td>
</tr>
<tr>
<td>Sample 5</td>
<td>3.992</td>
<td>4.037</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 6</td>
<td>3.992</td>
<td>4.036</td>
<td>3.840</td>
<td>-3.80</td>
<td>-4.85</td>
</tr>
</tbody>
</table>

**Table 5.3:** Out-of plane Lattice parameters of BTO and LSMO obtained with x-ray diffraction. The mismatches between BTO and LSMO with the a- and b-axis as well with the c-axis (no data for LSMO for Sample 5)

BTO and LSMO is -3.8 % with the a- and b-axis and -4.8 % with the c-axis. We note that the intensity of the LSMO peak is lower than for LSMO grown on e.g. STO or NGO. This is related to two effects. First, the crystalline quality of the BTO substrate is not as good as for STO and NGO as there are different directed domains. Secondly, the films do not grow layer-by-layer as on STO or NGO, but also consists of islands (see AFM results). Slight disorientations of these islands result in peak broadening and in a reduction of the peak height.
5.1 Results x-ray diffraction

Figure 5.1: X-ray $\omega - 2\Theta$ diffraction spectra taken from sample 1, 2, 3, 4, 6.
5.1 Results x-ray diffraction

The influence of an applied electric field was investigated at RT with XRD. A field of 6 kV cm\(^{-1}\) was applied to a blank BTO substrate for approximately 2 minutes and afterwards analysed (see Fig. 7.4). The intensity ratio of \(I_{(002)}\) and \(I_{(200,020)}\) increased to 12:1 from 1:3 before the application of the electric field. It has indeed been shown that the application of an electric field of about 6 kV cm\(^{-1}\) initiates a rotation of c-axis from in-plane to out-of plane, associated with 90° domain rotations in bulk BTO. This change can be attributed entirely to 90° rotation, regarding that 180°-domains switching can not be detected by XRD methods [51]. This effect is known to occur in electric fields between 3-10 kV cm\(^{-1}\) [52] and as seen, it is permanent since the scan was performed with no applied field. A small additional peak appears at \(2\Theta = 45.13°\) with a out-of-plane lattice parameter of 4.016 Å, which is related to the possibility of an orthorhombic (bulk BTO \(c=4.018\) Å [23]) or other phase.

![XRD ω − 2Θ scan](image)

**Figure 5.2:** XRD ω − 2Θ scan of a blank BTO substrate indicating the rotation of 90° domains (020,200) initiated by an applied electric field. The intensity of the (002) peak increases but the (020,200) peak decreases because of the increasing degree of c-axis orientation.
5.2 Results atomic force microscopy

Topographic images were made using atomic force microscopy (Digital Instruments) at room temperature. Information about the growth mode, roughness as well as structural anomalies were expected. To achieve comparable results, each sample was measured with scan sizes of 4.0–5.0 µm and of 700 nm. A blank BTO substrate was also investigated to see its influence on the film structure (Fig.5.3). The figures 5.4 to 5.9 show surface images from films grown under various conditions.

The root mean square (RMS, Rq) roughness of these films varied between 0.93 nm and 1.85 nm for an area of 5 x 5 µm. Thus the change in surface roughness when the deposition time and temperature were changed was small. The smooth film surface and the low roughness indicates good epitaxy. The observations of the figures show the presence of stripe-like features. Comparing the morphology with a pure BTO substrate surface Fig.5.3 shows that they are ferroelectric domain patterns from the BTO substrate. It has been reported, that 90° domain boundaries in ferroelectric PZT thin films have a step height of \( \approx 20 \, \text{Å} \) [53]. It can be assumed that this is the same in BTO domain boundaries. During deposition, the LSMO films follows these steps of the BTO surface and thus the stripes appear on the film surface as well. The morphology of the films suggests that films grown in Stranski-Krastanov mode. The transition in the growth mode from monolayers to three-dimensional islands could be due to strain relaxation in the film after a particular thickness. It is reported that the lattice strain in \( \text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3 \) is gradually relaxed with increasing film thickness [54].

