

PULSED-LASER DEPOSITION OF $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ EPITAXIAL THIN FILMS

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PULZNO-LASERSKO NANAŠANJE EPITAKSIALNIH TANKIH
PLASTI $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3$

Doktorska disertacija

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Abstract

(1- x)Pb(Mg_{1/3}Nb_{2/3})O₃- x PbTiO₃ (PMN-PT) thin films with three compositions ($x = 0.25$, $x = 0.33$ and $x = 0.40$) close to the morphotropic phase boundary (MPB) were grown on SrTiO₃ (STO) substrates by means of pulsed-laser deposition. Motivated by the higher potential power output of the d_{33} -mode energy-harvesters (EHs), the first part of the thesis is focused on the growth of PMN-PT ($x = 0.33$) thin films directly on STO substrates. Due to Pb-loss, pyrochlore-free growth could not be realized using a stoichiometric target. Therefore, Pb-rich targets were prepared in order to find the exact amount of Pb excess required for the growth of pure-perovskite films. I found that the addition of 20 mol. % was sufficient to ensure single-phase growth; however, the process window was extremely narrow, particularly regarding the substrate temperature and ambient pressure. X-ray diffraction measurements revealed a splitting of the PMN-PT peaks in the film prepared at 0.13 mbar. I found that the splitting was related to a high density of structural defects, such as out-of-phase boundaries (OPB), which was determined by atomic-resolution scanning-transmission electron microscopy. I have managed to significantly reduce the defect density by raising the process pressure to 0.27 mbar. By conducting an experiment with an Ar/O₂ mixture I showed that the total ambient pressure, rather than the partial pressure of oxygen, was the determining factor for the structural quality of the layers. I argued that for the given system a transition in the plasma plume expansion regime occurs between 0.13 mbar and 0.27 mbar. I achieved a twofold increase of the relative dielectric permittivity and the longitudinal piezoelectric response upon raising the process pressure to 0.27 mbar. Nevertheless, both films were found to grow in a combined 2D and 3D manner, forming Ruddlesden-Popper-type (RP-type) defects between the as-grown islands, to compensate for the small surplus of Pb. A slight Mg-deficit was also observed. I achieved a vast expansion of the process window by growing the films on LaNiO₃ (LNO) bottom electrodes, which is the focus of the second part of the thesis. Based on the results obtained by using other types of intermediate layers, I attributed the improved stability of the perovskite phase to the higher surface roughness of the LNO/STO system as compared to the bare STO substrates. The increased roughness improves the sticking probability for PbO, thereby suppressing the formation of the pyrochlore phase. Therefore, I selected the substrates with LNO electrodes for further investigations regarding the influence of the target composition on the structure and properties of the PMN-PT films. Due to the Mg deficit observed in films grown from targets with only PbO excess, I also used targets with both PbO and MgO excess. The film prepared from the target with 20 mol. % PbO and 10 mol. % MgO was very close to stoichiometric, its formula being $\text{Pb}_{1.04 \pm 0.01} \text{Mg}_{0.203 \pm 0.004} \text{Nb}_{0.44 \pm 0.01} \text{Ti}_{0.33 \pm 0.01} \text{O}_3$. As the perovskite ABB'B'O₃ structure is unable to accommodate the surplus of Pb on the A site, additional PbO layers are grown, forming RP-type defects. The improved overall stoichiometry of the film, as well as the slightly larger crystallite size are believed to be responsible for the superior piezoelectric properties of this film, with a $|d_{33,eff}^{max}|$ of 135 pm V⁻¹. Comparison of the films with a different PT content showed that the piezoelectric response in films with $x = 0.33$ and $x = 0.40$ was similar, implying a broader region of enhanced response as compared to bulk PMN-PT.

Povzetek

S tehniko pulznega-laserskega nanašanja sem na substratih SrTiO_3 (STO) pripravila tanke plasti $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ (PMN-PT) s tremi sestavami ($x = 0,25$, $x = 0,33$ in $x = 0,40$) blizu morfotropne fazne meje (ang.: morphotropic phase boundary, MPB). Motivacija za prvi del disertacije, ki je osredotočen na pripravo tankih plasti PMN-PT ($x = 0,33$) neposredno na substratih STO, je v potencialno višji izhodni moči naprav za zbiranje energije (ang.: energy-harvesters, EH), ki delujejo v načinu d_{33} . Zaradi izgube Pb priprava plasti brez piroklora z uporabo stehiometrične tarče ni bila izvedljiva. Za ugotavljanje natančne količine prebitka Pb, ki je potrebna za pripravo plasti z izključno perovskitno fazo, smo pripravili tarče, bogate s Pb. Ugotovila sem, da je dodatek 20 mol. % zadostoval za zagotovitev enofazne rasti, vendar je bilo procesno okno izjemno ozko, predvsem z ozirom na temperaturo substrata in tlak. Meritve z uklonom rentgenskih žarkov so razkrile cepitev vrhov PMN-PT pri plasteh, pripravljenih pri 0,13 mbar. Ugotovila sem, da so cepitve povezane z visoko gostoto strukturnih napak, kot so izven-fazne meje (ang.: out-of-phase boundaries, OPB), kar smo pokazali z uporabo vrstične-presevne elektronske mikroskopije z atomsko ločljivostjo. Z zvišanjem procesnega tlaka na 0,27 mbar mi je uspelo znatno zmanjšati gostoto napak. S pripravo plasti z uporabo mešanice Ar/O_2 sem pokazala, da je celokupni tlak, in ne parcialni tlak kisika, odločujoč faktor za strukturno kakovost plasti. Ti rezultati nakazujejo, da pri dotičnem sistemu obstaja prehod v režimu razširjanja plazme med 0,13 mbar in 0,27 mbar. Z zvišanjem procesnega tlaka na 0,27 mbar sem nadalje dosegla dvojno povečanje relativne dielektričnosti in longitudinalnega piezoelektričnega odziva. Ugotovila sem, da kljub temu obe plasti rasteta v kombiniranem 2D in 3D načinu, pri čemer nastajajo med otoki napake tipa Ruddlesden-Popper (RP), da se nadomesti majhen presežek Pb. Prav tako sem opazila rahel primanjkljaj Mg. Opazila sem, da se je procesno okno močno razširilo, ko sem plasti nanese na spodnje elektrode LaNiO_3 (LNO), kar je osrednja tema drugega dela disertacije. Z ozirom na rezultate, dobljene pri uporabi drugih tipov vmesnih plasti, sem izboljšano stabilnost perovskitne faze pripisala višji grobosti površine v sistemu LNO/STO v primerjavi z golimi substrati STO. Povečana grobost izboljšuje verjetnost vezave PbO na površino, s čimer je zavrt nastanek piroklorne faze. Iz tega razloga sem za nadaljnje raziskave, povezane z vplivom sestave tarč na strukturo in lastnosti plasti PMN-PT, izbrala substrate z elektrodami LNO. Z ozirom na primanjkljaj Mg, ki sem ga opazila pri plasteh, pripravljenih iz tarč, ki so vsebovale zgolj prebitek PbO, sem uporabila tudi tarče s prebitkom tako PbO kakor tudi MgO. Sestava plasti, pripravljene iz tarče z 20 mol. % PbO in 10 mol. % MgO, je bila zelo blizu stehiometrični, s formulo $\text{Pb}_{1.04 \pm 0.01}\text{Mg}_{0.203 \pm 0.004}\text{Nb}_{0.44 \pm 0.01}\text{Ti}_{0.33 \pm 0.01}\text{O}_3$. Perovskitna struktura $\text{AB}_2\text{B}'\text{O}_3$ ne dopušča vgraditve presežnega Pb na mestu A. Tako tvorijo nastale dodatne plasti PbO napake tipa RP. Za izboljšan piezoelektrični odziv ($|d_{33,eff}^{max}| = 135 \text{ pm V}^{-1}$) te plasti je verjetno odgovorna izboljšana celokupna stehiometrija plasti, skupaj z rahlo večjo velikostjo kristalitov. Primerjava plasti z različno vsebnostjo PT je pokazala, da je bil piezoelektrični odziv v plasteh z $x = 0,33$ in $x = 0,40$ podoben, kar nakazuje na širše območje izboljšane odziva v primerjavi z volumnim PMN-PT.

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Abbreviations

2D	...	two-dimensional
3D	...	three-dimensional
ABF	...	annular bright field
AFM	...	atomic force microscopy
DBLI	...	double-beam laser interferometer
EH	...	energy harvesting/er
FOM	...	figure-of-merit
FWHM	...	full width at half maximum
HAADF	...	high-angle annular dark field
HR-TEM	...	high-resolution transmission electron microscopy
HR-XRD	...	high-resolution X-ray diffraction
HV	...	crossed-polarized
IDE	...	interdigitated electrodes
IP	...	in-plane
LNO	...	lanthanum nickelate
LPFM	...	lateral piezoresponse force microscopy
MD	...	misfit dislocation
MEMS	...	micro-electro-mechanical system
ML	...	monolayer
MPB	...	morphotropic phase boundary
OP	...	out-of-plane
OPB	...	out-of-phase boundary
PFM	...	piezoresponse force microscopy
PNR	...	polar nanoregions
PLD	...	pulsed-laser deposition
PZT	...	lead zirconate titanate
PMN-PT	...	lead magnesium niobate lead titanate
PPC	...	parallel-plate capacitor
RC	...	rocking curve
RHEED	...	reflection high-energy electron diffraction
RSM	...	reciprocal space map
SC	...	single-crystal
SF	...	stacking fault
SOI	...	silicon-on-insulator
SRO	...	strontium ruthenate
STO	...	strontium titanate
STEM	...	scanning transmission electron microscopy
SEM	...	scanning electron microscopy
SF	...	stacking fault
TEC	...	thermal expansion coefficient
TEM	...	transmission electron microscopy
VPFM	...	vertical piezoresponse force microscopy
WDXS	...	wavelength-dispersive X-ray spectroscopy
XRD	...	X-ray diffraction

Chapter 1

Introduction

1.1 Functional Perovskite Oxides

Metal oxides with a perovskite crystal structure (ABO_3) are the key enabler for numerous important technologies, and are recognized for their potential as next-generation macro-, micro- and nano-electronic materials. They offer scientists and engineers a theme park of exciting new physics with intricate structure–property relations and a plethora of useful phenomena. They represent potential candidates to partially replace silicon and introduce complexity to solid-state technologies, including energy conversion, communication technologies, and microsensing/microactuation. Although Si-based technologies have achieved extraordinary success in the last century, international technology roadmaps point to new concepts and functionalities that the physics and chemistry of Si is unable to support. Numerous oxide properties are sensitive to strain, temperature, electric and magnetic fields. Specifically, perovskite oxides have been shown to exhibit record-high dielectric, ferroelectric and piezoelectric performances [1], colossal magnetoresistance [2], half-metallic and multi-ferroic properties [3], [4], resistive switching behavior, high-temperature superconductivity, giant magneto-caloric and thermoelectric effects, giant photoconductivity effects [5], giant ionic conduction and catalytic properties, field-induced Mott transitions, and topologically nontrivial behavior [6], [7].

For a given parent compound, a rich phase diagram is colored-in by the substitution of the A- and/or B-site cations. The term “morphotropic” that was originally coined in reference to phase transitions due to changes in composition has come to be used mostly for morphotropic phase boundaries (MPBs) that separate the regions of rhombohedral and tetragonal symmetry induced by compositional variation (mainly substitution of B-site cations) in ferroelectrics [8]. Oxides with MPB compositions have been found to exhibit interesting and highly useful behavior [1]. The broad range of functionalities can be further extended by preparing the materials in thin-film form.

1.1.1 Thin-film perovskite functional oxides

Owing to their rich physical phenomena, epitaxial complex oxide thin films have attracted enormous attention in both academia and the industry. The physical properties of these materials are highly sensitive to the chemical composition, crystal structure and defect structure, due to the strong coupling among charge, orbital, spin and lattice [9]–[11]. Advances in the epitaxial growth of thin films bring unprecedented possibilities of atomic engineering of these oxides and the interfaces they form with other materials. This brings exciting prospects of unravelling the underlying physics and transferring the knowledge into practical applications. Owing to their intrinsic chemical and crystal-structure similarities, functional oxides can be stacked in multilayer structures, exhibiting an astounding degree of epitaxial perfection. Thin-film strain engineering is a well-established method to enhance the material properties. Through strain engineering, certain ground states that would otherwise be unattainable become energetically preferred. This is conventionally accomplished through coherent epitaxy by using substrates, which have a similar crystal structure, but exhibit a lattice mismatch with the film. The lattice mismatch for a simple [001] out-of-plane (OP) oriented cubic unit cell is defined in Equation 1.1:

$$m = \frac{a_L^R - a_S}{a_S} \quad (1.1)$$

where m is the lattice mismatch, a_L^R is the lattice constant of the relaxed layer (i.e. the material's bulk lattice constant) and a_S is the lattice constant of the substrate. The lattice mismatch between the substrate and the film in hetero-epitaxial growth gives rise to biaxial strain. This results in elastic energy, which grows with increasing layer thickness. If the layer exceeds the critical thickness, the interface strain stemming from the lattice mismatch is released via the formation of misfit dislocations at the substrate–film interface [12]. Therefore, for relaxed layers, alternative strategies to accessing different strain states have been proposed, such as utilizing the difference in thermal expansion coefficients (TEC) between the substrate and the film [13]. The thermal strain ($\varepsilon_{\text{thermal}}$) is calculated using Equation 1.2:

$$\varepsilon_{\text{thermal}} = \int_{T_1}^{T_2} (\alpha_{\text{film}} - \alpha_{\text{substrate}}) dT \quad (1.2)$$

where T_2 is the deposition temperature and T_1 is the room temperature, and α_{film} and $\alpha_{\text{substrate}}$ are the TEC of the film and the substrate, respectively. The domain structure and the fractions of a polydomain state are influenced by the combined effects of the lattice and thermal expansion coefficient (TEC) mismatches between the film and the substrate, the structural phase transformation and the possibility of strain relaxation via the formation of misfit dislocations at the growth temperature [14].

Recently, alternative mechanisms of strain engineering have been proposed. It has been shown [15] that the deposition temperature has a critical impact on the growth kinetics and thermodynamic balance in PLD-derived BaTiO₃ epitaxial thin films. The temperature affects the strain in the BaTiO₃ polar axis, which has been demonstrated to exceed 2% in films thicker than 100 nm. This shows that the deposition temperature can be utilized as an efficient tool for tailoring the ferroelectric polarization. A similar approach was used by Zhang et al. [13] to continuously tweak the strain in STO films on Si by establishing an adsorption–controlled growth window. Unfortunately, the growth of PMN-PT does not allow for such temperature variations due to the thermodynamic instability of the perovskite phase relative to the pyrochlore phase. Residual stress, which is common in energetic techniques such as PLD, can be used to modify the lattice parameters of epitaxial thin films [16].

Thin films can be grown using a variety of techniques, which are classified into two main categories, depending on whether the process is primarily chemical or physical. In the former case, the films are deposited via a chemical reaction between the hot substrate and inert gases in the chamber. Depending on the phase of the precursor, chemical deposition is further classified into spin coating, chemical vapor deposition and atomic layer deposition. In physical deposition, the raw materials, which can be in either vapor, liquid or solid phase, are released and physically moved to the substrate surface. Examples of physical deposition techniques include molecular beam epitaxy, sputtering, thermal evaporation and pulsed laser deposition [16]. The latter, being the technique used in this work, will be presented in more detail in Section 3.2.2.

1.1.2 Piezoelectrics

Piezoelectrics are a group of materials in which polarization can be produced by application of mechanical stress. Alternatively, upon application of an electric field, the piezoelectric material will change its shape, as shown in Figure 1. In piezoelectrics, the electric, elastic and thermal parameters are coupled through different relationships that can be deduced from thermodynamics. The direct effect is described by $D_i = P_i = d_{ij} T_j$, where D is the electric charge displacement, P is the induced polarization, d is the piezoelectric coefficient and T is the mechanical stress. The subscripts i and j are matrix notations. The converse effect is

described by $S_j = d_{ij}E_i$ where S is the induced strain, d is the piezoelectric coefficient and E is the electric field. In total, there are four piezoelectric coefficients: d_{ij} , e_{ij} , g_{ij} and h_{ij} . We will focus on the first two coefficients, which are defined by Equations 1.3 and 1.4:

$$d_{ij} = \left(\frac{\partial D_i}{\partial T_j} \right)^E = \left(\frac{\partial S_i}{\partial E_j} \right)^T \quad (1.3)$$

$$e_{ij} = \left(\frac{\partial D_i}{\partial S_j} \right)^E = \left(\frac{\partial T_j}{\partial E_i} \right)^S \quad (1.4)$$

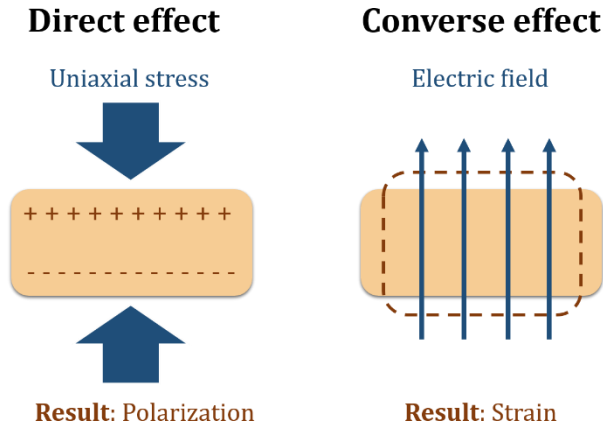


Figure 1: A schematic representation of the direct and converse piezoelectric effect.

If the sample is not mechanically restricted, the strain is caused by pure piezoelectric effect. On the other hand, if the sample is clamped (like a thin film on a thick substrate), the strain is a sum of the piezoelectrically induced strain and the mechanical strain imposed by the substrate [17]. The physical properties of piezoelectric thin films depend on several other parameters, such as secondary phases, composition, dopants, interface layers, crystalline structure, orientation, misfit strain, internal stress, film thickness and microstructure, etc.

1.1.3 From ferroelectrics and relaxors to relaxor-ferroelectrics

Among all known piezoelectrics, perovskite ferroelectrics exhibit the highest electromechanical activity. Ferroelectrics, such as PT, are polar materials with at least two equilibrium directions of the spontaneous polarization in the zero-field condition. Furthermore, the polarization directions can be switched via the application of an electric field. The direction of spontaneous polarization in a ferroelectric material is usually not uniformly aligned within a crystal (or a grain). Spontaneous polarization may arise with equal probability in any of the equivalent directions as dictated by the crystal symmetry of the material. In tetragonal materials there are six equivalent ferroelectric domains, in rhombohedral there are eight, and so forth. The polarization direction is dictated by the electrical and mechanical boundary conditions imposed on the material. Individual regions with a uniform spontaneous polarization direction are named ferroelectric domains. The boundary that separates two neighboring domains is called a domain wall [17]. The enhanced piezoelectric response of ferroelectrics is generally attributed to long-range cooperative phenomena near the MPB, as in this region different ferroelectric phases possess similar energies, which facilitates the variation of strain and polarization under external stimuli [18].

There has been considerable interest in ferroelectric materials, properties and devices over the past few decades. Problems related to applications of these materials have driven

intensive research of the fundamental properties of ferroelectric materials. Up to the 2000's, the large majority of the considered applications was based on ceramics and polycrystalline thin films, due to the ease of production and a larger variety of possible modifications as compared to single crystals. The downside of polycrystalline ferroelectrics lies in the fact that their properties are often strongly influenced by extrinsic contributions, whose theoretical treatment is highly challenging [17]. The advantages of epitaxial thin films over their polycrystalline counterparts lie in a lower leakage current and a higher piezoelectric response [19].

A common structural property of relaxors, such as PMN, is their compositional disorder, i.e. the disorder in the arrangement of the different ions at crystallographically equivalent sites. The ions are also off-centered, leading to the appearance of a polar distortion. At high temperatures, the off-centered ions switch freely between their positions, leaving the time average structure cubic. Upon lowering the temperature, their positions and motions become correlated and give rise to the formation of polar nanoregions (PNRs) [20]. Relaxors are distinguished from conventional ferroelectrics by a lack of a macroscopic phase transition. They are recognized by their broad, high and frequency dependent maximum in the dielectric permittivity over a wide temperature range. In spite of their polar character, they are optically isotropic. Ferroelectric hysteresis appears well below the temperature of the dielectric maximum, at the so-called freezing temperature (T_f). The Burns' temperature (T_B) is the temperature below which PNRs start to form. Their formation is conjectured from e.g. the non-linearity in the thermal expansion and refractive index [21].

Relaxor-based materials are more difficult to nucleate and grow. As the growth temperatures for relaxor thin films are relatively lower than bulk synthesis temperatures, the disordered B-site ions are not homogeneously distributed, leading to a lower dielectric permittivity. The high strain response of relaxors does not necessarily translate directly into stress response, because relaxors are soft [22].

PMN-PT therefore represents a relaxor-ferroelectric solid solution. Relaxor-ferroelectrics exhibit numerous interesting and useful phenomena, one of which is their exceedingly high piezoelectric response.

1.1.4 Ultra-high piezoelectricity in relaxor-ferroelectric solid solutions

Lead-based relaxor-ferroelectrics exhibit exceptional electromechanical coupling and high relative dielectric permittivities with weak temperature dependencies, which are desirable in many applications. Among the most remarkable breakthroughs in relaxor-ferroelectrics was the discovery of giant piezoelectricity and electromechanical coupling factors in relaxor-PT compounds with MPB compositions. Several qualitative mechanisms have been proposed to explain this unusually high piezoelectric response:

- Electric field induced phase transition [23],
- A monoclinic intermediate phase, which facilitates polarization rotation [24],
- Giant electromechanical response as a critical phenomenon [25] and
- Adaptive ferroelectric state [26].

Recently, the critical role of the electric-field-driven polarization rotation in the monoclinic plane on the performance of perovskite piezoelectrics has been revealed. It has been found that a strong tendency of the electric-field-driven polarization rotation causes peak piezoelectric performance and vice-versa. Additionally, it has been demonstrated that the monoclinic M_c structure is the main player in achieving the superior piezoelectric properties. A high piezoelectric response thus originated from the intrinsic lattice strain, with little contribution from extrinsic domain switching [27].

Nevertheless, these mechanisms have failed to explain the significantly higher piezoelectricity of relaxor-ferroelectrics, compared to conventional ferroelectrics such as $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT). Although a strong consensus exists on the coupling of the exceptional properties of Pb-based relaxor ferroelectrics and local symmetry breaking, the nature of the disordered ground states has been a controversial subject. Li et al. [18] have determined that the contribution of the PNRs to the room-temperature dielectric and piezoelectric response is in the range of 50–80%. It was argued that the PNRs aligned in a ferroelectric matrix can facilitate polarization rotation. The transverse dielectric and shear piezoelectric

properties are substantially higher than their longitudinal counterparts, thereby playing a dominant role in the extraordinary electromechanical performance of relaxor-PT crystals [18]. It is important to note that the high longitudinal piezoelectric coefficients reported in domain-engineered relaxor-PT crystals originate from the high shear piezoelectric coefficients in the corresponding single-domain state.

1.1.5 PMN-PT: bulk and thin-film

Crystalline solid solutions $(\text{PMN})_{1-x}(\text{PT})_x$ are formed for all PMN:PT ratios. The electromechanical properties of both endmembers are relatively poor, however, close to the MPB the response is anomalously large [28]. Depending on the chemical composition, PMN-PT undergoes several structural transitions with temperature. With the increasing PT content, the Curie temperature (T_C) increases. Although the nature of the MPB is still a subject of debate in the literature, a consensus seems to have emerged regarding the existence of a sequence of second-order phase transitions around the MPB, which allow for easy rotation of the polarization vector [24]. At $x = 0$, PMN-PT is in a non-ferroelectric, cubic symmetry, which transforms into a highly strained ferroelectric, tetragonal symmetry at $x = 100$. In lead-based perovskites, due to the strong orbital hybridization between the Pb $6s$ and the O $2p$ states, tetragonal or rhombohedral phases are favored, while the orthorhombic phase is suppressed [29]. It has been shown that the energy balance between the different crystal phases in PMN-PT is intrinsically more delicate than of related solid solutions exhibiting an MPB (e.g. PZT). The transition between the rhombohedral and tetragonal phase occurs via at least one monoclinic phase, which serves as a structural bridge between the two end-member phases. Noheda et al. [30] have observed an M_C -type monoclinic phase using high-resolution synchrotron X-ray powder diffraction. The proposed phase transition sequence together with the lattice parameters, is shown in Figure 2a). The notation M_C was introduced by Vanderbilt and Cohen [31], according to which this is one of the three known monoclinic phases, along with the M_A and M_B phase. Their unit-cell distortions along with the polarization vectors are shown in Figure 2b). The M_A and M_B phase (space group Cm) bear a large resemblance to the rhombohedral $R3c$ phase. They have a doubled unit cell, rotated by 45° about the c axis with respect to the pseudocubic cell, and the polarization vector lies in the $(1\bar{1}0)$ plane. The two phases differ in the magnitudes of the polarization components in the three axes directions corresponding to the pseudocubic unit cell. The structure of the M_C phase, on the other hand, is similar to that of the tetragonal phase. It belongs to the space group Pm and its polarization vector lies in the (010) plane. The two types of monoclinic phases can be distinguished by X-ray reciprocal space mapping (RSM). For example, the $h0l$ reflections split into two peaks for the M_A phase, while they split into three for the M_C phase. Singh et al. [32] proposed a new phase diagram for PMN-PT with two monoclinic phases, M_B and M_C .

Thin-film boundary conditions, such as substrate clamping can modify the position of the MPB. A wider compositional range of the MPB is usually observed in thin films as compared to bulk materials. This phenomenon is ascribed to the higher Gibbs free energy density in the case of epitaxial thin films on cubic single-crystal substrates [33]. Owing to its complexity, the exact crystal and domain structure of PMN-PT thin films at the MPB has not yet been elucidated.

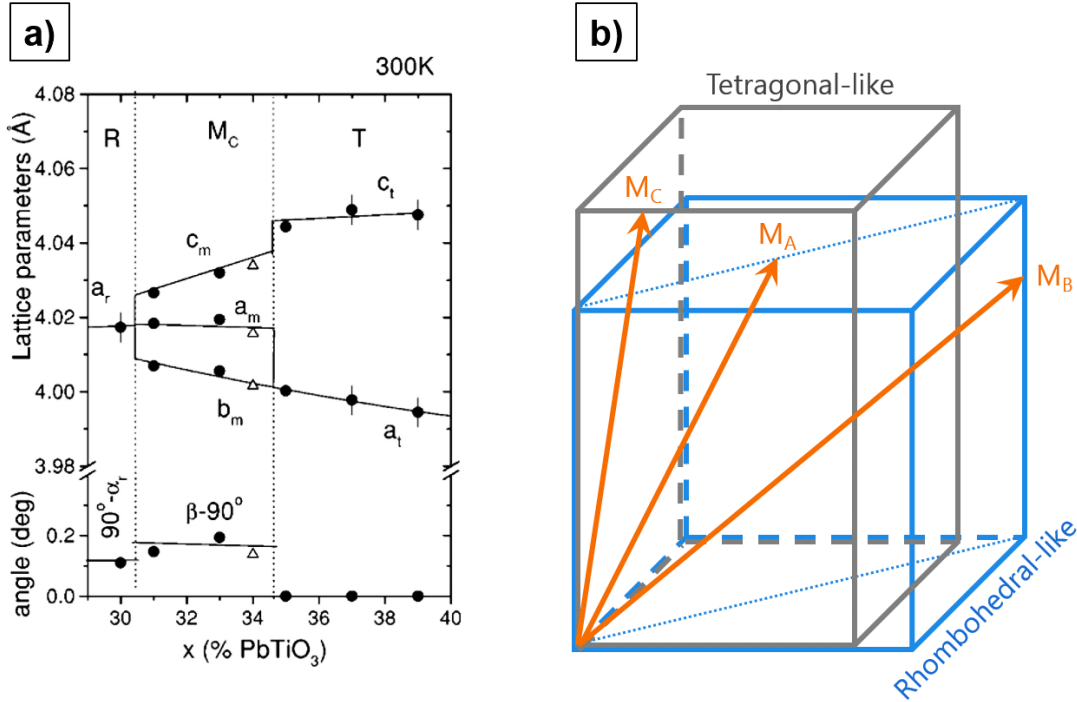


Figure 2: a) Lattice parameters of PMN-PT around the MPB [30]. b) Different proposed monoclinic variants.

Due to the chemical complexity of the PMN-PT solid solution, its growth is extremely challenging. Small deviations in the stoichiometry can lead to the formation of parasitic pyrochlore phases [34], [35]. The variation in stoichiometry is mainly a consequence of Pb- and Mg-loss during the material preparation procedure. While the widely adopted columbite procedure [34] and modified Bridgman technique [36] present a clear mechanism for the suppression of the pyrochlore phase in bulk ceramics and single crystals, respectively, the approaches to obtaining the correct stoichiometry in thin films described in the literature are rather vague. Pb-rich targets are often used to compensate the Pb-loss in PLD-growth (Figure 3); however, it seems that often an arbitrary amount of PbO excess is added to the targets. Furthermore, owing to the sensitive nature of PMN-PT, the use of several characterization techniques that tend to be relatively straightforward requires additional consideration. Because of the overlapping signals, commonly used techniques, such as energy-dispersive X-ray spectroscopy cannot offer reliable information about the chemical composition [37]. The preparation of PMN-PT samples for TEM analysis has also been shown to be very delicate and can lead to misinterpretations regarding the stoichiometry and crystal structure [38], [39].

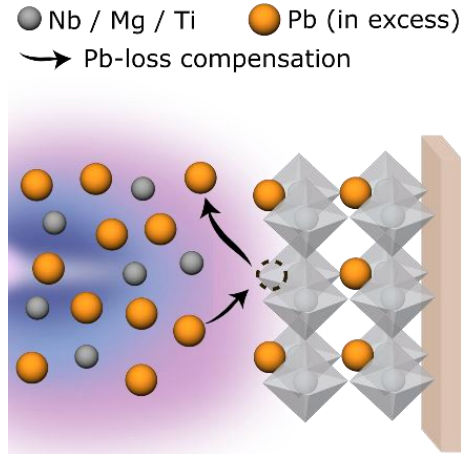


Figure 3: Schematic representation of the Pb-loss compensation mechanism.

PMN-33PT in single-crystal form has been shown to exhibit record-high longitudinal piezoelectric coefficient $d_{33} > 2500 \text{ pm V}^{-1}$, leading to strain levels up to 1.7%, along with high electromechanical coupling factor $k_{33} (> 90\%)$ and low dielectric losses ($< 1\%$) [23], [40]. The highest reported relative dielectric permittivity at constant stress is 8200 [40]. The first successful PLD-derived epitaxial PMN-PT thin films were grown by Maria et al. [41] using LaAlO_3 substrates. Thirteen years later, Baek et al. combined molecular beam epitaxy with radiofrequency magnetron sputtering to produce high-quality epitaxial PMN-33PT on STO-buffered silicon. A giant piezoelectric transverse coefficient $e_{31} = -27 \pm 3 \text{ C m}^{-2}$ was reported for the thin films in a cantilever configuration [42].

1.1.6 Applications of PMN-PT

It has recently been shown [43] that PMN-PT thin films can be utilized to harvest waste heat through pyroelectric energy conversion from low-grade thermal sources. The strong field- and temperature-induced polarization susceptibilities of PMN-PT are exploited here. The reported values are equivalent to the performance of a thermoelectric material with an effective $ZT \approx 1.16$ for $\Delta T = 10 \text{ K}$. The optimization of pyroelectric performance requires a suppression of the dielectric permittivity, while at the same time ensuring an independent enhancement of the pyroelectric coefficient. This is difficult to achieve in conventional materials, where the dielectric and piezoelectric susceptibilities are usually enhanced by the same generic features, such as the proximity to phase transitions driven by temperature, strain, chemistry, etc., such phase transitions are a hallmark of relaxor ferroelectric materials like PMN-PT. PMN-PT with an MPB composition is also a promising material for electro-optic applications, such as optical switches and waveguide modulators, due to its large electro-optic coefficient [44].

Giant electro-caloric response has also been observed in PMN-PT thin films with a low PT content [45]. PMN-10PT thin films have also been shown to exhibit a large recoverable energy density under high electric fields at room temperature, rendering them appropriate for energy-storage capacitor applications [46], [47].

1.1.6.1 Piezoelectric micro-electro-mechanical systems (MEMS) energy harvesters

The idea of MEMS was born as engineers wanted to improve the capabilities of integrated circuits based on Si technology by adding mechanical elements, which would be controlled by electronic signals. This opened up a much wider application range. Nowadays, the MEMS field has expanded even further by the notion of electro-mechanics, including chemical, biochemical, magnetic, optical, thermal and other functional properties. With the rapid development of new wireless sensors, wearable devices and even implantable electronics, the demand for small and durable power sources is becoming stronger and stronger. Standard electrochemical batteries are not keeping pace with these rapid advances.

Therefore, the energy-harvesting concept was proposed to power such standalone devices and systems. While energy sources, such as solar or wind energy are available and abundant outdoors, mechanical vibrations represent a viable source in indoor environments and remote locations. Mechanical vibrations are typically converted to electricity by exploiting electrostatic, electromagnetic induction or piezoelectric mechanisms. Among these, piezoelectric harvesters are most suitable for practical applications, due to superior energy densities produced. Owing to the inherent capability of piezoelectrics to directly convert strain into electrical energy, such devices are based on simpler architectures and can be fabricated with micromachining techniques and directly integrated into MEMS [48]. The produced power (up to the order of mW) is usually enough for powering most handheld devices and passive sensors. Compared to MEMS devices based on other physical principles, piezoelectricity also has the following advantages for application:

- Large actuation force and low operating voltage. Owing to the large piezoelectric coefficients of the active materials, large force actuation and large displacement can be achieved, especially by using the curvature of cantilever structures. Although low-voltage actuation switches have also been realized by implementing electrostatic actuation, such actuators lack the restoring force necessary for long cycle lifetimes.
- High efficiency and high quality factor Q . By optimizing the growth conditions, piezoelectric films with high piezoelectric coefficients, low dielectric losses and a high Q value can be achieved.
- Broad frequency range of operation. Shrinking the dimensions of MEMS devices offers the possibility to exploit different ambient frequencies. Using the non-linear part of the piezoelectric response the resonance frequency can be dynamically tuned via an application of a DC bias voltage.

The two main challenges to be addressed for high performance MEMS devices are the generated power and frequency bandwidth. The most important parameters concerning the active layers are the piezoelectric strain constants, the voltage constants and the electromechanical coupling factors. The first two are related via the dielectric permittivity, which is based on the ability of the material to store electric charge. The third parameter represents the effectiveness at converting mechanical energy into electrical energy. Under static conditions and at frequencies much lower than the resonant frequency, this parameter is directly related to the dielectric, piezoelectric and elastic properties of the material [48]. The figure-of-merit (FOM) for piezoelectric thin film material selection is presented in Equation 1.1. As it can be seen from this equation, the highest power output for MEMS energy harvesters can be generated by employing piezoelectric thin films with high $e_{31,eff}$ transverse piezoelectric coefficients and low dielectric permittivity [48].

$$FOM_{tf} = \frac{e_{31,eff}^2}{\epsilon_{33}^T} \quad (1.5)$$

PMN-PT exhibits a higher piezoelectric response as compared to the most widely known and implemented ferroelectric PZT, leading to a higher FOM_{tf} value. Furthermore, lower damping in PMN-PT-based devices leads to enhancement of the power output. It has been shown [49]–[51] by direct comparison that PMN-PT single crystals can substantially outperform those exploiting PZT ceramics. PMN-PT-based EHs showed better results in terms of voltage, as well as power output, and efficiency in both on-resonance and off-resonance conditions. The power output of PMN-PT-based devices was almost twice as high, despite PMN-PT having a higher Young's modulus and hardness. Applications of PMN-PT-based materials include flexible EHs for cardiac pacemakers [52], [53], cymbal-type EHs [54], PMN-PT/epoxy composites [55], and several others [56], [57]. Wide-range implementation of PMN-PT single crystals (and epitaxial thin films) is held back mainly by the complexity and cost of manufacturing. These are the main issues to be addressed, along with temperature instability, inhomogeneity and fatigue.

1.1.6.1.1 Different modes of EH operation

The two most common coupling modes for piezoelectric transducers are illustrated in Figure 4. The piezoelectric material is poled in the “3” direction. In the d_{31} mode, the charges are collected on the electrode surface, when a mechanical force is applied perpendicular to the poling direction. This structure is also referred to as the parallel-plate capacitor (PPC). In the d_{33} mode, an array of positive and negative electrodes, the so-called interdigitated electrodes (IDEs), is placed alternately on the film’s surface and the charges are collected on the electrode surface, when the piezoelectric is strained in parallel to the poling direction. Generally, the electromechanical coupling factor is higher in the d_{33} mode as compared to the d_{31} mode. Because of the poling directions, the d_{33} configuration is inappropriate for devices based on non-ferroelectric materials [29], [48]. Compared to PPC, the capacitance of a capacitor with IDEs is determined by a much larger number of geometrical parameters. Wang et al. [58] found that the electrode dimensions, spacing and number of “fingers” have different influences on the measured capacitance. Toprak et al. [59] presented a method for the optimization of parameters in IDE geometry to maximize the efficiency of such devices. They have shown that the efficiency can be improved by one order of magnitude for the specific modeled case. Kim et al. [60] reported that the use of IDEs results in a ten times higher voltage generation and similar power levels as in PPC-based devices. Note that these studies were performed on PZT-based systems or by implementing theoretical calculations. Given the demonstrated vast potential offered by the d_{33} -mode EHs, one of the focuses of this thesis is to study the growth and properties of PMN-PT thin films on an insulating template, such as STO. To my knowledge, a single literature report exists on the PLD-growth of PMN-PT directly on STO substrates [61]. The study lacks detailed structural analysis, and does not include any microstructural, chemical or electrical characterization.

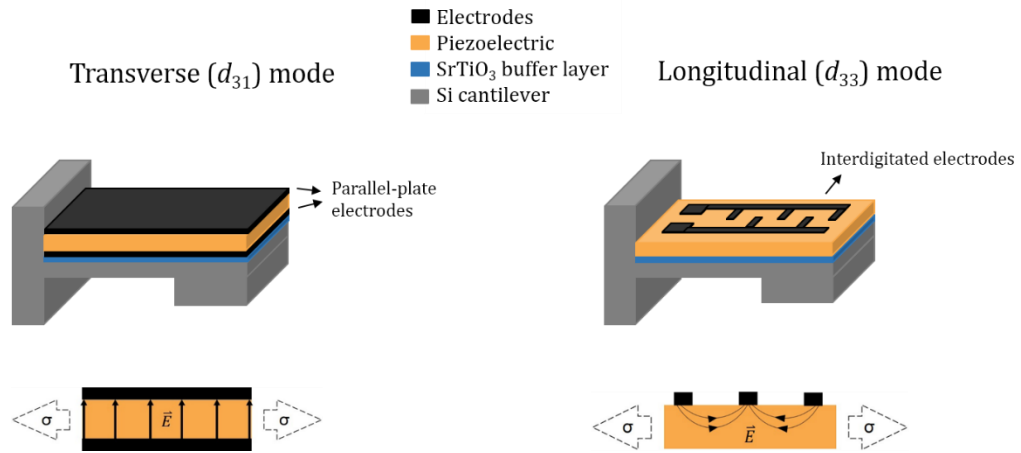


Figure 4: Capacitor geometries and principle of operation in d_{31} - and d_{33} -mode EHs.

Typically, top and bottom electrodes consisted of noble metals, such as gold or platinum. However, there are some downsides to using metallic electrodes, such as their high cost, limited processing options, strongly enhanced interdiffusion and inferior fatigue characteristics of the corresponding capacitors. Oxide electrodes can act as a sink for oxygen vacancies, thereby preventing their accumulation at the film/electrode interface. It has been shown [62] that LaNiO_3 (LNO) bottom electrodes can act as a seed layer for the growth of PMN-PT thin films on Si substrates, suppressing the formation of spurious phases and inducing a preferred orientation in the perovskite films. Compared to films grown on Pt bottom electrodes, the ferroelectric properties of the films grown on LNO are superior.

1.1.6.2 Integration of PMN-PT with Si

While oxide substrates enable the growth of high-quality epitaxial films, they are expensive, and owing to their brittle nature, they are not suitable for cantilever-type applications. Furthermore, monolithic integration with Si opens a route between oxide functionalities and microelectronics. In heteroepitaxy between oxides and semiconductors, in addition to the lattice and thermal mismatch, another factor that has to be accommodated is the transition between fundamentally different types of chemical bonds across the interface. Therefore, most functional oxides need to be grown on an oxide buffer layer, which can be grown epitaxially on Si. STO is one of the most commonly used buffer layers, along with yttria-stabilized zirconia. Both buffer layers have been grown by pulsed-laser deposition (PLD). As this thesis deals with the growth on PMN-PT on STO, we will focus on this approach. Firstly, it is important to note that Si is naturally coated with a thin layer of amorphous SiO_2 , which needs to be removed in order to obtain a clean, reconstructed Si surface, appropriate for oxide epitaxy [63]. This is normally done by flash annealing under ultra-high vacuum conditions; however, the resulting surface is thermodynamically unstable, when in contact with oxides. Therefore, an additional buffer layer needs to be prepared, in order to protect the interface from oxidation. Strontium silicide (SrSi_2) has proven to be the most suitable buffer [64]. At $\frac{1}{2}$ monolayer (ML) coverage, the Sr atoms assume positions between the Si dimer rows of the $(2 \times 1) + (1 \times 2)$ reconstructed surface, and inhibit the formation of an amorphous SiO_2 layer during subsequent growth of STO. The silicide can be formed by depositing metallic Sr or SrO on a clean Si surface. Alternatively, Sr or SrO can be deposited directly on the SiO_2/Si substrate at an elevated temperature. The deposited Sr or SrO will scavenge the oxide from the Si surface. The advantage of using SrO instead of Sr lies in the reduced reactivity of SrO, which allows for a simpler experimental set-up, rendering the procedure more industrially-appropriate. An oxide-free and atomically flat Si surface can be achieved using SrO-induced deoxidation [65], [66], which was the procedure used for the preparation of the Si surface in this work. The STO was then grown using the procedure from Díaz-Fernández et al. [67], [68], which enables the preparation of epitaxial STO on (001)-oriented Si by PLD.