Since the roughness and structure of the LSMO film did not vary much with growth temperature, we based our optimum growth temperature of 775°C on the combined results of AFM, XRD and VSM, as films grown at 775°C had the largest magnetisation (shown in Chapter 6).
5.2 Results atomic force microscopy

Figure 5.3: AFM image of a blank BTO substrate

Figure 5.4: AFM image of Sample 1 \( (d_{\text{film}} = 80 \, \text{nm}, T_{\text{substr}} = 750^\circ \text{C}) \) with scan size 5.0 nm and 700 nm
5.2 Results atomic force microscopy

**Figure 5.5:** AFM image of Sample 2 \((d_{\text{film}} = 80 \text{ nm}, T_{\text{subst}} = 700 ^\circ \text{C})\) with scan size 5.0 nm and 700 nm

**Figure 5.6:** AFM image of Sample 3 \((d_{\text{film}} = 40 \text{ nm}, T_{\text{subst}} = 775 ^\circ \text{C})\) with scan size 5.0 nm and 700 nm
5.2 Results atomic force microscopy

**Figure 5.7**: AFM image of Sample 4 ($d_{\text{film}} = 40$ nm, $T_{\text{subst}} = 800^\circ C$) with scan size 5.0 nm

**Figure 5.8**: AFM image of Sample 5 ($d_{\text{film}} = 20$ nm, $T_{\text{subst}} = 775^\circ C$) with scan size 5.0 nm and 700 nm
5.2 Results atomic force microscopy

Figure 5.9: AFM image of Sample 6 (d_{film} = 30 nm, T_{subst} = 775 °C) with scan size 5.0 nm and 700 nm
Chapter 6

Coupling between BTO and LSMO as a function of temperature

6.1 Introduction

Coupling between the BaTiO$_3$ substrate and the La$_{0.67}$Sr$_{0.33}$MnO$_3$ film was investigated as a function of temperature. A Princeton vibrating magnetometer was used to analyse the influence from the structural phase transitions of BTO on the magnetic behaviour of the film. BTO changes its structures at 410 K, 290 K and 190 K, however the transition at 410 K from cubic to tetragonal was of no relevance since LSMO is paramagnetic above $T_C = 370$ K.

For a full characterisation of the magnetic behaviour, additional to the $M$ vs. $T$; hysteresis loop measurements ($M$ vs. $H$) at various temperatures were performed. The samples were cooled from 470 K through the Curie temperature to 70 K in a magnetic field ($H = 8000$ Oe) to form a single domain in the film. During the measurement of $M$ vs. $T$, a magnetic field $H = 20$ Oe was applied along the [100] direction of the substrate. The actual output of $M$ is emu (electro magnetic unit), which was converted to the more standardised unit $\mu_B$ / unit cell (see Equ.6.1).

$$[\mu_B/\text{unit cell}] = [\text{emu}] \cdot 1.0783 \cdot 10^{20}/\text{number of unit cells} \quad (6.1)$$

with emu $= 1.0783 \cdot 10^{20} \mu_B$
The magnitude of magnetisation and lattice structure depends on the film thickness, oxygen pressure and annealing conditions. Consequently, the growth conditions had to be adjusted to achieve high magnetisation and clamping effects between the film and the substrate. We started with known deposition parameters for LSMO films on non-BTO substrates and changed them to approach the expected results. For reminding, only the substrate temperature and the deposition time were optimised, conditions like the laser energy ($350 \text{ mJ}$), laser frequency ($1 \text{ Hz}$), $\text{O}_2$ pressure ($15 \text{ Pa}$) and annealing (except Sample 1) were kept constant during all deposition runs. The single parameter adjustments are described in the Chapter 3 and the methods of the VSM measurements are detailed in the Chapter 4.

In some measurements of $M$ vs. $T$ it strikes out that the curve around $T_C$ is either higher or lower than zero. Negative magnetisation can be gathered from diamagnetic effects of the VSM sample holder and higher-than-zero magnetisation from either the silicon grease or silver paint residues which can be ferromagnetic.

### 6.2 Results magnetic characterisation

Magnetisation loops for Sample 1 ($d_{\text{film}} = 80 \text{ nm}, T_{\text{subst}} = 750 ^\circ \text{C}, \text{anneal:} 750-700 \text{ 5}^\circ \text{C \ per \ min, 30 \ min \ at \ 700^\circ \text{C}, \ cooling: \ 700-\text{RT \ randomly}}$) and Sample 2 ($d_{\text{film}} = 80 \text{ nm}, T_{\text{subst}} = 700 ^\circ \text{C}, \text{anneal:} \ 30 \text{ min \ at \ 700}^\circ \text{C, \ cooling:} \ 700-\text{RT \ 10}^\circ \text{C \ per \ min}$) obtained at RT and 77 K are shown in Fig.6.1. Sample 1 shows $M_S = 1.3 \mu_B/\text{unit cell}$ at 77 K which is lower than the bulk value of $3.6 \mu_B/\text{unit cell}$, but comparable to the value reported by Lee et al. [9] for LSMO on BTO. In comparison, Sample 2 has a lower $M_S = 0.3 \mu_B/\text{unit cell}$, which can be attributed to the low substrate temperature during deposition. Magnetisation as a function of temperature (Fig.6.2) shows no changes or jumps at the transitions temperatures of the BTO substrate (190 K, 290 K). The anomaly in the curve for Sample 1 at $\sim 150 \text{ K}$ is due to unstable temperature conditions. The thin film of Sample 2 only shows weak magnetic behaviour, resulting in an uncommon curve for LSMO.
6.2 Results ($M$ vs. $T$)

**Figure 6.1:** Magnetisation ($M$) as a function of magnetic field ($H$) at room temperature and 77 K of Sample 1, 2.

![Magnetisation vs Magnetic Field](image)

**Figure 6.2:** Magnetisation ($M$) as a function of temperature ($T$) of Sample 1, 2.

![Magnetisation vs Temperature](image)

As the sample grown at 750°C had a larger magnetisation than the sample grown at 700°C, the deposition conditions were changed by increasing the substrate temperature and by shortening the deposition time. A higher substrate temperature usually results in better crystalline and epitaxial film growth and a thinner layer should increase clamping and coupling effects. Magnetisation-vs.-temperature curves of Sample 3 ($d_{film} = 40$ nm, $T_{subst} = 775$ °C), Sample 4
6.2 Results ($M$ vs. $T$)

$(d_{film}=40 \text{ nm}, T_{subst}=800 ^\circ \text{C})$ and Sample 5 $(d_{film}=20 \text{ nm}, T_{subst}=775 ^\circ \text{C})$ are shown in Fig.6.3. None of the samples show any coupling to the substrate. The reduction of film thickness sheds light on the magnitude of the magnetisation, which is evidently dropping. The influence of the temperature can not be remarked.

![Figure 6.3: Magnetisation ($M$) as a function of temperature ($T$) of Sample 3, 4, 5.](image)

According to the previous result, a lower film thickness results in weak magnetisation, but thinner films are more likely to be clamped with the substrate. Hence, in Sample 6, the deposition time was set to 0.5 hr $(d_{film} \approx 40 \text{ nm})$ with a substrate temperature of 775$^\circ$C. Indeed, Fig.6.4 shows temperature dependent response at $T = 198 \text{ K}$ and $T = 295 \text{ K}$. These distinctive drops in magnetisation are similar to the ones illustrated in Lee’s report (see Discussion, Fig.6.6).

For reproducibility purposes, more sample were grown under the conditions of Sample 6. The results in Fig.6.5 only show the jump at 198 K, which clarifies the crucial behaviour of coupling between film and substrate. No evidence of coupling can be seen around the transition from tetragonal to orthorhombic near 295 K.
6.2 Results ($M$ vs. $T$)

**Figure 6.4:** Magnetisation ($M$) as a function of temperature ($T$) of Sample 6. The curve shows distinct drops of $0.32 \mu_B$ / unit cell ($T = 198$ K) and $0.2 \mu_B$ / unit cell ($T = 295$ K) in magnetisation.

**Figure 6.5:** Magnetisation ($M$) as a function of temperature ($T$) of Sample 7, 8, 9.
6.3 Discussion

Magnetoelectric coupling between the ferroelectric BaTiO$_3$ and the ferromagnetic La$_{0.67}$Sr$_{0.33}$MnO$_3$ has been achieved at the phase transitions of the substrate. Huge discontinuous magnetic jumps in magnetisation can be found at 199 K (17%) and at 295 K (28%). However, the coupling at 295 K has been achieved only with one sample, coupling at 199 K was reproducible in several samples. The results also show a slight decrease of $T_C \approx 300 - 350$ K (bulk BTO $T_C \approx 393$ K). The reason is expected to be from deformations of epitaxial stress in the thin film [55], which can influence the Curie temperature. This decrease in $T_C$ for LSMO films is notable for $d_{film} \leq 100$ nm [56].