Silicon-on-insulator (SOI) substrates were also used in this work. SOI is a structure, in which a layer of Si is separated from the bulk crystal by an insulating (SiO_2) layer. The thickness of the Si layer can be varied to suit a specific application. Likewise, the buried oxide thickness can also range from tens of nm to several μm . Two main manufacturing methods are used for the production of SOI wafers. The first is “bonded silicon on insulator” (BSOI), and the second is “separation by implantation of oxygen” (SIMOX) [69]. SIMOX SOI substrates were used in this work, due to their superior quality, as compared to wafer-bonded SOI. As described, the advantage of SOI substrates as compared to monolithic Si crystals is that they enable more complex device structures with precisely controlled layer thicknesses. The Si layer can be released by a simple etching procedure, producing a cantilever structure, such as the one used in e.g. EHs.

In the early stages, PZT and PMN-PT thin films on single-crystal substrates exhibited superior properties (e_{31}) as compared to those integrated on Si. Now, as the integration and seeding issues have largely been solved, films on Si have been shown to outperform the ones on single crystals [42]. A possible explanation for this is that in epitaxial thin films, the lattice is perfect, the film can be single c-domain. However, the ferroelastic domains do not cooperate in the response. The domain configuration is also different, because the single crystal substrates exhibit larger thermal expansion coefficients than Si [29].

Chapter 2

Aim and Hypothesis

2.1 Aim

The aim of this thesis was to gain an understanding of the growth mechanism of PMN-PT thin films deposited by PLD. A large part of published research on PMN-PT thin films is focused on improving its performance; however, the underlying science has not been holistically addressed. Detailed chemical and structural studies on the nano- to macroscopic scale, especially in conjunction with the processing conditions and functional properties, were lacking. Due to the complexity of the PMN-PT solid solution, the preparation of high-quality PMN-PT thin films is not straightforward. The main challenge is associated with the high vapor pressure of Pb, which demands a fast deposition regime in order to prevent excessive evaporation and consequently the formation of non-piezoelectric pyrochlore inclusions. Such a fast growth regime prevents the realization of a fully two-dimensional growth mode. This leads to the appearance of structural defects, which in turn adversely affect the electrical properties of the films. Additionally, excess quantities often need to be added to the PLD targets. However, the amount of PbO and MgO (rarely added) additions is quite scattered in the literature data; there is no comprehensive study on the compensation of the volatile constituents. In a large fraction of studies, an ideal $(1-x)\text{PMN}-x\text{PT}$ stoichiometry is assumed in the absence of pyrochlore. Few studies contain chemical characterization of the thin-film samples, and the techniques used are unreliable or the detailed results are not reported.

2.2 Hypothesis

The main hypothesis of this work was that by understanding the growth mechanism of the PMN-PT epitaxial thin films on STO substrates, it is possible to optimize the PLD growth, as to achieve a significant improvement of the structural and consequently functional properties of the films.

Hypothesis 1: The process window for producing high-quality PMN-PT thin films is extremely narrow.

Based on the available literature data and given the complexity of the PMN-PT solid solution, I expected that strict control over the deposition parameters will be necessary in order to ensure the growth of single-phase films a low defect concentration. There are several highly intertwined parameters that strongly influence the stoichiometry and crystalline quality of the films. Due to different absorption spectra of the constituents, it is important to adjust the energy density of the laser to ensure an even distribution of all components in the plasma plume. Because of the evaporation of Pb (and also Mg to a lesser extent) at high substrate temperatures, needed for obtaining PMN-PT with high crystalline quality, finding the optimal temperature is a challenging task. The evaporation dynamics can be controlled by adjusting the laser-pulse frequency. As PMN-PT is an oxide material, the partial oxygen pressure during the deposition also plays an important role in the film growth. Additionally, the total background pressure affects the dynamics of the plasma plume, which can affect the growth regime of the film.

Hypothesis 2: Despite meticulous optimization of the PLD parameters, the stoichiometry of the target is not preserved during the deposition, and some components need to be compensated for.

While generally speaking stoichiometric transfer is one of the main advantages of the PLD technique, for some multicomponent materials this is not necessarily the case. Literature concerning the growth of PMN-PT suggests that PbO and MgO additions are often necessary to compensate for the loss. Several questions arise here:

- Is it possible to completely replace the individual deficits by modifying the target composition?
- How much addition is necessary?
- It is known that Pb and Mg deficits can lead to pyrochlore formation. What about excess quantities of individual components? How are they accommodated within the structure?

As off-stoichiometry and the presence of other defects can affect the functionality of thin films, it is important to address these issues.

Hypothesis 3: The growth of PMN-PT thin films is strongly influenced by the underlying material.

Due to the large scattering of data in the literature regarding the growth conditions and the quality of the layers, I assumed that the underlying layers also play an important role in the stabilization of certain structures. A distinction is systematically made between films prepared on different single crystals; however, the role of the bottom electrode on the phase purity, crystal structure and functional properties is most commonly overlooked. Due to the different morphological, chemical and electronic characteristics of the different interfaces, I hypothesized that the nucleation and growth of the active layers are strongly affected by the underlying layer material.

Chapter 3

Experimental Work

3.1 Materials

Different types of (001)-oriented STO substrates that were used for the thin-film growth are shown in Table 1, along with the Si and silicon-on-insulator (SOI) substrates. The Si substrates were in fact a (111)Pt/TiO₂/SiO₂/Si heterostructure. The thicknesses were 150 nm, 20 nm and 300 nm for the Pt, TiO₂ and SiO₂, respectively.

Table 1: Substrate specifications.

Material	Dimensions	Miscut	Doping	Supplier
STO	10 × 10 × 0.5 mm ³	< 0.5°	none	SurfaceNet, Crystec
STO	10 × 5 × 0.5 mm ³	4°	none	SurfaceNet
STO	10 × 10 × 0.5 mm ³	< 0.5°	0.5 wt.% Nb	SurfaceNet, Crystec
(111)Pt/TiO ₂ /SiO ₂ /Si	5 × 5 × 0.5 mm ³	< 0.5°	<i>p</i> -type	INOSTEK
SOI	20 × 20 × 0.5 mm ³	< 0.5°	<i>p</i> -type	SINTEF

Deionized water and ammonium fluoride etching mixture (AF 875-125, VLSI purity grade, Honeywell), i.e. buffered hydrofluoric acid (BHF) were used for the preparation of TiO₂-terminated STO surfaces. The treated substrates were then cleaned with acetone and ethanol, and glued to the resistive heater using silver paint (Leitsilber 200, Ted Pella), which assured temperature uniformity across the surface.

The SRO (Beijing Goodwill Metal Technology Co.), LNO (SolMateS), ceramic stoichiometric PMN-33PT (SolMateS) and single-crystal STO (Plasmaterials) and PMN-33PT (CTG Advanced Materials) targets were obtained commercially. All targets containing an excessive amount of PbO and MgO were prepared in-house by means of solid-state synthesis. The starting materials were MgO (99.95%, Alfa Aesar), Nb₂O₅ (99.9%), TiO₂ (99.8%, Alfa Aesar) and PbO (99.99%, Alfa Aesar) powders. The targets were glued to stainless-steel target holders using base resin and hardener (Torr Seal, Varian), which are appropriate for vacuum applications. SiC papers were used to grind the surface of the targets in order to prepare a fresh surface prior to each ablation.

60-nm-thick Au electrodes were sputtered on the surface of the as-grown thin films using a shadow mask.

The bulk lattice parameters and TECs of all the materials are listed in Table 2.

Table 2: Bulk material parameters.

Material	a [Å]	b [Å]	c [Å]	V [Å ³]	PDF card	TEC [ppm K ⁻¹]
STO	3.905	3.905	3.905	59.55	00-035-0734	8.8 [70] – 11.1 [71]
SRO ¹	3.929	3.929	3.929	60.65	00-043-0472	10.3 [72]
LNO ¹	3.835	3.835	3.835	56.40	01-070-8027	8.2 [71] – 16.2 [73]
PZT (52/48) ²	4.077	4.077	4.077	67.76	01-080-7944	2-9 [74]
PMN-25PT	4.021	4.025	4.025	65.16	04-014-1573	2.0 ⁵ [75]
PMN-33PT ³	4.019	4.019	4.019	64.92	01-076-9083	2.8 ⁵ [75]
PMN-40PT ⁴	3.992	3.992	4.052	64.57	01-083-8176	4.4 ⁵ [75]
Si	5.431	5.431	5.431	160.19	00-026-1481	2.6 [70]

¹ Pseudocubic parameters.

² Crystallographic data for the $Pm\bar{3}m$ space group.

³ Crystallographic data for PMN-32PT.

⁴ Crystallographic data for PMN-39PT.

⁵ The TECs of PMN-PT were obtained by interpolation and extrapolation of the TECs in the given reference.

STO belongs to the $Pm\bar{3}m$ space group (cubic), SRO belongs to $Pnma$ (orthorhombic), LNO belongs to $R\bar{3}c$ (rhombohedral), and the space group of cubic Si is $Fd\bar{3}m$. Table 2 lists pseudocubic parameters for the SRO and LNO. As the PZT (52/48) and PMN-33PT compositions are at the MPB, several crystal structures can exist. In the table, the data for the tetragonal phase (space group $P4mm$) of PZT is given. A tetragonal (space group $P4mm$, 01-070-4060) and a monoclinic structure (space group Ia , PDF card number 01-074-7024) also exist. For PMN-33PT and PMN-40PT, no entries were found in the database, therefore, the data for the closest-matching composition are listed, i.e. for PMN-32PT and PMN-39PT, respectively. The PMN-25PT is monoclinic (space group Cm). The PMN-32PT is cubic (space group $Pm\bar{3}m$). A tetragonal structure (space group $P4mm$) was also found for the same composition (PDF card number 01-076-9082). The structure of PMN-39PT is tetragonal (space group $P4mm$). Where several similar PDF cards were found, the one with the highest (star) quality was selected.

The TEC of the different PMN-PT solid solutions given in Table 2 was calculated based on the data reported by Wongmaneeerung et al. [75] using interpolation and extrapolation of a second order polynomial, which yielded an R^2 value of 1.0. The TEC values for PMN-PT found in the literature are highly scattered, which is a consequence of the complex structure of PMN-PT. Furthermore, the TEC of PMN-PT is highly temperature-dependent, as it undergoes a non-ferroelectric – ferroelectric phase transition during heating/cooling. Similar applies to PZT. Maria et al. [41] reported that the TEC of PMN-PT is <1 ppm/°C at low T and 10 ppm/°C at high temperatures. Keech [76] presented the temperature dependence of the TEC of PMN-30PT, Si, STO. The data for the former three materials is presented in Figure 5. The measurement of Uršič et al. [77] yielded a TEC of 6.3 ppm K⁻¹ for PMN-35PT bulk ceramics. Sehirliouglu et al. [78] found that in an MPB single crystal the lower-temperature rhombohedral phase has a TEC of 4 ppm K⁻¹, while the TEC of the higher-temperature tetragonal phase is 14 ppm K⁻¹. Their measurements also revealed that despite the fact that all three $\langle 001 \rangle$ directions were indistinguishable by XRD, they were macroscopically inequivalent. A unique direction with different thermal strain characteristics compared to the remaining two directions was identified, and found to be related to the domain structure of the crystal.

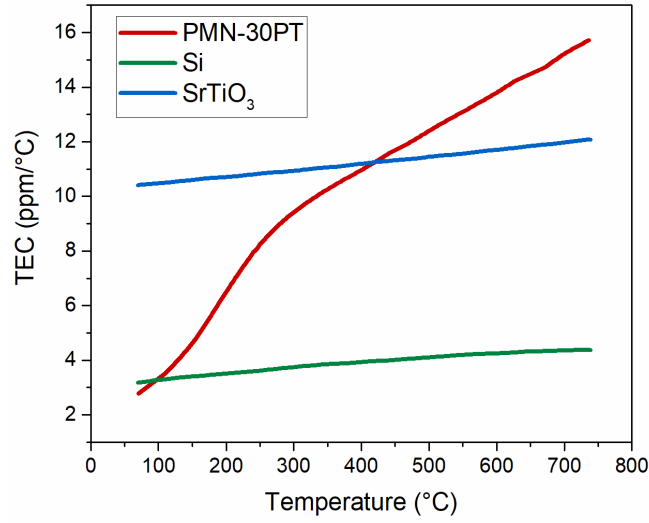


Figure 5: Comparison of the temperature dependence of the TEC of PMN-30PT and commonly used substrates. Reproduced using the data from Ref. [76].

3.2 Synthesis Methods

3.2.1 Solid-state synthesis (target preparation)

In order to obtain pure-perovskite PMN-PT, i.e. free of pyrochlore impurities, the columbite procedure developed by Swartz and Shrout [34] was followed. In the first step, MgO and Nb₂O₅ powders were mixed and fired at 1150°C for a duration of 4 h. This was followed by ball-milling and drying at 500 °C for 30 min. In the second step, stoichiometric amounts of TiO₂ and PbO were added to the mixture and fired at 750 °C for 4 h, ball-milled, fired at 1100 °C for 4 h, and ball-milled once again before the final firing step, which was performed at 1200 °C for 2 h. Prior to each firing, the powders were uniaxially pressed into pellets with 100 MPa. After the final ball-milling step, a particle size analyzer was used to determine whether the desired particle size, which was below 1 μm, was reached. The as-prepared powder was then dried at 500 °C for 30 min. The powder was then weighed and the desired amounts of PbO (and MgO) excess were added. The homogenized mixture was uniaxially pressed with 100 MPa into pellets with a diameter of 20 mm. The pellets were then placed in a confined corundum crucible and completely covered with PbO powder, in order to compensate for the PbO loss, caused by the high temperature during the firing, which was performed at 840 °C for 30 min. The temperature was carefully selected to prevent excessive evaporation of lead, whilst providing relatively high-density targets. The target list is shown in Table 3.

Table 3: Composition of in-house prepared targets.

PMN:PT	Excess PbO [mol. %]	Excess MgO [mol. %]
75:25	20	/
75:25	20	10
67:33	20	/
67:33	15	/
67:33	10	/
67:33	20	10
67:33	10	10
60:40	20	/
60:40	20	10

3.2.2 Pulsed-laser deposition (thin-film preparation)

3.2.2.1 About the technique

PLD is a physical vapor deposition technique widely used to deposit several types of materials, from metals, insulators and semiconductors, to polymers, and even biological materials. PLD possesses numerous characteristics that render it remarkably competitive in the research arena of complex-oxide thin films. First and foremost, it is the simplicity in the initial set-up and the flexibility in the choice of materials. Other attractive features include a high deposition rate, stoichiometric transfer of material from the target to the substrate surface (an exception will be discussed shortly), generation of energetic species and compatibility with a vast range of background pressures. For example, in the deposition of oxides, an oxygen background pressure up to 1 mbar can be used. The ability of the PLD technique to realize stoichiometric transfer from a multicomponent target stems from the nonequilibrium nature of the ablation process. The exception is in case if any of the cation species in the target have a high vapor pressure. When elevated temperatures are used for the thin-film growth, sticking of the volatile species becomes an issue. Such cations include: Pb, Mg, Zn, Cd, Li, K, Na and Tl. One means of compensating for the loss of these species is to use a target that contains an additional phase with the volatile component. Lastly, it is important to point out that PLD is an industrially appropriate technique. While there are some technical differences between lab-scale and industrial tools, the latter are starting to be used to produce thin films on large Si wafers. Uniform film thickness can be achieved over large areas by manipulating the plume-substrate positioning. Droplet filters are often installed in large-scale systems, which enable the growth of thin films with a reduced droplet density by removing the part of the plume with a lower velocity, i.e. the heavier droplets [16], [79].

PLD growth is carried out in a vacuum chamber, such as the one shown in Figure 6. A pulsed laser is focused onto a target, ablating a small amount of the material and creating a plasma plume, which provides the material flux for the film growth. Lasers with ultraviolet (UV) wavelength and nanosecond pulse widths are used to grow epitaxial multicomponent inorganics, as such lasers are able to produce atomic, diatomic and other low-mass species in the ablation plume. Under typical conditions, the deposition rate per pulse is between 0.001 and 1 Å. A multiple-target carousel allows sequential deposition of different materials in a single run. For growing multication materials, target selection can have a strong effect on the film growth properties, such as phase formation, epitaxy, particulate/droplet density and deposition rate. The substrate can be heated to the deposition temperature using an infrared laser or resistive heating. The growth can be monitored *in-situ* using reflection high-energy electron diffraction (RHEED).

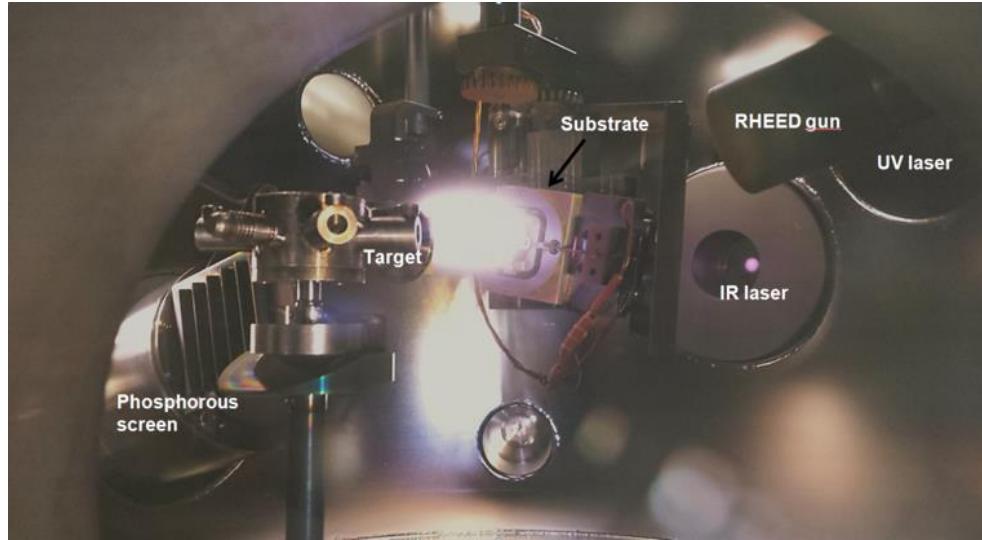


Figure 6: PLD vacuum chamber and its functional components.

Nucleation and growth of islands are two independent processes in PLD, separated in time and determined by kinetics, as they take place far from thermodynamic equilibrium. Surface steps of the deposited material are formed by nucleation and lateral movement of these steps is caused by subsequent growth. Different growth modes can be distinguished, depending on the bonding between the substrate and the growing film. If the free energies of the film surface and the interface between the film and the substrate are smaller than the free surface energy of the bare substrate, the film will grow in a layer-by-layer or Frank-Van der Merve mode. In case of poor bonding between the film and the substrate, on the other hand, three-dimensional (3D) islands are formed. In other words, here the film does not wet the substrate, as this would increase the total surface energy. This growth mode is called the Volmer-Weber growth mode. If the material of the film differs from the material of the substrate (i.e. in case of heteroepitaxial growth), the Stranski-Krastanov growth mode may occur, where the growth mode changes from layer-by-layer to island growth. One of the reasons for this is the limited surface diffusion in PLD, preventing the deposited material from fully rearranging itself in order to minimize the surface energy. The high supersaturation of vapor results in a large nucleation rate, and different growth modes will arise due to the kinetic effects [16].

3.2.2.2 Synthesis procedure

All thin-film samples were prepared using a PLD system (Figure 7) from Twente Solid State Technology (TSST), equipped with a KrF excimer laser from Coherent (COMPex 205, wavelength 248 nm, pulse-length 20 ns). Prior to deposition, the STO substrates were cleaned and dipped in deionized water, etched with a buffered hydrofluoric acid (BHF) solution, and annealed in a tube furnace with oxygen flow at 950 °C. This procedure, which was developed by Koster et al. [80], is used to ensure TiO_2 termination of STO and is described in more detail in Section 4.1. The treated and cleaned substrate was then attached to a resistive heater using silver paint and heated up to ~ 100 °C to evaporate most of the solvent from the paint, to avoid excessive contamination of the vacuum chamber. The base pressure was $\sim 1 \times 10^{-7}$ mbar for all depositions. Some deposition parameters were kept constant for all samples. A spot-size of 2.3 mm^2 was selected for all depositions. The target-to-substrate distance was fixed at 55 mm, and the cooling to room temperature was always carried out immediately after finishing the depositions, in an atmosphere of 700 mbar O_2 at a rate of $10 \text{ }^\circ\text{C min}^{-1}$. 100-nm-thick LNO was grown at 570 °C and 0.13 mbar, with a pulse frequency of 5 Hz and a fluency of 2.5 J cm^{-2} . 100-nm-thick SRO was grown at 600 °C and 0.13 mbar, with a pulse frequency of 8 Hz and a fluency of 2.5 J cm^{-2} . PMN-PT (600–1000-nm-thick) was grown at 8 Hz. These initial conditions for the growth were selected based on literature reports and some preliminary results, while the rest of the parameters were

varied. The dynamic oxygen pressure was varied from 0.065 mbar to 0.5 mbar. The substrate temperature was varied from 550 °C to 570 °C.

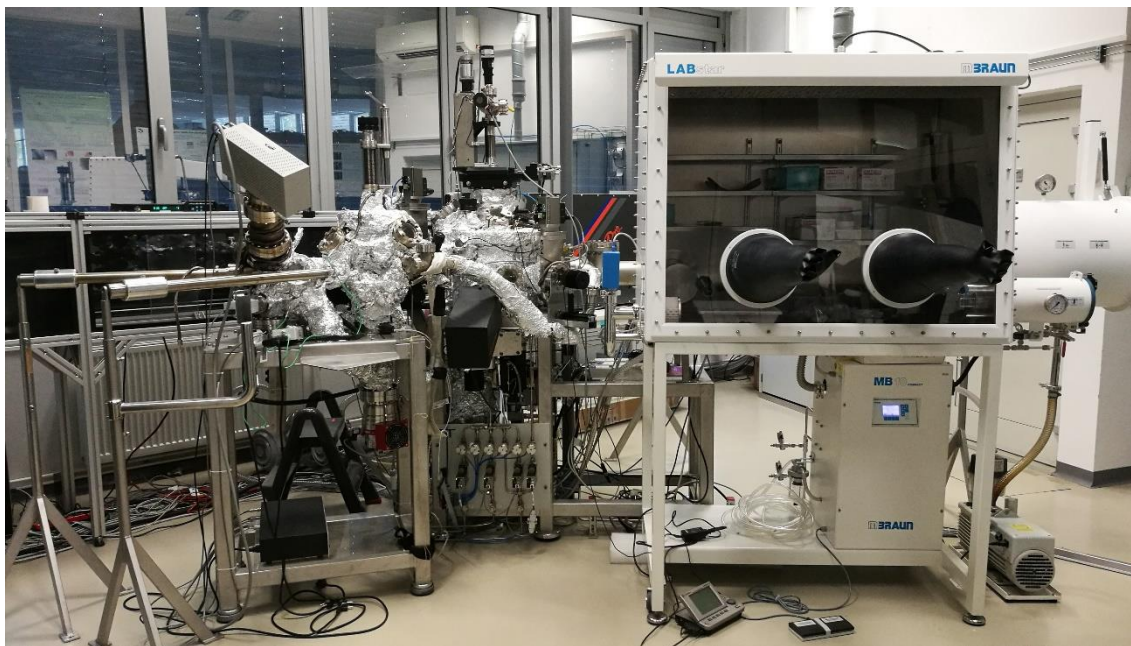


Figure 7: PLD system at the Advanced Materials Department of the Jožef Stefan Institute.

3.3 Characterization Methods

In this subsection the analysis techniques relevant for understanding the results of this thesis are presented, with an emphasis on X-ray diffraction. In addition to the methods presented in the following subsections, optical microscopy was used to analyze the surface of the thin films.

3.3.1 Reflection high-energy electron diffraction

Reflection high-energy electron diffraction (RHEED) is a surface-sensitive technique, most often used to study the mechanisms and surface processes during film growth. The finely collimated electron beam reaches the surface at a grazing incidence angle, typically between 0.1 and 5°, penetrating a few atomic layers into the sample. The irradiated area on the sample surface is 1–3 mm along the beam. The coherence length is typically in the order of several hundreds of nanometers. Scattered electrons result in a characteristic diffraction pattern on the phosphorous screen, which acts as a detector [16]. RHEED was initially limited to low background pressures. The development of high-pressure RHEED systems made it possible to monitor *in-situ* growth of oxides at high pressures. The typical energy of the electron beam in a RHEED system is 10–100 keV. Although such high energy would in principle enable a penetration depth of several hundreds of nm, the electrons only interact with the topmost layer of atoms, owing to the low incident angle [12]. Due to this geometrical arrangement, RHEED can be used to monitor dynamic changes during sample heating, deposition or desorption of species from the surface [81]. In case of atomic layer-by-layer growth, oscillations in the intensity of the diffraction spots indicate when a layer has been completed. The intensity of the specular spot depends on the spatial coherence of the surface atoms. During the deposition at sub monolayer coverages, the intensity decreases, while for completed layers, the intensity is high [16]. This way, the number of atomic layers grown and the growth-mode of the layer can be determined. Furthermore,

from the arrangement, intensity and profile of the diffraction spots in the pattern, other information can be extracted:

- flatness of surfaces,
- sizes of the surface structures (grains, domains, etc.),
- information on structural phase transitions,
- periodicity (unit cells) in atomic arrangements,
- epitaxy of the film with respect to the substrate and
- individual atomic positions in the unit cells [81].

As this thesis is not dealing with ideal, atomically flat surfaces (with the exception of the single-crystal substrates), this subsection focuses more on the various modifications of the RHEED pattern that arise due to imperfections on the sample surface, as illustrated in Figure 8. In an ideal case (shown in Figure 8a), all of the diffraction spots lie on the so-called Laue zones (circles) and have the same intensity. If the surface is composed of small out-of-phase (OP) domains (Figure 8b), the diffraction spots (streaks) in the RHEED pattern are broadened (more elliptical). In case of a two-level stepped surface, as shown in Figure 8c, the diffraction spots get split into satellite spots/streaks. A rough surface with multilevel terraces of different widths, as the one shown in Figure 8d, produces a RHEED pattern with elongated streaks, whose intensity is modulated in the perpendicular direction. As shown in Figure 8e, if the crystal is cut under an angle, the resulting RHEED pattern is similar to that shown in Figure 8c; however, the spots/streaks are inclined. If the surface roughness is very high, i.e. 3D islands are formed on the surface, the electron beam is no longer reflected from the sample surface. Instead, the beam is transmitted through the protruded parts of the islands, producing a transmission diffraction pattern. If the islands are epitaxially grown, the reciprocal lattice matches that of a 3D crystal. The diffraction pattern is then the usual one as obtained from bulk crystals. If the islands are nonepitaxial, i.e. random, one obtains a Debye-Scherrer ring pattern [81].

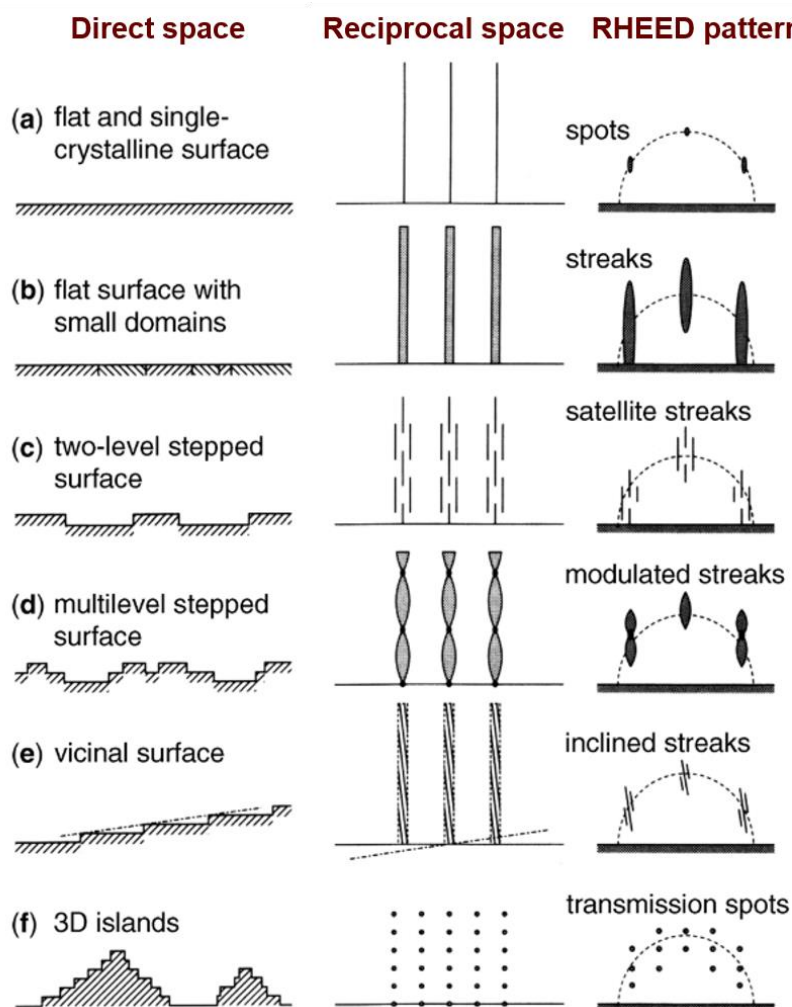


Figure 8: Different types of RHEED patterns [81].

Equipment and parameters used:

A RHEED gun with differential pumping from STAIB instruments, coupled with kSA 400 RHEED analysis system from k-Space Associates, Inc., was used. The energy of the beam was 30 keV, corresponding to a wavelength of $0.069 \text{ \AA}$ (with relativistic correction), and the current was $\sim 1.5 \text{ A}$.

3.3.2 X-ray diffraction

X-ray diffraction (XRD) was used for crystallographic characterization of the thin film samples. Different types of measurements were carried out in order to obtain as much information as possible about the structure and crystalline quality of the samples.

Equipment and parameters used:

All X-ray diffraction (XRD) measurements were carried out using an Empyrean diffractometer (Malvern PANalytical) with $\text{CuK}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$). All measurements were carried out at 45 kV and 40 mA in parallel beam geometry with a double-bounce Ge(220) hybrid monochromator on the incident-beam side. The diffracted beam was captured by a PIXcel3D detector operating in different modes, depending on the measurement type. A 4-mm-wide mask was used in all measurements, while the size of the divergence- and anti-scatter slits depended on the specific measurement type. The XRD setup, together with the geometrical relations, is shown in Figure 9.

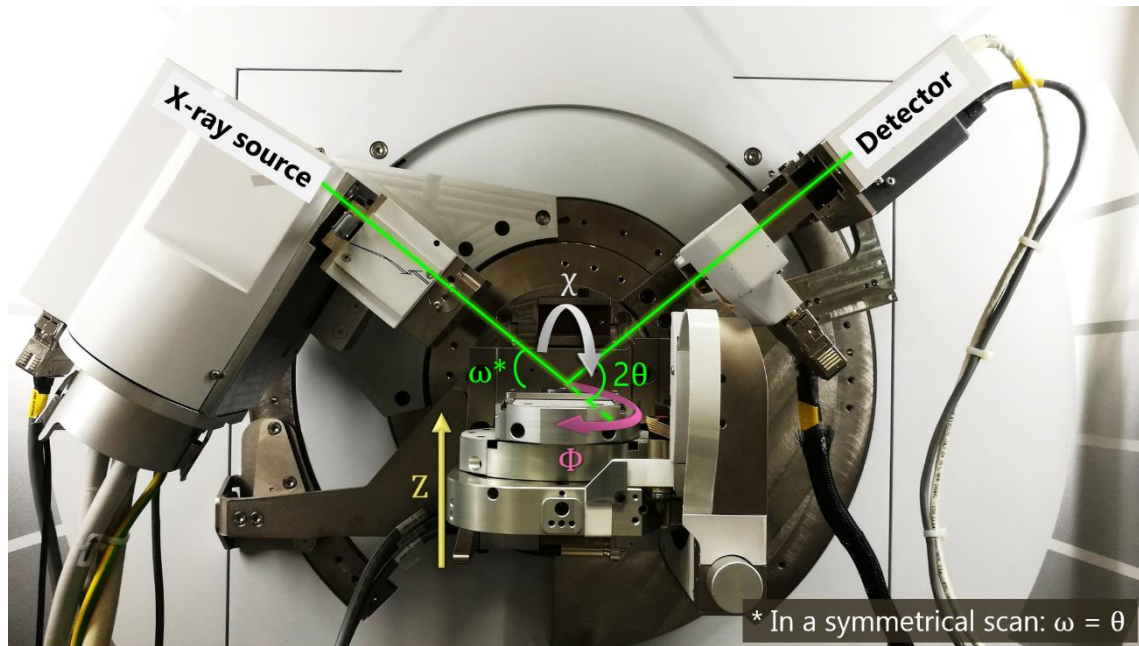


Figure 9: XRD setup.

3.3.2.1 θ - 2θ measurements

Symmetric or θ - 2θ measurements (sometimes also called specular scans) were performed for the purpose of phase analysis and determination of the out-of-plane (OP) orientation of the layers. In this type of scan, diffraction peaks corresponding to the lattice spacings perpendicular to the sample surface are observed.

Equipment and parameters used:

Prior to the measurements a three-step alignment procedure was carried out. First, the direct beam was aligned, placing the 2θ axis on an absolute scale. The second step consisted of iterations of ω and Z scans in order to place the ω angle on an absolute scale. In the final step, the sample source and the detector were placed under the critical angle with respect to the sample surface, in order to bring the sample surface plane exactly perpendicular to the diffraction plane by performing an iteration of ω , Z and χ scans. Divergence- and anti-scatter slits with a $1/16^\circ$ opening were used. The PIXcel3D detector was set to scanning line (1D) mode. The measurement range was 10 – 80° along the 2θ axis, with a step size of 0.0131° and a time-per-step of 400 s.

3.3.2.2 Azimuthal measurements (Φ -scans)

Azimuthal measurements are used to determine the in-plane orientation of a film and its crystallographic relationship with the substrate. In other words, they are used to determine whether a film is grown in an epitaxial manner. The scans are performed with the sample placed under an angle, so that one of the asymmetric (not parallel to the sample surface) planes is placed in the diffraction plane, since an in-plane component is required. Several scans are performed – one for the substrate and one for each of the layers. The ω and 2θ angles are selected in such a way that the diffraction condition for the asymmetric reflection of interest is fulfilled – first for the substrate and then for the layers. During each scan, the sample is rotated for the whole 360° range. An epitaxial film exhibits diffraction peaks exclusively at specific Φ angles, which are symmetry-related to similar asymmetric peaks from the substrate.

Equipment and parameters used:

The measurements were performed on a PANalytical Empyrean XRD system. The sample alignment procedure was the same as that described in the previous subsection, with some additional steps consisting of tilting the sample to reach the asymmetrical crystal planes and aligning the beam to those specific planes. The divergence- and anti-scatter-slit openings were $1/2^\circ$, and the detector was set to open (OD) mode. A step size of 0.01° was used, and the time-per-step was selected in such a way that a sufficient amount of signal was acquired for the individual components of the sample.

3.3.2.3 Rocking curve measurements (ω -scans)

A rocking curve (RC) measurement is an ω scan. As the name implies, in this type of scan, the incident beam angle (ω) is varied and the diffracted beam intensity is measured in each step. The 2θ position is fixed to a value corresponding to the position of the reflection of interest. The full-width-at-half-maximum (FWHM) values obtained from the RC measurements serve as a measure of crystal perfection or crystallinity. The slight misorientation, which can be observed in an RC measurement, is also called mosaicity. Mosaicity is commonly equated with the standard deviation of the Gaussian distribution of crystallite orientations. An alternative to performing a separate RC measurement is to extract the appropriate FWHM of a reciprocal space spot, which is how the FWHMs were collected in this thesis.

Equipment and parameters used:

See the following subsection.

3.3.2.4 Reciprocal-space mapping

Reciprocal-space mapping (RSM) is a 2-axis scan where 2θ is sequentially scanned for each step of ω . RSM enables the calculation of many parameters related to the quality and structure of a thin film and its epitaxial relationship with the substrate. Lattice mismatch, strain, relaxation, crystalline quality and lattice parameters can be calculated from the data collected in a map. Usually, at least two sets of reciprocal spots are collected: (i) symmetrical – the planes are parallel to the sample surface, and (ii) asymmetrical – the planes are inclined. Ideally, each set contains spots from both the substrate and the layer(s). Symmetric spots are located above the point of origin in reciprocal space. They contain information on the size and spread of the out-of-plane (OP) lattice parameters, crystallographic tilts and some information on the mosaic spread. By also mapping the asymmetrical spots, a more generous amount of information can be acquired, such as the lateral correlation length, unit cell distortion and in-plane (IP) lattice parameters, from which the lattice mismatch and the % of relaxation can be calculated.

An exemplary scheme of the reciprocal space of a single crystal sample is shown in Figure 10. The grey areas in the scheme represent areas of the reciprocal space, which are inaccessible in standard commercial diffractometers, such as the Empyrean. Only a limited number of reflections can occur within the radius of twice of Ewald's sphere, called the limit sphere. Using a smaller wavelength, such as at a synchrotron light source, a larger volume of the reciprocal space can be explored, as $|K| \leq 2/\lambda$. The other two limitations are related to the accessibility of the incident and diffracted beam. In the first case, the incident beam is located below the sample surface ($\omega < 0$), and in the second case, the detector is located below the sample surface ($2\theta < \omega$).

The output of a RSM measurement, which is given in 2θ and ω angles versus the intensity, can be transformed into reciprocal space coordinates using Equations 3.1 and 3.2, where the commonly used values of R are 1, $1/2$, $1/\lambda$ and $2\pi/\lambda$. The reciprocal space coordinates Q_x and Q_z of an asymmetrical reflection are used to calculate the IP and OP lattice parameters, respectively. If $R = 1/2$, Equations 3.3 and 3.4 can be used, where h and l are the Miller indices of the diffracting planes.

$$Q_x = R(\cos\omega - \cos(2\theta - \omega)) \quad (3.1)$$

$$Q_z = R(\sin\omega + \sin(2\theta - \omega)) \quad (3.2)$$

$$a = \frac{\lambda h}{2 Q_x} \quad (3.3)$$

$$c = \frac{\lambda l}{2 Q_z} \quad (3.4)$$

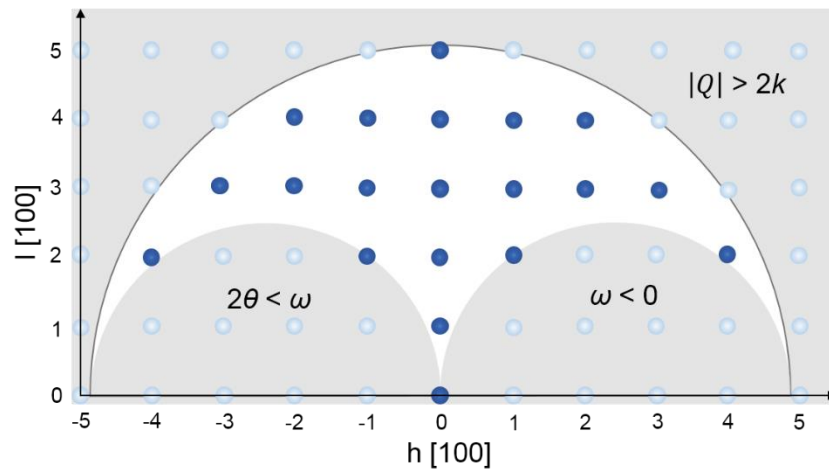


Figure 10: An exemplary scheme of the reciprocal space.

The mosaic spread and lateral correlation length are derived from the shape of an asymmetrical spot, as shown in Figure 11. The mosaicity is calculated by taking the angle that the layer peak subtends at the origin of the reciprocal space measured perpendicular to the reflecting plane normal. The lateral correlation length is calculated from the reciprocal of the FWHM of the peak measured parallel to the interface.

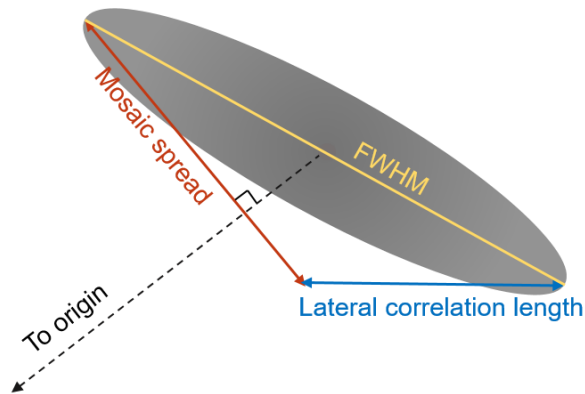


Figure 11: Mosaic spread and lateral correlation length.

Equipment and parameters used:

The measurements were performed using $1/8^\circ$ divergence slits and the detector operating in scanning line (1D) mode. The slits and step size were selected in such a way that the peak width was unaffected by the instrumental resolution. The Epitaxy software (Malvern PANalytical, version 4.3a) was used to determine the peak positions (by finding the centroids of the spots), the FWHMs, mosaic spread and lateral correlation length. The lattice parameters were determined from RSMs around the asymmetric reflections by finding the Gaussian peak centroids. The uncertainties in the estimation of the peak centroids were determined using a calculation method derived by Garnir et al. [82]. The uncertainty is calculated using the following equation: $s(b) = 0.412 \sqrt{f/a}$, where f is the full width at half maximum (FWHM) of the peak and a is the amplitude of the peak.

3.3.3 Raman spectroscopy

Raman spectroscopy is a scattering technique based on the so-called Raman effect, i.e. that the frequency of a small fraction of scattered radiation is different from the frequency of the monochromatic incident radiation. The main difference between infrared spectroscopy and Raman spectroscopy is in the fact that in infrared spectroscopy the phonons are detected directly, while in Raman spectroscopy the energy difference between the incident and the scattered photon is captured. Therefore, equipment with a visible or near-visible light source can be used. Raman spectroscopy is one of the most powerful techniques used to study lattice vibrations and other elementary excitations. This provides important information about the composition, structure, strain, phase transitions and defects. The dynamics of the crystal lattice is of central importance for understanding the fundamental properties of ferroelectric materials. The soft-mode theory has established the relationship between ferroelectric polarization and polar optical vibration modes [83]. The soft-mode (the lowest-frequency transverse optical phonon) involves the atomic displacements, which are also responsible for the appearance of spontaneous polarization. The soft-mode behavior is related to many technologically-important applications, such as a high dielectric permittivity, high piezoelectric coefficients, dielectric nonlinearity and dielectric losses [84].