The distortion of magnetic anisotropy can be attributed to in-plane strain, controlled by the substrate. At the ferroelectric phase transitions of barium titanate the dimensions of the lattice parameters differ dramatically, associated with a large ferroelastic strain inducement. For example, at the transition from cubic to tetragonal, the c-axis changes from 3.95 Å to 4.03 Å resulting in a strain of $\epsilon_s = (c_{tetragonal} - c_{cubic})/c_{cubic} = 1.0 \%$. Since there are six possible orientation states of the unit cell in a BTO crystal (see 2.4b), three distinct strain orientation could arise. Thus, this strain is geometrically complex and inhomogeneous. Analogous behaviour can be found at the transitions which are relevant in this project, from tetragonal to orthorhombic and from orthorhombic to rhombohedral. The strain here, is even more complex due to multible low energy domain walls. In the epitaxial heterostructure of LSMO and BTO with in-plane lattice clamping, these temperature dependent lattice strains of the substrate are transmitted to the thin film, causing a lattice distortion. Since the magnetic anisotropy is dominated by stress effects [57], the direction of the magnetic moments slightly shifts causing a drop in magnetisation.

In contrast to the work by Lee [9] et al. (illustrated in Fig.6.6), we only observed a jump in $M$ around 295 K in one sample and the jump was lower than reported. One possibility is the presence of 90° domains in our substrate, as shown in Fig.5.1. As Lee et al. used poled substrates and did not report XRD data, it is not known if their substrates contained 90° domains. Furthermore, the magnetisation in the Sample 7, 8, 9 was distinctively lower than in Sample 6 which can be attributed to defects and lower film crystallinity.
Summarised, our findings reveal that the magnetic anisotropy can be controlled by induced ferroelastic lattice strain from the ferroelectric phase transition.

\textbf{Figure 6.6:} Magnetisation as a function of temperature of a 50 nm $La_{0.67}Sr_{0.33}MnO_3$ film grown on (001) $BaTiO_3$ substrate in a magnetic field of 20 Oe applied along [100] direction. (from Lee report [9])
Chapter 7

Magnetoelectric coupling between BTO and LSMO as a function of electric field

7.1 Introduction

Magnetoelectric measurements between the $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ film and the $\text{BaTiO}_3$ substrate were performed by applying an electric field across the substrate (4 mm x 4 mm x 0.5 mm) while performing magnetic measurements with the VSM. The magnetic poling process was performed likewise as in the previous chapter. Voltages between 200-500 V (equivalent to an electric field of 4-10 kV cm$^{-1}$) were applied along the [001] direction of the substrate at a temperature range of 89-298 K. Since Sample 3 ($T_{\text{subst}}=775{^\circ}\text{C}$, $t_{\text{dep}}=0.5$ hr, $d_{\text{film}}=40$ nm) had the largest magnetisation and shown coupling to the substrate, Sample 7-9 were grown under the same conditions. More experimental details can be found in Chapter 4.3.

7.2 Results magnetic characterisation

Thirteen VSM measurements of magnetisation plotted as a function of time at various temperatures were performed with Sample 7-9. Four representative graphs are shown in Fig.7.1. Sample 7-9 were magnetised at different temperatures and after approximately 20 s, the electric field was switched on. The black bar indicates when the electric field was switched off for each measurement. The
application of an electric field shows huge and sharp changes in magnetisation. The variations of temperature shows that this effect arises at any temperature below the \( T_C \) of LSMO. In each measurement, the electric field was increased from zero to the value where the magnetic response occurred. This value depends on the coercive field \( E_c \) and the initial domain state in the substrate. Thus, the values for \( E \) differed for each sample. The magnetic jump was identified for Sample 7 at a field of 4 kV cm\(^{-1}\), for Sample 8 at 10 kV cm\(^{-1}\) and for Sample 9 at 6 kV cm\(^{-1}\). The curves also show that the change in magnetisation is persistent, as it remains after the field has been removed. A re-switch or even a reversal of the electric field after the magnetic switching did not affect the curve at all.

\[ Figure 7.1: \text{VSM measurements of magnetisation vs. electric field at various temperatures. The electric field was applied after approximately 20 s and the black bar indicates the turn-off time. The applied fields when the changes in magnetisation occurred were 4 kV cm\(^{-1}\) for Sample 4, 10 kV cm\(^{-1}\) for Sample 8 and 6 kV cm\(^{-1}\) for Sample 9.} \]

The persistent of the change over a longer time was confirmed by extending the measuring time after the magnetic switch to 10 minutes (Fig.7.2). Sample 9
was analysed at 245 K and with an applied field of 7 kV cm\(^{-1}\). It was not taking note of the turn-of time. Indeed, even after 10 minutes the effect is still persistent.

![Figure 7.2: Magnetisation vs. E-field, measured for 10 minutes. Sample 9 was poled in a 7 kV cm\(^{-1}\) field at 245 K. The drop in magnetisation was tracked for 10 minutes, confirming the persistent](image)

Altogether, thirteen magnetoelectric measurements (not all curves are shown here) has been observed and the analysis of all switching events is summarised in Table 7.1. The magnitudes of the jumps that we measured show considerable spread, even when a given sample was remeasured at the same temperature. Fig.7.3(a) shows all the jumps $\Delta M$ between stable states as a percentage of the zero $E$-field starting value $M_0$. The magnetic change occurs over a wide range of temperature, highlighting the occurrence at room temperature. This spread is particularly pronounced near the ferroelectric transition around 200 K, likely due to enhanced domain mobility [58]. It is at this temperature that we recorded our largest value of $\Delta M/M_0 = 65\%$ (Sample 7, 199 K). The larger value of change in $M$ at 199 K is mainly due to a combination of the non-180° domain rotation and the structural phase transition which takes place at 199 K.

As coupling occurs via the combined effect of electric field induced strain in the substrate and the influence of that strain on the magnetic properties of the
film, the mechanism is different than in single phase multiferroics. In those materials a direct coupling between magnetisation and polarisation exists and $\alpha = \frac{\Delta P}{\Delta M}$. In order to make a comparison to single phase multiferroics, we have calculated ME coupling coefficient from the jumps in magnetisation $\Delta M (\mu_B / \text{unit cell})$ in electric fields $\Delta E \text{ (kV cm}^{-1}\text{)}$ with $\alpha = \mu_0 \Delta M / \Delta E$. The values of $\alpha$ for each measurement can be seen in Table 7.1. For a single switch, the largest value of $\alpha = 2.3 \cdot 10^{-7} \text{s m}^{-1}$ recorded in our LSMO/BTO structure is obtained from Sample 7 at 199 K.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T$ (K)</th>
<th>$M_0$ ($\mu_B / \text{u.c.}$)</th>
<th>$\Delta M$ ($\mu_B / \text{u.c.}$)</th>
<th>$\Delta M / M_0$ (%)</th>
<th>$\Delta E$ (kV cm$^{-1}$)</th>
<th>$\alpha = \mu_0 \Delta M / \Delta E$ (s m$^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td>7*</td>
<td>199.0</td>
<td>0.68</td>
<td>0.45</td>
<td>0.66</td>
<td>4</td>
<td>2.3 \cdot 10^{-7}</td>
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<td>7</td>
<td>199.5</td>
<td>0.60</td>
<td>0.09</td>
<td>0.15</td>
<td>4</td>
<td>4.5 \cdot 10^{-8}</td>
</tr>
<tr>
<td>7</td>
<td>199.5</td>
<td>0.52</td>
<td>0.16</td>
<td>0.31</td>
<td>4</td>
<td>8.0 \cdot 10^{-8}</td>
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<tr>
<td>7</td>
<td>199.5</td>
<td>0.75</td>
<td>0.17</td>
<td>0.23</td>
<td>4</td>
<td>8.5 \cdot 10^{-8}</td>
</tr>
<tr>
<td>8*</td>
<td>295.0</td>
<td>0.42</td>
<td>0.11</td>
<td>0.26</td>
<td>10</td>
<td>2.2 \cdot 10^{-8}</td>
</tr>
<tr>
<td>8</td>
<td>199.1</td>
<td>0.77</td>
<td>0.36</td>
<td>0.47</td>
<td>10</td>
<td>7.2 \cdot 10^{-8}</td>
</tr>
<tr>
<td>8</td>
<td>199.6</td>
<td>0.77</td>
<td>0.23</td>
<td>0.30</td>
<td>10</td>
<td>4.6 \cdot 10^{-8}</td>
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<tr>
<td>9*</td>
<td>89.0</td>
<td>1.63</td>
<td>0.41</td>
<td>0.25</td>
<td>6</td>
<td>1.4 \cdot 10^{-7}</td>
</tr>
<tr>
<td>9*</td>
<td>157</td>
<td>1.26</td>
<td>0.69</td>
<td>0.55</td>
<td>6</td>
<td>2.3 \cdot 10^{-7}</td>
</tr>
<tr>
<td>9</td>
<td>251</td>
<td>0.63</td>
<td>0.2</td>
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<td>6</td>
<td>6.7 \cdot 10^{-8}</td>
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<tr>
<td>9</td>
<td>251</td>
<td>0.53</td>
<td>0.12</td>
<td>0.23</td>
<td>6</td>
<td>4.0 \cdot 10^{-8}</td>
</tr>
<tr>
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<td>0.09</td>
<td>0.35</td>
<td>7</td>
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</tr>
<tr>
<td>9*</td>
<td>245</td>
<td>1.3</td>
<td>0.32</td>
<td>0.25</td>
<td>7</td>
<td>9.2 \cdot 10^{-8}</td>
</tr>
</tbody>
</table>