The assignment and exploitation of Raman spectra is a challenging task, as the Raman activity seems to stem from both the ionic off-centering [85] and the occupational ordering [86]. Furthermore, the effects are often very material-dependent, thereby adding a great deal of importance to comparative studies and well-documented examples of polarized Raman spectra of individual complex perovskites. It has been shown [87] that Raman scattering is able to capture the development of rhombohedral ferroelectric order in complex perovskites. The spectral signature for this specific feature is related to the HV Raman intensity of the most pronounced first-order Raman scattering band in the high frequency range. This relatively well known mode is generally ascribed to the breathing mode of the oxygen octahedra. Furthermore, it has been observed that its intensity systematically scales with the degree of ferroelectric order, when the incident and scattered polarization directions are oriented along the pseudocubic axes. This analysis is valid for perovskite relaxors with a rhombohedral ferroelectric ground state [88].

The application of conventional Raman spectroscopy on ferroelectric thin films to study the lattice dynamics is especially challenging, because the visible phonon energy is much smaller than the bandgap. Consequently, light absorption is extremely poor and the penetration depth is large, resulting in light travelling through the film and into the substrate. The large substrate therefore generates overwhelming signals in the Raman spectra. To alleviate this issue, films have previously been grown on reflective substrates or substrates with low Raman activity at the given frequency [84]. In this study, the LaNiO_3 bottom electrode layer served as a barrier to eliminate the substrate contribution.

Angular dispersion of Raman spectra enables the unravelling of the symmetry in the measured area. This is done by comparing the relative intensities of chosen bands. It has been shown [89] that the differences between different areas in single crystal PMN-PT are best seen in HV geometry, where polarizations of incident and scattered light are oriented along two perpendicular pseudocubic axes. The difference is most pronounced when comparing the shapes and intensities of the bands near 600 cm^{-1} or 800 cm^{-1} . It is possible to quantify the difference by calculating the ratios of intensities between different bands. In

order to distinguish between the M_A (rhombohedral-like) and M_C (tetragonal-like) phase in PMN-33PT, the ratios $I_{570/510}$ and $I_{780/720}$ of intensities at respective frequencies in the subscripts have been found to be most informative. These bands were selected in such a way, as to have the most pronounced changes of intensities in the numerator, while the intensities in the denominator are practically constant or changing in the opposite manner with respect to the numerator. Bands with frequencies 270 cm^{-1} and 510 cm^{-1} may refer to E(TO) modes, and bands with frequencies 570 cm^{-1} and 780 cm^{-1} refer to $A_1(\text{TO})$ modes.

In this study, a micro-Raman setup was used, the advantages of which are: (i) the possibility to optically observe the measured area of the sample, (ii) simplicity and ease of use, and (iii) the possibility to obtain a high Raman signal, as the laser can be focused into a small spot.

Equipment and parameters used:

All measurements were performed on a Renishaw RM 1000 micro-Raman spectrometer with a He-Ne laser, which has a wavelength of 6328 Å . Laser power of 10 mW was focused on a $2\text{ }\mu\text{m}$ spot; the spectral resolution was better than 2 cm^{-1} . A single grating monochromator is connected to a Leica microscope. The main problem in backscattering geometry (which is the only geometry available in this configuration) is the large amount of Rayleigh scattering entering the monochromator. To suppress the Rayleigh scattering, a triple monochromator is used, combined in a compact module called Near-Excitation Tunable filter (NExT). To determine the crystal symmetry of the thin film, it was necessary to perform measurements with different sample orientations with respect to the polarization of the incident and scattered light. For this purpose, a motorized rotation table was used. The spectra were measured at angles from 0° to 180° with a 5° step. The angles refer to the angles between the polarizer and the pseudocubic crystal axes. Different scattering geometries can be employed to measure different Raman components with specialized equipment for forward and right-angle scattering. In our case, such measurements were enabled by custom-made parts.

The spectra were recorded using polarized laser light with the analyzer on the scattered beam parallel (VV) or perpendicular (HV) with respect to the polarization of the incident light.

3.3.4 Scanning electron microscopy with wavelength-dispersive spectroscopy

Scanning electron microscopy (SEM) was used to examine the microstructures of targets and the thin films and determine the thickness and density of the films by inspecting their cross-sections. The topography of the samples was examined by employing a detector for capturing the secondary electrons, which are emitted from the sample's surface. The chemical homogeneity of the samples was checked by using a detector for capturing backscattered electrons. The exact chemical composition of several thin-film samples was determined using quantitative electron-probe microanalysis, employing wavelength-dispersive X-ray spectroscopy (WDXS), as energy-dispersive X-ray spectroscopy, though widely employed in the literature, was found to yield highly unreliable results, due to the overlapping of the Pb and Nb lines.

Equipment and parameters used:

The microstructures of the thin films were examined using a Jeol JSM-7600F SEM with an in-lens thermal field emission gun. An accelerating voltage of 15 kV was used. The WDXS spectrometer (INCA WAVE, Oxford Instruments) was attached to the SEM instrument. The WDXS procedure, which was based on the analytical procedure that was applied and described in detail for bulk PMN-PT, [37] was carefully optimized for the analysis of PMN-PT thin films. Monte Carlo simulations were carried out to estimate the size of the electron-interaction volume, and the X-ray generation depth for different primary energies of the incident electrons. It was found that using a beam energy of 8 keV , the maximum X-ray-generation depth was $0.21\text{ }\mu\text{m}$ for the Ti-K α line, $0.27\text{ }\mu\text{m}$ for the Nb-L α line, $0.28\text{ }\mu\text{m}$ for the Pb-M α line and $0.30\text{ }\mu\text{m}$ for the Mg-K α line. Therefore, only X-rays from the PMN-PT were excited, i.e. there was no contribution from the substrate or the electrode layer. It is also shown that at 8 keV sufficient X-ray ionization yield was achieved for all cations. The intensities of the X-ray lines Ti-K α , Nb-L α and Pb-K α were measured using a PET crystal

with a sealed Xe-filled proportional counter, while the Mg-K α line was measured on a TAP crystal using a gas-flow (P-10) proportional counter. The detector settings were optimized in a sense of finding the optimum bias, accurate peak and background positions and the correct pulse height. Focused point-beam measurements were performed at 8 keV and with an electron dose of 3.0 μC per point. This way, a sufficient number of X-ray counts were achieved to keep the standards counting error under $\pm 2\%$ relative for each element. The standards used for quantification of Ti, Nb, Pb and Mg were pure stoichiometric oxide compounds (SrTiO_3 , Nb_2O_5 , PbO and MgO , respectively). The oxygen content was calculated from the stoichiometry to nominal cation valences. The quantitative matrix correction algorithm that was used was an optimized off-line $\Phi(\rho z)$ -based method. The reliability of the employed set-up was verified by measurements on a bulk PMN-33PT single-crystal reference material. The obtained elemental concentrations showed excellent agreement with the nominal composition within the range of experimental uncertainty.

3.3.5 Transmission electron microscopy

Transmission electron microscopy (TEM) was used to inspect the cross-sections of the samples on different length scales. Under relatively small magnifications, the density and macroscopic structure of the film can be examined, along with potential defects threading across the thickness of the film. Initial information on the potential presence of any structural or ferroelectric domains can also be collected. In atomic-resolution images, it is possible to identify the origin of the features observed under smaller magnifications. Different types of structural defects can be identified, such as point defects, lines defects, and so forth. In thin film investigations, the interfaces between the substrate and the individual layers are of special interest.

Geometric phase analysis (GPA) is an algorithm used to determine the lattice strains in high-resolution TEM images. It is particularly attractive for the analysis of aberration-corrected scanning TEM (ac-STEM) images, where every atom column is resolved, as it uses Fourier transforms and therefore real-space peak detection and assignment to appropriate sublattices is not required [90].

Careful preparation of the TEM samples is of utmost importance, as various techniques and/or preparation parameters can lead to artefacts, which are not always obvious, i.e. can easily be interpreted as the virgin structure of the sample. It has been shown that ion-milling can induce microdomains in PMN-PT single-crystal samples, due to the surface stress induced by the ion-milling procedure [91]. It has also been reported that focused ion beam (FIB) sample preparation can induce relaxation mechanisms in epitaxial thin films. Specifically, it can lead to flipping of the crystal by 90° [39]. Elastic relaxation that tends to occur at the free surfaces of epitaxial films is a common problem in all preparation techniques [92].

Equipment and parameters used:

In order to avoid any artefacts induced by the preparation procedure, the samples were prepared following the procedure developed by Srot et al. [38], which consisted of polishing the sample using a tripod and short Ar^+ -ion milling at low acceleration voltages. During the preparation procedure, the sample was cooled to liquid-nitrogen temperatures.

Atomic-resolution TEM imaging was performed using a probe-aberration corrected JEM-ARM200CF (Jeol) microscope, equipped with a cold field-emission gun, a scanning unit (STEM), annular bright-field (ABF) and high-angle annular dark-field (HAADF) detectors, and a US1000 CCD camera for the HR-TEM.

GPA analysis was performed using a plug-in for the image-processing package Gatan Digital Micrograph. The main goal of the analysis was to qualitatively visualize the positioning and distribution pattern of the observed structural defects formed in the films. Therefore, the selection criterion for the analysis parameters (1.5 nm resolution with a Fourier mask of $r = \frac{1}{4} a$) was enhancement of the visual structures on the map of the in-plane strain component.

3.3.6 Atomic force microscopy

Atomic force microscopy (AFM) is a technique used to image the shape of a surface in 3D detail down to the nanometer scale. Surface height is measured at each point or pixel in a 2D array using a sharp solid force probe. AFM operates in two general modes: (i) static (contact) and (ii) dynamic (non-contact and tapping) mode. The contact mode is based on repulsive forces, while non-contact mode utilizes attractive forces. A combination of attractive and repulsive forces is used in the tapping mode. Here, the cantilever oscillates with a constant amplitude at the resonance frequency in intermittent contact with the sample [93].

Equipment and parameters used:

AFM imaging was carried out on a Digital Instruments Dimension™ 3100 microscope, using silicon probes with reflective aluminum coating (OTESPA-R3, Bruker). Tapping mode was employed in all of the measurements. The images were processed using WSxM 5.0 software [94]. The distribution of equivalent diameters of the surface structures, assuming spherical shapes, was determined using MIPAR software.

3.3.7 Dielectric measurements

The relative dielectric permittivity and dielectric loss are important parameters for most practical material applications. The dielectric properties are strongly coupled with the ferroelectric and piezoelectric properties of a material. Through the studies of dielectric properties, information on the mechanism of the electrical polarization in ferroelectric materials can be provided. The anomalous material properties around the MPB are associated with a large dielectric anisotropy, $\varepsilon_{11}^T \gg \varepsilon_{33}^T$, where ε_{11}^T is the dielectric permittivity perpendicular to the spontaneous polarization and ε_{33}^T is the dielectric permittivity parallel to the spontaneous polarization. The perpendicular component exhibits a strong maximum upon reaching the MPB composition, while the value of the parallel component barely changes. Furthermore, the large dielectric anisotropy leads to a very high shear piezoelectric constant d_{15} [95].

Equipment and parameters used:

In accordance with the two different desired device configurations, two distinct measurement geometries were used to determine the dielectric properties of the samples: (i) PPC and (ii) IDE. The PPC measurements were conducted using Nb:STO as the bottom electrode. Here, circular top electrodes were fabricated by sputtering a 50-nm-thick layer of Au through a shadow mask with holes 600 μm in diameter. The electric field in these films was therefore applied across their thickness, i.e. along the [001] crystallographic axis of the substrate. Prior to the measurements, the samples were dried in a flow of dry air inside a probe station (Cascade Microtech, Inc.) in order to avoid any potential artefacts due to moisture. The relative permittivity was measured using an Agilent 4284 LCR meter, connected to the sample through Cascade DCP-HTR probes. The values were measured along a logarithmic frequency scale from 20 Hz to 1 MHz, with an AC excitation voltage of 100 mV. The same devices and settings were used to determine the relative permittivity with IDEs, where the electric field was applied along the thickness of the films, i.e. along the [100] crystallographic axis of the pure, non-conductive STO substrate. The pattern of the 70-nm-thick Cr-Au alloy electrodes, which were patterned by laser lithography (LPKF Proto-Laser LDI), consisted of 10 fingers, each 11.5 μm wide and 3 mm long, with a gap width of 8.5 μm . The relative permittivity of the samples with IDEs was calculated according to the method developed by Kidner et al. [96].

Temperature-dependent dielectric characterization was carried out by measuring the dielectric permittivity as a function of temperature ($T = 25^\circ\text{C} - 200^\circ\text{C}$, 5°C steps) at different frequencies (100 Hz, 200 Hz, 1 kHz, 2 kHz, 10 kHz, 20 kHz and 100 kHz) using an AC excitation voltage of 100 mV. At each temperature a DC sweep was conducted, from -7.2 V to +7.2 V with steps of 0.36 V.

3.3.8 Ferroelectric measurements

Measurements of ferroelectric hysteresis loops provide valuable information, such as the maximum or saturation polarization (P_{sat}) value under an applied external electric field, the value of the remnant polarization (P_r), which is left after the removal of the DC field, and the coercive field (E_c), which is the value of the electric field, where the polarization value reaches zero. The shape of the loop is indicative of the degree of the ferroelectric or relaxor nature. The potential vertical and/or lateral shift of the loop can be related to many effects, such as the electrode configuration, internal fields or defects in the sample. Owing to the small grain sizes, large residual stresses and a relatively high concentration of point and line defects, the mobility of the domain walls and phase boundaries are heavily diminished in thin films as compared to bulk. Consequently, thin films usually act as hard piezoelectrics [125].

Equipment and parameters used:

The ferroelectric properties were determined using a ferroelectric test system (Radiant Precision LC materials analyzer), which operates on the virtual ground principle. A series of double triangular bipolar waveforms was applied at a frequency of 10 Hz and an amplitude of between 1 V and 10 V. The integration of current to and from the sample was used to measure the polarization.

3.3.9 Piezoelectric measurements

Two techniques were used to determine the piezoelectric response of the PMN-PT thin films: laser interferometry and piezoresponse force microscopy. The former is used to measure the piezoelectric properties on a macroscopic scale, whereas the latter is used to examine the domain structure and measure the local piezoelectric response.

3.3.9.1 Laser interferometry

Piezoelectric measurements were performed in order to determine the longitudinal effective piezoelectric $d_{33,f}$ coefficient of the thin films. The suffix “33” is a matrix notation, which indicates that this coefficient correlates an electrical excitation in the direction of the polarization with a mechanical deformation response in the same direction. The suffix “f” indicates that this is the effective value of the coefficient, as affected by the properties of the substrate and electrode layers. Generally, the measured effective parameters of the films are diminished as compared to bulk values due to clamping to the substrate. It has been shown that laser interferometry is the most accurate technique for determining the $d_{33,f}$ of a piezoelectric thin film. The high resolution of the technique is appropriate for the tiny mechanical deformations of thin-film structures. A common issue in standard laser interferometers are wafer bending effects, which represent a potential cause of measurement errors. These can be avoided by the use of double-beam laser interferometers (DBLI) with a differential measurement method [97]–[99]. The operation principle of a DBLI instrument is presented in Figure 12.

Equipment and parameters used:

The samples were not polarized prior to the measurements. Measurements of the converse piezoelectric response were performed using an aixACCT DBLI system, which offers a resolution better than 1 pm. The system was used to measure (i) the large-signal polarization and displacement, and (ii) small-signal dielectric and piezoelectric properties. The small-signal measurements were performed at DC bias fields up to $\pm 150 \text{ kV cm}^{-1}$ with a superimposed AC signal with an amplitude of 500 mV and a frequency of 1 kHz. The size of the top electrodes ($d = 600 \text{ }\mu\text{m}$) was selected in accordance with studies [100], [101], which show that the real material properties are measured when the ratio of the electrode diameter and the thickness of the substrate is close to 1.

DBLI was also used to determine the large signal strain S . These measurements were performed by applying a triangular signal with a frequency of 100 Hz and a maximum amplitude corresponding to 200 kV cm^{-1} .

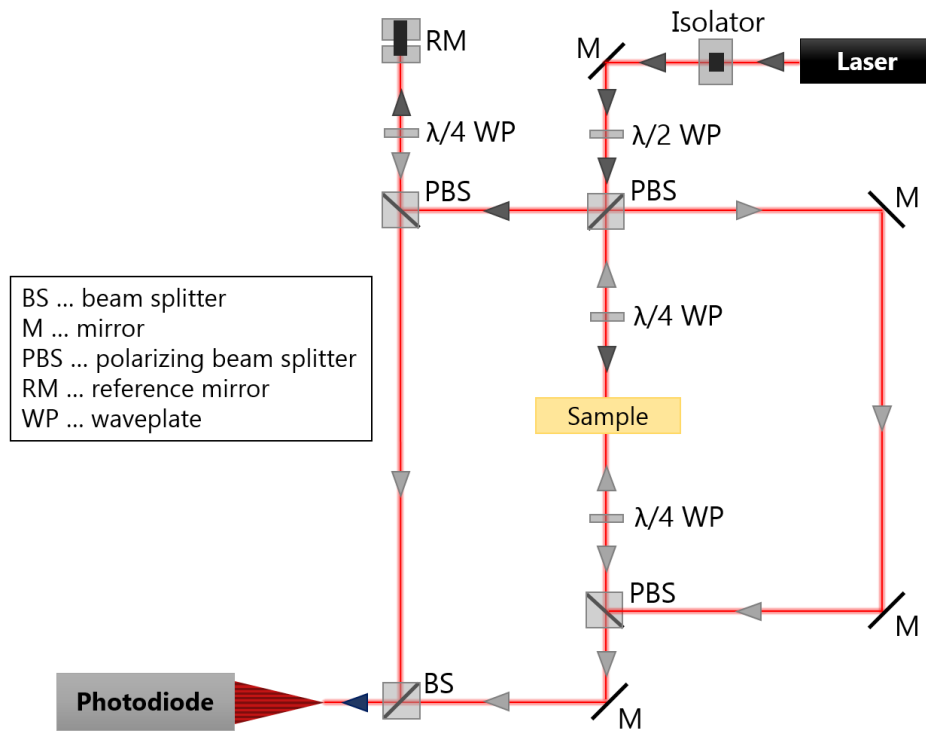


Figure 12: Operation principle of a DBLI instrument.

3.3.10 Piezoresponse force microscopy

Piezoresponse force microscopy (PFM) is actually a modification of AFM, which was presented in subsection 3.3.6. PFM is based on the detection of local bias-induced piezoelectric deformation of a ferroelectric sample. The deformation is induced by an external electric field. Depending on the relative orientations of the sample's polarization vector and the applied field, the sample deformation can occur in the form of contraction, elongation or shear. Due to the linear coupling between the piezoelectric and ferroelectric parameters, the domain polarity can be deduced from the sign of the field-induced strain. If a uniform electric field is applied along the polar direction, the domains with the polarization parallel to the direction of the applied field are elongated, while the domains with the opposite polarization are contracted. The sample deformation ΔZ is proportional to the piezoelectric coefficient d_{33} and the applied voltage V , as seen from this equation $\Delta Z = \pm d_{33} V$. The $\pm$ sign reflects the d_{33} coefficients with opposite signs for antiparallel domains. In addition to domain imaging, a conductive probing tip can also be used for the modification of the initial domain structure (PFM lithography). Application of a small dc voltage between the PFM tip and the sample's bottom electrode can be used to generate an electric field higher than the coercive field, inducing local polarization reversal. Another important application of PFM is local piezoelectric spectroscopy, i.e. measurement of local hysteresis loops. This way, information on the local electromechanical activity and coercive voltage variation between different grains can be obtained. However, extreme care should be taken in attempts to quantify the response in PFM spectroscopy [102].

Equipment and parameters used:

The PFM images were recorded using a molecular Force Probe 3D microscope (Asylum Research). An electric field was applied between the conductive AFM tip and the bottom electrode, which was either a Nb-doped STO substrate or thin-film LNO. A Pt-coated Si tip (OMCL-AC240TM-R3) with a curvature radius of ~ 10 nm was used. The in-situ poling experiments were conducted in PFM Lithography mode. The PFM amplitude and phase hysteresis loops were measured using the switching-spectroscopy off-loop mode. The waveform parameters for the loop measurements were the following: the sequence of the

increasing DC field steps was 20 Hz with a maximum amplitude of 35 V; the frequency of the triangle envelope was 200 mHz; and there was an overlapping AC sinusoidal signal with an amplitude of 4 V and a frequency of 350 kHz. The local piezoelectric values were determined in a PFM Single Frequency mode by applying an AC voltage with 1 V amplitude and a frequency of 280 kHz, which was a few tens of kHz away from the contact resonance frequency. Prior to the measurements the response was tested using a standard quartz sample (x -cut SiO_2 crystal, MTI Corporation).

Chapter 4

Results and Discussion

4.1 Characteristics of the Targets

The sintered targets were ground, and the resulting powder was measured using XRD in order to examine the phase purity and structure. Targets with all PMN:PT ratios were found to be pyrochlore-free (Figure 13a)). The PMN-25PT target showed a pseudocubic/rhombohedral structure, the PMN-40PT was tetragonal, while PMN-33PT consisted of a mixture of phases (Figure 13b)). The PMN-40PT was clearly tetragonal, while the PMN-33PT did not exhibit a distinct tetragonal splitting. Therefore, it is possible that the c/a ratio is smaller in this composition and/or that the PMN-33PT consists of a mixture of phases. In order to identify the exact structures, Rietveld refinement should be applied to the XRD patterns, obtained from measurements of the targets in powder form, which was outside the scope of this work.

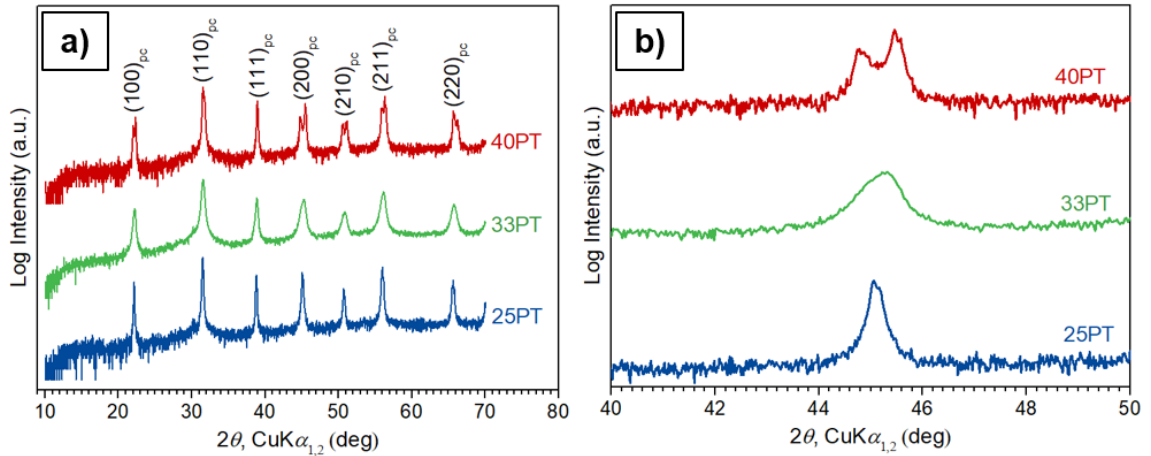


Figure 13: XRD patterns of the targets. a) XRD patterns of the targets with different PMN:PT ratios. (b) A magnified view of the region around the $(002)_{pc}$ peaks, revealing the different crystal symmetries.

Figure 14 shows the XRD pattern of the PMN-33PT target after the addition of PbO excess and firing. It can be seen that no undesired phases were formed during the densification of the lead-rich target at high temperatures. A final examination of the targets was performed by means of SEM to ensure that the targets were dense and that the added PbO excess was uniformly distributed throughout the volume of the target. From the micrographs in Figure 15, showing the polished surface of the target, it is evident that the density of the targets was satisfactory and that the PbO distribution is homogeneous. An analogous result was obtained for the cross-section of the target (not shown here).

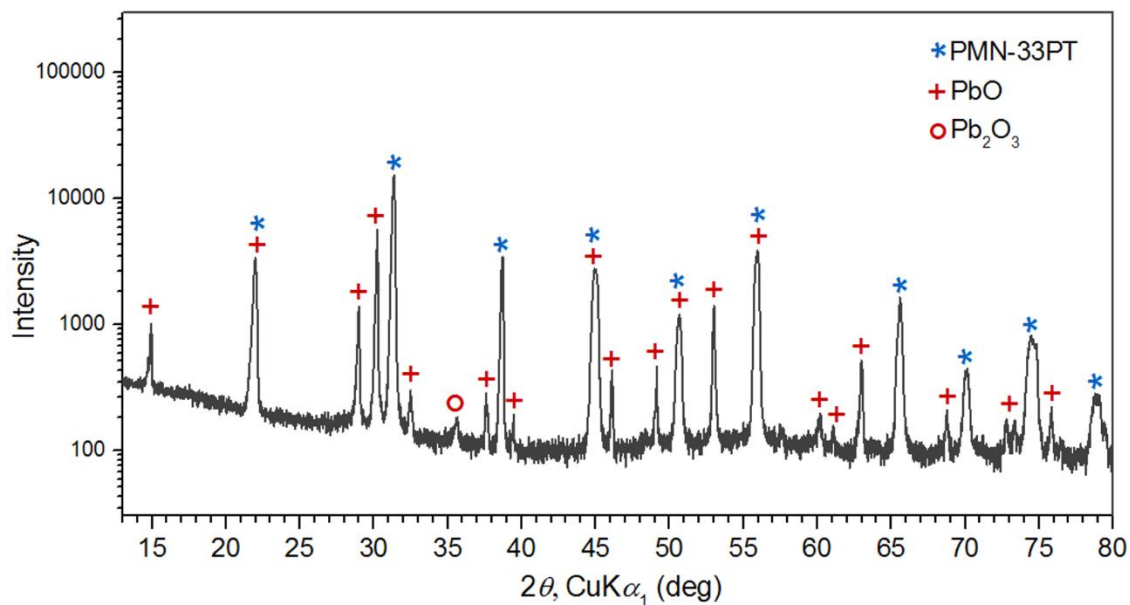


Figure 14: XRD pattern of the PMN-33PT target with 20 mol. % PbO excess.

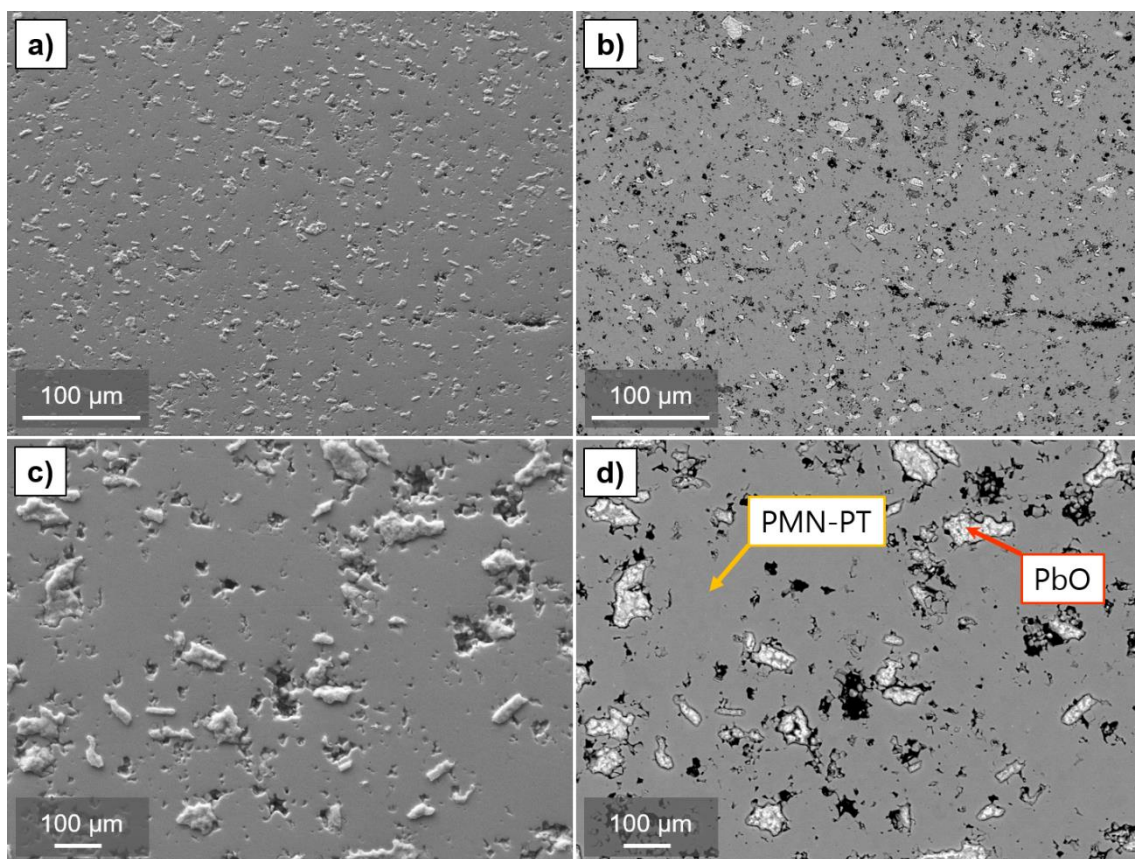


Figure 15: SEM micrographs of the PMN-33PT target with PbO excess. a) Secondary-electron image of the surface. b) Back-scattered-electron image of the surface shown in panel a). c) Secondary-electron image of the surface under larger magnification. d) Back-scattered-electron image of the surface shown in panel c).

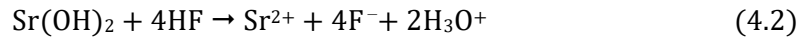
4.2 Treatment of SrTiO₃ Substrates

Regular as-supplied STO substrates have a mixed termination, i.e. the terminating planes on the surface are both SrO and TiO₂, where their lateral distribution is roughly 50:50. It has been shown that for reproducible growth of high quality epitaxial thin films, it is important to ensure a single termination of the surface, as the nucleation process depends strongly on the chemical composition of the surface. Shell-model calculations by Chen et al. have revealed that the TiO₂ surface termination is energetically favorable in STO. The underlying explanation is that the surface ions rumple and induce surface dipoles. The polarization stabilizes the surface and therefore affects the stability and properties of the epitaxial films. Specifically, the polarization that develops along the surface normally exhibits relatively long-range Coulomb interactions, which can repel or attract charged species from the surroundings. The surface dipoles for a TiO₂-terminated surface are negative, while for SrO termination they are positive [103].

Koster et al. [80] developed a procedure to prepare a quasi-ideal TiO₂-terminated STO surface. They used deionized water to enhance the etch-selectivity of SrO with respect to TiO₂ in a buffered hydrofluoric acid (BHF) solution. The enhanced etch selectivity is based on the hydroxylation of SrO, i.e. the formation of Sr(OH)₂:



The Sr(OH)₂ is then removed by soaking the substrate in BHF, which results in a TiO₂-terminated surface:



After the chemical treatment, the surface is chemically ordered, however, the morphology of the surface should also be improved. Thermal treatment is required to obtain an ordered surface with flat steps and straight step edges. The annealing time depends on the lateral dimensions of the steps, i.e. the miscut; the larger the steps, the longer the time required for annealing. For the substrates used in this thesis, it was found that an annealing time of 90 min was optimal. The annealing should be performed in a flow of pure oxygen gas to prevent the formation of oxygen vacancies.

Prior to deposition of any layer by PLD, all STO substrates were treated chemically and thermally, in order to ensure a single-terminated surface and smooth step edges (Figure 16).

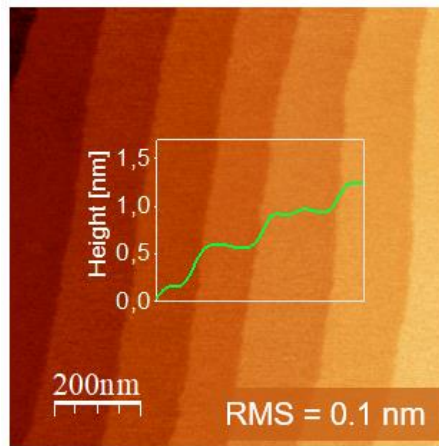


Figure 16: AFM image of a treated STO substrate. The inset shows the height profile of the steps. The individual step height corresponds to the unit cell of STO, confirming single termination of the surface.

4.3 Growth of PMN-33PT Thin Films Directly on STO

4.3.1 Phase purity of the PMN-33PT thin films

It is well known from the literature that the acquisition of high-quality PMN-PT thin films is difficult, mainly owing to pyrochlore impurities. The process window for obtaining perovskite phase pure films has been shown to be extremely narrow in different systems [41], [104]. Table 4 lists deposition parameters for the PLD growth of PMN-PT on STO substrates, which were used as a starting point for the optimization process of the growth conditions for the films in this thesis.

Table 4: Deposition parameters from the literature.

PMN:PT	Electrode	T [°C]	$p(O_2)$ [mbar]	ν [Hz]	Fluency [J cm ⁻¹]	Thickness [nm]	Target-to-substrate [mm]	Ref.
67:33	SRO	600	0.24	4	2.25	300	60	[105]
70:30	SRO	780	0.10	5	N/A	200	50	[106]
80:20	without	781	0.26	5	N/A	N/A	N/A	[61]
67:33	without	748	0.26	5	N/A	N/A	N/A	[61]
50:50	without	748	0.26	5	N/A	N/A	N/A	[61]
70:30	LSMO*	550	0.40	3	1.5	65	55	[107]

* $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$

4.3.1.1 Ablation parameters

Congruent ablation of the PLD target is crucial for the realization of stoichiometric transfer of material from the target to the substrate surface. If the laser energy density (fluency) were too low, the laser pulse would simply heat the target. Therefore, the flux would be determined solely by the vapor pressure of the constituents. By increasing the laser fluency, the ablation threshold is reached, where the ablated species absorb the energy and form a plasma at the target surface. Furthermore, non-uniform ablation can lead to droplet formation in the plasma plume, which can be incorporated into the growing film [108]. Droplets, leading to the formation of macroparticles, are one of the major causes for electrical shorts in films [105]. Also, if the penetration depth of the laser pulse into the target is large, often micron-sized particles are ejected from it. Such particles present obvious problems in the formation of multilayer device structures [16]. Therefore, the energy density of the laser should be optimized prior to optimization of other deposition parameters. Due to the large difference in the volatility of the individual elements in PMN-33PT, preferential ablation of certain components can occur, which is manifested in the form of conical structures, which are visible on the target surface under an SEM.

We ablated the target with 20 mol. % PbO excess using different energy densities of the UV laser (1.5 J/cm², 1.75 J/cm², 2.25 J/cm², 3.0 J/cm², 3.75 J/cm² and 4.25 J/cm²). The comparison of backscattered-electron micrographs of targets for three different energy densities is shown in Figure 17. The insets show the secondary-electron micrographs of the respective regions. For all tested energy-density values specific surface structures were observed at the laser-target interaction sites. These surface structures do not resemble the very distinct cones associated with incongruent erosion [108]–[110]. Nevertheless, the body of the cones formed at energy densities below 2.25 J/cm² is more pronounced in comparison to the cones formed at higher energy densities. In all cases, the surface of the cones is covered with PbO-rich droplets. At higher energy-density values the target contained numerous cracks. Therefore, an energy density of 2.25 J/cm² was selected for all experiments in order to ensure sufficient material transfer and a reasonable growth rate.

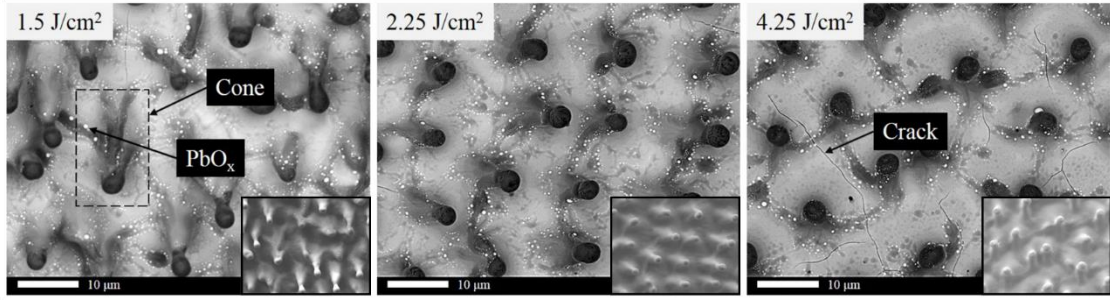


Figure 17: Backscattered-electron micrographs of the target taken after ablation using different energy densities. The insets contain the corresponding secondary-electron micrographs.

4.3.1.2 Influence of the PbO excess and the deposition temperature

Given that several literature reports exist on the growth of PMN-PT thin films on STO substrates from stoichiometric targets [111]–[114], the initial experiments were also carried out using stoichiometric PMN-33PT. Despite varying numerous parameters, we were not able to achieve pyrochlore-free growth. As it is known that the appearance of this undesired phase is most likely caused by lead-loss, we tried to compensate for it by using an additional target made from pure PbO. We programmed the deposition process in such a way that after every 120 pulses of PMN-PT the target was switched and 12 pulses of PbO were deposited. No improvement was achieved by using this procedure. As shown in Figure 18, where the PMN-PT reflections are marked with “P”, the STO is denoted by “S” and “Py” stands for pyrochlore, the sample still contained a large amount of secondary phase. We believe that the reason for this lies in the prolonged exposure of the growing sample to high temperatures during the switching of the targets, which actually resulted in additional PbO loss, which could not be efficiently replaced by the deposition from the PbO target.

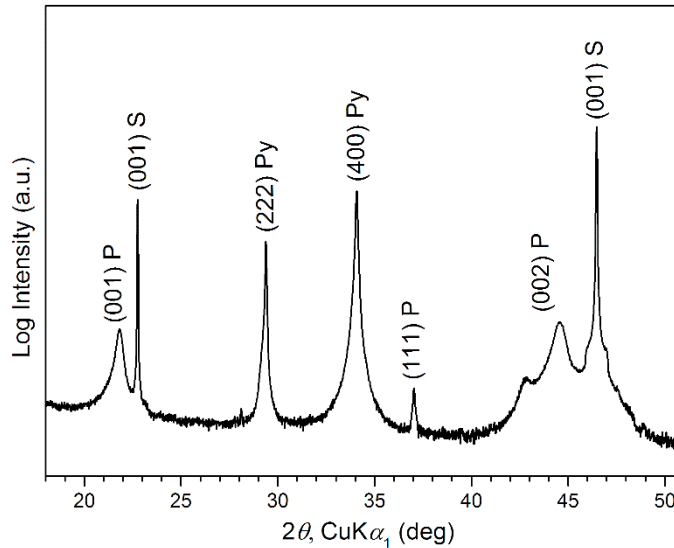


Figure 18: XRD pattern of the sample deposited by alternating ablation of PMN-33PT and PbO.

From these initial results it was concluded that it is necessary to use PMN-33PT targets with PbO excess. However, there existed no literature data on the exact amount of PbO excess required. It seems that in most studies an arbitrary amount was added. For this reason, we prepared targets with different amounts of PbO excess. The thin films were prepared using the targets with 10, 15 and 20 mol. % PbO excess at an oxygen partial

pressure of 0.13 mbar and a temperature of 560 °C. The phase composition of the films is shown in Figure 19a), where “_{pc}” signifies a pseudocubic notation for PMN-PT. The main diffraction peaks for the PMN-PT correspond to the (001)_{pc}-oriented perovskite structure. The diffraction peaks appearing at 29.2°, 34.2° and 37.2° 2θ belong to the (222), (400) and (331) planes of the cubic pyrochlore (Pb₃Nb₄O₁₃) impurity phase, respectively. Films prepared from targets with < 20 mol. % PbO excess contain relatively large amounts of pyrochlore, as well as some PMN-PT with a secondary orientation, (110)_{pc}, as seen from the peak at 31.5°. The sample prepared from the target with 20 mol. % excess (sample *P13* hereinafter) is completely single-phase and epitaxial. These results indicate that for the given system 20 mol. % of PbO excess is necessary to obtain pyrochlore-free epitaxial PMN-PT thin films.

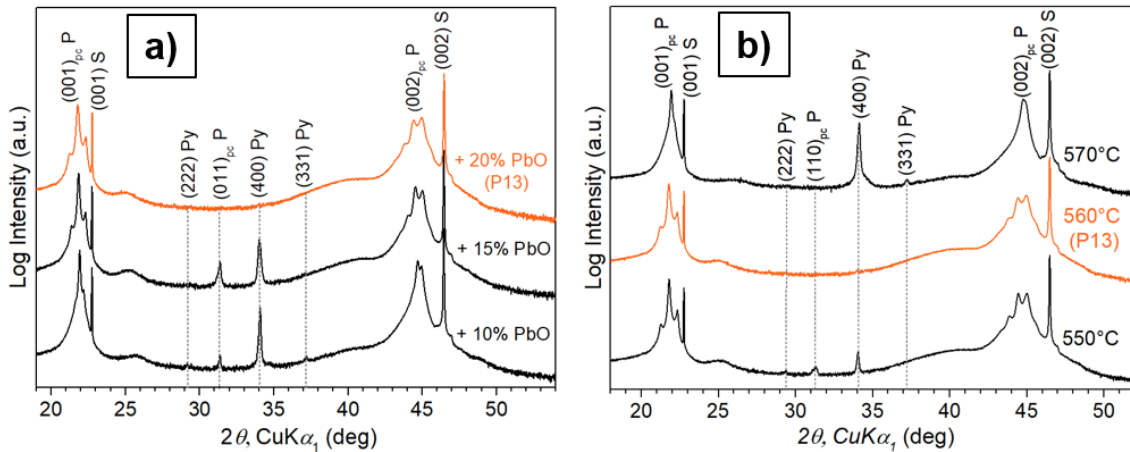


Figure 19: θ - 2θ scans of samples a) prepared from targets with different quantities of PbO excess, and b) deposited at different temperatures using the target with 20 mol. % PbO excess.

While this demonstrates that it is possible to obtain phase-pure films using a PbO-enriched target, it was also found that the appropriate deposition conditions are severely limited. Several parameters, particularly the substrate temperature, should be considered. The immense influence of the temperature on the phase purity of the films was demonstrated in a set of experiments, where the target with 20 mol. % PbO excess was used to prepare samples at an oxygen partial pressure of 0.13 mbar (Figure 19b)). The sample grown at 560 °C (sample *P13*) is pyrochlore-free and (001)-oriented. At 570 °C a large amount of pyrochlore is detected. As only the (400) reflection is seen, the pyrochlore phase seems to be textured as well. At temperatures below 550 °C the (222) peak of the Pb₃Nb₄O₁₃ is also identified. From these results it can be concluded that the temperature window for the growth of pure-perovskite films is smaller than ± 10 °C. Furthermore, it was found that the size heated area of the PLD heater has a substantial influence on the growth of the films. We tested two heaters, one with the heated area of 1.8 cm² and the other with an area of 12.5 cm². Note that in both cases, the diameter is larger than the substrate dimensions. We found that the use of the heater with a larger heater area diameter substantially facilitated the growth of pure-perovskite films, in some samples, we did not succeed in finding the appropriate deposition parameters for pyrochlore-free growth on the smaller heater at all. There are two possible explanations for this: (i) the temperature on the smaller heater is inhomogeneous, i.e. smaller at the edges - we could not test this hypothesis, since the STO substrates are largely transparent for the wavelength of the pyrometer on the PLD system; and (ii) the large heated mass of the larger heater affects the behavior of the plasma arriving to the substrate surface.

The formation of pyrochlore could be recognized already *in-situ* by examining the RHEED pattern after the sample was cooled and the chamber evacuated. The RHEED patterns of samples containing pyrochlore inclusions (Figure 20a) were always 3D

transmission patterns, similar to the pattern shown in Figure 8f), as these inclusions tend to protrude the sample surface to heights above 100 nm, as shown on the AFM image in Figure 20b). The growth of these inclusions was further clarified by examining the cross-section of the samples using TEM (Figure 21). The inclusions nucleate at the interface and extend throughout the layer in a conical shape. Therefore, their volume increases with increasing film thickness. Furthermore, new pyrochlore inclusions can be formed during prolonged exposure to high temperatures in the growth of thicker films. The electron diffraction pattern of the inclusion confirmed the results of the XRD measurements, i.e. that the structure of the secondary phase is indeed $\text{Pb}_3\text{Nb}_4\text{O}_{13}$ with a cubic $\text{Fd}\bar{3}\text{m}$ structure and a lattice parameter $a = 10.6 \text{ \AA}$.

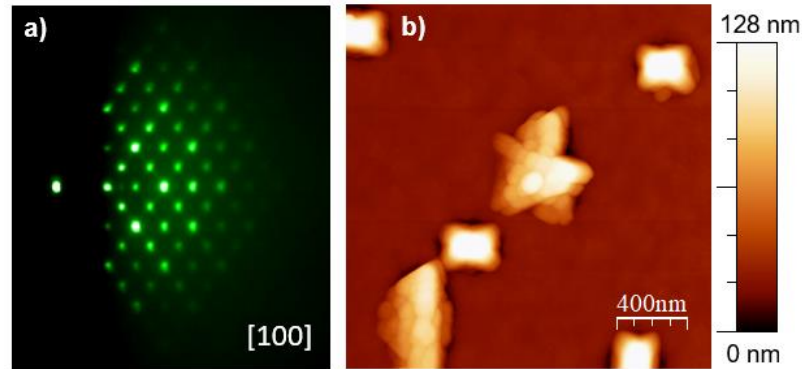


Figure 20: RHEED pattern (a) and AFM image (b) of a sample containing a large amount of pyrochlore.

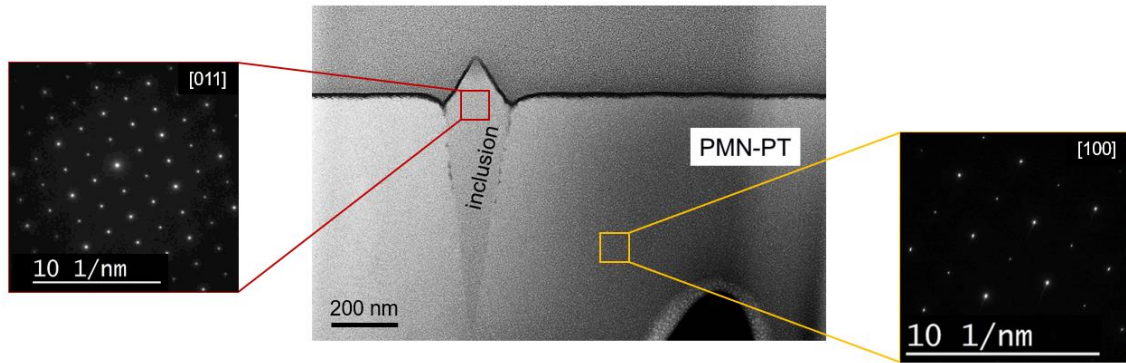


Figure 21: Cross-sectional TEM micrograph of a sample containing pyrochlore inclusions. The diffraction patterns of the $\text{Pb}_3\text{Nb}_4\text{O}_{13}$ and PMN-33PT phases in the labelled zone-axes are shown in the red and yellow squares, respectively.

4.3.2 Morphology, crystal structure and stoichiometry of the PMN-33PT thin films

In contrast to the samples containing pyrochlore, the phase pure sample ($P13$) has a smooth surface with a root-mean-square (RMS) roughness of 1.5 nm over a $2 \mu\text{m} \times 2 \mu\text{m}$ scan area. The AFM image of the sample is shown in Figure 22, along with the RHEED pattern (inset). The modulated streaks, similar to those shown in Figure 8d), indicate that (i) the film was grown epitaxially, and (ii) the surface consists of uncorrelated multilevel steps, with a width smaller than the coherence length, and, implying that the growth mode was a combination of 2D and 3D [115]. Monitoring of the intensity of the RHEED specular spot did not show

any clear oscillations. This indicates that the growth quickly transitions into island growth, however, the resulting surface is relatively smooth.

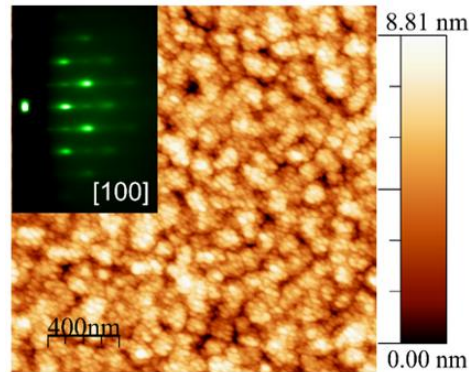


Figure 22: AFM image of sample *P13* with the RHEED pattern shown in the inset.

Despite the smoothness of the film, and the fact that there was no pyrochlore phase detected in this sample, the results of the preliminary relative-permittivity measurements did not meet my expectations. This encouraged me to examine the structure and stoichiometry of the PMN-33PT itself more profoundly. The first obvious peculiarity is the splitting of the $(00l)_{pc}$ peaks in the θ - 2θ scans. In principle, the peak profiles can be influenced by a large variety of structural peculiarities, such as non-uniform strain, the presence of lower-symmetry crystal structures, stacking faults or dislocations, etc. In order to investigate the effect of the deposition parameters, and to try and find the origin of this splitting, we carried out some additional experiments. The results of these experiments, where the deposition pressure was varied, are presented in the following subsection.

4.3.2.1 Influence of the process pressure

We have found that by raising the oxygen partial pressure from 0.13 mbar to 0.27 mbar (sample *P27*), while keeping the remaining parameters constant, the splitting of the $(00l)_{pc}$ PMN-PT peaks vanishes (Figure 23). The additional peak, which appears at 31.5° , corresponds to the (110) orientation of PMN-PT. Therefore, raising the deposition pressure leads to the growth of a small amount of misoriented crystallites. Nevertheless, the RHEED pattern and the morphology of the surface are similar to those of sample *P13*.

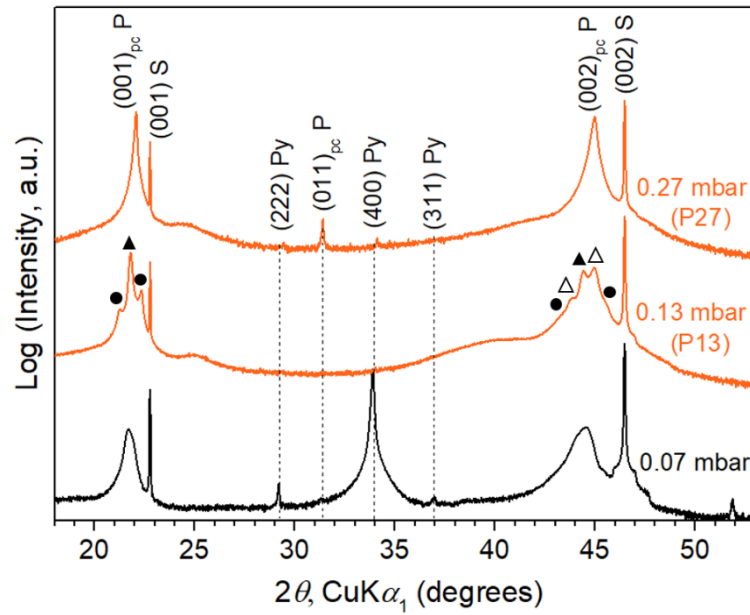


Figure 23: θ - 2θ scans of samples prepared at different oxygen partial pressures. The sample prepared at 0.07 mbar contains a very large amount of pyrochlore. Samples *P13* and *P27* are pyrochlore-free. Sample *P27* contains some (110)-oriented grains. The individual peaks in sample *P13* are marked with different symbols, the meaning of which is discussed in Section 4.3.2.1.2.

Unlike PLD growth of thin films in vacuum, the interaction of the plasma flux with the environmental gas changes the chemistry, dynamics and energy spectrum of the plasma species. The presence of a background gas can change the substrate and film surface energies and may even change the growth mode [116]. In a simplified view, the role of oxygen in PLD growth of oxides is double: (i) oxygen serves as a reactive gas, and (ii) oxygen (like any other gas) affects the propagation of the plume, i.e. it influences the plume dynamics. Let us focus on the former role first. The oxygen content from the target is generally not transferred to the thin film, if grown in vacuum. The metal-oxygen bonds can be broken directly by the laser or during collisions in the plume. Furthermore, oxygen is light and therefore easily scattered. In any case, additional oxygen has to be provided during deposition or in the post-annealing step to adjust the oxygen stoichiometry, i.e. to incorporate the oxygen from the surrounding atmosphere into the growing film. Going back to the results shown in Figure 23, given that the peak splitting is only observed in the sample prepared at a lower oxygen pressure (comparing only pure-perovskite samples), it would be tempting to conclude that the splitting arises from oxygen deficiency, i.e. it indicates the presence of oxygen vacancies. In order to exclude thermodynamic reduction processes as the origin of the splitting, we performed an experiment with an O_2/Ar gas mixture. The partial pressure of oxygen was fixed at 0.13 mbar, whereas the total pressure was 0.27 mbar. Oxygen and argon were selected for this experiment due to their similar atomic weights and PLD plasma expansion dynamics [117]. The pattern of the film prepared under these process parameters did not exhibit any splitting, indicating that oxygen vacancies are not the origin of the splitting. From this it could be concluded that the species are fully oxidized at 0.13 mbar. Therefore, the second role of the oxygen should be taken into consideration. Different models have been proposed to describe the flux propagation, such as the “drag force” and the “shock wave” model. The former assumes that the flux velocity decreases linearly with distance due to the viscosity of the gas. The latter describes how the confined part of the plume stops as a result of energy loss due to shock wave formation, and the particles within the plume become thermalized [118]. A more complex model, designed specifically for PLD-growth was presented by Strikovski and Miller [119]. Their model offers a physical definition of the plume range, which depends on the individual PLD system and also explains why the appropriate deposition rate is very important in PLD. Amoroso et al. [117] explained that three separate regimes exist:

- **a vacuum-like regime** at low pressures with a forward-directed flow and little scattering,
- **a transition regime**, where the plume is increasingly broadened, due to a strong momentum transfer to the background gas. Here, the plume ions and neutrals are split into a slow and fast component, where the fast part of the plume consists of particles that have suffered fewer collisions with the background gas. Finally, shock wave formation can occur in this regime.
- **a diffusion-like regime** with a broad angular distribution in the highest pressure range. Here, only the slow part of the plume remains, and the expansion can be described using a simple model based on diffusion from a confined plume.

In the pressure range in question here (10^{-1} mbar) the plasma plume expansion is no longer in the vacuum-like (ballistic) regime. Given the low kinetic energy of the species in this pressure range, sputtering and implantation can be disregarded as the origin of the observed anomalies. The kinetic model for the pressure-dependent propagation presented by Geohegan et al. [118] and Strikovski and Miller [119] proposes a transition in the propagation behavior from ballistic to drag to thermalized between 10^{-2} mbar and 10^{-1} mbar. While Kumar et al. [120] found that in PZT growth the energy of all the species in the plume is approximately equal at exactly 0.1 mbar, Amoroso et al. [117] showed that the transition regime exists between 0.01 mbar and 0.2 mbar. The observed splitting of the plume was reported for the ablation of pure Ag. The transition pressure from one regime to another is dependent on the specific gas used in the process [117]. The exact pressure range seems to be material-dependent, and its determination for complex materials, such as PMN-PT is challenging. The end values reported in these studies could also be related to the limited number of data points, the location of the pressure sensor, the gas flow, etc. Finally, the combined effect of both roles of oxygen should also be considered, as the sticking and mobility of the species on the surface of the substrate are in strong relation with their oxidation state [121], which in turn is associated with the reactions between the ejected metastable species and the gas molecules from the environment. As explained earlier, a higher ambient pressure can lead to the formation of a shock-wave front, thereby activating a chemical reaction in the plume [120]. Therefore, the plasma dynamics can influence the oxidation of the species in an indirect way, affecting the diffusion and relaxation behavior. Although plasma propagation studies are not within the scope of this work, the obtained results do imply that for this specific experimental set-up, the transition from one regime to the other lies in the pressure range between 0.13 mbar and 0.27 mbar, thereby yielding substantial differences in the structures of the samples prepared at these respective ambient pressures. The nature of these structural differences will be further discussed in the following subsections.

4.3.2.1.1 Analysis of the elemental composition by means of WDXS

The difference in the local adhesion energy and in the surface diffusion of the different adsorbed species can cause chemical inhomogeneity. This can lead to the formation of point-defect clusters or to phase separation, while the mean stoichiometry remains relatively unaffected [12]. The elemental composition of samples *P13* and *P27* was examined by means of WDXS analysis. According to the results shown in Table 5, the composition of the films was found to be uniform across the whole area, the concentration variations being lower than the experimental uncertainty of the method. Small deviations from the stoichiometric composition were found for Mg and Pb in both samples. The deviations are slightly larger in sample *P13*. Both samples contain a deficit in Mg and a surplus of Pb. Sample *P13* also has a slight Ti deficit. The calculated oxygen concentration is close to stoichiometric in both films, indicating that there are little or no oxygen vacancies, assuming the preservation of electric charge neutrality. The calculated chemical formula for sample *P27* was $\text{Pb}_{1.068 \pm 0.009} \text{Mg}_{0.185 \pm 0.004} \text{Nb}_{0.44 \pm 0.01} \text{Ti}_{0.324 \pm 0.007} \text{O}_3$. It should be noted that the formula is normalized to O_3 . The stoichiometry variations, including the surplus of Pb on the A-sites, is further explained in Section 4.3.2.1.3.

Table 5: The concentration (C) of individual elements in atomic percent (at. %), along with standard deviations, which include the standard deviations between individual measurement points and the counting errors for individual elements. Values are given for samples *P13* and *P27* and the reference single-crystal sample, and compared to the nominal PMN-33PT composition.

	Mg	Ti	Nb	Pb	O*
Average C in <i>P13</i> [at.%]	3.16	6.2	9.0	21.8	60.0
σ	± 0.02	± 0.2	± 0.3	± 0.5	-
Average C in <i>P27</i> [at.%]	3.68	6.5	8.8	21.3	59.8
σ	± 0.06	± 0.1	± 0.3	± 0.4	-
Average C in ref. sample [at.%]	4.54	6.4	9.0	20.0	60.0
σ	± 0.02	± 0.1	± 0.3	± 0.4	-
Nominal C for PMN-33PT [at.%]	4.4	6.7	8.9	20	60

4.3.2.12 Analysis of the average crystal structure by means of HR-XRD

The determination of the crystal structure and exact lattice parameters in oxide epitaxial thin films is anything but straightforward, especially with lab-sale diffractometers. The constituent crystallographic phases in materials with an MPB composition are usually determined by employing Rietveld analysis of X-ray or neutron diffraction patterns. Due to the preferred crystal orientation, it is impossible to apply the Rietveld analysis, as the number of diffracting planes is heavily reduced and the intensities are changed [122]. XRD-RSM is an effective approach to determining the crystal structure of most epitaxial thin films. RSM was performed around the (003), ($\bar{1}$ 03) and ($\bar{1}$ $\bar{1}$ 3) reflections of STO. The RSMs of the STO and corresponding PMN-PT reflections (found at lower Q_z values as compared to the STO) for sample *P27* are shown in Figure 24. The Q_z values of the symmetric and asymmetric PMN-33PT reflections match, indicating that there are no significant angular distortions in the crystal structure. The calculated IP and OP lattice parameters were $a = 4.021 \pm 0.006 \text{ \AA}$ and $c = 4.031 \pm 0.002 \text{ \AA}$, respectively. Therefore, the film is in a relaxed state, and the average crystal structure of the film seems to be pseudocubic with a slight OP tetragonal distortion. Despite the film being relaxed of lattice misfit strain, it is compressed due to the differences in TECs. As seen from Figure 5, the TECs of PMN-PT (around the MPB) and STO are equal at 450 °C. Below this temperature, the STO shrinks faster, imposing compressive strain onto PMN-33PT. Nevertheless, the distortion is small, the c/a ratio of the bulk tetragonal phase is 1.0104, while in sample *P27* it is 1.0025. It is important to keep in mind that the spot is broad and the given parameters just describe the position of the centroid. In principle, a mixture of different structural modifications could account for the broadening of the reciprocal spot, as shown later in Section 4.4.2, since the individual structural variants with the MPB composition are not easily distinguishable by XRD-RSM. There are also other possible origins for the broadening, such as strain relaxation along the film thickness, a low lateral correlation length and high mosaicity.

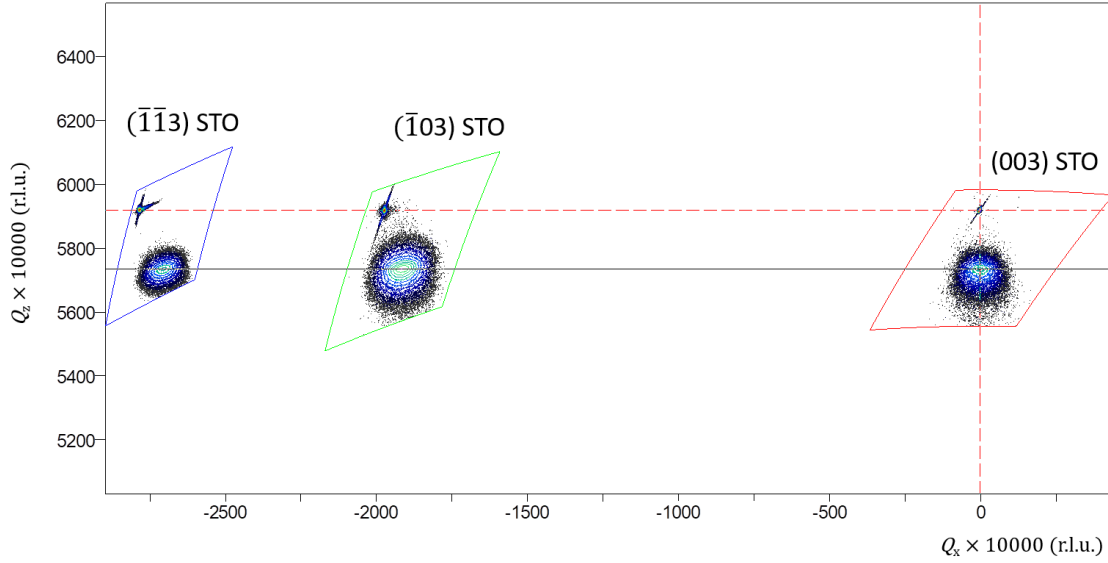


Figure 24: RSMs around two asymmetric and one symmetric reflection of STO and PMN-33PT. The vertical dashed red line marks the $Q_x = 0$ value. The center of the PMN-PT (003) reflection does not deviate strongly from this line, indicating that there is no significant tilting present in the out-of-plane direction. The horizontal dashed red line marks the Q_z value corresponding to the $(hk3)$ reflections of the STO. Matching Q_z peak positions confirm that the sample was well-aligned for all the measurements. The horizontal solid black line marks the Q_z value for the (003) PMN-PT reflection. The Q_z values of the $(hk3)$ PMN-PT reflections exhibit a good match.

As discussed in Section 4.3.2.1, the structure of sample *P13* is more complex. In some literature reports [123], [124], it has been argued that the peak splitting could be an indication of the presence of the MPB. As mentioned earlier, the structural distortions in bulk PMN-PT around the MPB are subtle. Nevertheless, it is also well known that different crystal systems can be stabilized in thin films under certain conditions. The clamping of the films to the substrate may hinder typical phase transformations during the cool-down from the deposition temperature. One can find numerous reports on BiFeO_3 , which is rhombohedral in bulk form, and the thin films exhibit a variety of crystal structures, even in thicker films (up to 2 μm) [125]–[128]. The MPB in PMN-PT thin [129], [130] and thick [77] films is also often shifted. It has also been shown [131] that crystal structures different from bulk can be stabilized by creating designer defects. Specifically, ultralow incident flux conditions, i.e. slower growth rate, can lead to the formation of nanoscale “defect pockets”. This results in the formation of local compressive strain, which cumulatively leads to macroscale strain, preserving the designer crystal structure even at higher thicknesses.

The markings (the circles and the triangles) in Figure 23 indicate the positions of the individual PMN-PT peaks in sample *P13*. The peaks in $(001)_{\text{pc}}$ do not match the parameters of any of the structural variants in bulk PMN-33PT, as the interplanar distances (d) calculated from the diffractogram are 4.18 Å, 4.08 Å and 3.98 Å. The lattice parameters for PMN-PT around the MPB (32-34PT) found in the Inorganic Crystal Structure Database are between 3.99 Å and 4.033 Å. Therefore, only the calculated distance of 3.98 Å does not deviate significantly from the known bulk values of MPB PMN-PT. Two additional peaks (marked with white triangles), with interplanar distances of 4.13 Å and 4.03 Å, are resolved from the central peak (black triangle) of $(001)_{\text{pc}}$ at 2θ higher angles. While 4.03 Å matches well the values from the database, 4.13 Å does not. Such large d -values could be explained by the presence of a separate phase of (001)-oriented PT, the existence of which was not confirmed by any of the techniques used in this work. A possible origin of lattice expansion in perovskite oxides is the presence of oxygen vacancies, in which case the equally charged cations move further away from each other. As explained in Section 4.3.2.1, oxygen deficiency is not expected to arise directly because of a lower oxygen partial pressure, yet it could arise indirectly due to the dynamics of the plasma plume affecting the chemical

reactions in the plume. The oxygen concentration cannot be probed directly by means of WDXS analysis. Nevertheless, if we assume that the electric charge neutrality will be preserved in the sample, the calculated oxygen stoichiometry is very close to the stoichiometric value. Furthermore, it is unclear why ordered domains with different concentrations of oxygen vacancies would be formed. On the other hand, given the large deviations of these parameters with respect to bulk PMN-33PT, it is also unlikely that this splitting is related to the presence of different structural modifications with the same stoichiometry, i.e. the presence of the MPB. Therefore, the origin of the splitting remains unclear.

In order to examine the IP orientation of sample *P13*, we performed an azimuthal (Φ) scan of the $\{101\}$ family of planes of the substrate and the film (Figure 25). IP epitaxy with the substrate was revealed, i.e. $[100]_{\text{pc}}$ PMN-33PT $\parallel$ $[100]$ STO. The film therefore exhibits a fourfold symmetry. However, from the asymmetrical peak shapes in the Φ -scan it is also evident that the structure of the film is complex.

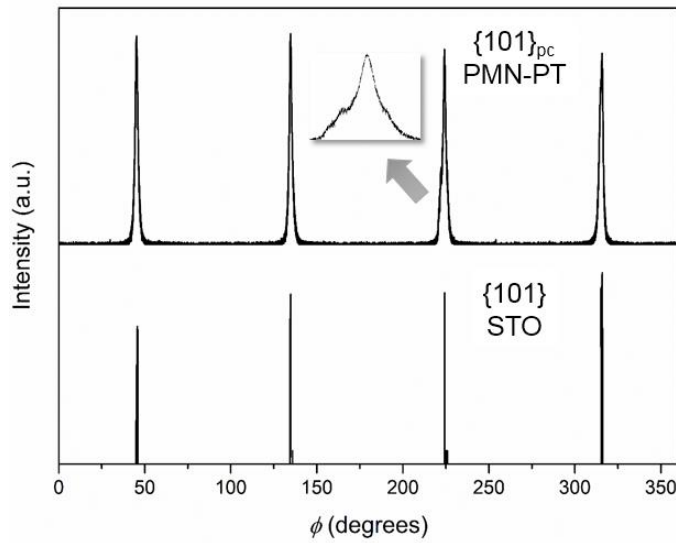


Figure 25: Azimuthal XRD measurement of the $\{101\}$ family of planes in sample *P13*. A magnification of the region around $225^\circ \Phi$ is shown in the inset, revealing the irregular peak shape.

From the $(001)_{\text{pc}}$ PMN-PT reflections shown in Figure 26 it is clear that there is no significant domain tilting present in the sample, as all three distinct peaks are centered around $Q_x = 0$. Domain tilting is very common in tetragonal PZT thin films with an a/c domain structure, and it has also been reported for PMN-PT [39], [132].

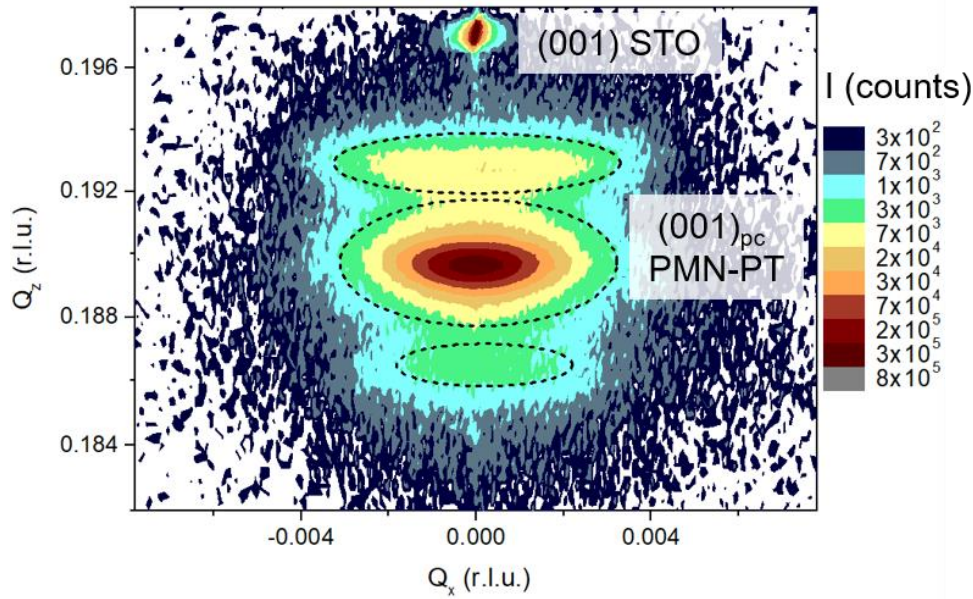


Figure 26: RSM around the $(001)_{\text{STO}}$ and $(001)_{\text{pc}}$ PMN-33PT reflections.

The entire mapped areas of the asymmetric reflections are shown in Figure 27 (panels a and b). Panel c shows a magnified region around the $(\bar{1}\bar{1}3)_{\text{pc}}$ PMN-PT reflection. Two distinct reflections are seen, as well as a very faint reflection at a higher Q_z value. A magnified region around the $(\bar{1}03)_{\text{pc}}$ PMN-PT reflection is shown in panel d. Three distinct peaks were identified, the one with the lowest Q_z value being the least intense. The purple line marks the Q_z value of the most intense $(003)_{\text{pc}}$ peak (not shown here). Deviations of the peak positions from the purple line indicate either (i) an angular distortion within the crystal structure or (ii) the presence of defects in the structure. On the one hand, given that the spitting of the peaks does not corroborate with any known tetragonal, rhombohedral or monoclinic structure of PMN-33PT or related compounds [133], the former option does not seem very likely. On the other hand, the presence of individual defects should not affect the diffraction of X-rays, as large ordered domains are required to produce a signal in XRD.

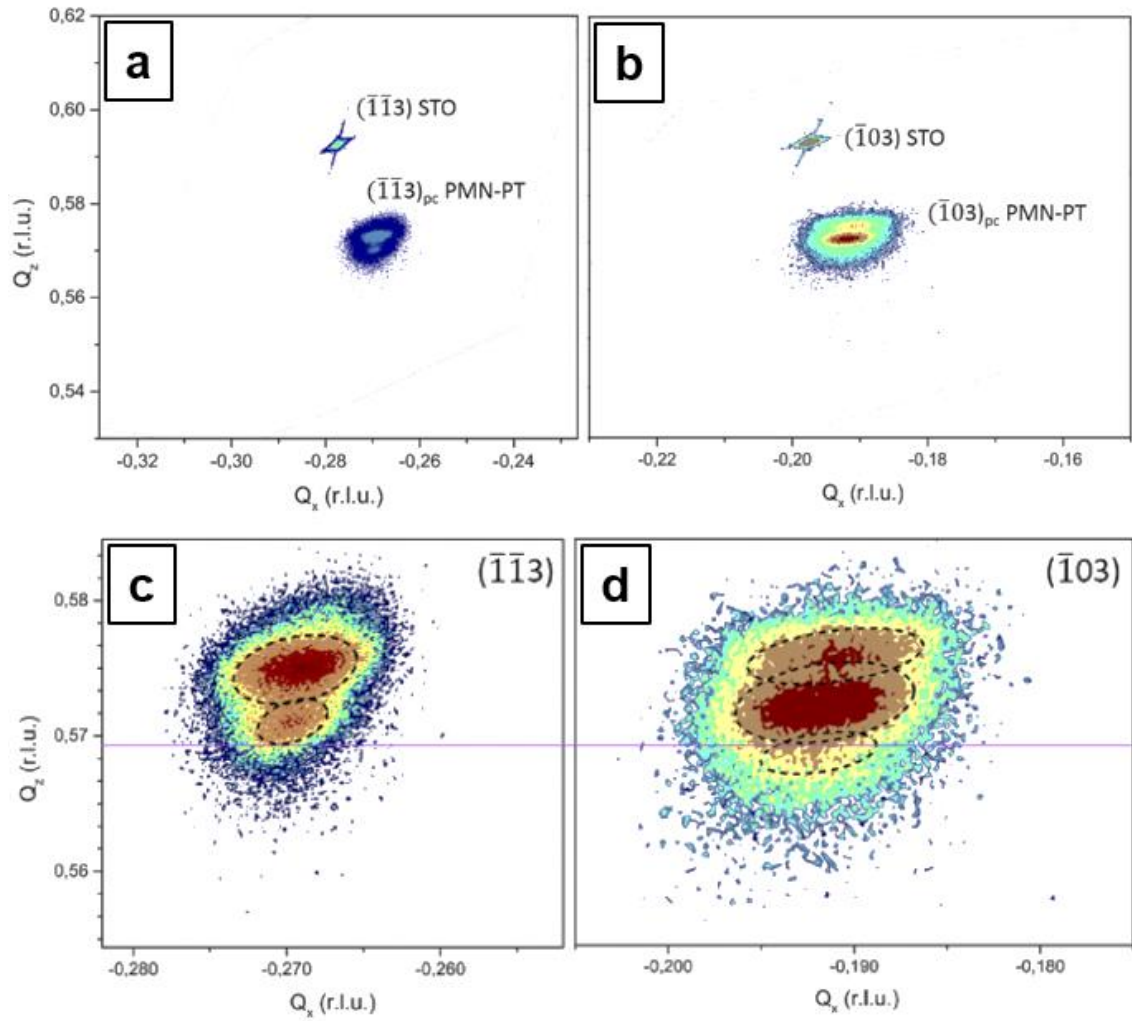


Figure 27: RSMs around the a) $(\bar{1}\bar{1}3)$ and b) $(\bar{1}03)$ reflections. c) Zoomed-in region from panel a. d) Zoomed-in region from panel b.

The splitting of the PMN-PT reflections was also observed by Mietschke et al. [124] in films grown from a PMN-32PT single-crystal target with on-axis and off-axis PLD at a partial oxygen pressure of 0.1 mbar. Furthermore, they observed that the splitting appears at lower temperatures, where the pyrochlore-phase formation is suppressed. Given that the pressure used was similar as in this study, the assumption that the splitting is related to the plasma dynamics under these conditions is reinforced. In contrast to other reports, we believe that the structural peculiarities in study [124], as well as this study, are brought about by peculiarities of the transition regime, such as limited diffusion, particle energetics, etc. In the next step, TEM analysis was performed in order to find out how the splitting is reflected in the microstructure, and to examine the local atomic structure of samples *P13* and *P27*.

4.3.2.13 Local structural analysis with TEM

TEM cross-sectional micrographs of *P13* and *P27* shown in Figure 28 exhibit a substantial difference in the microstructure of the two samples. Sample *P13* consists of more lamellar-like features, whereas wedge-like features are present in sample *P27*.

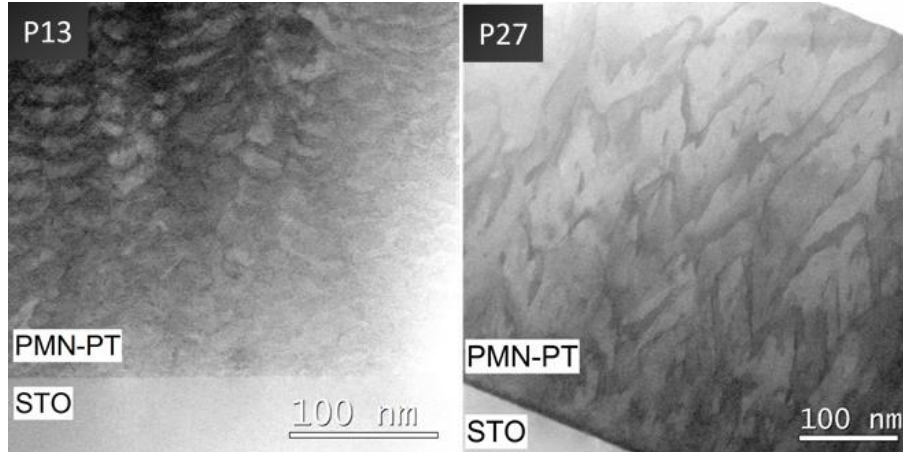


Figure 28: Cross-sectional TEM image of samples *P13* and *P27*, revealing their different microstructure.

Closer inspection by means of atomic resolution STEM-HAADF imaging revealed that the interface between the TiO_2 -terminated STO substrate and the PMN-33PT is atomically sharp in both samples. Good crystallinity and coherent growth with the substrate was achieved. The interface in sample *P27* is shown in Figure 29.

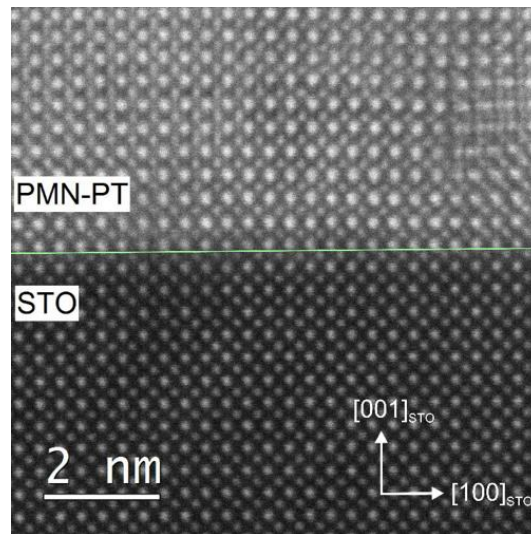


Figure 29: STEM-HAADF image of the atomically abrupt STO/PMN-PT interface in sample *P27*.

Structural defects can nevertheless be seen to start appearing a few monolayers into the thin film. In order to study their origin, STEM-HAADF images of the interfaces in both samples were post-processed by means of GPA. The original and processed images are shown in Figure 30. The intensity distribution in the maps corresponds to the relaxed structure of PMN-33PT, as already indicated the XRD-RSM measurements. In sample *P13* the compressive stress is accommodated via a network of stacking faults (SFs) that form out-of-phase boundaries (OPBs) close to the interface as well as in the bulk of the film. No localized dislocation centers were found at the interface. In *P27*, on the other hand, the stress is released through the formation of defined misfit dislocations (MDs) spaced about 10 nm apart. The strain-line density is also significantly higher in the bulk of sample *P13* (see strain map insets in Figure 30). The strain lines correspond to the positions of the defective structure areas in the film, such as different types of SFs. The rest of the strain components are shown in Figure 31.

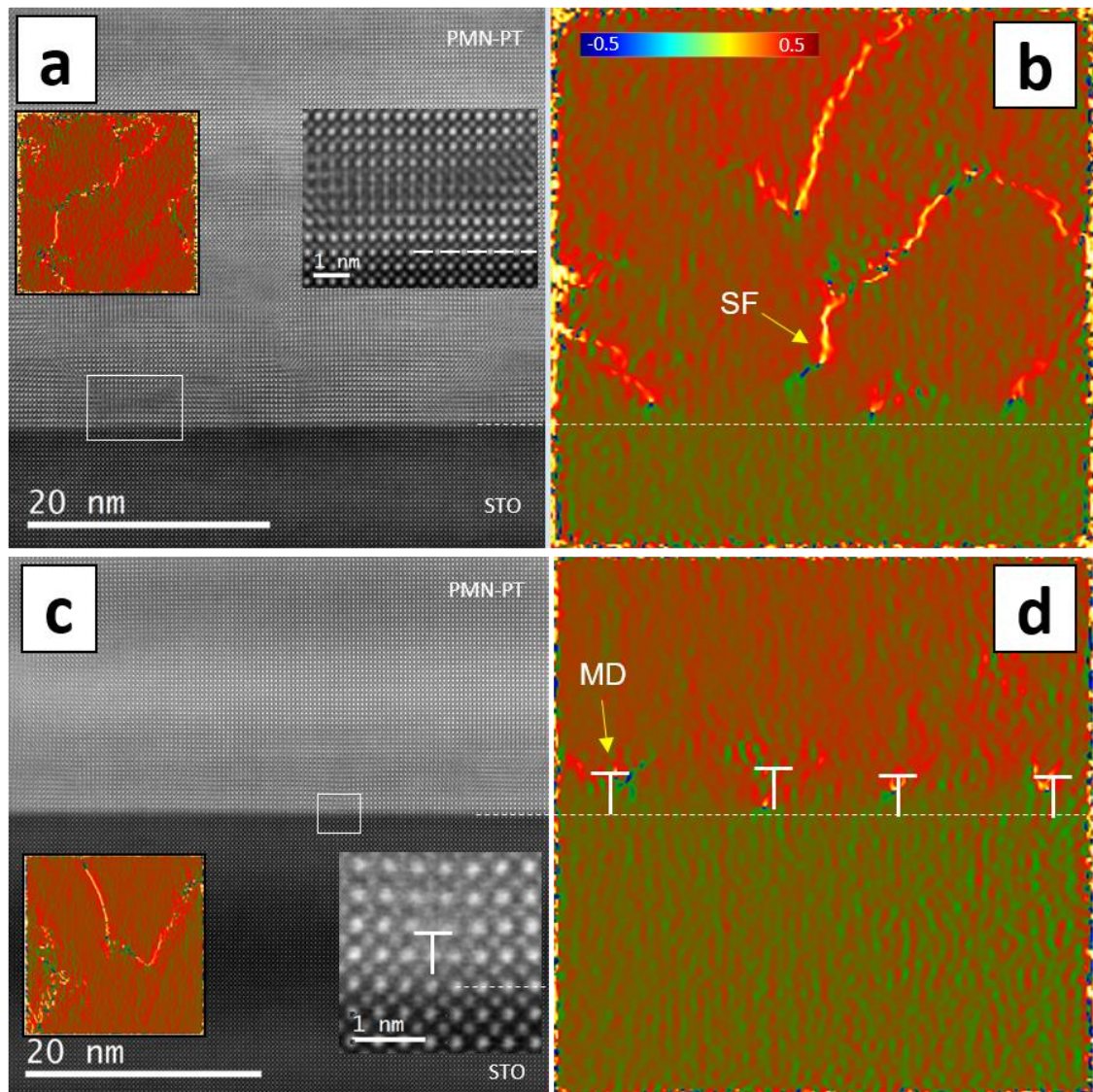


Figure 30: a) STEM-HAADF image of the interface in *P13*. A magnified region of the interface is shown in the inset on the right. b) Analysis of the xx component of the strain map on the region from panel a. c) STEM-HAADF image of interface in *P27*. The magnified region of the interface (inset on the right) reveals the presence of misfit dislocations, spaced about 10 nm apart, and starting within the first 2-4 ML of PMN-33PT. Strain maps of the bulk part of the *P13* and *P27* films are shown as left insets in panels a and c, respectively. The rainbow scale represents the intensity variations on the map, with green corresponding to the regular structure.