Table 7.1: Magnetoelectric data summary. The following table summarises the data for all magnetoelectric switching events that we observed. Entries with * correspond to the data presented in Fig.7.1 and Fig.7.2.
7.2 Results ($M$ vs. $E$)

Figure 7.3: a) Spread of the observed magnetic changes at various temperatures. The jump $\Delta M$ between stable states as a percentage of the zero field starting value $M_0$. b) Spread of the magnetoelectric coupling constant $\alpha$. 
The large strain, induced by the \( E \)-field during measurements occasionally led to cracking of the substrate, resulting in destruction of the samples. Furthermore at high electric fields sparks were observed in consequence of water vapour in the VSM tube. This made it difficult to achieve a complete data set for a particular sample. The electronic contacts at the backside of the BTO and on the top of LSMO films can be considered as tricky. Silver paint was used to attach the sample to the home-made VSM holder and parallel to make conducting contacts. Due to the small dimensions of the sample, a deliberate handling was necessary to avoid a shortcut between the substrate and the film.

### 7.3 Discussion

The results show sharp and persistent changes in film magnetisation of up to 65\%, by applying small electric fields (4-10 kV cm\(^{-1}\)) at any temperature below the \( T_C \) of LSMO, corresponding to magnetoelectric coupling constants of \( \alpha \sim 10^{-7} - 10^{-8} \text{ m}^{-1} \). The operative mechanism is the induction of a large strain in the BaTiO\(_3\) substrate and the transfer of this induced strain to the \( \text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3 \) film. The large strain is related to the rotation of non-180° domains into the direction of the electric field. The actual rotation of 90° domains at RT was confirmed by the XRD scan of a blank BTO substrate before and after applying an electric field of 6 kV cm\(^{-1}\) (Fig. 7.4). The peak height of the (002) reflection increases and the peak height of the (200)/(020) reflection decreases, such that the intensity ratio of \( I_{(002)} \) and \( I_{(200,020)} \) changes from 1:3 to 12:1. This domain rotation is associated in-plane strain of 1\% [52]. From Fig.7.4, it can be seen that almost all 90° domains [(200)/(020)] have changed into 180° domains [(002)].