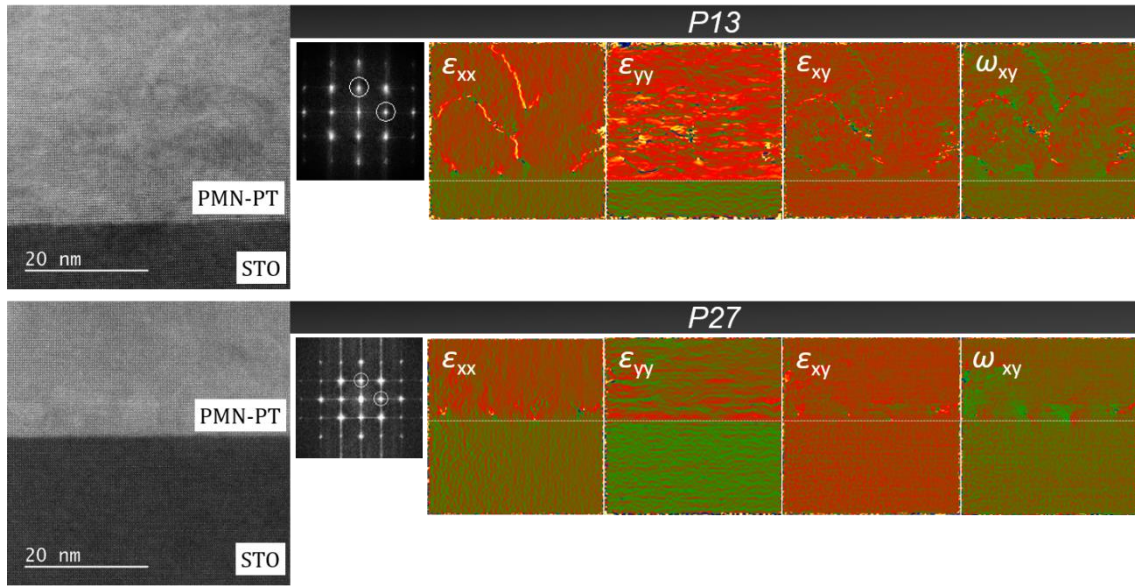


Figure 31: The in-plane (ϵ_{xx}), out-of-plane (ϵ_{yy}), shear (ϵ_{xy}) and rotation (ω_{xy}) strain components. The asymmetric Bragg spots used for the analysis are marked with white circles. Generated GPA strain maps illustrate the locations of the relative strain by color contours.

An example of an A-site OPB in sample *P27* is shown in panel a) of Figure 32. Panel b) shows a magnified image of the boundary region, together with marked atomic positions. According to these observations, a possible mechanism for the formation of such OPBs could be the kinetically limited growth of Pb-rich PMN-33PT, similar to what has been observed in other A-site rich perovskites. Actually, interweaving slabs of the rock-salt structure within the parent perovskite structure are a typical accommodation mode for excess alkaline-earth oxides. A-site Ruddlesden-Popper (RP) planar faults have been found in BaTiO_3 thin films, supposedly representing a mechanism of accommodating the excess quantities of barium ions [134], [135]. A randomly arranged RP structure has also been observed in SrO-excess-STO thin films [136]. The RP faults usually do not form an ordered structure in thin films, while this is frequently observed in sintered ceramics [137], [138]. The difference is attributed to the differences in thermodynamic equilibrium.

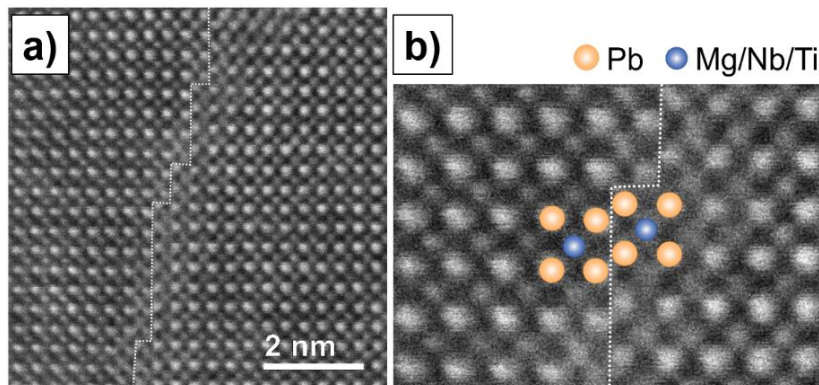


Figure 32: a) Atomic-resolution STEM-HAADF image of sample *P27*. The OPB is marked with a dashed line. b) Magnification of the boundary region with marked atomic positions, revealing a PbO/PbO boundary, where the PMN-33PT unit cell is shifted vertically by approximately 1/3 of a unit cell.

As WDXS analysis has shown, the overall composition of the two films is slightly Pb-rich. This is probably related to the local excess of PbO and the 3D growth mode. A layer of PbO rock-salt structure is formed on the surface of the growing islands. A lattice shift occurs where the two islands meet. In principle, another mechanism for the compensation of smaller quantities of A-site surplus in perovskite thin films could be the formation of vacancies on the B-sites [12]. This mechanism could explain the Mg (as well as Ti in sample *P13*) vacancies. It would make sense for B-site vacancies to be preferentially formed on Mg-sites, due to equivalent valences of Pb and Mg ions (X^{2+}). However, owing to the close packing of oxygen in the perovskite structure, any A-site excess should be difficult to accommodate, leading to the formation of a separate AO layer as soon as the atomic ratio between Pb and O is larger than 1:3. Owing to the low vapor pressure of Mg, it is not expected that the Mg be lost during the deposition through the same mechanism as Pb. Due to its relatively high melting point, one of the possible reasons for Mg deficiency could be non-uniform ablation of the target, which would leave excess Mg behind. As explained in Section 4.3.1.1, the energy density was selected carefully, in order to avoid non-uniform ablation. Mg being the lightest among the cations in PMN-PT, it is most affected by the collisions with other particles in the plume, as well as the collisions with the ambient gas. This could lead to Mg deficiency, especially in the ballistic regime. In the diffusion-like regime, however, the plume particles are thermalized, when they reach the substrate, i.e. they should have the same energy and spread on the substrate surface. However, the thermalization does not occur instantaneously. In the nascent plume, the angular distribution of the lighter and heavier species may not be the same. At higher energy density values, this effect should be less pronounced. Furthermore, it has been suggested that the atomic masses may not reflect the mass of the so-called carrier species that transport the atom [139], [140]. As spectroscopic measurements of the plasma plume are outside the scope of this work, the origin of the Mg deficiency cannot be determined with confidence. As spectroscopic measurements of the plasma plume are outside the scope of this work, the origin of the Mg deficiency cannot be determined with confidence.

We have also considered the possibility that the observed defects are related to the TEM sample preparation procedure, however, we do not believe that is the case. The observed stacking faults strongly resemble those grown by Chekhonin et al. [141]. In contrast to my samples, the samples in their study were prepared using FIB. Several other interesting comparisons between the studies can be made. Their films were grown on low- and high-miscut substrates at 0.3 mbar and 0.1 mbar, respectively. They argued that the appearance of the MDs around the SFs is a mechanism of strain relaxation in the films. They proposed a different mechanism of MD formation for the two types of samples, supposedly giving rise to the observed microstructural differences. Based on my results, I believe that the mechanism is related to the deposition pressure, rather than the substrate miscut and the mechanical strain accommodation. It should be emphasized that in both studies, the samples with the higher defect density were prepared at lower pressures (~ 0.1 mbar).

The observation of a much higher density of OPBs in sample *P13* actually offers a possible explanation for the peak splitting observed in the XRD pattern of this sample. According to some literature reports, a high density of SFs, such as OPBs, could result in peak splitting, i.e. the modulation of the diffracted intensity could in fact be caused by regions of diffracting volume in out-of-phase alignment [142]–[144].

4.3.3 Functional properties of PMN-33PT/STO samples

As already explained in Subsection 3.3.7, the electrical characterization was performed on two types of samples: (i) PMN-33PT grown on pure STO substrates (samples *P13* and *P27*) and (ii) PMN-33PT grown on Nb:STO (samples *P13Nb* and *P27Nb*). The former samples were measured using a set of IDEs, which is used in the d_{33} -mode, while the latter samples were measured in the standard PPC configuration, as implemented in the d_{31} -mode EHs. The results of the measurements are shown in Table 6. The ε_r of the samples prepared at a higher deposition pressure is increased by more than 100% as compared to those prepared at a lower pressure. This reinforces the assumption that the peak splitting observed in XRD does not indicate the presence of the MPB in samples prepared at 0.13 mbar. Additionally, the relative permittivity measured in IDE configuration (ε_r^{IP}) is also approximately twice as high as in the PPC geometry (ε_r^{OP}). From the results of the XRD measurements (Figure 33) and the AFM images, together with the corresponding SEM cross-sectional micrographs

(Figure 34) it is evident that the substrate doping does not have a significant effect on the crystal structure, surface morphology or the density of the films. All films exhibit a dense, non-columnar structure. The results are shown for samples *P13* and *P13Nb*. The results for *P27* and *P27Nb* are similar. From this it can be concluded that the differences in the ε_r values can be attributed to the anisotropic nature of the PMN-33PT thin films [145], [146]. The higher ε_r^{IP} values (as compared to (ε_r^{OP})) imply that the net polarization in both types of samples is in the OP direction, i.e. tetragonal *c*-domains would be expected to prevail in the films.

Table 6: Relative permittivity and dielectric losses of PMN-33PT/(Nb:)STO samples measured at 1 kHz.

Sample	ε_r	$\tan \delta$
P13	$900 \pm 60 (\varepsilon_r^{IP})$	0.007
P27	$1900 \pm 150 (\varepsilon_r^{IP})$	0.013
P13Nb	$410 \pm 10 (\varepsilon_r^{OP})$	0.041
P27Nb	$980 \pm 30 (\varepsilon_r^{OP})$	0.051

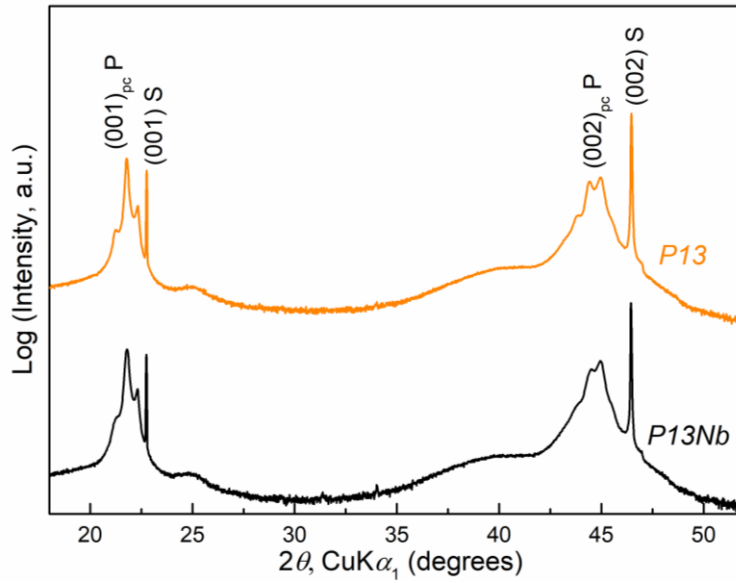


Figure 33: XRD patterns of samples *P13* and *P13Nb*, revealing that the average crystal is unaffected by the substrate doping.

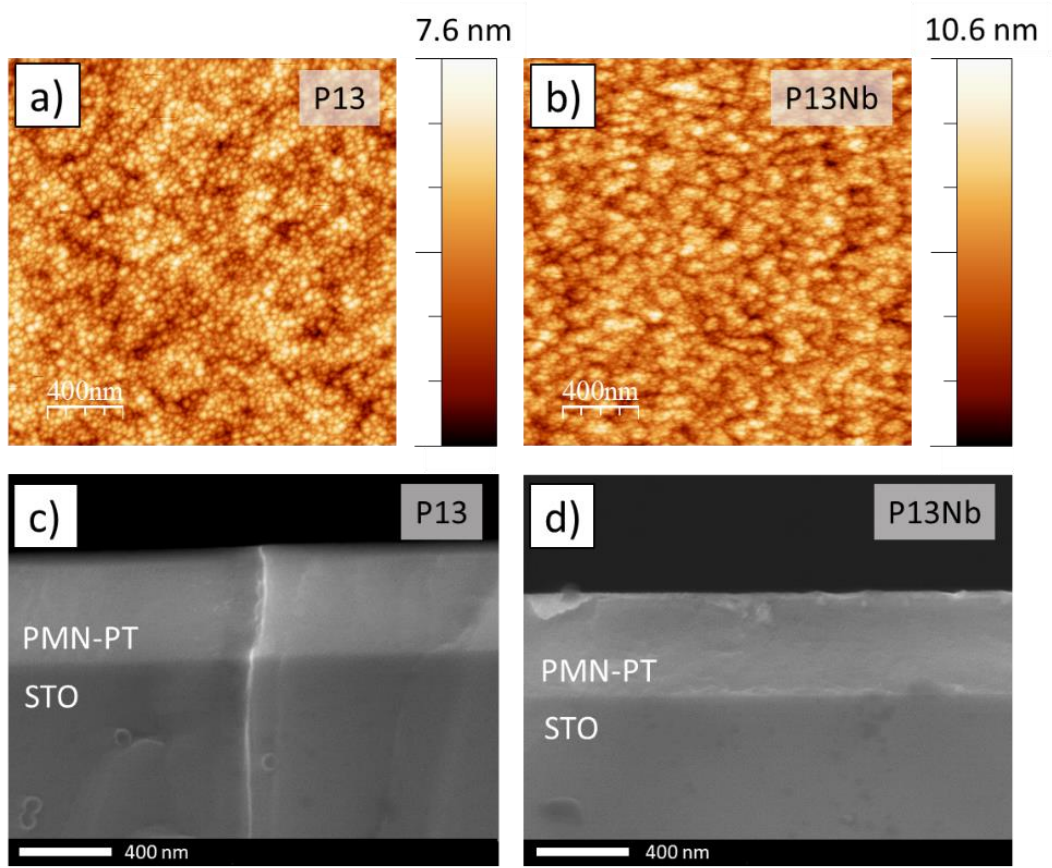


Figure 34: a), b) AFM micrographs of the surfaces of samples *P13* and *P13Nb*, respectively. c), d) Secondary-electron SEM micrographs of the cross-sections of samples *P13* and *P13Nb*, respectively.

In order to probe the local piezoelectric response, and also to find out whether the features observed with XRD and TEM are related to the domain structure of the films, we carried out PFM analysis. Note that PFM was performed on the surfaces of the films, as opposed to TEM, where the cross-sections were studied. We are aware that due to the boundary conditions, the properties of the surface can differ from the bulk. However, due to the thinness of the films it is impossible to probe the cross-sections by PFM. In thick films it is possible to reach the internal domain structure by polishing the sample surface, which is also not feasible in thin films.

The topography and map of the piezoelectric responses for sample *P27Nb* are shown in Figure 35a) and b), respectively. The bright regions in the PFM amplitude image correspond to the areas with an enhanced piezoelectric response, while the dark regions mainly belong to pores and non-active boundaries of the surface structures. The surface structures appear to be single-domain, but note that the tip radius is only a few times smaller than the structures themselves. Therefore, the resolution limit of the PFM technique hinders the distinction of individual domains. A line profile extracted from Figure 35b) is shown in panel c), where it is shown that the local piezoelectric response (d_{33}^{local}) can reach values as high as 140 pm V^{-1} . Figure 35d) shows the distribution of the PFM amplitude values. The most common value of the piezoelectric response is $\sim 20 \text{ pm V}^{-1}$. The average piezoelectric value was calculated to be 28 pm V^{-1} .

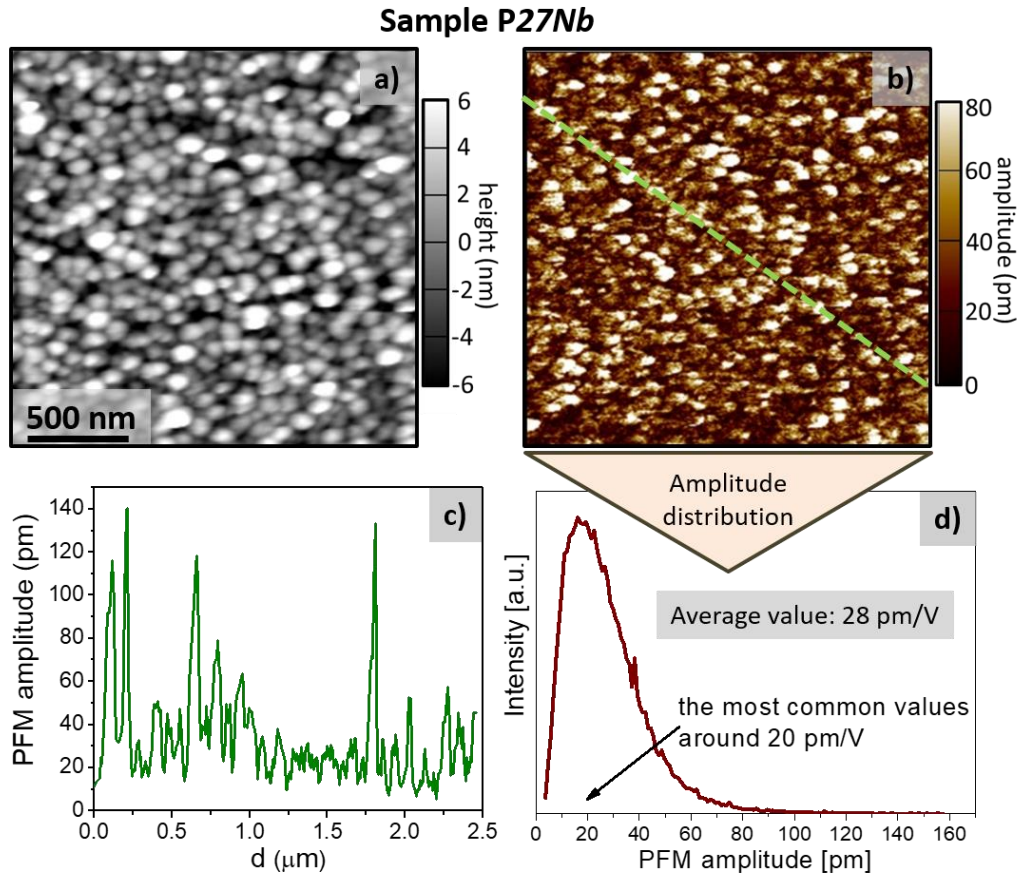


Figure 35: a) Height (topography) image. b) OP PFM amplitude image at an AC amplitude of 1 V (10 kV cm^{-1}). c) Line profile extracted from the dashed line in panel b). d) The distribution of the PFM amplitude values extracted from the image in panel b).

The inferior local piezoelectric response in sample *P13Nb*, as shown in Figure 36, serves as additional confirmation that the XRD peak splitting does not indicate the presence of the MPB, and that the high density of SFs strongly deteriorated the local piezoelectric response.

In order to further probe the piezoelectric response, PFM local domain-switching experiments were performed, one of which is shown in Figure 37 for sample *P27Nb*. Local amplitude and hysteresis loops can be observed. The domain nucleation voltages $V_{\text{DN}+}$ and $V_{\text{DN}-}$ are $\sim 11 \text{ V}$ and $\sim -4 \text{ V}$, respectively. For this reason, all the PFM scans presented in this work were performed with an AC amplitude of 1 V so as not to modulate the domain structure during the scanning. In the following step a PFM *in-situ* poling experiment was performed. The marked area was scanned with the PFM tip under a DC poling voltage of $\pm 30 \text{ V}$, which is significantly higher than the V_{DN} , aiming to switch as many domains as possible. After the *in-situ* poling, the entire area was scanned using an AC voltage with the amplitude of 1 V. As shown in Figure 37c)-e), the scanning area was poled almost perfectly, thereby providing evidence that the domains can be effectively switched. Good domain mobility and successful *in-situ* poling was also achieved for sample *P13Nb* (the results are not shown here, due to the similarity with those shown in Figure 37). According to the results of the PFM analysis, the films are self-poled, i.e. in the PFM phase image of the virgin part of the sample, the contrast is almost completely uniform.

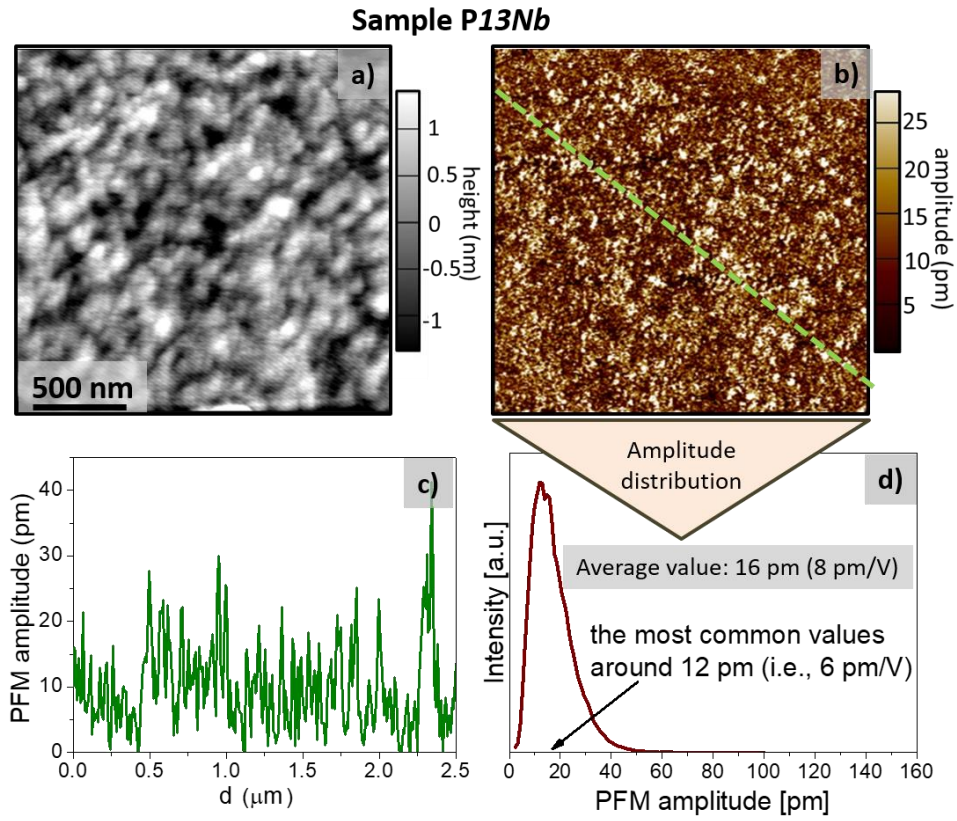


Figure 36: a) Height (topography) image and b) OP PFM amplitude image at an AC amplitude of 2 V (36 kV cm^{-1}). c) Line profile extracted from the dashed line marked in panel b). d) The distribution of PFM amplitude values extracted from the image in panel b).

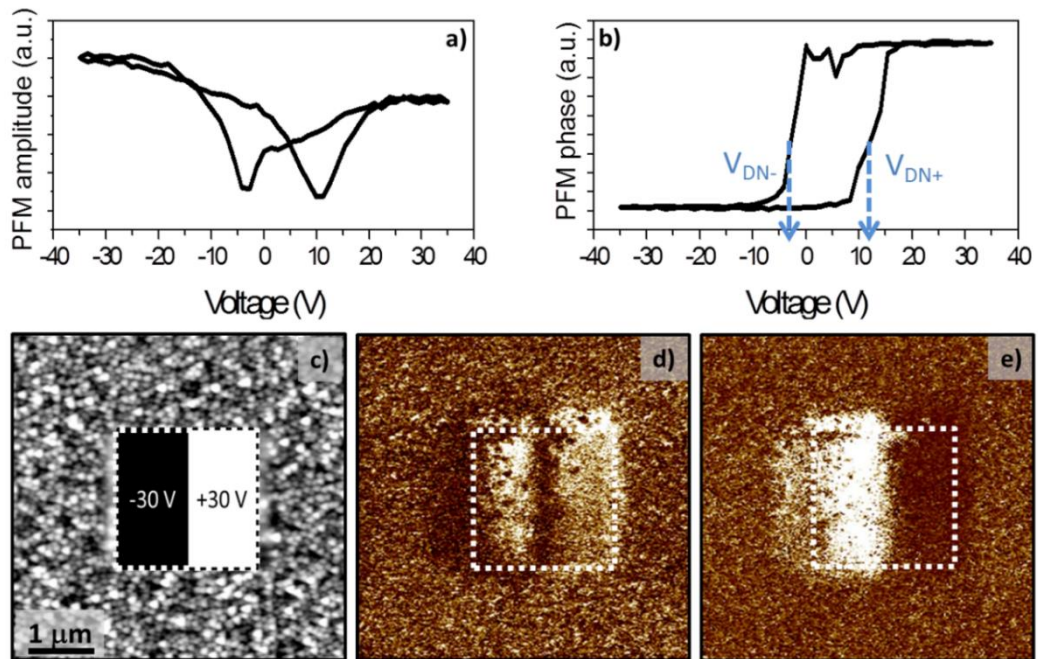


Figure 37: PFM a) amplitude and b) phase local hysteresis loops. c) Height (topography) image, d) PFM OP amplitude and e) phase images after the *in-situ* poling experiment. The two different areas of poling with negative and positive voltage are marked in panel c).

The macroscopic electrical properties of sample *P13Nb* were quite poor, with the maximum absolute value of $d_{33,\text{eff}}$ reaching only 35 pm V^{-1} , the highest value of the large signal strain at 400 kV cm^{-2} being 0.09% and the polarization reaching $25 \text{ } \mu\text{C cm}^{-2}$. The macroscopic longitudinal piezoelectric response of sample *P27Nb* is shown in Figure 38a). Figure 38b) shows the large signal strain and polarization loops. The sample again exhibits superior properties as compared to sample *P13Nb*. The loops are off-set horizontally and also slightly vertically. This self-bias or imprint can be caused by different reasons.

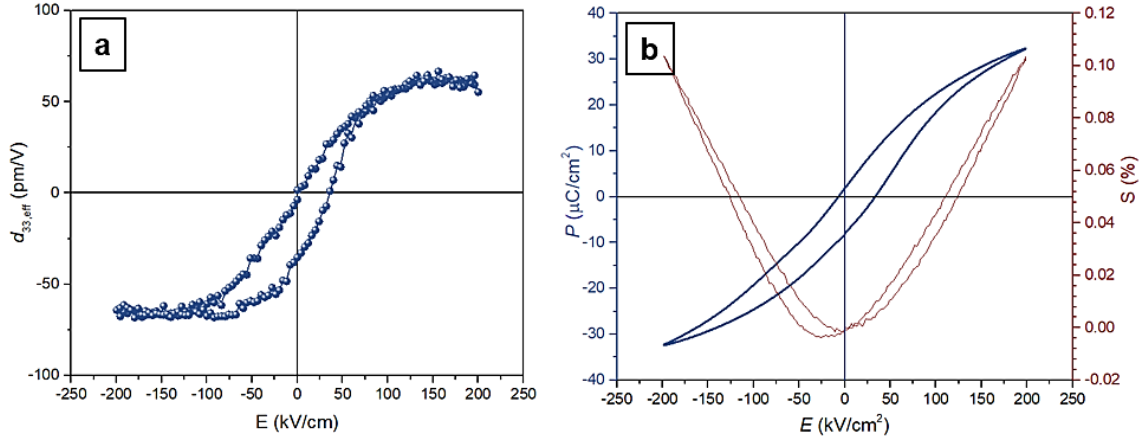


Figure 38: a) Piezoelectric coefficient $d_{33,\text{eff}}$ and b) polarization and strain in sample *P27*.

Imprint or asymmetry of switching parameters, such as the remnant polarization (P_r) and coercive field (E_c) have often been reported in the literature [42], [112], [147]–[151]. The origin of the imprint is usually ascribed to the presence of an internal electric field within the capacitor. The field supports the given polarization state, while opposing the antiparallel one. Different models have been proposed to explain this asymmetric behavior: trapped charge carriers [152], domain pinning [153], a built-in electric field or a non-switching layer at the interface [150], [151], and the aligned dipolar defect complexes and asymmetric distribution of charged defects through the bulk of the thin film.

Abe et al. [151] argued that the voltage offset originates from the non-switching (dead) layer that exists at the interface, with a spontaneous polarization that cannot be switched by the applied voltage. Here, the crystal structure could be asymmetrically deformed by the relaxation of the lattice misfit strain.

Misfit strain accommodation via the formation of misfit dislocations, similar as presented in Section 4.3.2.1.3, has also been found to play a role. It has been shown [154] that the presence of dislocations at the interface can lead to the preferential formation of ferroelectric domains around the misfit dislocations. It was also found that the types of the domain variants depend on the directions of the dislocation lines and their Burger's vectors. Furthermore, Wu et al. [155] have demonstrated that the annealing conditions have an enormous influence on the voltage shift in PZT thin films on various electrodes. Annealing in high- and low-oxygen-pressure conditions revealed that the bulk film parameters are the same, therefore the oxygen loss could take place at the interface alone. Specifically, at the sites near the threading dislocations. With the increase of the lattice-misfit strain, a larger density of dislocations will be formed, leading to a larger concentration of oxygen vacancies. This will result in a larger internal field, manifested as a voltage shift. A shift caused by an asymmetry in the oxygen vacancy content was also proposed by Lee et al. [149]. Supposedly, the concentration of oxygen vacancies in and near the top electrode changes with the cooling conditions after the deposition, while that at the bottom electrode is independent of the cooling conditions.

Wong et al. [156] followed up the idea of a passive layer by modeling a thin film using ferroelectric-dielectric and ferroelectric-ferroelectric bilayer structures. They demonstrated that the horizontal shift of the P-E loop from the central position is strongly related to the asymmetry of the electrical conductivities, thickness of the passive layer and the applied AC field. Other degradation phenomena, such as vertically shifted and

asymmetrically deformed loops can be modeled by introducing a ferroelectric-ferroelectric bilayer. The imprint could also be caused by asymmetric electrodes due to differences in screening properties and work functions of the electrodes [157].

The latter seem to be the most likely cause for the shift of the loop in sample *P27*, the bottom electrode being the Nb:STO and the top electrode consisting of Au. Furthermore, the sputtering deposition of the Au electrode could introduce defects into the PMN-PT thin film structure, resulting in the observation of an imprint [158]. In light of the surface domain imaging with PFM, it is also possible that the as-grown film is already self-poled. Self-poling has been observed in many different types of thin films [159]–[165].

A built-in bias can be beneficial from an application standpoint in many ways. A positive self-bias increases the value to the negative remnant polarization, for example. This in turn may enhance the piezoelectric response at zero applied field. Self-bias stabilizes the polarization in a given direction and aids in slowing down the aging of the piezoelectric response. Devices, based on films with a built-in bias, are more robust against depolarization due to voltage or temperature excursions [166]. Furthermore, the self-bias also decreases the dielectric permittivity at zero applied field, leading to an enhancement of the FOM value in EHs.

4.4 Growth of PMN-33PT Thin Films on LNO/STO

In the second part, the PMN-33PT thin films were grown on STO substrates covered with thin-film LNO electrodes, in order to study them for the application in d_{31} -mode EHs. It has been shown [167], [168] that the substrate symmetry and the electrical properties of the bottom interface have a more pronounced influence on the domain variants, as compared to the sign and magnitude of the epitaxial strain. Owing to the electrical properties of the bottom-electrode material, a reduced number of domain variants was formed upon its introduction. Shelke et al. [169] observed a strain effect in BFO films deposited directly on STO substrates, while layers deposited on SRO/STO were unstrained. Peräntie et al. [170] observed an electrode-controlled strain relaxation in PbTiO_3 epitaxial thin films, where thin films grown on thicker bottom electrodes exhibited significantly larger polarization values as compared to those grown on a thinner layer. On the other hand, Alpay et al. [171] did not find any effects of the bottom electrode on the domain structure or population in the PZT thin films, arguing that depolarization charges do not affect the domain structure.

In light of the interesting reports from the literature, mainly showing that the insertion of a thin layer between the substrate and the piezoelectric film changes many parameters of the system, we have also focused on the secondary role of the electrode layers in the preparation of PMN-PT thin films. Furthermore, my hypothesis was that the electrode layer influences the sticking properties of the PMN-PT. The hypothesis was formed on the basis of the results on the growth of PMN-PT directly on STO. Here, a substantial amount of PbO excess was required, while in the literature growth from stoichiometric targets yielded pyrochlore-free films on STO with bottom-electrode layers.

4.4.1 Growth and crystal structure of LNO

LNO is the only rare-earth nickelate that exhibits metallic behavior at all temperatures, making it a viable candidate for electrodes in oxide-based devices [172]. A remarkable improvement of the ferroelectric properties of PZT thin films has been observed upon changing the bottom electrode material from SRO to LNO [173]. We did not find many literature reports for the growth of LNO on STO substrates, therefore, the starting deposition parameters were selected on the basis of the growth of PMN-33PT. The optimum parameters for the growth of epitaxial (001)-oriented LNO were found to be a substrate temperature of 570 °C, oxygen partial pressure of 0.13 mbar, a pulse repetition frequency of 5 Hz with an energy density of 2.5 J cm⁻². 5400 pulses were needed to obtain a 100-nm-thick film.

The surface morphology of an LNO film, along with the grain-size distribution is shown in Figure 39. The spotty RHEED pattern, which is shown in the inset, reflects the 3D nature of the surface. Interestingly, the roughness of the surface is comparable to that of the PMN-33PT/STO samples, where a modulated streaky pattern was observed.

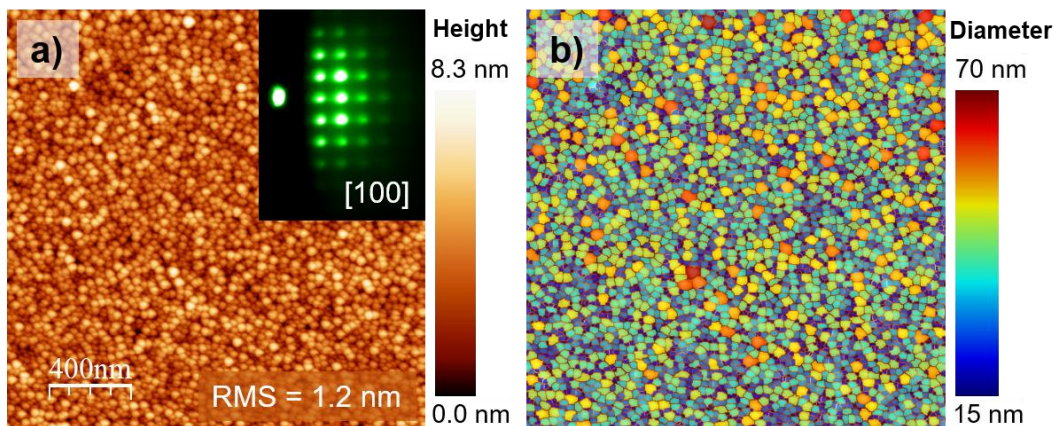


Figure 39: a) AFM image of an LNO layer with the RHEED pattern in the inset. b) Equivalent diameter distribution of the surface structures, calculated from the image in panel a).

From the XRD-RSM we calculated that the OP lattice parameter of the LNO film was 3.830 Å, which is nearly identical to the bulk pseudocubic lattice parameter. Therefore, on the basis of the measured OP lattice parameter, which could also be determined by a simple θ - 2θ measurement, one could come to the conclusion that the LNO film is relaxed. However, the RSM revealed that the LNO is in fact fully strained to the STO substrate, i.e. its IP lattice parameter equals 3.905 Å. According to the general elasticity theory, lattice expansion in the in-plane direction should be accompanied by a shrinkage in the out-of-plane direction. Hwang et al. [174] experimentally determined that STO/LNO superlattices grown on $(\text{LaAlO}_3)_{0.3}(\text{SrAl}_{0.5}\text{Ta}_{0.5}\text{O}_3)_{0.7}$ substrates exhibited a larger OP lattice parameter, as compared to bulk LNO, despite the IP tensile strain imposed on the layers by the substrate. With a tensile IP strain ($\varepsilon_{xx} + \varepsilon_{yy} > 0$), an increase in the OP lattice parameter ($\varepsilon_{zz} > 0$) means that the Poisson's ratio, given by $\nu = -\varepsilon_{zz} / (\varepsilon_{xx} + \varepsilon_{yy})$, is negative. They ascribed this phenomenon to the oxygen octahedra of the two materials maintaining corner-connectivity across both interfaces, i.e. to interfacial coupling of the tilted LNO with the non-tilted STO. McBride et al. [175] used first principles calculations based on density functional theory to investigate the structural properties of LNO/STO superlattices. They also found that for tensile biaxial stresses, the LNO layer exhibits a negative Poisson's ratio, despite bulk LNO exhibiting a positive Poisson's ratio. However, they found that these changes would not be expected from strain considerations alone. They demonstrated that the effects of the octahedral connectivity can be decoupled from the strain effects and lead to a negative Poisson's ratio, thus adding a theoretical explanation to the experimental observations reported by Hwang et al. A simpler and likely explanation for the increase of the unit-cell volume could be a deviation of the oxygen concentration from the stoichiometric value. Rakshit et al. [176] argued that the structure of perfectly stoichiometric LaNiO_3 is actually an ideal cubic structure with $a = 3.851$ Å, since, if ionic radii with their proper coordination number are taken into consideration when calculating the tolerance factor, one obtains a value of 1.003. However, upon heating to high temperatures, the LaNiO_{3-x} loses a small amount ($x \geq 0.05$) of oxygen and it gradually transforms into the hexagonal (rhombohedral) phase. Ni^{3+} is reduced to Ni^{2+} and the oxygen vacancies are ordered. It has been shown [177] that in thin layers the rhombohedral symmetry of LNO is broken and lowered to tetragonal. Cation off-stoichiometry could also lead to a change of the unit-cell volume. Another possible explanation for this observation could be chemical interdiffusion across the interface during the high-temperature growth process [178].

In order to try and find the origin of the unit-cell expansion, the samples were investigated using TEM. The STEM-HAADF images of the cross-sections along the STO [100] direction are shown in Figure 40. The micrograph of the interface at a smaller magnification (panel a)) revealed that the LNO layer contains a high density of anti-phase boundaries (APB) in the [001] direction. Two APBs are marked with solid yellow lines. Furthermore, as seen more clearly from the micrograph in Figure 39b), a thin (3-5 nm) single-crystal layer of LNO, marked with dashed yellow lines, at the interface is grown completely coherently with the STO substrate. After that, the LNO seems to form thin domains, which extend throughout the thickness of the film, and are separated from each other by APBs.

4.4.2 Structural and functional properties of PMN-33PT thin films on LNO

We deposited the PMN-33PT thin films using the same deposition parameters as in samples *P13* and *P27*. Starting with the former, we found that the peculiarity, i.e. the XRD peak splitting, observed in sample *P13*, which was prepared directly on STO, was also present in the sample prepared on LNO/STO (Figure 42) leading to the conclusion that the formation of the high density of structural defects is not related to the chemistry or the surface morphology of the underlying material.

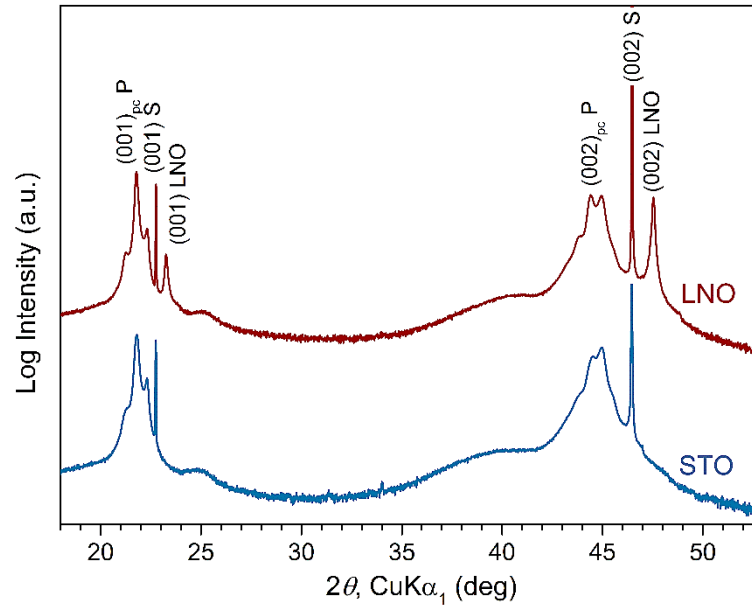


Figure 42: XRD patterns of PMN-33PT deposited at 0.13 mbar on STO and LNO/STO.

Moving on to the results of the growth using the same parameters as in *P27*, I have found that the use of LNO strongly suppressed the formation of the pyrochlore phase in the PMN-PT films. Pyrochlore-free growth was achieved even when using the stoichiometric target. Owing to the expanded process window for the fabrication of pure-perovskite films, the structure and properties of films prepared from a larger variety of targets were studied. In addition to the stoichiometric ceramic target and targets with PbO excess, targets with both PbO and MgO excess were used. Additionally, the growth using a single-crystal target was also studied. Their annotations of the prepared samples are explained in Table 7. MgO-enriched targets (which also contained PbO excess) were used for two reasons: (i) It has been argued that MgO loss is more detrimental to the forming of the perovskite structure than the loss of PbO [179]. MgO excess has been used in thin-film growth studies of PMN-PT, where it has been shown to contribute to improving the stoichiometry and properties of the films [180]. (ii) WDXS analysis of sample *P27* showed that the film was slightly Mg-deficient. The single-crystal target was used in addition to the stoichiometric ceramic target, because thin films grown from single-crystal targets reportedly exhibit higher crystallinity and a smoother surface, due to their higher purity, density, and absorption coefficient. Consequently, better dielectric and ferroelectric properties have also been observed [113].

Table 7: Sample annotations.

Sample	Target
<i>C20</i>	20 mol. % PbO excess
<i>C2010</i>	20 mol. % PbO excess + 10 mol. % MgO excess
<i>C1010</i>	10 mol. % PbO excess + 10 mol. % MgO excess 03
<i>C0</i>	Stoichiometric ceramic
<i>SC0</i>	Single crystal

The XRD patterns of the samples prepared from different targets are shown in Figure 43a). As mentioned earlier, the films are phase pure. Most of the films contain a small amount of (110)-oriented PMN-PT grains. The peak shapes of samples *C20*, *C2010* and *C1010* are symmetrical, while the peaks belonging to *C0* and *SC0* are slightly asymmetrical, i.e. exhibit shoulders. Disregarding the small amount of (110)-oriented grains, the films were grown cube-on-cube with the substrate. Using pseudocubic notations, the measurements of the {101} family of planes confirmed the following crystallographic relations: PMN-PT(001)||LNO(001)||STO(001) and PMN-PT[100]||LNO[100]||STO[100]. The result of an azimuthal XRD measurement is shown in Figure 43b).

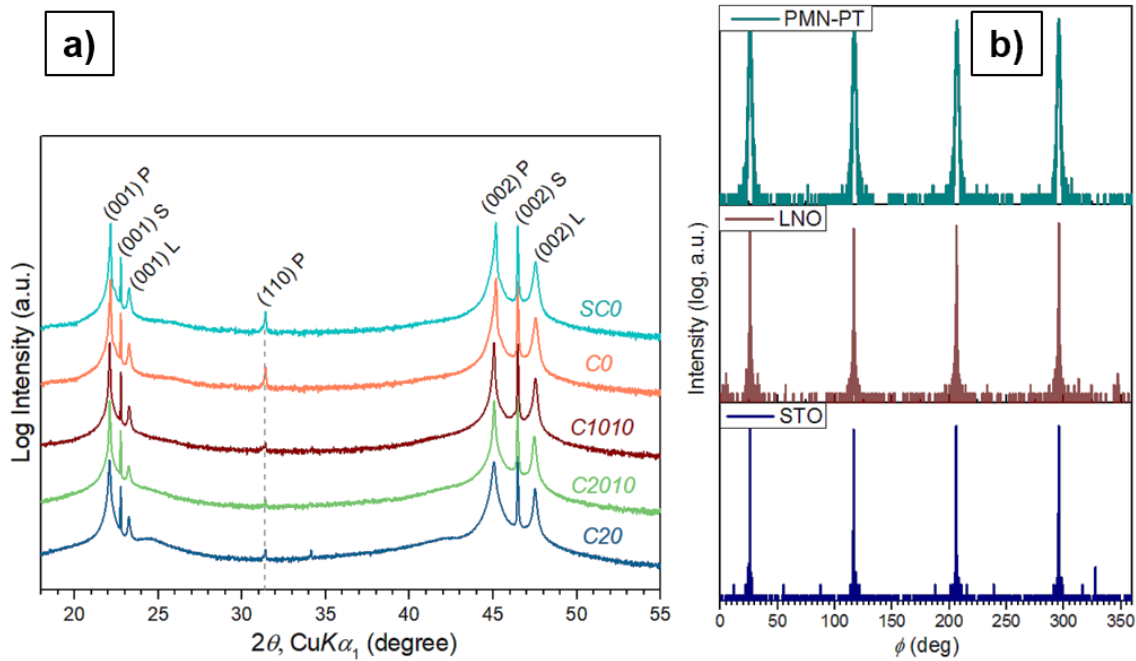


Figure 43: a) θ - 2θ scans of PMN-33PT/LNO/STO samples prepared from different targets. b) Azimuthal scan of the {101} family of planes in sample *C2010*.

The lattice parameters and full-widths-at-half maximum (FWHM) measured in the ω and 2θ directions are shown in Figure 44. The pseudocubic lattice parameters (a_{pc}) were calculated as $\sqrt[3]{a^2c}$, where a and c are the IP and OP lattice parameters, respectively, determined from the peak positions of the asymmetrical reflections in RSMs. The a_{pc} values of all samples are comparable, and seem to be unrelated to the stoichiometry of the target. All a_{pc} values are higher than the bulk value, which is marked with the grey dashed line. In

principle, the lattice expansion could be a consequence of off-stoichiometry or structural defects. The FWHM values measured in a symmetrical RSM spot also do not show a clear correlation with the target stoichiometry. The broadening of the spot in the 2θ direction (along Q_z) is related to the distribution of d -spacings across the thickness of the film, and could indicate the presence of a strain or compositional gradient. The FWHM is the largest in the *SCO* sample, therefore, the shoulder observed in Figure 43 could be related to a strain/compositional gradient. The broadening of the spot in the ω direction (along Q_x), which is commonly called a rocking curve, is related to the degree of crystalline perfection and is the most commonly used quantitative measure for determining how much the layer is single-crystal-like. A high FWHM value indicates that the layer is not well crystallized and/or numerous crystallites with different tilt angles exist in the thin film. It should be kept in mind that the FWHM of the rocking curve does not necessarily reflect the functional properties of the material, as in MPB (relaxor) ferroelectrics, a wider peak could indicate a mixture of crystal phases, which collaboratively contribute to the piezoelectric response. The highest FWHM in the ω direction was again obtained for sample *SCO*, while the lowest value belonged to sample *C1010*.

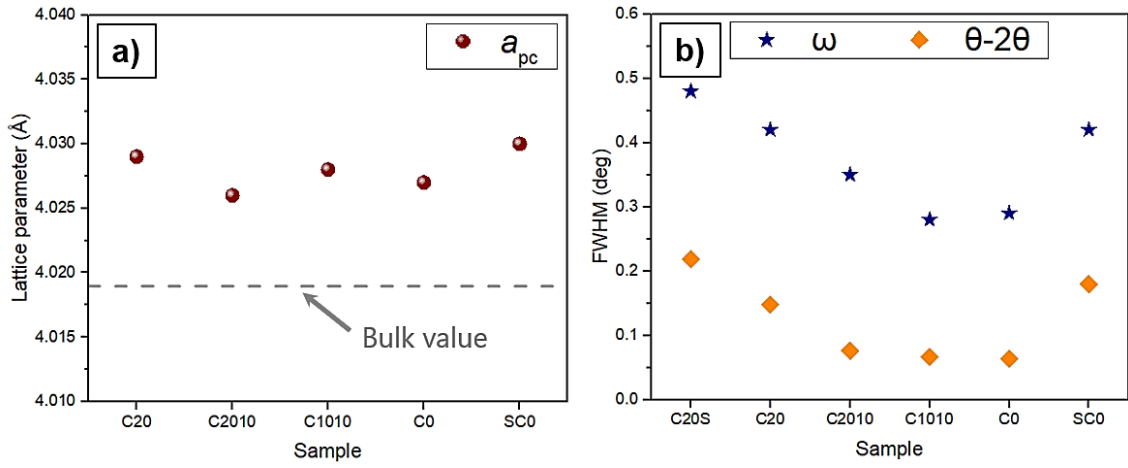


Figure 44: a) Pseudocubic lattice parameters of the PMN-33PT films on LNO/STO. b) FWHMs of the same samples as in panel a).

The widening of a symmetrical spot in the ω direction (parallel to Q_x), contains two contributions: (i) mosaic spread and (ii) lateral correlation length, which can only be separated by mapping an asymmetrical spot. The measured values are shown in Table 8.

Table 8: The mosaic spread and lateral correlation length of PMN-33PT/LNO/STO samples prepared from different targets.

Sample	Mosaic spread [°]	Lateral correlation length [Å]
<i>C20</i>	0.30	100
<i>C2010</i>	0.40	100
<i>C1010</i>	0.03	180
<i>C0</i>	0.05	200
<i>SCO</i>	0.40	80

As mentioned earlier, the widening of the reciprocal spots in PMN-33PT could also be brought about by the presence of different structural variants, due to the MPB composition. Figure 45 shows the RSM around the $(\bar{1}03)_{pc}$ PMN-PT spot. In the magnified image, the peak positions for the individual crystal structures are marked with different colors. The sample peak position is marked with violet, the position corresponding to the pseudocubic/rhombohedral (PC/R) bulk structure is marked with blue, “T c” stands for tetragonal *c*-domains and is marked with black, the peak for the monoclinic (M) structure is marked with red, and the tetragonal *a*-domain (T a) peak is marked with green. The PC/R peak position is the closest to the peak position of the sample. The peak positions of all the structures fall within the measured spot, making it difficult to define the thin-film crystal structure. In PZT, tetragonal and rhombohedral phases can be distinguished by XRD-RSM [181], even close to MPB compositions [182]. In PMN-PT this is not quite the case. Furthermore, it has been shown [130] that in PMN-PT thin films the mixed-phase region exists in a shifted and broader range ($x = 0.40$ - 0.55) as compared to single crystals. To sum up, the results of the RSM analysis do not exclude the presence of any PMN-33PT structural variant.

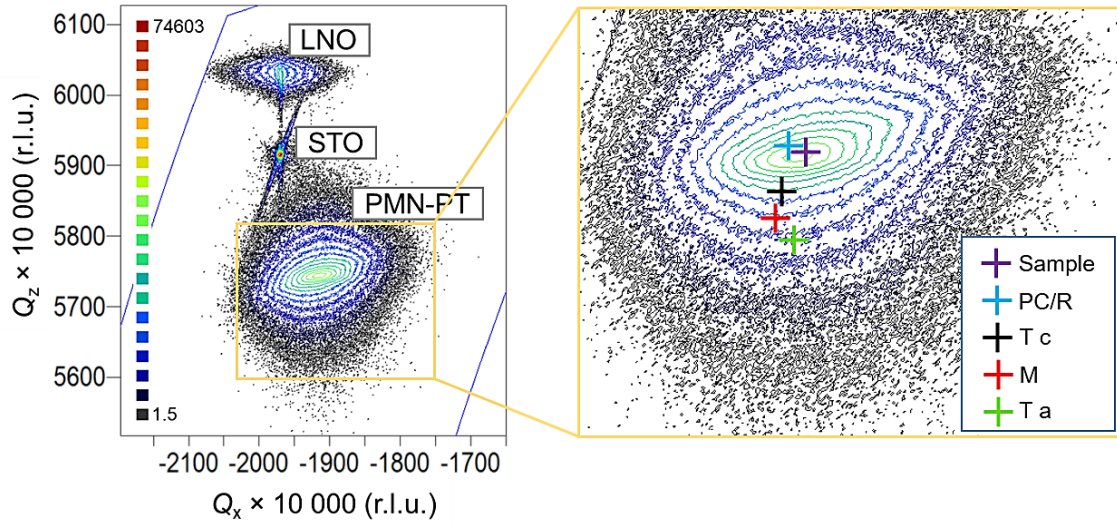


Figure 45: RSM around the $(\bar{1}03)_{pc}$ reflections of STO, LNO and PMN-PT in sample *C2010*. The intensity of the diffracted beam is shown in color scale. The streaks in the STO peak correspond to the monochromator, detector and sample surface streaks. The latter confirms the high crystalline quality of the STO substrate. A magnified region around the PMN-PT spot with marked positions for different bulk crystal structures is shown.

To find out whether the deviation of the lattice parameters from the bulk originates from the differences in the stoichiometry, and to find out whether the addition of MgO to the target helped improve the composition of the film as compared to sample *P27*, WDXS analysis was performed on sample *C2010*, which revealed that the chemical formula of the sample was $\text{Pb}_{1.04 \pm 0.01}\text{Mg}_{0.203 \pm 0.004}\text{Nb}_{0.44 \pm 0.01}\text{Ti}_{0.33 \pm 0.01}\text{O}_3$. In comparison with sample *P27*, sample *C2010* has less PbO surplus, and a smaller Mg deficiency. Therefore, the addition of MgO was beneficial for improving the stoichiometry of the film. As seen from Figure 44, the addition of MgO (to PbO-rich targets) also contributed to the lowering of the FWHMs. It has been observed [183] that the addition of excess MgO in the synthesis of bulk ceramics strongly affects the growth mechanism. Abnormal grain growth observed in MgO-doped samples has been attributed to the presence of singular interfaces between the liquid phase and the grain boundaries. Guha [184] reported that the simultaneous addition of MgO and PbO to the solid solution led to the formation of a dense and homogeneous microstructure. We have examined the microstructure and the surface morphology of the samples. Cross-sectional SEM imaging revealed that all of the samples were dense and homogeneous. An interesting difference was observed in the surface morphology, which was imaged by AFM.

Sample *C2010* (Figure 46) exhibited larger surface crystallites as compared to the rest of the samples (Figure 47). The diameters of the surface structures in sample *C2010* are up to 170 nm (Figure 46b)). The surface of the remaining samples consists of smaller structures, which are aggregated into larger ones.

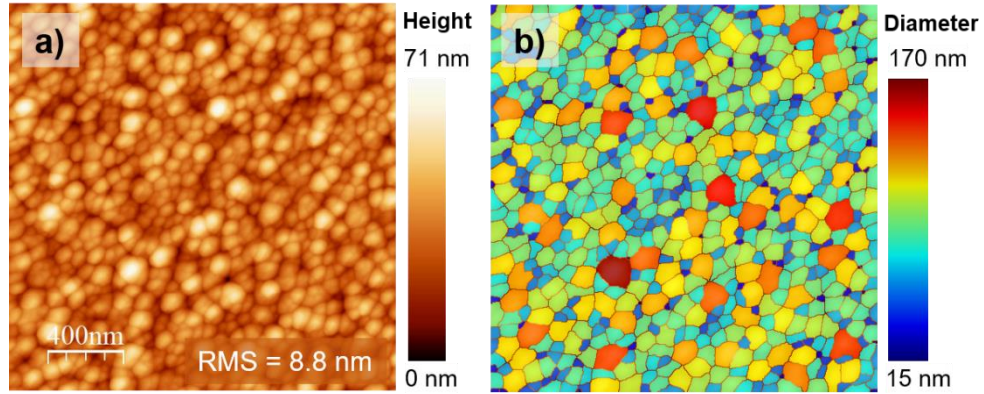


Figure 46: a) AFM image of sample *C2010*. b) Equivalent diameter distribution of the surface structures, calculated from the image in panel a).

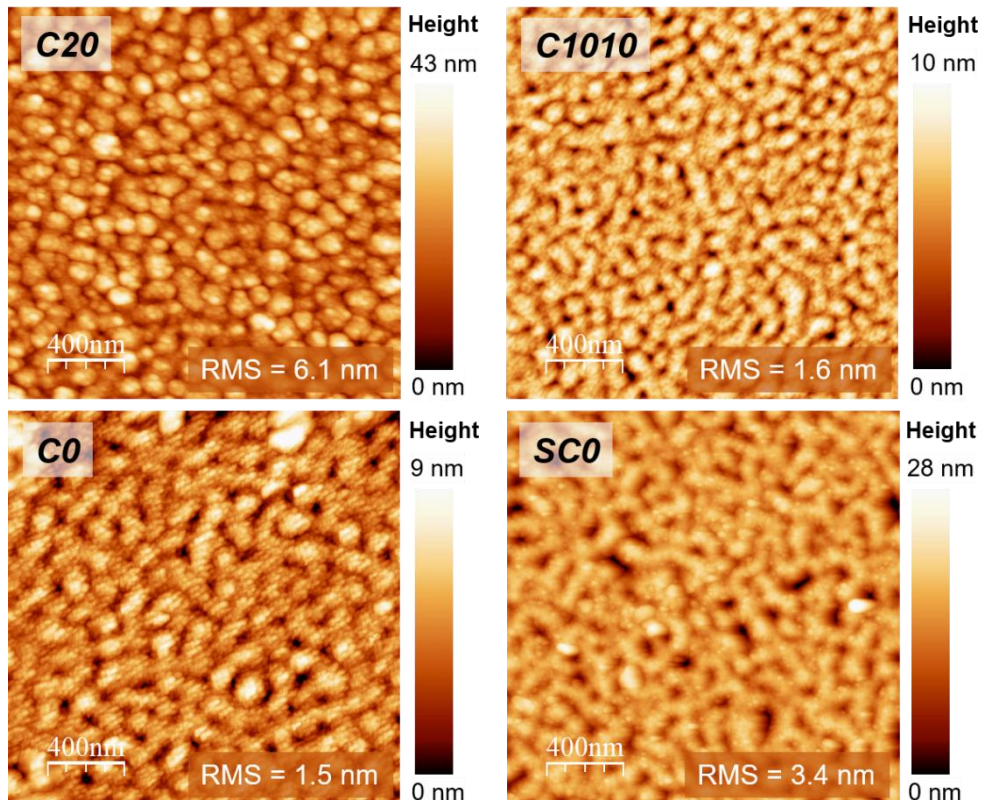


Figure 47: AFM images of PMN-33PT/LNO/STO samples prepared from different targets.

In the next step, we performed electrical measurements in order to study the influence of the structural properties on the electrical response of the samples. The first observation was that the samples prepared from stoichiometric targets (*CO* and *SCO*) contained conductive pathways, which prevented any ferroelectric or piezoelectric measurements from being performed. Their relative dielectric permittivities were 2350 and 1300, respectively. There are several possible origins of conductivity in thin films. The first one is porosity, which is usually found in films that grow in a columnar manner. We have not observed columnar growth, as seen from the STEM-HAADF image of sample *SCO* in Figure 48. Although the films grow in a 3D mode, no gaps have been observed between the islands in analyzing the cross-sections of the samples. Some porosity is observed in the AFM images of the surfaces; however, the holes are relatively shallow. It is not very likely that the cause of the conductive behavior lies in the porosity of the samples.

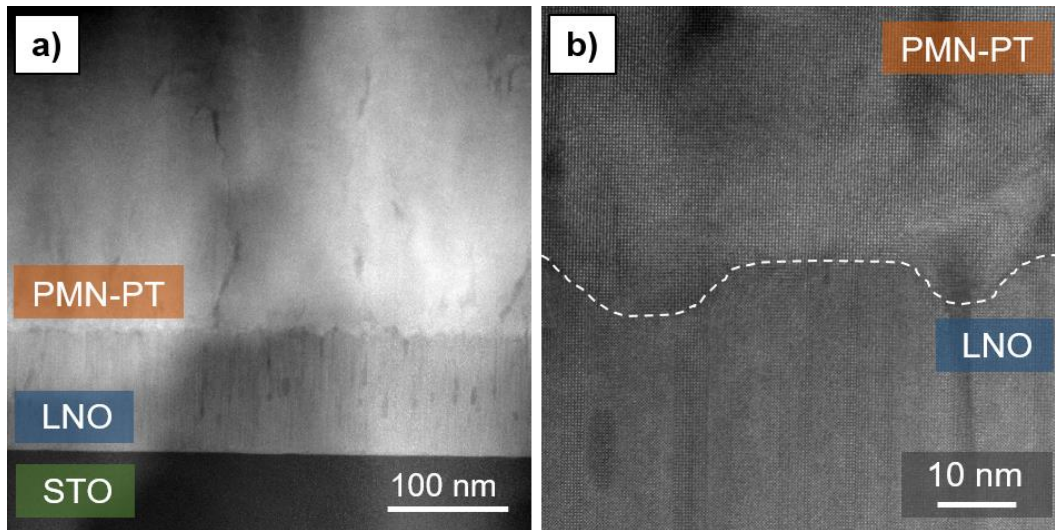


Figure 48: a) STEM-HAADF image of the cross-section of sample *SCO* along the STO [100] direction. b) A magnified region of the interface between the LNO and the PMN-PT.

The second possibility is the presence of particulates. As discussed in Section 4.3.1.1, macroscopic particles can be ejected from the target and incorporated into the film, which can lead to the formation of conductive pathways. Despite the extensive optimization of the laser energy parameters, droplet/particulate formation could be possible, due to the chemical complexity of PMN-PT. The optical quality of the sample surfaces is shown in Figure 49. All samples contain a relatively large amount of particulates, the concentrations are similar, with the concentration in *C2010* being slightly lower than in the rest. The particulate density in sample *SCO* is the largest; however, the particles are small. Sample *CO* contains a larger amount of bigger particles. However, a larger particulate density would be expected for the samples deposited using the targets enriched with PbO (and MgO), as their density was lower compared to the commercial stoichiometric targets, as in general, less particulates are ejected from denser targets. Single-crystal targets should further reduce the droplet density, which was in fact the motivation for the preparation of sample *SCO*. The concentration of droplets also depends on the target surface roughness, laser fluency, target-to-substrate distance and number of pulses on a particular target location. As the rest of the parameters are the same in all samples, the surface roughness is the only parameter that could cause a difference. The target surface of all the samples was prepared in the same manner, i.e. using SiC papers with the same grit size, which reduces the chances of variation in the surface roughness between targets. Another source of particle generation is in the gas phase, when the background pressure is high enough for heterogeneous particle nucleation. This generates nanoparticles, which can also be incorporated into the growing film [16]. Again, as the pressure used is the same for all samples, the same density of particulates would be expected to be generated via this mechanism. In summary, on the basis of the

optical micrographs, it is not quite obvious why only samples *C0* and *SC0* exhibit a conductive behavior.

In the previous paragraphs, only extrinsic conduction mechanisms were discussed. Another possible mechanism is ionic conduction, i.e. the movement of charge carriers through the defects in the crystal lattice. In ferroelectrics, oxygen vacancies generally act as such charged carriers. Under a given applied electric field, the carriers can hop among different oxygen positions in the lattice [62].

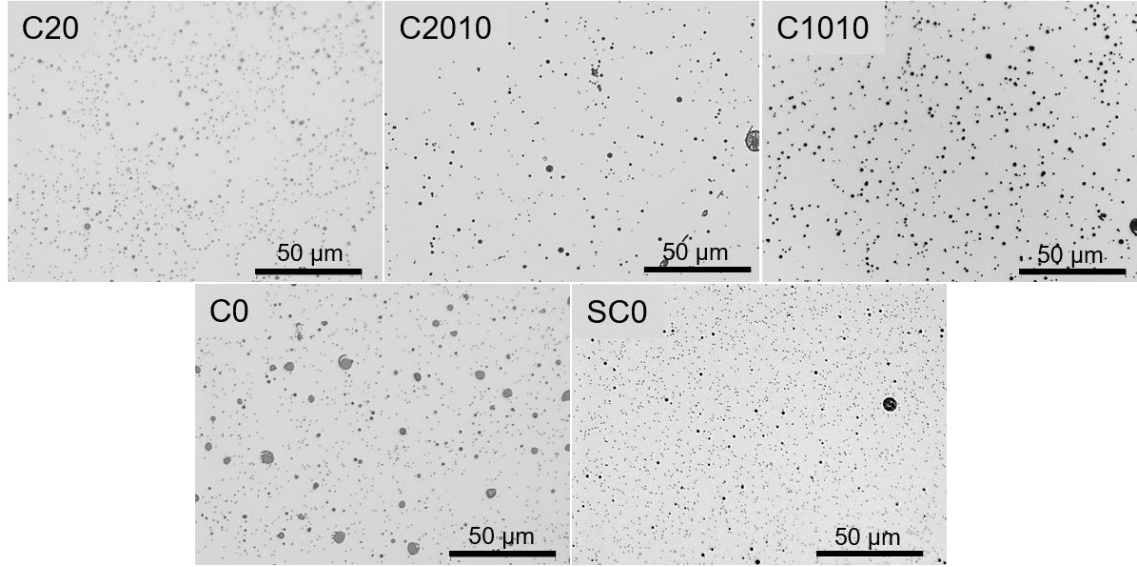


Figure 49: Optical micrographs of samples prepared from different PMN-33PT targets.

The dielectric and piezoelectric properties of samples *C20*, *C1010* and *C2010* are shown in Figure 50. The highest dielectric permittivity (up to 2000) was measured in sample *C2010*. This sample also exhibited the largest piezoelectric response with a $|d_{33,eff}^{max}|$ of 135 pm V⁻¹. Its dielectric tunability and polarization-electric field (*P-E*) loop are shown in Figure 51. The P_{max} value was 22 μC cm⁻². The superior functional properties of sample *C2010* could be related to the difference in stoichiometry, and/or to the larger density and/or crystallite size observed with AFM. Films with larger crystallites contain fewer defects, such as SFs, which accumulate on the boundaries between the crystallites.

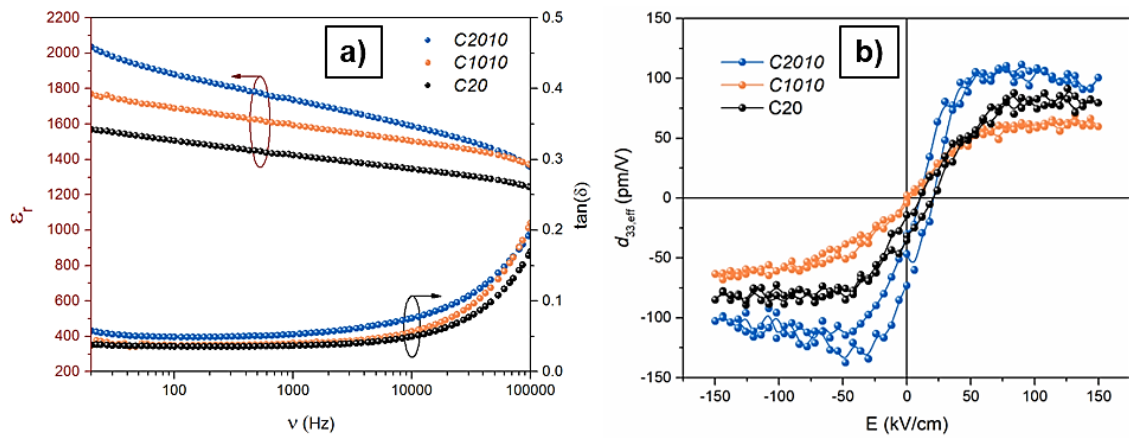


Figure 50: Frequency dependence of the dielectric permittivity and dielectric loss tangent (a) and piezoelectric coefficient $d_{33,eff}$ (b) in samples *C20*, *C1010* and *C2010*.

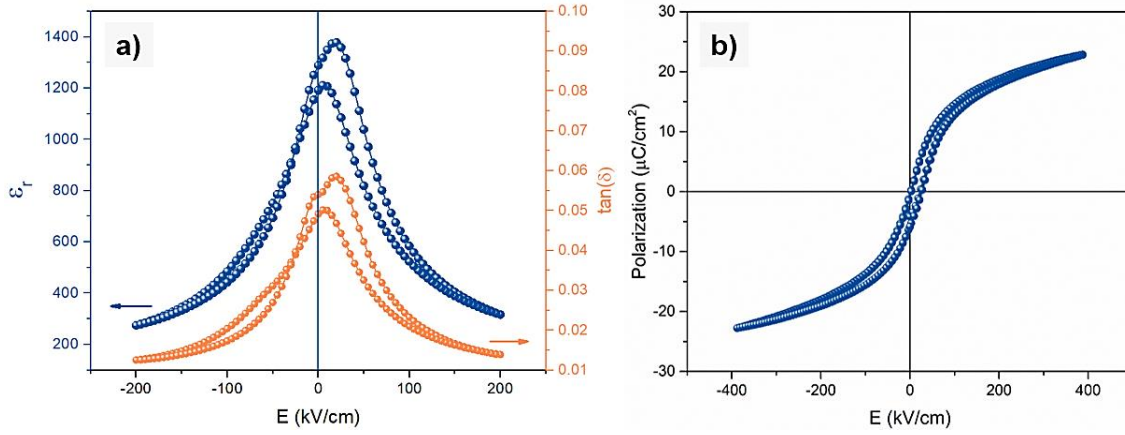


Figure 51: Dielectric tunability (a) and P - E loop (b) of sample *C2010*.

Imprint, which has already been discussed in Section 4.3.3, was also observed in samples *C2010* and *C1010*. Given that the relative permittivity is proportional to dP/dE , the dielectric response in imprinted films is also shifted along the E -axis in accordance with the direction and magnitude of the internal fields. In order to understand the dielectric properties of imprinted samples, an external DC bias should be applied to compensate for the internal fields during the measurement of the temperature dependence of the dielectric response [185]. Therefore, the dielectric phase transition behavior of the imprinted films was mapped as a function of temperature and DC bias. A 3D dielectric map, such as the one shown in Figure 52 for sample *C2010*, offers insight into the phase transition of the thin film, as well as the temperature stability of the imprint. The relative dielectric permittivity in sample *C2010* is maximized at $\sim 145 \pm 5$ °C, which is comparable to bulk PMN-33PT ceramics, where the T_{max} , derived from the phase diagram, is 155 °C [30], [186]. In bulk single crystals $T_{\text{max}} = 140$ °C and $T_{\text{max}} = 165$ °C have been measured for PMN-31PT and PMN-35PT, respectively [187]. The observed broad maximum was consistent with my expectations, as PMN-33PT is a relaxor ferroelectric, where the ferroelectric-paraelectric phase transition occurs at different temperatures in different regions of the sample (because of the structure disorder in the lattice). The peak is broader in thin films as compared to bulk.

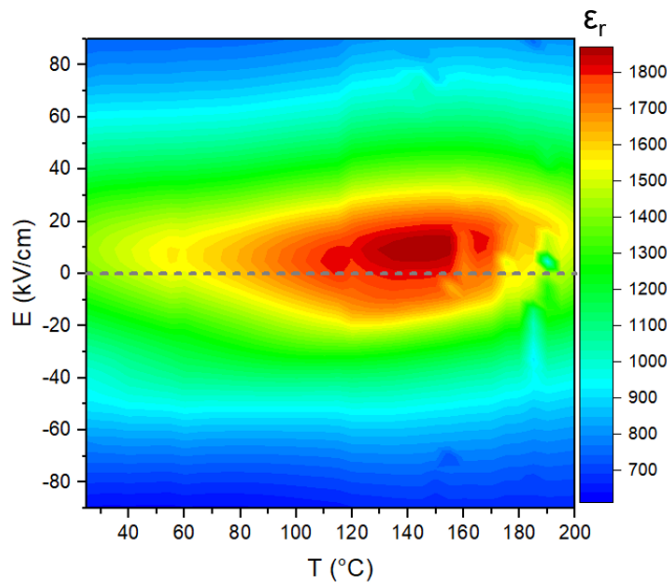


Figure 52: 3D relative dielectric permittivity map of sample *C2010*.

Care should also be taken regarding the AC amplitude used for the dielectric measurements. A small AC amplitude that is used to measure dielectric properties may no longer be small in thin films. It is important to keep it under the coercive field value. The dielectric permittivity was found to increase with the increasing oscillation amplitude, as shown in Figure 53 for sample *C2010*, measured at 1 kHz. The dielectric measurements were therefore performed using an amplitude of 100 mV, since at higher amplitudes, the response also contained extrinsic contributions.

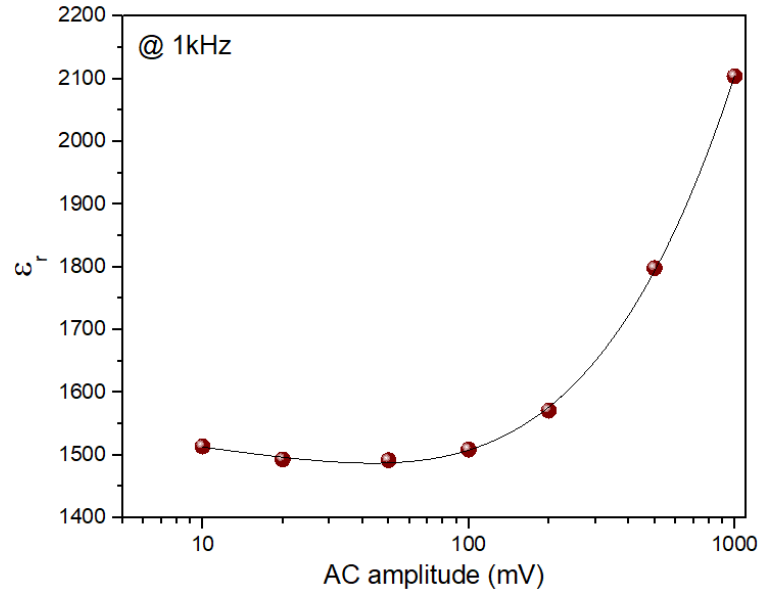


Figure 53: Dependence of the relative permittivity in sample *C2010* on the small-signal amplitude. The measurements were performed at 10, 20, 50, 100, 200, 500 and 1000 mV.

The ϵ_r and $d_{33,eff}$ of the films grown on LNO/STO are higher as compared to the ones of the samples grown directly on STO. The ϵ_r of the sample grown on Nb:STO from the PMN-33PT target with 20 mol. % PbO excess (*P27Nb*) is approximately 1000, while the ϵ_r of the sample grown from the same target on LNO/STO (*C20*) is about 1400. The $d_{33,eff}^{max}$ of sample *P27Nb* is 65 pm V⁻¹, while in sample *C20* it is 90 pm V⁻¹. The difference is even more pronounced, when comparing the values of *P27Nb* to those of *C2010*. In the latter case, one of the possible reasons for this is the slightly improved stoichiometry, as seen from the results of the WDXS analysis, which are shown on pages 40 and 61. The difference could also be brought about by the different nature of the bottom electrodes. Sama et al. [188] grew PZT with different top and bottom electrodes (Pt, LNO) grown with magnetron sputtering. They found that the nature of the bottom electrode influences the dielectric properties of the samples. The piezoelectric response of both types of samples was significantly reduced compared to values reported for bulk crystals, which is not at all unusual for thin films. In general, there are several reasons for deterioration of functional response in thin films. The discrepancies between the properties of thin films and single crystals have often been ascribed to the changes in the grain boundary properties and concentration, where defects are expected to accumulate. Slight off-stoichiometry could cause the formation of localized screening charges, hampering the polarization rotation, and affecting the dielectric permittivity and the polarization [105]. TEC mismatch can lead to the destabilization of specific polarization directions. The part of the piezoelectric material located beneath the top electrode is bonded to non-actuated material, imposing elastic constraints to the ideal piezoelectric deformation. Sama et al. [188] also found that the top electrode affects the device properties as well. When LNO was used as the top electrode, the dielectric permittivity and the piezoelectric response were substantially enhanced, and the average coercive fields were strongly lowered. Additionally, the maximum polarization was increased by up to 20%. Last but not least, due to the attachment to a thick, passive

substrate, the OP displacement is limited by the coupled and frustrated lateral contraction, proportional to the d_{31} coefficient. It has been demonstrated [189] that upon application of constant strain to PMN-33PT single crystals, the measured dielectric permittivity dropped from 8200 to 680. Taking into consideration that the dielectric permittivity is related to the piezoelectric response by the relation $d_{33} = 2\epsilon_0\epsilon_r QP_s$, the diminished piezoelectric response in thin films should come as no surprise. Substrate removal or thinning has been proven as an effective way to declamp the piezoelectric response in thin films [190], [191]. Keech et al. [192] demonstrated that clamping of the intrinsic response and decreased domain mobility in blanket PMN-PT thin films are responsible for a diminished piezoelectric response; an issue that can be solved by lateral subdivision of the film to dimensions smaller than 1 μm . This way, a threefold increase in the $d_{33,f}$ was achieved.

4.5 Growth of PMN-33PT on Other Surfaces

In light of the improved phase purity of the films grown on LNO, where also an enhancement of the functional properties was observed, we decided to try and find the underlying cause and also achieve an improvement in the films grown on STO with different buffer layers or surface modifications. First, we grew the PMN-33PT on ultra-thin layers of LNO and SrO to try and determine the effect of the surface chemistry on the stability of the perovskite phase. A 100-nm-thick layer of SrRuO_3 (SRO) was also tested as a possible route to achieve SrO-termination. SRO could also serve as a bottom electrode. A PZT buffer layer was also tested. The potential benefits of the PZT layer include an engineered electrical imprint, which could improve the FOM of the capacitor structure. Finally, an STO buffer layer and vicinal STO substrates were used to determine the influence of the surface morphology on the stabilization of the perovskite phase.

4.5.1 4-ML-thick LNO buffer layer

In order to find whether the surface chemistry of the LNO was responsible for the improved sticking probability of PbO on LNO/STO, we deposited only 4 ML of LNO, on top of which we again grew PMN-33PT from the stoichiometric target. The resulting XRD pattern, shown in Figure 54 revealed a large quantity of pyrochlore phase was present in the film. Therefore, 4 ML of LNO, which is approximately 65-times thinner as compared to the LNO electrodes from Section 4.4, was insufficient to stabilize the perovskite phase.

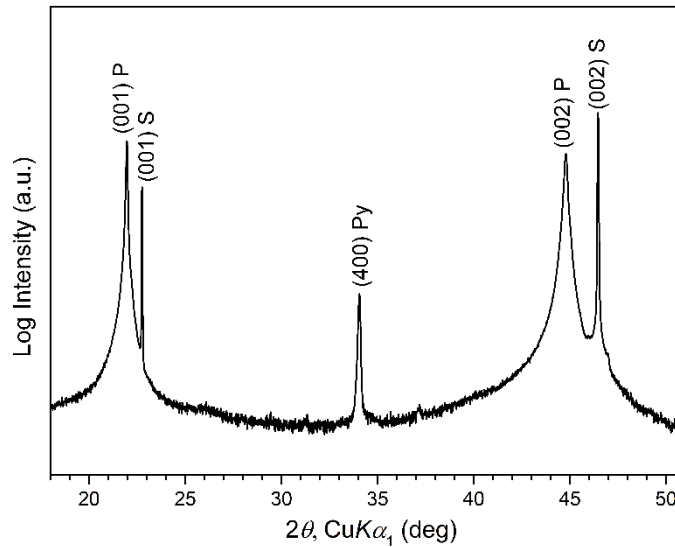


Figure 54: XRD pattern of PMN-33PT/4 ML LNO/STO.

4.5.2 SrO buffer layer

Owing to the relatively much simpler procedure necessary for the preparation of TiO_2 -terminated STO substrates, growth on SrO-terminated STO is rarely studied. Nevertheless, there are some studies comparing the growth of different perovskite films using both possible STO terminations, where it has been reported that the surface termination can have a pronounced influence on the growth of the films. Huijbregtse et al. [193] found that the substrate termination determined both the starting and the terminating layer of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. A different mechanism of incorporating off-stoichiometry was found to exist in films grown on SrO-terminated substrates. Pesquera et al. [194] reported a difference in the properties of $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ thin films grown on either one or the other terminating layer. Solmaz et al. [195] found that BiFeO_3 thin films have different morphologies as well as different ferroelectric domain structures when grown on STO with different terminations.

They attributed the difference to the different sticking properties of the BiFeO_3 species on SrO or TiO_2 surfaces.

It was hypothesized that the perovskite phase in PMN-PT thin films should also be relatively more stabilized on SrO-terminated STO as compared to the TiO_2 -terminated surface, due to the improved sticking of the species. For the purpose of testing this hypothesis, we have tried to deposit one monolayer of SrO on TiO_2 -terminated STO. However, as we did not observe any oscillations in the RHEED pattern, the deposited amount was most probably larger, and the final layer was probably not completed. Nevertheless, we used this template to deposit PMN-33PT from the target without PbO excess in order to find whether the sticking has been improved by the change of the substrate surface. We did not observe any improvement in the phase purity of the film, imposed by this SrO buffer layer. Therefore, an alternative route to obtaining SrO-terminated STO was taken, which is presented in the following subsection.

4.5.3 SrRuO_3 buffer layer

PLD-derived epitaxial SRO thin films have been shown to grow uniformly on TiO_2 -terminated STO substrates with a high crystalline quality [196], and exhibit A-site, i.e. SrO termination [167], [168]. The BFO films deposited directly on STO substrates reportedly grew in a 3D manner, while growing on an SRO electrode layer, they remained atomically flat. The difference could possibly be attributed to a different surface termination. Additional benefits of SRO are its low mismatch with standard substrates, including STO, and many functional oxides, good stability and good metallic behavior.

The starting parameters for the growth of SRO electrodes were selected on the basis of literature reports listed in Table 9. All of the SRO films were prepared on STO substrates and with a 248 nm KrF laser. Spot size was not reported in any case.

Table 9: Parameters for the growth of SRO thin films on STO from the literature.

T [°C]	$p(\text{O}_2)$ [mbar]	ν [Hz]	Fluency [J cm^{-1}]	Thickness [nm]	Target-to-substrate [mm]	Ref.
600	0.13	4	2.5	100	49	[105]
680	N/A	10	1.1	100	80	[197]
780	0.08	5	N/A	50	50	[106]
600	0.07	10	~ 2	11-22	40	[198]
600	0.13	2	2.5	ultrathin	N/A	[199]

I found that in our PLD system phase-pure epitaxial SRO films are grown by using a substrate temperature of 600 °C, oxygen partial pressure of 0.13 mbar, a frequency of 8 Hz, a fluency of 2.5 J cm^{-2} and a target to substrate distance of 55 mm. From the RHEED pattern, which is reminiscent of the RHEED scheme in Figure 8b), and the AFM micrograph, shown in Figure 55, it can be seen that the 100-nm-thick SRO layers grew in a 2D manner. The steps from the underlying STO substrate are still visible, the step height corresponds to one unit cell of SRO. Therefore, the surface is single terminated; however, we have not confirmed that the terminating plane is in fact SrO. The roughness of the surface is increased by the large density of small pits. The measured depth of the pits matches 2–3 unit cells of SRO. The pits may be deeper; however, it is unlikely, as their lateral dimensions are 30–50 nm, while the maximum tip diameter is 10 nm. Despite these surface imperfections, we decided to use such SRO/STO heterostructures for the growth of PMN-PT.

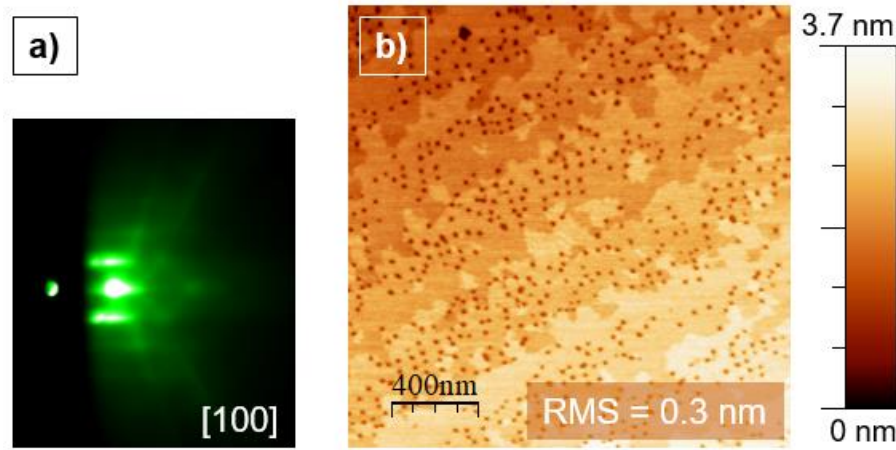


Figure 55: a) RHEED pattern of the SRO layer. b) AFM image of the SRO layer.

The analysis of the PMN-PT layer grown on SRO/STO showed that only a slight suppression of the pyrochlore phase was achieved by the use of the SRO buffer layer, still requiring the use of PbO-rich targets to grow phase-pure PMN-PT. Furthermore, the films grown on SRO/STO were found to contain conductive defects, the potential causes of which have already been discussed in Section 4.4.2.

4.5.4 PZT buffer layer

Another buffer layer that was tested was PZT (52/48). Although PZT also contains the volatile component PbO, its nucleation is simpler as compared to PMN-PT, and the process window for obtaining phase-pure films is reportedly larger. It was hypothesized that a thin layer of PZT will serve as a good buffer layer for the subsequent growth of PMN-PT, as the sticking will improve. Furthermore, the role of the PZT buffer layer would also be to bring additional functionality to the sample. It has been shown [112] that a thin seed layer of PZT can introduce a large self-bias (up to 101 kV cm^{-1}) to the overgrown PMN-PT thin films. The self-bias was arguably related to a strain gradient layer in the PZT seed layer.