This is in agreement with the strain vs. electric field curve of BTO as shown in Fig.7.5. The values of the electric fields we used, agree within the shown curve. The strain reaches its maximum close to the coercive field associated with the completely rotation of the non-180° domains. Thus, this gives rise to a very discrete jump in magnetisation. As the strain is almost saturated just above \( E_c \), the application of a larger electric field does not yield any significant increase in strain. Beyond, the strain is hysteretic, i.e. it does not go back to zero as non-180° rotation is irreversible [59], which explains the persistent change.
7.3 Discussion ($M$ vs. $E$)

in magnetisation. The electrically driven switching of ferroelectric non-180° domains in the BTO produces in-plane piezostrictive strains that are expected to modify the overlying ferromagnetic LSMO by locally switching its strain. This in turn locally switches the magnetic anisotropy of the film, and thus the direction of the local magnetisation, such that the component detected by the magnetometer is altered. Although we applied no external stresses, the ferroelastic nature of BTO is exploited indirectly, given that ferroelastics necessarily possess the non-180° domains required for switching strain states in an overlying epitaxial film, and given also the more general point that ferroelastics display pronounced piezoelectric effects. There is evidence to suggest that all these statements can to be transferred to every temperature below the $T_C$ of the BTO.

Figure 7.4: XRD $\omega-2\Theta$ scan of a blank BTO substrate indicating the rotation of 90° domains (020,200) initiated by an applied electric field of 6 kV cm$^{-1}$. The intensity of the (002) peak increases but the (020,200) peak decreases because of the increasing degree of $c$-axis orientation.
7.3 Discussion (M vs. E)

The persistent of the magnetic change has been experimentally confirmed and can be explained by the hysteresis behaviour of strain vs. electric field [52]. It has been reported that this “irreversibility in domain switching makes the electrostrain effect futile” [59]. However in our work this one-time effect is the significant contribution regarding possible applications. This reversible reorientation [51] illustrates that we had to realign the ferroelectric domains in the substrate after each measurement by our heat and cooling treatment. Going above the $T_c$ of BTO and cooling through it again, leads to the initial domain state again.

The values of the ME coupling constant $\alpha = 10^{-7} - 10^{-8} \text{ s m}^{-1}$ recorded in our epitaxial heterostructure significantly exceed the values obtained in single phase materials, i.e. $\text{Cr}_2\text{O}_3$ ($4.1 \cdot 10^{-12} \text{ s m}^{-1}$) [60] or $\text{Tb}_2(\text{MoO}_4)_3$ ($\sim 10^{-9} \text{ s m}^{-1}$) [61]. Our largest value $\alpha = 2.3 \cdot 10^{-7} \text{ s m}^{-1}$ is a factor of 100 larger than for $\text{Tb}_2(\text{MoO}_4)_3$, clearly demonstrating the advantage of two phase strain coupled ME interaction.

Our measurements are the first to measure the effect of an applied electric field on the magnetisation in a two phase system directly. Most reports of ME effects in heterostructures report the converse effect, i.e. an induced voltage as a function of applied magnetic field ($E/H$). This makes it difficult to compare our

![Figure 7.5: Strain vs. eclectic field curve of a [001] oriented BTO crystal at RT. (from [52])]
values of $\alpha$ with other work on heterostructures. To establish values of $\alpha$ for absolute comparison requires knowledge of the relative dielectric permittivity $\varepsilon$. The best value of $\Delta E/\Delta H = 4800$ mV cm$^{-1}$ Oe$^{-1}$ [12] was obtained with laminated Pb(Zr,Ti)O$_3$/terfenol-D, and taking e.g. $\varepsilon = 300$ for a typical film of Pb(Zr,Ti)O$_3$ gives $\alpha \sim 10^{-8}$ s m$^{-1}$. Thus, our results of the epitaxial heterostructure LSMO-BTO presents an order of magnitude improvement over values associated with two phase systems with clean and sharp ME switching.
Chapter 8

Summary and future work

*I may not have gone where I intended to go,
but I think I have ended up
where I intended to be.*
Douglas Adams (1952 - 2001)