First, a few experiments were carried out to ensure that the growth of the PZT layer itself yielded phase-pure films. Such PZT/Nb:STO templates, the surface morphology of which is shown in Figure 56a), were then used for the growth of PMN-PT films from targets with and without PbO excess. From the θ - 2θ measurements (Figure 56b)) it is evident that the phase-pure PZT buffer layer successfully suppressed the pyrochlore phase in the PMN-PT layer, enabling the growth of pure-perovskite PMN-PT even from the target without PbO excess. Similar to the film grown on SRO/STO, the electrical properties of the films grown on PZT/Nb:STO were not as good as expected. Due to the high dielectric losses and leakage currents, it was impossible to determine the influence of the PZT layer on the self-bias of the PMN-PT films.

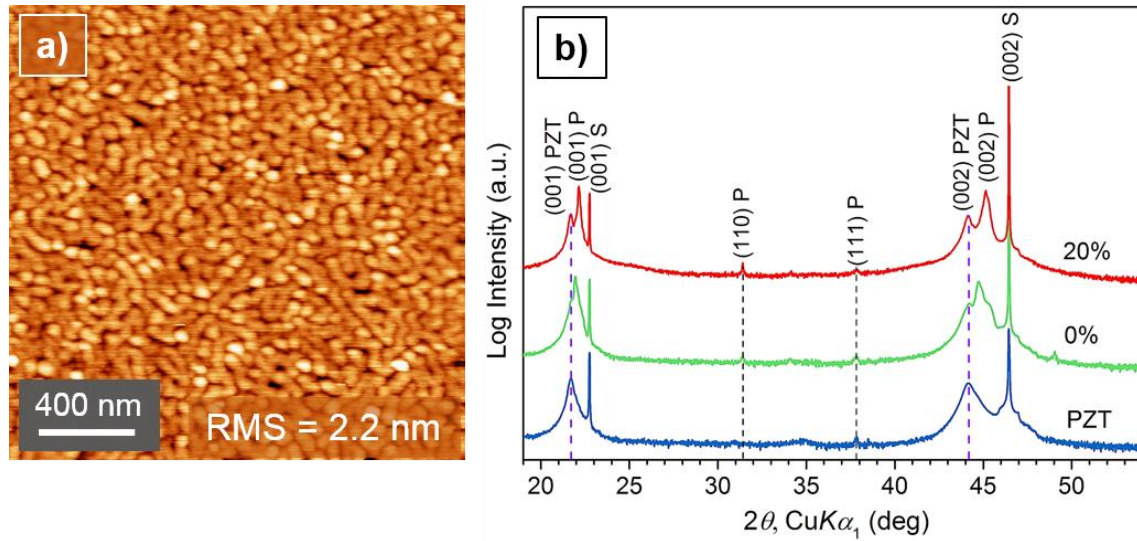


Figure 56: a) AFM micrograph of the PZT thin film. b) θ - 2θ measurements of PMN-PT samples grown on PZT/Nb:STO from different PMN-33PT targets. The dashed violet line traces the positions of the PZT peaks.

4.5.5 STO buffer layer

From the previous experiments with thin buffer layers of LNO and SrO it seems that the surface chemistry might not be the key factor in determining the phase purity of the overgrown PMN-33PT thin films. As improved phase stability was achieved on rougher surfaces, such as the thicker LNO layer and the PZT layer, it was postulated that the increased surface roughness with a larger effective surface area facilitates the sticking of volatile species on the surface, thereby contributing to the phase purity. Using the results of the study on the homoepitaxial growth of STO by Diaz-Fernandez et al. [68] we have selected the set of parameters (515 °C, 0.08 mbar O₂) that produced stoichiometric STO with a relatively rough surface. As shown in Figure 57a), the surface of the STO buffer layer is indeed relatively rough. This was already clear from the RHEED pattern taken *in-situ* (shown in the inset of the figure), where the streaks were strongly modulated, indicating a 2D-to-3D growth-mode transition. The RMS roughness of the STO, as calculated from the AFM image falls between that of the low-miscut TiO₂-terminated substrate and the 100-nm-thick LNO layer. This template was then used to grow a PMN-33PT thin film from the target without PbO excess. Comparing the phase compositions of the films grown with and without this buffer layer (Figure 57b)), it is clear that the STO buffer layer strongly suppresses the formation of the pyrochlore inclusions.

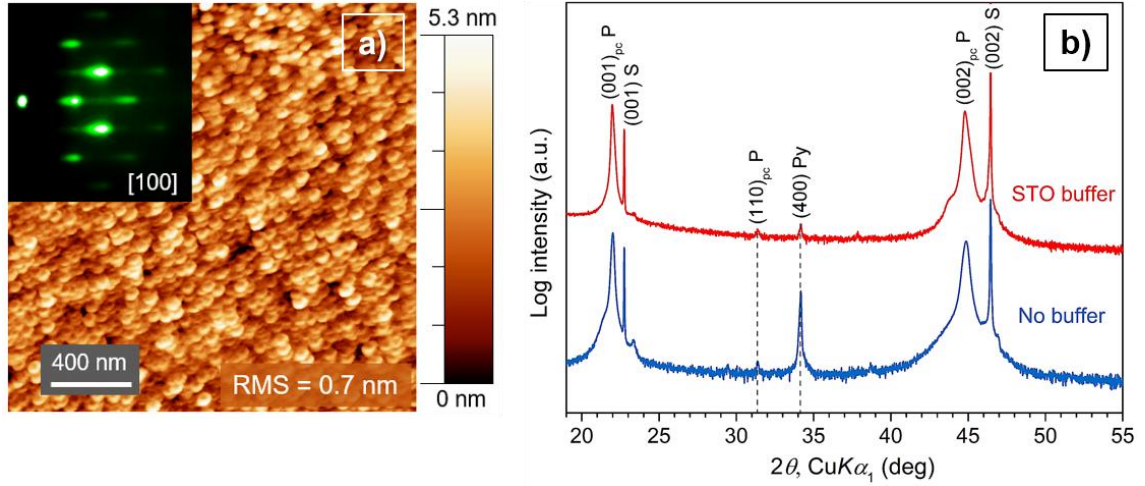


Figure 57: a) AFM image of the STO buffer layer, with the RHEED pattern shown in the inset. b) Comparison of the XRD patterns of the samples with and without the STO buffer layer.

As the sample was actually grown on an Nb:STO substrate, its electrical properties could also be examined. Despite the promising results of the structural analysis, the dielectric, ferroelectric and piezoelectric response was modest. The maximum dielectric permittivity was below 700, P_{sat} was $19 \mu\text{C cm}^{-2}$ and the $|d_{33,eff}^{max}| \sim 50 \text{ pm V}^{-1}$. A possible explanation for the relatively poor response was revealed upon inspection of the sample surface. The extremely large roughness of the surface was evident already by examining the sample with optical microscopy (Figure 58) which also revealed the presence of numerous macroparticles.

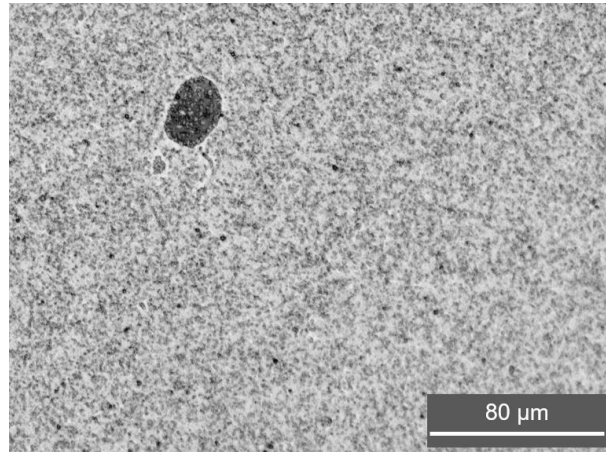


Figure 58: PMN-PT/STO/Nb:STO rough surface with macroscopic defects.

4.5.6 Vicinal STO substrates

Based on the results presented in the previous subsections, we can conclude that surface roughness, i.e. enhanced surface area, is the determining factor for the improved sticking. The surface area can also be enhanced by the use of higher-miscut (vicinal) substrates. It is known that the epitaxial quality, the domain structures and the dielectric properties can also be affected by the surface structure of the substrate; specifically, steps, terraces and surface defects. The surface step structure can alter the microstructure of the film [12]. Improved phase purity and properties have previously been obtained by the use of vicinal STO or Si substrates [42], [104], [123], [141], [179].

My results, which are shown in Figure 59, showed that the higher density of steps on the vicinal STO substrate surface slightly improved the sticking probability of PbO, enabling the growth of phase-pure films from the target with 15 mol. % of PbO excess, as compared to the 20 mol. % required on flat STO substrates.

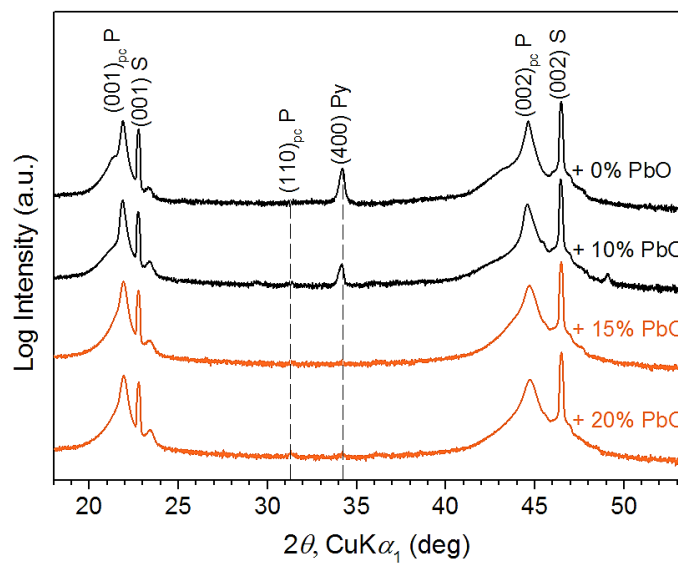


Figure 59: XRD patterns of the films grown on 4° miscut STO.

To summarize, the PMN-33PT thin films were grown on different buffer layers and surfaces in order to determine the underlying mechanism for the stabilization of the perovskite phase. It was found that a mere change of the surface chemistry as compared to the TiO₂-terminated STO substrates used for the samples presented in Section 4.3, did not suffice for the preparation of phase-pure PMN-33PT films from a stoichiometric target. The results show that the roughness of the surface plays a major role in the stabilization of the perovskite phase, probably by enhancing the sticking probability of Pb-based species, thereby suppressing the nucleation of the pyrochlore phase. The stability of the perovskite phase was the highest on rough STO, PZT and thick LNO layers. As shown earlier, the properties of the films grown on LNO are superior, as compared to those grown on STO. Therefore, the samples grown from targets with 25 % PT and 40 % PT, presented in the following section, were also grown on LNO. This way, a direct comparison of the properties in the PPC configuration could be made.

4.6 Comparison of Samples with Different PMN:PT Ratios

It has been shown that the MPB is often shifted in thin films [130] and that different crystal structures can be stabilized in thin films as compared to bulk [200]. This was the motivation behind the work presented in this subsection. Two compositions around the MPB were selected, one (PMN-25PT) with a bulk rhombohedral and the other (PMN-40PT) with a bulk tetragonal structure. The films were grown on LNO/STO substrates from PbO- (and MgO)-enriched targets. The structure and properties of the samples with a different PT content (25PT, 33PT and 40PT) were compared.

4.6.1 Structure of the PMN-25PT and PMN-40PT samples

The first interesting observation was that the PMN-PT ratio also did not influence the peak splitting that was always observed in the XRD patterns of the films deposited at 0.13 mbar, as shown in Figure 60a). Figure 60b) shows that the PMN-25PT films prepared from the targets with 20 mol. % PbO, and 20 mol. % PbO and 10 mol. % MgO excess were phase-pure and almost completely (001)-oriented. A slight asymmetry of the PMN-PT peaks observed in the specular scans was more pronounced in the asymmetrical RSM spots, where the main peak position in the sample prepared from the target with 20 mol.% PbO corresponded to lattice parameters $a = 4.033 \text{ \AA}$ and $c = 4.024 \text{ \AA}$. In the sample prepared from the target with 20 mol.% PbO and 10 mol.% MgO, the lattice parameters were $a = 4.021 \text{ \AA}$ and $c = 4.040 \text{ \AA}$.

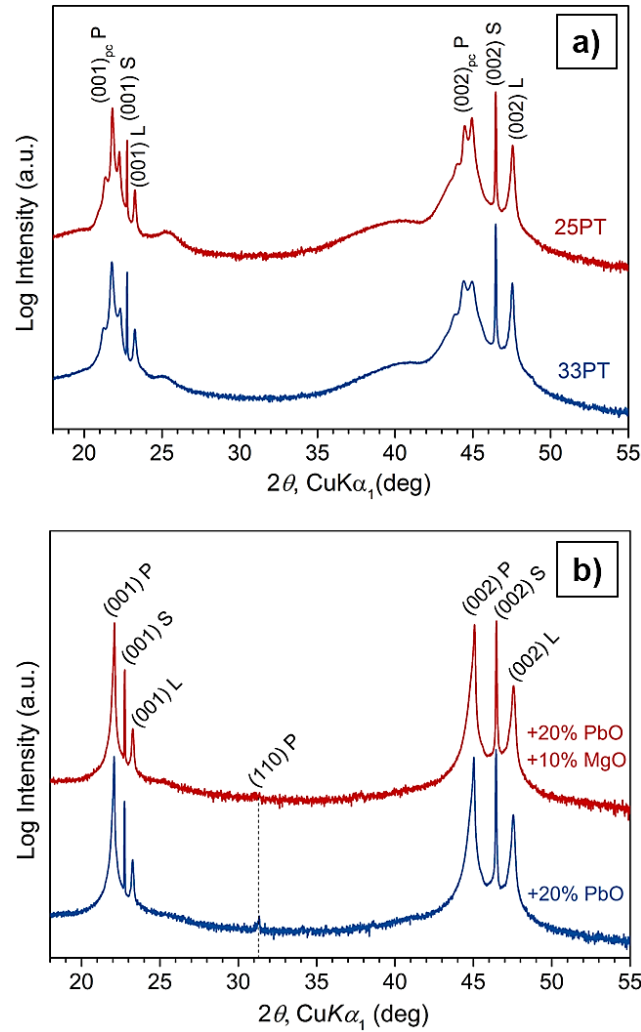


Figure 60: XRD patterns of (a) PMN-33PT and PMN-25PT films prepared at 0.13 mbar of oxygen, and (b) PMN-25PT films prepared from different targets.

The films prepared from the PMN-40PT targets with 20 mol. % PbO, and 20 mol. % PbO and 10 mol. % MgO excess also exhibited a pure-perovskite structure (Figure 61). The asymmetric nature of the peaks was more pronounced than in the PMN-25PT samples. The main peak position of the asymmetrical RSM reflection in the sample prepared from the target with 20 mol. % PbO excess corresponded to lattice parameters $a = 4.019 \text{ \AA}$ and $c = 4.009 \text{ \AA}$, while in the sample prepared from the target with 20 mol. % PbO and 10 mol. % MgO excess the main peak position corresponded to lattice parameters $a = 4.025 \text{ \AA}$ and $c = 4.004 \text{ \AA}$.

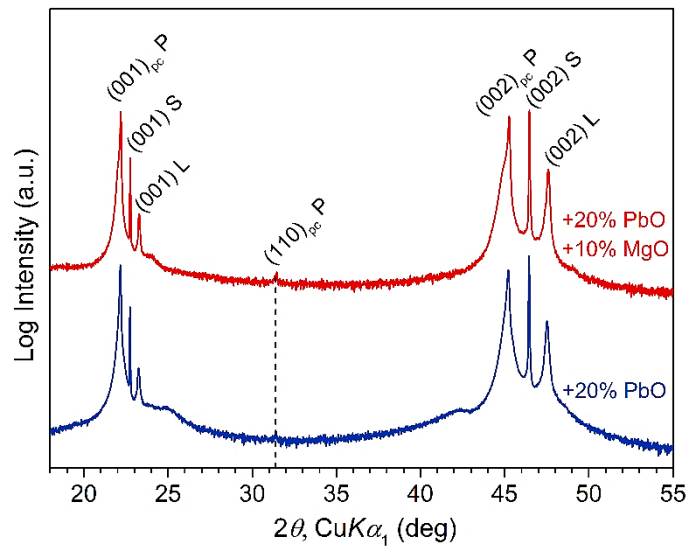


Figure 61: XRD patterns of the PMN-40PT samples prepared from different targets.

The measured pseudocubic parameters, i.e. the unit cell volumes, decreased monotonically from 25PT to 40PT, which is in accordance with the bulk cell volumes of the different compositions. Both the 25PT and the 40PT samples exhibited a slight tetragonal distortion with the average unit cell being very slightly elongated in the IP direction. Unambiguous and exact crystal structure identification of the PMN-PT thin films was not achievable by RSM alone.

4.6.1.1 Raman spectroscopy of PMN-PT thin films on LNO/STO

We have been fortunate to collaborate with Dr. I. Rafalovskyi and Dr. J. Hlinka from the Institute of Physics, Academy of Sciences of the Czech Republic in Prague, who conducted the Raman spectroscopy study. The experiments were performed on samples that contained an LNO bottom electrode, as this 100-nm-thick layer served as a barrier to suppress the Raman scattering signal from the STO substrate.

In their previous study [89] it was shown that the two optically differing phases in a PMN-PT single crystal sample consist of different crystal symmetry domains, which can be distinguished by angular-dependent Raman measurements. The rhombohedral phase has maxima at $\varphi = \pi n/2$, $n = 0, 1, 2$, etc., same as pure PMN and other rhombohedral ferroelectric crystals. In the tetragonal phase, on the other hand, i.e. the maxima are located at $\varphi = \pi(2n+1)/4$, $n = 0, 1, 2, \dots$, i.e. shifted by 45° with respect to the rhombohedral phase. All possible Raman tensors of the different rhombohedral ferroelastic domain states can be obtained by rotating the sample around the fourfold axis parallel to the [001] direction. Therefore, the shift is always 90° . In the tetragonal phase, the domains can only be oriented perpendicularly (rotated by 90°) with respect to each other.

The angular dependence (between the incident light polarization and the pseudocubic axis of the PMN-PT with the most intense signal) of the Raman scattering spectra for one of the films (PMN-33PT, C20) studied here, is shown in Figure 62. In the case of the single

crystal sample [89], there was a pronounced intensity modulation in the mode at 780 cm^{-1} for both the VV and the HV configuration, whereas in the case of my thin film samples, the systematic angular dependence is absent. At the same time, a clear angular dependence exists in both types of samples for the lower-frequency spectral bands. Altogether, all of the measured angular profiles exhibit a fourfold rotational symmetry.

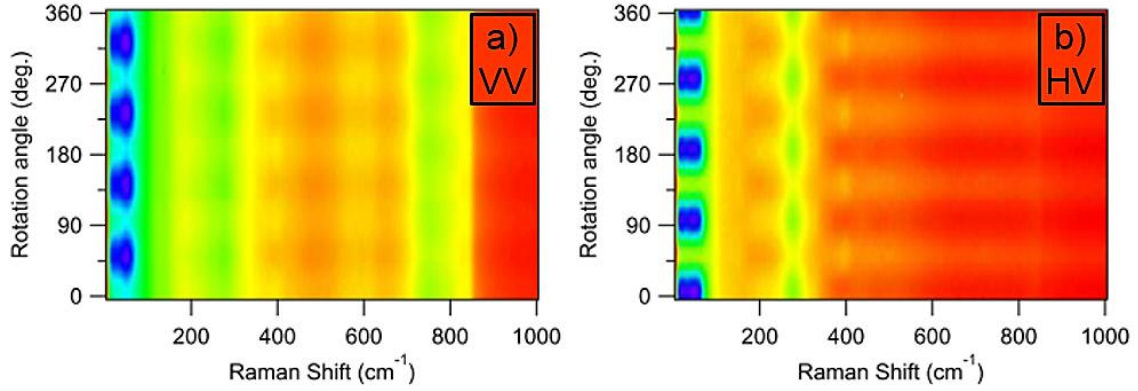


Figure 62: Intensity maps showing the dependence of the Raman signal of sample *C20* on the angle between the transmission direction of the analyzer and the one of the IP pseudocubic axes. (a) VV configuration, (b) HV configuration (Courtesy of Dr. I. Rafalovskyi, [201]).

In order to extract further information from the angular-dependent intensity maps, the depolarization ratio, i.e. the normalized HV intensity, was calculated using the equation $\eta = I_{HV} / (I_{HV} + I_{VV})$, where I_{VV} is the complementary scattering intensity in the VV channel). The results from films with different PMN:PT ratios were compared to the data obtained for bulk PMN-PT single crystals with an MPB composition [89], [202]. The comparison, which is shown in Figure 63, strongly suggests that the tetragonal crystal phase was stabilized in the thin films, even in compositions that fall to the rhombohedral side of the established phase diagram in bulk crystals. These results are supported by the measurements of the relative permittivity in the IP and OP direction presented in Section 4.3.3. The twice lower value of the permittivity in the OP direction, as compared to the IP direction, indicates, that the polarization is pointing in the OP direction, i.e. tetragonal domains are prevailing in the film.

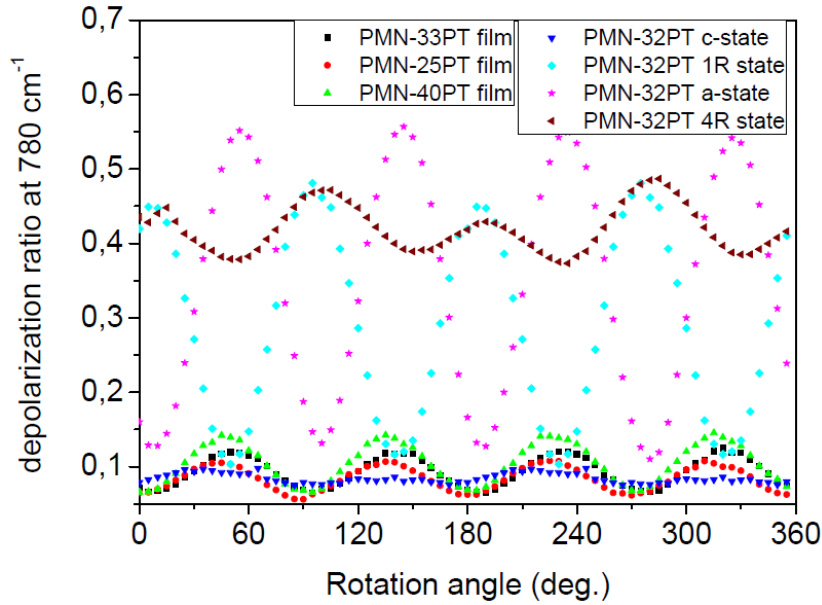


Figure 63: Raman scattering depolarization ratio for the characteristic PMN-PT phonon band, which is found at 780 cm^{-1} , as a function of the angle between the incident light polarization and the pseudocubic crystallographic axis of the PMN-PT. The single crystal data correspond to different crystallographic states: (i) the field-induced tetragonal state with the OP oriented tetragonal axis (*c*-state), (ii) the ambient rhombohedral state (*1R*-state), (iii) the tetragonal state with the IP oriented tetragonal axis (*a*-state), and (iv) the frustratively poled rhombohedral state (*4R*-state), analyzed in the plane perpendicular to the poling field (Courtesy of Dr. I. Rafalovskyi).

4.6.1.2 Comparison of the functional properties of the films with a different PT content

The *P-E* loops together with large signal strain loops are shown in Figure 64. Panel a) shows the results for the films prepared from the targets with 20 mol. % PbO excess, where it is shown that the strain and polarization increase with increasing PT content. Panel b) shows the results for the films prepared from the targets with 20 mol. % PbO and 10 mol. % MgO excess. Here, the highest polarization and strain were also obtained for the PMN-40PT sample. The strain was the lowest in the PMN-25PT sample, while the polarization was the lowest in the PMN-33PT sample. All of the films exhibit clear relaxor-like properties. The loops are slanted and slim, the slimmest one expectedly being the one for the PMN-25PT sample, as the nanodomains of the PMN component, which is more abundant there, mostly re-acquire their random orientation after the applied electric field is removed, resulting in a low remnant polarization value. Some of the loops are slightly pinched, the pinching being most pronounced in the PMN-40PT sample prepared from the target with both PbO and MgO excess, as indicated by the red arrows in Figure 64b). The pinching could mean that some domains contain dipoles oriented along the positive direction, while others contain dipoles along the negative direction of the measuring field. One could think of a pinched loop as being composed of two partial loops, one with a positive and the other with a negative internal field. Pinched loops are usually not horizontally shifted, as the net polarization equals zero, i.e. there is no self-bias. However, the loop in question is shifted. Furthermore, an antiferroelectric alignment of domains is not expected for a PMN-40PT film. The alignment of defect dipoles is not the only mechanism that can cause hardening and apparent internal fields. Diffusion of defects into strained or charged domain walls can lead to pinning of the domain walls and hardening. A concentration of defects at grain boundaries can lead to internal fields, as well as pinched loops [148], [203]–[205]. The defects can be introduced by the electrode deposition process. Matavž et al. [206] have shown that capacitors with inkjet-printed LNO as the top electrode exhibited superior characteristics as compared to those with sputtered Au top electrodes. The capacitors with LNO exhibited better polarization switching, improved fatigue and a significantly higher

dielectric permittivity. It was argued that the improvement of the dielectric response possibly originated from (a) effective compensation of oxygen vacancies by the electrode, (b) a thinner depletion layer at the ferroelectric-electrode interface and (c) a lower concentration of charged defects, owing to the fundamental differences of the processing technique for the preparation of both types of electrodes. Capacitors with LNO top electrodes exhibited symmetrical polarization loops with no evident shift of the coercive field, while the ones with Au top electrodes were pinched and shifted towards negative fields, indicating the presence of an internal bias field. It was argued that the internal field probably arises from the presence of charged defects introduced by the sputtering. Their study has shown that the main contribution to the improved characteristics of capacitors with LNO top electrodes comes from the enhanced mobility of ferroelectric domain walls.

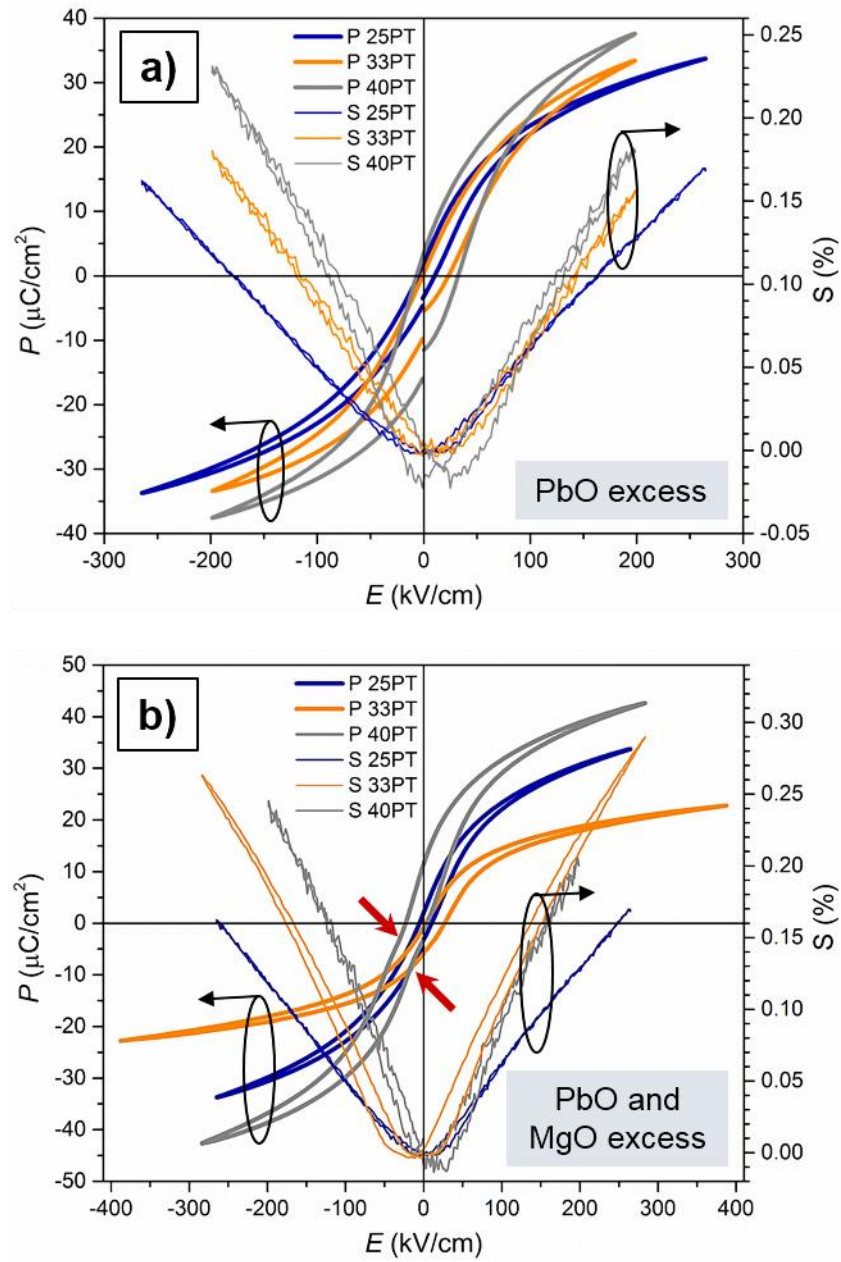


Figure 64: P - E loops together with strain loops of the field induced sample strain versus electric field for (a) samples prepared from targets with PbO excess and (b) samples prepared from targets with PbO and MgO excess.

The $d_{33,\text{eff}}$ coefficients of the same samples as in Figure 64 are presented in Figure 65. The highest $d_{33,\text{eff}}$ values among the samples prepared from the targets with only PbO excess are obtained in the PMN-40PT sample, while the PMN-33PT sample had the highest $d_{33,\text{eff}}$ value among the samples prepared from the targets with both PbO and MgO excess. Nevertheless, the piezoelectric responses of all PMN-33PT and PMN-40PT thin films are comparable, despite the available data on bulk PMN-PT reporting on a much higher response in the PMN-33PT. Nevertheless, the results are not unusual, as the MPB is often shifted in thin films, as mentioned earlier, shifting also the composition with the maximized response. In fact, my results corroborate quite well with those obtained from Yokoyama et al. [130], who found that the highest piezoelectric response was achieved in the PMN-39PT thin film. On the other hand, Wang et al. [180] also compared thin films with PMN:PT ratios of 70:30, 65:35 and 60:40. They found that the values of $d_{33,\text{eff}}$ were approximately the same in all films. The value of P_{sat} of the films decreased monotonically from 30PT to 40PT. The E_c value was the highest for the 40PT composition. They also observed that the dielectric permittivity dropped monotonously with increasing PT content, which was also observed in this work.

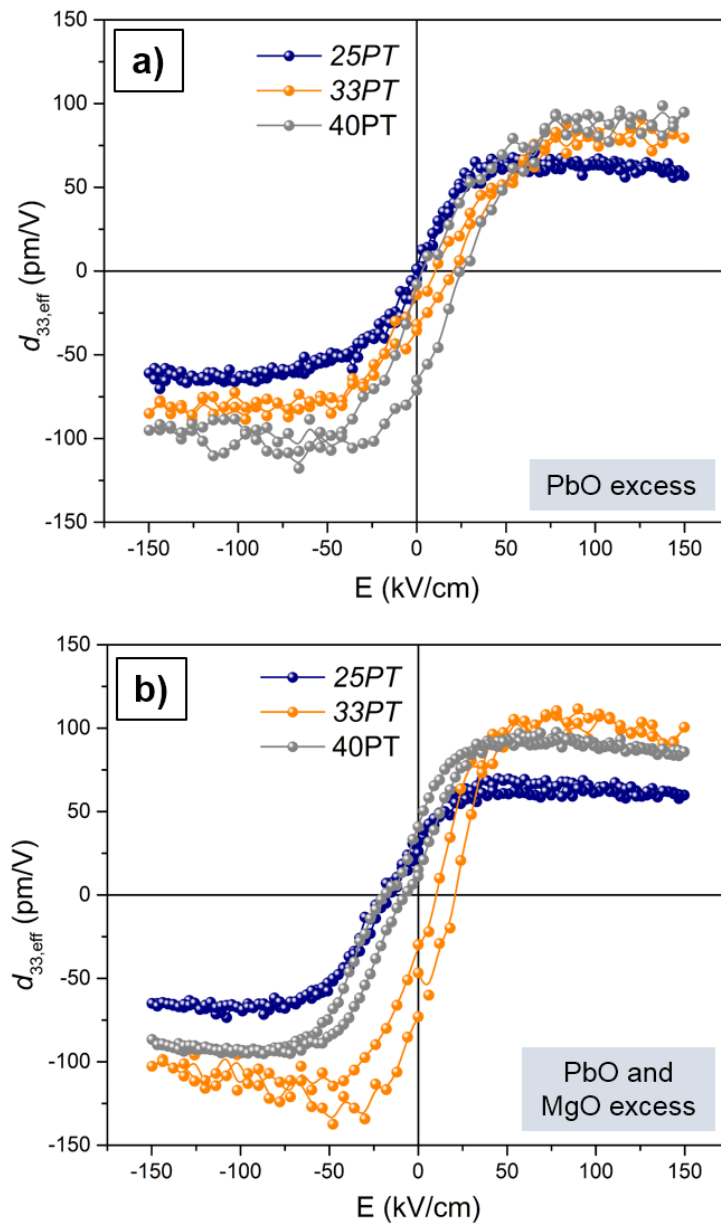


Figure 65: Effective longitudinal piezoelectric coefficients for (a) samples prepared from targets with PbO excess and (b) samples prepared from targets with PbO and MgO excess.

4.7 Growth of PMN-33PT Thin Films on Si Substrates

As stated previously, the majority of applications call for integration with Si, therefore, we have tried to transfer my PMN-33PT films onto Si as well. Two types of samples were grown on Si: (i) PMN-PT/STO/Sr/SOI and (ii) PMN-PT/LNO/Pt/Si, which are appropriate for d_{33} - and d_{31} -mode EHs, respectively. The first type was grown using the procedure described in Section 1.1.6.2, followed by a continuously-grown 50-nm-thick STO layer grown as described in Section 4.5.3, and PMN-33PT using the target with 20 mol. % PbO and 10 mol. % MgO excess. The second type was grown on a platinized Si, covered with a 20-nm-thick PLD-deposited layer of LNO, on top of which PMN-33PT was grown using the target with 20 mol. % PbO excess. As shown in Figure 66, the films were phase-pure; however, they were not grown epitaxially. Polycrystalline growth was expected for the sample grown on LNO, while the sample grown on the STO buffer layer was expected to be highly textured or epitaxial. Most probably, the reason behind this is technical in nature, as the growth of STO/Sr/Si templates was optimized on smaller Si substrates and using infrared laser heating, while the growth of PMN-PT was done on larger samples and using resistive heating.

The $d_{33,eff}$ of the sample prepared on the STO buffer layer could not be measured, due to the geometry of the sample, i.e. the lack of a bottom electrode. The $|d_{33,eff}^{max}|$ of the sample prepared on LNO/Pt/Si was 50 pm V⁻¹, which was significantly inferior to the response of the epitaxial thin film prepared on LNO/STO using the same target, where the value was 90 pm V⁻¹.

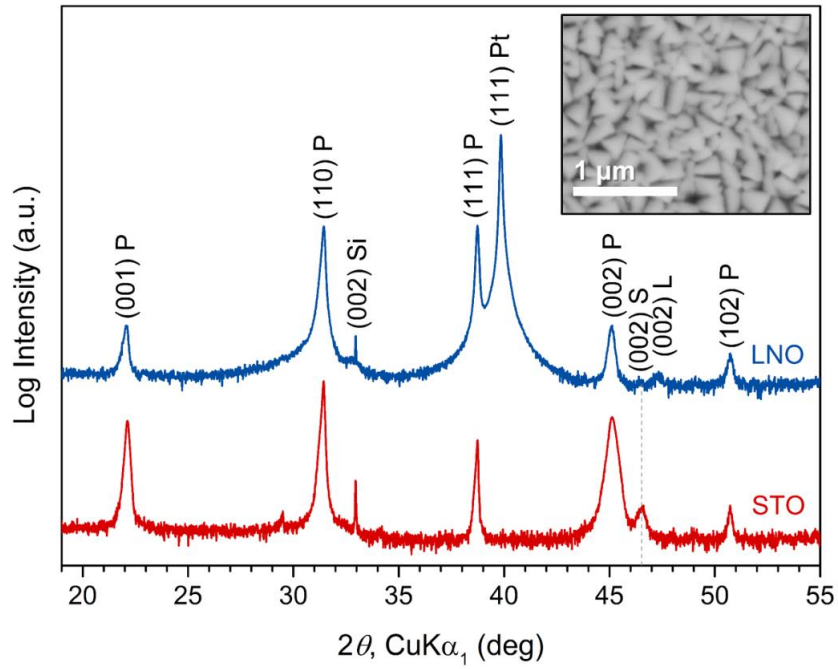


Figure 66: XRD patterns of PMN-33PT films grown on Si substrates.

Chapter 5

Conclusions

This thesis dealt with several issues concerning the PLD growth of epitaxial PMN-PT thin films with compositions around the MPB on (001)-oriented STO substrates. I studied two main types of samples: (i) PMN-PT/STO for d_{33} -mode EHs and (ii) PMN-PT/LNO/STO for d_{31} -mode EHs. I gave particular attention to the issue of the incorporation of Pb into the film, which I systematically addressed by the use of targets with different amounts of PbO excess. I studied the chemical and crystal structure of the films in detail, along with their relation to the functional properties.

In the first step, I examined the in-house prepared Pb- and Mg-rich targets and STO substrates after the chemical and thermal treatment. The targets were found to be phase-pure, relatively dense and homogeneous. The substrates exhibited a purely TiO₂-terminated surface with straight and smooth steps.

In the next part, the growth of the PMN-33PT/STO samples is presented, starting with the optimization of the parameters for obtaining pure-perovskite films. Despite extensive variations of several deposition parameters, trying to achieve pyrochlore-free growth using stoichiometric targets was an effort in futility. I found that 20 mol. % PbO were necessary to suppress the formation of the pyrochlore phase in PMN-PT/STO samples. Furthermore, I observed a large sensitivity to the deposition temperature, with variations of ± 10 °C leading to the formation of pyrochlore impurities, which grow in the shape of cones. The phase-pure sample exhibited a relatively smooth surface, giving rise to a modulated streaky pattern in RHEED.

A peculiar feature, namely a splitting of the PMN-33PT peaks, can be seen in the XRD pattern of the sample prepared at 0.13 mbar (*P13*). Upon raising the process pressure to 0.27 mbar (*P27*), the peak splitting was no longer present. An experiment with an Ar/O₂ mixture revealed that the total pressure, rather than the oxygen partial pressure, influenced the peak splitting behavior. Hence, I argued that for the given system the pressure 0.13 mbar falls into the transition regime between vacuum-like (ballistic) regime and the diffusion-like regime. In the transition regime, the plume is split into two parts, and shock-wave formation can occur, severely affecting the growth of the film. While this left the mean stoichiometry of the film relatively unaffected, the microstructures of the two films prepared under the two pressure conditions differ substantially. Atomic-resolution STEM-HAADF imaging revealed that while both films exhibited atomically-sharp interfaces, the strain was relaxed via different mechanisms. Whereas MDs were formed in sample *P27*, the strain in sample *P13* was released through SFs. While SFs, such as OPBs were observed in both films, the density was much higher in sample *P13*. It had been argued in the literature that the splitting is related to the MPB composition of the films, i.e. to the presence of different types of ferroelectric domains, which should enhance the functional response of the films. This hypothesis was not supported by the results obtained in this thesis, as sample *P27* was found to exhibit superior dielectric and piezoelectric properties.

As mentioned, OPBs were also observed in sample *P27*. These defects are most probably a consequence of the partially 3D-like growth of the film and a small surplus of PbO, which was determined by WDXS analysis. RP-type defects form between the as-grown islands.

During the preparation of LNO electrodes, I stumbled upon several interesting structural features. The unit-cell volume of the films was largely increased as compared to bulk LNO. While the layer was fully strained IP to the STO, the OP lattice parameter remained almost the same as in bulk. STEM-HAADF imaging revealed that the first few MLs of the LNO are single-crystal-like. Afterwards, a large density of APBs is formed, which extend throughout the thickness of the film. These observations corroborate with the measured RHEED specular-spot intensity oscillations.

The main conclusion, which I have drawn from the growth of PMN-PT/LNO/STO samples, is the remarkably enhanced stability of the perovskite phase as compared to PMN-PT/STO samples. Based on the experiments I carried out on other buffer layers, it seems that the relatively larger surface roughness of the LNO is responsible for the enhanced sticking probability of PbO, thereby suppressing the growth of pyrochlore. Given the enhanced stability of the PMN-PT, I studied the growth from different types of targets. I found that the unit-cell volume was increased with respect to bulk in all samples. The use of PbO- and MgO-rich targets led to improved stoichiometry of the films, yielding a film (sample *C2010*) with the overall composition $\text{Pb}_{1.04 \pm 0.01} \text{Mg}_{0.203 \pm 0.004} \text{Nb}_{0.44 \pm 0.01} \text{Ti}_{0.33 \pm 0.01} \text{O}_3$, which is very close to stoichiometric. This sample exhibited the best piezoelectric response among the PMN-33PT samples.

I have shown that the structural peculiarity observed in sample *P13* is independent of the underlying material and the PMN:PT ratio, i.e. the splitting was observed in all of the samples prepared at 0.13 mbar.

All of the PMN-PT films exhibited a pseudocubic structure, with a slight tetragonality, as measured from the centroid positions of the reciprocal spots. Distinct crystal structures were not resolved from the RSMs. The comparison of the Raman scattering depolarization ratio at 780 cm^{-1} for the thin films with a different PMN:PT ratio, and bulk crystals, strongly suggests that the tetragonal crystal structure is stabilized in the thin films. This argument is supported by the measurements of the dielectric permittivity, where a strong anisotropy was observed. Measurements of the ferroelectric hysteresis loops expectedly revealed the slimmest loops for PMN-25PT samples, while PMN-40PT samples exhibited the highest $|E_c|$ values. The highest large signal strains were achieved in PMN-40PT samples, while the longitudinal piezoelectric response was high in both PMN-40PT and PMN-33PT, pointing to a larger region of augmented response as compared to bulk.