This thesis describes an experimental study of an epitaxial heterostructure La$_{0.67}$Sr$_{0.33}$MnO$_3$ on BaTiO$_3$ and characterises the coupling effects in this system. The multiferroic BTO-LSMO exhibits strong coupling of ferroelectricity and magnetism through the heteroepitaxy of the two lattices. A manipulation of strain obtained via structural phase transitions or an electric field (ferroelectric domain rotation) can change the film magnetisation significantly. The lattice changes in the BTO substrate couple directly to strain changes in the LSMO film. The use of BTO is particularly attractive here because over a wide range of temperatures it displays large (1%) piezoelectric strains associated with ferroelastic non-180° domains, both of which are not present in all ferroelectric materials. Furthermore, the presence of in-plane ferroelectric domains facilitates the electric field induced strain changes and therefore poled BTO (which is much more expensive than un-poled) is not required. Similarly, LSMO is suitable as the ferromagnetic constituent, since the magnetic properties of these films are extremely sensitive to in-plane strain.

It has been shown in this system, that at the phase transitions of BTO (199 K and 295 K), huge changes in magnetisation occur via ferroelastic strain changes induced by the substrate. Upon that, a new approach towards two phase multiferroics with giant and persistent magnetoelectric effects at room temperature.
has been demonstrated by applying a small electric field (4-10 kV cm$^{-1}$) along the [001] direction of the BTO substrate. A specially designed VSM sample holder enables direct measurements of magnetisation as a function of applied electric field. Giant and discrete switching of up to 65% in magnetisation can be attributed to the induced strain in the LSMO film due to ferroelastic non-180° domain rotation in the BTO substrate. The coupling requires an in-plane component of the strain. This occurs here as the $c$-axis of the non-180° domains in the BTO substrate rotate from in-plane to out-of-plane. We presume, that this strain is a combination of piezostriction and ferroelasticity. Unlike ME effects observed in most single phase multiferroics, the change in the magnetisation is persistent. The corresponding value of the magnetoelectric coefficient is not only a improvement compared to existing single and two phase systems, but it corresponds to a large ME switching in small electric fields over a wide range of temperatures including room temperature. Our results show that an epitaxial bilayer of LSMO on a BTO substrate is a simple solution for a two phase system with a large ME effect. It is simple to fabricate and offers an easy control mechanism due to the significant elastic strain-mediated coupling between the two ferroic components.

8.1 Future work

Further work should be carried out to obtain more reproducible and quantitative results. A full characterisation of the LSMO-BTO system should include in situ magnetic domain observation to verify the magnetisation rotation and in situ XRD as a function of electric field at various temperatures to investigate ferroelastic changes of both the BTO and LSMO lattice parameters.

A device fabricated with thin films of BTO and LSMO could also permit the investigation of the converse effect, whether an applied magnetic field could lead to changes in the polarisation. This converse effect has been studied in an epitaxial PZT film on a La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ substrate [62, 63]. A large ME effect was indeed found near the transition temperature (105 K) of the substrate. Since the PZT film was fully $c$-oriented, non-180° domains were not present and the coupling is thus not equivalent to the coupling described in this thesis. Epitaxial BTO films can contain non-180° domains, depending on thickness [64] and deposition conditions [65]. It has been shown that the application of a compressive
stress can indeed lead to the formation and growth of non-180° domains in single crystal BTO [66], showing that the converse effect might indeed be possible. Thus, a multilayer structure of BTO-LSMO-BTO is promising for observations of the converse coupling effect via an applied magnetic field.

8.2 Possible applications

According to our results, promising applications include actuators and sensors, but the biggest potential application of multiferroics is in data storage devices. Conventionally, information has been stored in ferromagnetic or ferroelectric layers with read/write cycles performed by magnetic or electric fields respectively. Using the ME effect that exists in multiferroics, data in ferromagnetic layers could be written or reorientated by an electric field. This could lead to closer spaced data elements, improving capacity and possibly improving data transfer rates as well [67].

The multilayer approach to multiferroics not only has promise for technological applications, but also contains exciting new physics. It is our hope that the structures we have made and continue to improve will be multifunctional and versatile in the next generation of electronic devices.
Declaration / Erklärung

I hereby declare that this diploma thesis was composed by myself and all work included has been done by me, except where otherwise stated. Other sources are acknowledged by giving explicit references. This work has been carried out in the Department of Materials Science and Metallurgy, University of Cambridge, U.K. from April till September 2006.


Weissenhorn,

.................................................................
Date, Signature
Datum, Unterschrift
References


REFERENCES