In the final part, results of the integration with Si are presented. While phase-pure growth was achieved on both types of templates, the films were polycrystalline, thereby exhibiting inferior properties as compared to the ones grown on STO substrates.

In summary, the results presented in this thesis offer an insight into the correlation between the synthesis process, the chemical composition, and the atomic-scale structural properties of the films, as well as their functional characteristics.

References

- [1] S. E. Park and T. R. Shrout, "Ultrahigh strain and piezoelectric behavior in relaxor based ferroelectric single crystals," *J. Appl. Phys.*, vol. 82, no. 4, pp. 1804–1811, 1997.
- [2] A. P. Ramirez, "Colossal magnetoresistance," *J. Phys. Condens. Matter*, vol. 9, no. 39, pp. 8171–8199, Sep. 1997.
- [3] J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, "Epitaxial BiFeO₃ multiferroic thin film heterostructures," *Science*, vol. 299, no. 5613, pp. 1719–1722, Mar. 2003.
- [4] N. A. Spaldin and R. Ramesh, "Electric-Field Control of Magnetism in Complex Oxide Thin Films," *MRS Bull.*, vol. 33, no. 11, pp. 1047–1050, Nov. 2008.
- [5] A. Tebano, E. Fabbri, D. Pergolesi, G. Balestrino, and E. Traversa, "Room-temperature giant persistent photoconductivity in SrTiO₃/LaAlO₃ heterostructures," *ACS Nano*, vol. 6, no. 2, pp. 1278–1283, Feb. 2012.
- [6] M. Z. Hasan and C. L. Kane, "Colloquium: Topological insulators," *Rev. Mod. Phys.*, vol. 82, no. 4, pp. 3045–3067, Nov. 2010.
- [7] X. Wan, A. M. Turner, A. Vishwanath, and S. Y. Savrasov, "Topological semimetal and Fermi-arc surface states in the electronic structure of pyrochlore iridates," *Phys. Rev. B - Condens. Matter Mater. Phys.*, vol. 83, no. 20, p. 205101, May 2011.
- [8] B. Jaffe, R. S. Roth, and S. Marzullo, "Piezoelectric Properties of Lead Zirconate-Lead Titanate Solid-Solution Ceramics," *J. Appl. Phys.*, vol. 25, no. 6, pp. 809–810, Jun. 1954.
- [9] S. M. Wu, S. A. Cybart, P. Yu, M. D. Rossell, J. X. Zhang, R. Ramesh, and R. C. Dynes, "Reversible electric control of exchange bias in a multiferroic field-effect device," *Nat. Mater.*, vol. 9, no. 9, pp. 756–761, Sep. 2010.
- [10] H. Y. Hwang, Y. Iwasa, M. Kawasaki, B. Keimer, N. Nagaosa, and Y. Tokura, "Emergent phenomena at oxide interfaces," *Nat. Mater.*, vol. 11, no. 2, pp. 103–113, Feb. 2012.
- [11] P. Zubko, S. Gariglio, M. Gabay, P. Ghosez, and J.-M. Triscone, "Interface Physics in Complex Oxide Heterostructures," *Annu. Rev. Condens. Matter Phys.*, vol. 2, no. 1, pp. 141–165, Mar. 2011.
- [12] G. Koster, M. Huijben, and G. J. H. M. Rijnders, *Epitaxial Growth of Complex Metal Oxides*, 76th ed., Woodhead Publishing, 2015.
- [13] L. Zhang, Y. Yuan, J. Lapano, M. Brahlek, S. Lei, B. Kabius, V. Gopalan, and R. Engel-Herbert, "Continuously Tuning Epitaxial Strains by Thermal Mismatch," *ACS Nano*, vol. 12, no. 2, pp. 1306–1312, 2018.
- [14] S. P. Alpay and A. L. Roytburd, "Thermodynamics of polydomain heterostructures. III. Domain stability map," *J. Appl. Phys.*, vol. 83, no. 9, pp. 4714–4723, May 1998.
- [15] J. Lyu, I. Fina, R. Solanas, J. Fontcuberta, and F. Sánchez, "Tailoring Lattice Strain and Ferroelectric Polarization of Epitaxial BaTiO₃ Thin Films on Si (001)," *Sci. Rep.*, vol. 495, no. December 2017, pp. 1–19, 2018.
- [16] R. Eason, Ed., *Pulsed Laser Deposition of Thin Films*. Hoboken, NJ, USA: John Wiley & Sons, Inc., 2006.
- [17] D. Damjanovic, "Hysteresis in piezoelectric and ferroelectric materials," in *The Science of Hysteresis*, vol. 3, 2006, pp. 337–465.
- [18] F. Li, S. Zhang, T. Yang, Z. Xu, N. Zhang, G. Liu, J. Wang, J. Wang, Z. Cheng, Z.-G. Ye, J.

- Luo, T. R. Shrout, and L.-Q. Chen, "The origin of ultrahigh piezoelectricity in relaxor-ferroelectric solid solution crystals," *Nat. Commun.*, vol. 7, p. 13807, 2016.
- [19] R. Ramesh, A. Inam, W. K. Chan, B. Wilkens, K. Myers, K. Remschnig, D. L. Hart, and J. M. Tarascon, "Epitaxial cuprate superconductor/ferroelectric heterostructures," *Science*, vol. 252, no. 5008, pp. 944–946, May 1991.
- [20] M. A. Helal, M. Aftabuzzaman, S. Tsukada, and S. Kojima, "Role of polar nanoregions with weak random fields in Pb-based perovskite ferroelectrics," *Sci. Rep.*, vol. 7, p. 44448, 2017.
- [21] N. Setter, "What is a ferroelectric—a materials designer perspective," *Ferroelectrics*, vol. 500, no. 1, pp. 164–182, Aug. 2016.
- [22] L. E. Cross, "Relaxor Ferroelectrics," in *Piezoelectricity*, Berlin, Heidelberg: Springer Berlin Heidelberg, 2008, pp. 131–155.
- [23] S. Park and T. R. Shrout, "Ultrahigh strain and piezoelectric behavior in relaxor based ferroelectric single crystals," *J. Appl. Phys.*, vol. 82, no. 4, pp. 1804–1811, 1997.
- [24] H. Fu and R. E. Cohen, "Polarization rotation mechanism for ultrahigh electrochemical response in single-crystal piezoelectrocs," *Lett. to Nat.*, vol. 403, pp. 281–283, 2000.
- [25] Z. Kutnjak, J. Petzelt, and R. Blinc, "The giant electromechanical response in ferroelectric relaxors as a critical phenomenon," *Nature*, vol. 441, no. 7096, pp. 956–959, Jun. 2006.
- [26] Y. Zhang, D. Xue, H. Wu, X. Ding, T. Lookman, and X. Ren, "Adaptive ferroelectric state at morphotropic phase boundary: Coexisting tetragonal and rhombohedral phases," *Acta Mater.*, vol. 71, pp. 176–184, 2014.
- [27] H. Liu, J. Chen, L. Fan, Y. Ren, Z. Pan, K. V Lalitha, J. Rödel, and X. Xing, "Critical Role of Monoclinic Polarization Rotation in High-Performance Perovskite Piezoelectric Materials," *Phys. Rev. Lett.*, vol. 119, no. 1, p. 017601, 2017.
- [28] M. J. Krogstad, P. M. Gehring, S. Rosenkranz, R. Osborn, F. Ye, Y. Liu, J. P. C. Ruff, W. Chen, J. M. Wozniak, H. Luo, O. Chmaissem, Z.-G. Ye, and D. Phelan, "The relation of local order to material properties in relaxor ferroelectrics," *Nat. Mater.*, vol. 17, pp. 718–724, 2018.
- [29] W. Wersing, W. Heywang, H. Beige, and H. Thomann, "The Role of Ferroelectricity for Piezoelectric Materials," in *Piezoelectricity*, vol. 114, Berlin, Heidelberg: Springer Berlin Heidelberg, 2008, pp. 37–87.
- [30] B. Noheda, D. E. Cox, G. Shirane, Z.-G. Ye, and J. Gao, "Phase diagram of the ferroelectric-relaxor $(1-x)\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ - $x\text{PbTiO}_3$," *Phys. Rev. B*, vol. 66, no. 5, p. 054104, 2002.
- [31] D. Vanderbilt and M. H. Cohen, "Monoclinic and triclinic phases in higher-order Devonshire theory," *Phys. Rev. B*, vol. 63, no. 9, p. 094108, Jan. 2001.
- [32] A. Singh, D. Pandey, and O. Zaharko, "Powder neutron diffraction study of phase transitions in and a phase diagram of $(1-x)[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]$ - $x\text{PbTiO}_3$," *Phys. Rev. B*, vol. 74, pp. 1–18, 2006.
- [33] V. G. Koukhar, N. A. Pertsev, and R. Waser, "Thermodynamic theory of epitaxial ferroelectric thin films with dense domain structures," *Phys. Rev. B*, vol. 64, no. 21, p. 214103, Nov. 2001.
- [34] S. L. Swartz and T. R. Shrout, "Fabrication of perovskite lead magnesium niobate," *Mater. Res. Bull.*, vol. 17, no. 10, pp. 1245–1250, 1982.
- [35] J. P. Guha, "Reaction chemistry and subsolidus phase equilibria in lead-based relaxor systems: Part I Formation and stability of the perovskite and pyrochlore compounds in the system PbO - MgO - Nb_2O_5 ," *J. Mater. Sci.*, vol. 4, pp. 4985–4994, 1999.
- [36] H. Luo, G. Xu, P. Wang, and Z. Yin, "Growth and characterization of relaxor ferroelectric PMNT single crystals," *Ferroelectrics*, vol. 231, no. 1, pp. 97–102, Jun. 1999.
- [37] Z. Samardžija, J.-H. Jeon, and M. Čeh, "Microstructural and compositional study of a

- bulk $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ single crystal grown from a BaTiO_3 seed," *Mater. Charact.*, vol. 58, pp. 534–543, 2007.
- [38] V. Šrot, M. Gec, P. A. van Aken, J. H. Jeon, and M. Čeh, "Influence of TEM specimen preparation on chemical composition of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ single crystals," *Micron*, vol. 62, pp. 37–42, 2014.
 - [39] T. Denneulin, W. Maeng, C.-B. Eom, and M. Hÿtch, "Lattice reorientation in tetragonal PMN-PT thin film induced by focused ion beam preparation for transmission electron microscopy," *J. Appl. Phys.*, vol. 121, p. 55302, 2017.
 - [40] R. Zhang, B. Jiang, and W. Cao, "Elastic, piezoelectric, and dielectric properties of multidomain $0.67\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.33\text{PbTiO}_3$ single crystals," *J. Appl. Phys.*, vol. 90, no. 7, pp. 3471–3475, 2001.
 - [41] J.-P. Maria, W. Hackenberger, and S. Trolier-McKinstry, "Phase development and electrical property analysis of pulsed laser deposited $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (70/30) epitaxial thin films," *J. Appl. Phys.*, vol. 84, no. 9, pp. 5147–5154, 1998.
 - [42] S. H. Baek, J. Park, D. M. Kim, V. A. Aksyuk, R. R. Das, S. D. Bu, D. A. Felker, J. Lettieri, V. Vaithyanathan, S. Bharadwaja, N. Bassiri-Gharb, Y. B. Chen, H. P. Sun, C. M. Folkman, H. W. Jang, D. J. Kreft, S. K. Streiffer, R. Ramesh, X. Q. Pan, S. Trolier-McKinstry, D. G. Schlom, M. S. Rzchowski, R. Blick, and C. B. Eom, "Giant piezoelectricity on Si for hyperactive MEMS," *Science*, vol. 334, no. 6058, pp. 958–961, 2011.
 - [43] S. Pandya, J. Wilbur, J. Kim, R. Gao, A. Dasgupta, C. Dames, and L. W. Martin, "Pyroelectric energy conversion with large energy and power density in relaxor ferroelectric thin films," *Nat. Mater.*, vol. 17, no. 5, pp. 432–438, 2018.
 - [44] K. Shinozaki, S. Hayashi, N. Wakiya, T. Kiguchi, J. Tanaka, and N. Ishizawa, "Fabrication and Optical Properties of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ Thin Films on Si Substrates Using the PLD Method," vol. 55, no. 5, 2008.
 - [45] M. A. Hamad, "Room temperature giant electrocaloric properties of relaxor ferroelectric $0.93\text{PMN}\text{-}0.07\text{PT}$ thin film," *AIP Adv.*, vol. 3, p. 032115, Mar. 2013.
 - [46] X. Wang, L. Zhang, X. Hao, S. An, and B. Song, "Dielectric properties and energy-storage performances of $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}x\text{PbTiO}_3$ relaxor ferroelectric thin films," *J. Mater. Sci. Mater. Electron.*, vol. 26, no. 12, pp. 9583–9590, 2015.
 - [47] X. Wang, L. Zhang, X. Hao, and S. An, "High energy-storage performance of $0.9\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3\text{-}0.1\text{PbTiO}_3$ relaxor ferroelectric thin films prepared by RF magnetron sputtering," *Mater. Res. Bull.*, vol. 65, pp. 73–79, 2015.
 - [48] M. T. Todaro, F. Guido, V. Mastronardi, D. Desmaele, G. Epifani, L. Algieri, and M. De Vittorio, "Piezoelectric MEMS vibrational energy harvesters: Advances and outlook," *Microelectron. Eng.*, vol. 183–184, no. November, pp. 23–36, 2017.
 - [49] Z. Yang and J. Zu, "Comparison of PZN-PT, PMN-PT single crystals and PZT ceramic for vibration energy harvesting," *Energy Convers. Manag.*, vol. 122, pp. 321–329, 2016.
 - [50] M. A. Karami, O. Bilgen, D. J. Inman, and M. I. Friswell, "Experimental and analytical parametric study of single-crystal unimorph beams for vibration energy harvesting," *IEEE Trans. Ultrason. Ferroelectr. Freq. Control*, vol. 58, no. 7, pp. 1508–1520, 2011.
 - [51] Y. H. Fu, W. H. Tang, S. C. Lin, T. K. Lin, C. T. Chen, and W. J. Wu, "Comparison of electrical and mechanical properties between PMN-PT and PZT thin films in energy harvester application," in *21st International conference on Composite Materials*, 2017.
 - [52] G. T. Hwang, H. Park, J. H. Lee, S. Oh, K. Il Park, M. Byun, H. Park, G. Ahn, C. K. Jeong, K. No, H. Kwon, S. G. Lee, B. Joung, and K. J. Lee, "Self-powered cardiac pacemaker enabled by flexible single crystalline PMN-PT piezoelectric energy harvester," *Adv. Mater.*, vol. 26, no. 28, pp. 4880–4887, 2014.
 - [53] D. H. Kim, H. J. Shin, H. Lee, C. K. Jeong, H. Park, G. T. Hwang, H. Y. Lee, D. J. Joe, J. H. Han, S. H. Lee, J. Kim, B. Joung, and K. J. Lee, "In Vivo Self-Powered Wireless Transmission Using Biocompatible Flexible Energy Harvesters," *Adv. Funct. Mater.*,

- vol. 1700341, pp. 1–8, 2017.
- [54] B. Ren, S. Wing Or, X. Zhao, and H. Luo, “Energy harvesting using a modified rectangular cymbal transducer based on single crystal,” *J. Appl. Phys.*, vol. 107, p. 34501, 2010.
 - [55] K. Ren, Y. Liu, X. Geng, H. F. Hofmann, and Q. M. Zhang, “Single Crystal PMN-PT / Epoxy 1-3 Composite for Energy-Harvesting Application,” *IEEE Trans. Ultrason. Ferroelectr. Freq. Control*, vol. 53, no. 3, 2006.
 - [56] G. Tang, B. Yang, J.-Q. Liu, B. Xu, H.-Y. Zhu, and C.-S. Yang, “Development of high performance piezoelectric d_{33} mode MEMS vibration energy harvester based on PMN-PT single crystal thick film,” *Sensors Actuators A Phys.*, vol. 205, pp. 150–155, 2014.
 - [57] B. Yang, Y. Zhu, X. Wang, J. Liu, and C. Yang, “Fabrication and Characterization of d_{33} Mode Energy Harvester,” *Sensors Mater.*, vol. 26, no. 8, pp. 591–598, 2014.
 - [58] Y. Wang, N. Chong, Y. L. Cheng, H. L. W. Chan, and C. L. Choy, “Dependence of capacitance on electrode configuration for ferroelectric films with interdigital electrodes,” *Microelectron. Eng.*, vol. 66, no. 1–4, pp. 880–886, 2003.
 - [59] A. Toprak and O. Tigli, “Interdigitated-electrode-based mems-scale piezoelectric energy harvester modeling and optimization using finite element method,” *IEEE Trans. Ultrason. Ferroelectr. Freq. Control*, vol. 60, no. 10, pp. 2162–2174, 2013.
 - [60] M. Kim, J. Dugundji, and B. L. Wardle, “Effect of electrode configurations on piezoelectric vibration energy harvesting performance,” *Smart Mater. Struct.*, vol. 24, no. 4, p. 045026, Apr. 2015.
 - [61] J. Shang, H. Zhang, Y. Li, X. Zhou, and P. Zhang, “Fabrication of pure-perovskite PMN-PT thin films on SrTiO_3 substrates using pulsed laser deposition,” *J. Cryst. Growth*, vol. 312, pp. 1925–1928, 2010.
 - [62] Y. W. Li, Z. G. Hu, F. Y. Yue, G. Y. Yang, W. Z. Shi, X. J. Meng, J. L. Sun, and J. H. Chu, “Properties of highly (100) oriented $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ films on LaNiO_3 bottom electrodes,” *Appl. Phys. Lett.*, vol. 91, no. 23, pp. 89–92, 2007.
 - [63] J. W. Reiner, K. F. Garrity, F. J. Walker, S. Ismail-Beigi, and C. H. Ahn, “Role of Strontium in Oxide Epitaxy on Silicon (001),” *Phys. Rev. Lett.*, vol. 101, no. 10, p. 105503, 2008.
 - [64] M. P. Warusawithana, C. Cen, C. R. Sleasman, J. C. Woicik, Y. Li, L. Fitting Kourkoutis, J. A. Klug, H. Li, P. Ryan, L.-P. Wang, M. Bedzyk, D. A. Muller, L.-Q. Chen, J. Levy, and D. G. Schlom, “A Ferroelectric Oxide Made Directly on Silicon,” *Science*, vol. 423, pp. 367–369, 2009.
 - [65] Z. Jovanović, M. Spreitzer, J. Kovač, D. Klement, and D. Suvorov, “Silicon Surface Deoxidation Using Strontium Oxide Deposited with the Pulsed Laser Deposition Technique,” *ACS Appl. Mater. Interfaces*, vol. 6, no. 20, pp. 18205–18214, Oct. 2014.
 - [66] Z. Jovanović, M. Spreitzer, U. Gabor, and D. Suvorov, “Control of SrO buffer-layer formation on Si(001) using the pulsed-laser deposition technique,” *RSC Adv.*, vol. 6, no. 85, pp. 82150–82156, 2016.
 - [67] D. Diaz-Fernandez, M. M. Spreitzer, T. T. Parkelj, J. Kovač, K. Kovač, and D. Suvorov, “The importance of annealing and stages coverage on the epitaxial growth of complex oxides on silicon by pulsed laser deposition,” *RSC Adv.*, vol. 7, no. 40, pp. 24709–24717, 2017.
 - [68] D. Diaz-Fernandez, M. Spreitzer, T. Parkelj, and D. Suvorov, “Multi-stage pulsed laser deposition of high quality epitaxial ultra-thin SrTiO_3 on Si substrates,” *Appl. Surf. Sci.*, vol. 455, pp. 227–235, Oct. 2018.
 - [69] J. Mäkinen, “Thick-Film SOI Wafers,” in *Handbook of Silicon Based MEMS Materials and Technologies*, Elsevier, 2010, pp. 107–136.
 - [70] K. Munakata and A. Okazaki, “Ultra-high-angle double-crystal X-ray diffractometry (U-HADOX) for determining a change in the lattice spacing: Experiment,” *Acta Crystallogr. Sect. A Found. Crystallogr.*, vol. 60, no. 1, pp. 33–39, 2004.
 - [71] K. S. Hwang, B. A. Kang, Y. S. Jeon, J. H. An, B. H. Kim, K. Nishio, and T. Tsuchiya, “AFM

- study of LaNiO_3 thin films on various single crystal substrates prepared by using a metal naphthenate precursor," *Surf. Coatings Technol.*, vol. 190, no. 2–3, pp. 331–335, 2005.
- [72] S. Yamanaka, T. Maekawa, H. Muta, T. Matsuda, S. I. Kobayashi, and K. Kurosaki, "Thermophysical properties of SrHfO_3 and SrRuO_3 ," *J. Solid State Chem.*, vol. 177, no. 10, pp. 3484–3489, Oct. 2004.
 - [73] G. Gou, I. Grinberg, A. M. Rappe, and J. M. Rondinelli, "Lattice normal modes and electronic properties of the correlated metal LaNiO_3 ," *Phys. Rev. B*, vol. 84, no. 14, p. 144101, 2011.
 - [74] S. N. Kallae, G. G. Gadzhiev, I. K. Kamilov, Z. M. Omarov, S. A. Sadykov, and L. A. Reznichenko, "Thermal properties of PZT-based ferroelectric ceramics," *Phys. Solid State*, vol. 48, no. 6, pp. 1169–1170, 2006.
 - [75] R. Wongmaneeerung, R. Guo, A. Bhalla, R. Yimnirun, and S. Ananta, "Thermal expansion properties of PMN-PT ceramics," *J. Alloys Compd.*, vol. 461, no. 1–2, pp. 565–569, 2008.
 - [76] R. R. Keech, "Dimensional scaling of perovskite ferroelectric thin films," The Pennsylvania State University, 2016.
 - [77] H. Uršič, M. Hrovat, J. Holc, J. Tellier, S. Drnovšek, N. Guiblin, B. Dkhil, and M. Kosec, "Influence of the substrate on the phase composition and electrical properties of 0.65PMN-0.35PT thick films," *J. Eur. Ceram. Soc.*, vol. 30, no. 10, pp. 2081–2092, 2010.
 - [78] A. Sehirlioglu, D. A. Payne, and P. Han, "Thermal expansion of phase transformations in $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\text{PbTiO}_3$: Evidence for preferred domain alignment in one of the 001 directions for melt-grown crystals," *Phys. Rev. B - Condens. Matter Mater. Phys.*, vol. 72, no. 21, 2005.
 - [79] T. Yoshitake, G. Shiraishi, and K. Nagayama, "Droplet-Free Thin Films Prepared by Pulsed Laser Deposition Using a Vane Velocity Filter," *Jpn. J. Appl. Phys.*, vol. 41, no. Part 1, No. 2A, pp. 836–837, 2002.
 - [80] G. Koster, B. L. Kropman, G. J. H. M. Rijnders, D. H. a Blank, and H. Rogalla, "Quasi-ideal strontium titanate crystal surfaces through formation of strontium hydroxide," *Appl. Phys. Lett.*, vol. 73, no. 20, pp. 2920–2922, 1998.
 - [81] S. Hasegawa, *Characterization of Materials*. John Wiley & Sons, Inc., 2012.
 - [82] H. P. Garnir, Y. Baudinet-Robinet, and P. D. Dumont, "Error in the determination of Gaussian peak centroids," *Nucl. Inst. Methods Phys. Res. B*, vol. 28, no. 1, pp. 146–153, 1987.
 - [83] W. Cochran, "Crystal stability and the theory of ferroelectricity," *Adv. Phys.*, vol. 9, no. 36, pp. 387–423, Oct. 1960.
 - [84] D. A. Tenne and X. Xi, "Raman spectroscopy of ferroelectric thin films and superlattices," *J. Am. Ceram. Soc.*, vol. 91, no. 6, pp. 1820–1834, 2008.
 - [85] M. Iwata, N. Tomisato, H. Orihara, N. Arai, N. Tanaka, H. Ohwa, N. Yasuda, and Y. Ishibashi, "Raman Scattering in $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\text{PbTiO}_3$ Mixed Crystal System II," *Jpn. J. Appl. Phys.*, vol. 40, no. Part 1, No. 9B, pp. 5819–5822, Sep. 2001.
 - [86] N. Setter and L. E. Cross, "An optical study of the ferroelectric relaxors $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$, $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$, and $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$," *Ferroelectrics*, vol. 37, no. 1, pp. 551–554, Oct. 1981.
 - [87] B. Maier, B. Mihailova, C. Paulmann, J. Ihringer, M. Gospodinov, R. Stosch, B. Güttler, and U. Bismayer, "Effect of local elastic strain on the structure of Pb-based relaxors: A comparative study of pure and Ba- and Bi-doped $\text{PbSc}_{0.5}\text{Nb}_{0.5}\text{O}_3$," *Phys. Rev. B*, vol. 79, no. 22, p. 224108, Jun. 2009.
 - [88] J. Pokorný, I. Rafalovskyi, I. Gregora, F. Borodavka, M. Savinov, J. Drahokoupil, M. Tyunina, T. Kocourek, M. Jelinek, Y. Bing, Z.-G. Ye, and J. Hlinka, "Polarized Raman scattering study of PSN single crystals and epitaxial thin films," *J. Adv. Dielectr.*, vol. 5, no. 2, p. 1550013, 2015.
 - [89] I. Rafalovskyi, M. Guennou, I. Gregora, and J. Hlinka, "Macroscopic lamellar

- heterophase pattern in $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{1/3})\text{O}_{1/3}$ - $\text{PbTiO}_{1/3}$ single crystals," *Phys. Rev. B*, vol. 93, p. 064110, 2016.
- [90] J. J. P. Peters, R. Beanland, M. Alexe, J. W. Cockburn, D. G. Revin, S. Y. Zhang, and A. M. Sanchez, "Artefacts in geometric phase analysis of compound materials," *Ultramicroscopy*, vol. 157, pp. 91–97, 2015.
- [91] K.-H. Kim, D. A. Payne, and J.-M. Zuo, "Ion-beam induced domain structure in piezoelectric PMN-PT single crystal," *Appl. Phys. Lett*, vol. 97, p. 261910, 2010.
- [92] J. M. Gibson, R. Hull, J. C. Bean, and M. M. J. Treacy, "Elastic relaxation in transmission electron microscopy of strained-layer superlattices," *Appl. Phys. Lett*, vol. 46, no. 7, pp. 649–651, 1985.
- [93] G. Haugstad, *Atomic Force Microscopy*. Hoboken, New Jersey: John Wiley & Sons, Inc., 2012.
- [94] I. Horcas, R. Fernández, J. M. Gómez-Rodríguez, J. Colchero, J. Gómez-Herrero, and A. M. Baro, "WSXM: A software for scanning probe microscopy and a tool for nanotechnology," *Rev. Sci. Instrum.*, vol. 78, no. 1, p. 013705, 2007.
- [95] W. Wersing, W. Heywang, H. Beige, and H. Thomann, "The Role of Ferroelectricity for Piezoelectric Materials," in *Piezoelectricity*, Berlin, Heidelberg: Springer Berlin Heidelberg, pp. 37–87.
- [96] N. J. Kidner, Z. J. Homrighaus, T. O. Mason, and E. J. Garboczi, "Modeling interdigital electrode structures for the dielectric characterization of electroceramic thin films," *Thin Solid Films*, vol. 496, no. 2, pp. 539–545, Feb. 2006.
- [97] K. Prume, P. Muralt, F. Calame, T. Schmitz-Kempen, and S. Tiedke, "Piezoelectric Thin Films: Evaluation of Electrical and Electromechanical Characteristics for MEMS Devices," *IEEE Trans. Ultrason. Ferroelectr. Freq. Control*, vol. 54, no. 1, pp. 8–14, 2007.
- [98] K. Prume, P. Muralt, F. Calame, T. Schmitz-Kempen, and S. Tiedke, "Extensive electromechanical characterization of PZT thin films for MEMS applications by electrical and mechanical excitation signals," *J. Electroceramics*, vol. 19, no. 4, pp. 407–411, Dec. 2007.
- [99] K. Prume, S. Tiedke, and T. Schmitz-Kempen, "Double-Beam and four-point," *Microniek*, vol. 4, pp. 31–35, 2010.
- [100] P. Gerber, A. Roelofs, C. Kügeler, U. Böttger, R. Waser, and K. Prume, "Effects of the top-electrode size on the piezoelectric properties (d_{33} and S) of lead zirconate titanate thin films," *J. Appl. Phys.*, vol. 96, no. 5, pp. 2800–2804, 2004.
- [101] K. Prume, P. Gerber, C. Kugeler, a. Roelofs, U. Bottger, R. Waser, T. Schmitz-Kempen, and S. Tiedke, "Simulation and measurements of the piezoelectric properties response (d_{33}) of piezoelectric layered thin film structures influenced by the top-electrode size," *14th IEEE Int. Symp. Appl. Ferroelectr. 2004. ISAF-04. 2004*, vol. 00, no. c, pp. 7–10, 2004.
- [102] A. Gruverman, "Piezoresponse force microscopy and recent Piezoresponse force microscopy and recent advances in nanoscale studies of ferroelectrics," *J. Mater. Sci.*, vol. 41, no. 1, pp. 107–116, 2006.
- [103] S. P. Chen, "Compositional and physical changes on perovskite crystal surfaces," *J. Mater. Res.*, vol. 13, no. 7, pp. 1848–1852, 1998.
- [104] S. D. Bu, M. K. Lee, C. B. Eom, W. Tian, X. Q. Pan, S. K. Streiffet, and J. J. Krajewski, "Perovskite phase stabilization in epitaxial $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 films by deposition onto vicinal (001) SrTiO_3 substrates," *Appl. Phys. Lett*, vol. 79, no. 21, pp. 3482–3484, 2001.
- [105] M. Boota, E. P. Houwman, M. D. Nguyen, G. Lanzara, and G. Rijnders, "Effect of fabrication conditions on phase formation and properties of epitaxial $(\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3)_{0.67}$ - PbTiO_3 thin films on SrTiO_3 ," *AIP Adv.*, vol. 6, no. 5, p. 055303, 2016.
- [106] S. Jiao, Y. Tang, X. Zhao, T. Wang, Z. Duan, F. Wang, D. Sun, H. Luo, and W. Shi, "Growth

- and electrical properties of epitaxial $0.7\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.3PbTiO_3 thin film by pulsed laser deposition," *J. Mater. Sci. Mater. Electron.*, 2018.
- [107] A. Chopra, E. Panda, Y. Kim, M. Arredondo, and D. Hesse, "Epitaxial ferroelectric $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 thin films on $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ bottom electrode," *J. Electroceramics*, vol. 32, no. 4, pp. 404–408, 2014.
- [108] A. B. Brailovsky, S. V. Gaponov, and V. I. Luchin, "Mechanisms of melt droplets and solid-particle ejection from a target surface by pulsed laser action," *Appl. Phys. A Mater. Sci. Process.*, vol. 61, no. 1, pp. 81–86, Jul. 1995.
- [109] D. Mukherjee, R. Hyde, M. Hordagoda, N. Bingham, H. Srikanth, S. Witanachchi, and P. Mukherjee, "Challenges in the stoichiometric growth of polycrystalline and epitaxial $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3/\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ multiferroic heterostructures using pulsed laser deposition," *J. Appl. Phys.*, vol. 112, no. 6, p. 064101, 2012.
- [110] D. Mukherjee, R. Hyde, P. Mukherjee, H. Srikanth, and S. Witanachchi, "Role of dual-laser ablation in controlling the Pb depletion in epitaxial growth of $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ thin films with enhanced surface quality and ferroelectric properties," *J. Appl. Phys.*, vol. 111, no. 6, p. 064102, 2012.
- [111] M. Boota, E. P. Houwman, M. D. Nguyen, G. Lanzara, and G. Rijnders, "Effect of fabrication conditions on phase formation and properties of epitaxial $(\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3)_{0.67}$ - $(\text{PbTiO}_3)_{0.33}$ thin films on (001) SrTiO_3 ," *AIP Adv.*, vol. 6, no. 5, p. 055303, 2016.
- [112] M. Boota, E. P. Houwman, M. Dekkers, M. Nguyen, and G. Rijnders, "Epitaxial $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (67/33) thin films with large tunable self-bias field controlled by a $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ interfacial layer," *Appl. Phys. Lett.*, vol. 104, no. 18, p. 182909, 2014.
- [113] J. Jiang, H. J. Jung, and S. G. Yoon, "Epitaxial PMN-PT thin films grown on buffered Si substrates using ceramic and single-crystal targets," *J. Alloys Compd.*, vol. 509, no. 24, pp. 6924–6929, 2011.
- [114] C. Tantigate, J. Lee, and A. Safari, "Processing and properties of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 thin films by pulsed laser deposition," *Appl. Phys. Lett.*, vol. 66, no. 13, pp. 1611–1613, 1995.
- [115] F. Niu and B. W. Wessels, "Surface and interfacial structure of epitaxial SrTiO_3 thin films on (001) Si grown by molecular beam epitaxy," *J. Cryst. Growth*, vol. 300, no. 2, pp. 509–518, Mar. 2007.
- [116] W. K. A. Kumuduni, Y. Nakayama, Y. Nakata, T. Okada, and M. Maeda, "Transport of YO molecules produced by ArF laser ablation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in ambient oxygen gas," *J. Appl. Phys.*, vol. 74, p. 33107, 1993.
- [117] S. Amoroso, B. Toftmann, and J. Schou, "Thermalization of a UV laser ablation plume in a background gas: From a directed to a diffusionlike flow," *Phys. Rev. E - Stat. Physics, Plasmas, Fluids, Relat. Interdiscip. Top.*, vol. 69, no. 5, p. 6, 2004.
- [118] D. B. Geohegan, "Physics and diagnostics of laser ablation plume propagation for high-Tc superconductor film growth," *Thin Solid Films*, vol. 220, no. 1–2, pp. 138–145, Nov. 1992.
- [119] M. Strikovski and J. H. M. Jr., "Pulsed laser deposition of oxides: Why the optimum rate is about 1 Å per pulse," *Appl. Phys. Lett.*, vol. 73, no. 12, p. 1733, Sep. 1998.
- [120] S. S. Kumar, R. Reshmi, N. V. Joshy, A. C. Saritha, and M. K. Jayaraj, "Optical Emission Spectroscopic Analysis of Plasma Plume during Pulsed Laser Deposition of PZT," *J. At. Mol. Phys.*, vol. 2014, p. 125843, 2014.
- [121] R. Groenen, J. Smit, K. Orsel, A. Vailionis, B. Bastiaens, M. Huijben, K. Boller, G. Rijnders, and G. Koster, "Research Update: Stoichiometry controlled oxide thin film growth by pulsed laser deposition," *APL Mater.*, vol. 3, no. 7, p. 070701, Jul. 2015.
- [122] P. Yang, H. Liu, Z. Chen, L. Chen, and J. Wang, "Unit cell determination of epitaxial thin films based on reciprocal space vectors by high-resolution X-ray diffractometry," *J. Appl. Crystallogr.*, vol. 1311, p. 3382, 2013.

- [123] M. Mietschke, S. Oswald, S. Fähler, L. Schultz, and R. Hühne, "Tuning structure in epitaxial $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 thin films by using miscut substrates," *Thin Solid Films*, vol. 589, pp. 792–797, 2015.
- [124] M. Mietschke, S. Fähler, L. Schultz, and R. Hühne, "Influence of the deposition geometry on structural and ferroelectric properties of epitaxial PMN-PT films," *2014 Jt. IEEE Int. Symp. Appl. Ferroelectr. Int. Work. Acoust. Transduct. Mater. Devices Work. Piezoresponse Force Microsc. ISAF/IWATMD/PFM 2014*, pp. 1–3, 2014.
- [125] W.-I. Liang, C.-Y. Peng, R. Huang, W.-C. Kuo, Y.-C. Huang, C. Adamo, Y.-C. Chen, L. Chang, J.-Y. Juang, D. G. Schlom, and Y.-H. Chu, "Epitaxial integration of a nanoscale BiFeO_3 phase boundary with silicon," *Nanoscale*, vol. 8, no. 3, pp. 1322–1326, 2016.
- [126] A. Huang, A. D. Handoko, G. K. L. Goh, S. R. Shannigrahi, and C. K. Tan, "Hydrothermal synthesis of BiFeO_3 films on SrTiO_3 substrates," *Prog. Cryst. Growth Charact. Mater.*, vol. 57, no. 4, pp. 109–116, 2011.
- [127] H. Béa, M. Bibes, S. Petit, J. Kreisel, and A. Barthémey, "Structural distortion and magnetism of BiFeO_3 epitaxial thin films: A Raman spectroscopy and neutron diffraction study," *Philos. Mag. Lett.*, vol. 87, no. 3–4, pp. 165–174, Mar. 2007.
- [128] D. Kan and I. Takeuchi, "Effect of substrate orientation on lattice relaxation of epitaxial BiFeO_3 thin films," *J. Appl. Phys.*, vol. 108, no. 1, p. 014104, Jul. 2010.
- [129] A. R. Damodaran, S. Pandya, Y. Qi, S. L. Hsu, S. Liu, C. Nelson, A. Dasgupta, P. Ercius, C. Ophus, L. R. Dedon, J. C. Agar, H. Lu, J. Zhang, M. Andrew, A. M. Rappe, and L. W. Martin, "Large polarization gradients and temperature-stable responses in compositionally-graded ferroelectrics," *Nat. Commun.*, vol. 8, p. 14961, 2017.
- [130] S. Yokoyama, S. Okamoto, H. Funakubo, T. Iijima, K. Saito, H. Okino, T. Yamamoto, K. Nishida, T. Katoda, and J. Sakai, "Crystal structure, electrical properties, and mechanical response of (100)-/(001)-oriented epitaxial $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 films grown on (100)_c SrRuO_3 || (100) SrTiO_3 substrates" *J. Appl. Phys.*, vol. 100, no. 5, p. 054110, 2006.
- [131] D. Sando, T. Young, R. Bulanadi, X. Cheng, Y. Zhou, M. Weyland, P. Munroe, and V. Nagarajan, "Designer defect stabilization of the super tetragonal phase in >70-nm-thick BiFeO_3 films on LaAlO_3 substrates," *Jpn. J. Appl. Phys.*, vol. 57, p. 0902B2, 2018.
- [132] K. Saito, T. Kurosawa, T. Akai, T. Oikawa, and H. Funakubo, "Structural characterization and 90° domain contribution to ferroelectricity of epitaxial $\text{Pb}(\text{Zr}_{0.35}\text{Ti}_{0.65})\text{O}_3$ thin films," *J. Appl. Phys.*, vol. 93, no. 1, pp. 545–550, 2003.
- [133] Z. Chen, Z. Luo, C. Huang, Y. Qi, P. Yang, L. You, C. Hu, T. Wu, J. Wang, C. Gao, T. Sritharan, and L. Chen, "Low-symmetry monoclinic phases and polarization rotation path mediated by epitaxial strain in multiferroic BiFeO_3 thin films," *Adv. Funct. Mater.*, vol. 21, no. 1, pp. 133–138, 2011.
- [134] T. Suzuki, Y. Nishi, and M. Fujimoto, "Ruddlesden-Popper planar faults and nanotwins in heteroepitaxial nonstoichiometric barium titanate thin films," *J. Am. Ceram. Soc.*, vol. 95, pp. 3185–3195, 2000.
- [135] M. Fujimoto, "Defects in epitaxially grown perovskite thin films," in *Journal of Crystal Growth*, 2002, vol. 237–239, no. 1–4 I, pp. 430–437.
- [136] T. Suzuki, Y. Nishi, and M. Fujimoto, "Defect structure in homoepitaxial non-stoichiometric strontium titanate thin films," *Philos. Mag. A Phys. Condens. Matter, Struct. Defects Mech. Prop.*, vol. 80, no. 3, pp. 621–637, 2000.
- [137] M. A. McCoy, R. W. Grimes, and W. E. Lee, "Phase stability and interfacial structures in the SrO - SrTiO_3 system," *Philos. Mag. A*, vol. 75, no. 3, pp. 833–846, Mar. 1997.
- [138] M. Fujimoto, T. Suzuki, Y. Nishi, K. Arai, and J. Tanaka, "Calcium-Ion Selective Site Occupation at Ruddlesden-Popper-Type Faults and the Resultant Dielectric Properties of A-Site-Excess Strontium Calcium Titanate Ceramics," *J. Am. Ceram. Soc.*, vol. 81, no. 1, pp. 33–40, Jan. 2005.
- [139] K. L. Saenger, "On the origin of spatial nonuniformities in the composition of pulsed-laser-deposited films," *J. Appl. Phys.*, vol. 70, no. 10, pp. 5629–5635, 1991.

- [140] M. C. Foote, B. B. Jones, B. D. Hunt, J. B. Barner, R. P. Vasquez, and L. J. Bajuk, "Composition variations in pulsed-laser-deposited Y-Ba-Cu-O thin films as a function of deposition parameters," *Phys. C Supercond.*, vol. 201, no. 1–2, pp. 176–182, Oct. 1992.
- [141] P. Chekhonin, M. Mietschke, D. Pohl, F. Schmidt, S. Fähler, W. Skrotzki, K. Nielsch, and R. Hühne, "Effect of substrate miscut on the microstructure in epitaxial $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 thin films," *Mater. Charact.*, vol. 129, pp. 234–241, 2017.
- [142] M. A. Zurbuchen, W. Tian, X. Q. Pan, D. Fong, S. K. Streiffer, M. E. Hawley, J. Lettieri, Y. Jia, G. Asayama, S. J. Fulk, D. J. Comstock, S. Knapp, A. H. Carim, and D. G. Schlom, "Morphology, structure, and nucleation of out-of-phase boundaries (OPBs) in epitaxial films of layered oxides," *J. Mater. Res.*, vol. 22, no. 06, pp. 1439–1471, 2007.
- [143] E. E. Fullerton, I. K. Schuller, H. Vanderstraeten, and Y. Bruynseraede, "Structural refinement of superlattices from x-ray diffraction," *Phys. Rev. B*, vol. 45, no. 16, p. 9292, 1992.
- [144] A. Malachias, T. U. Schülly, G. Medeiros-Ribeiro, L. G. Cançado, M. Stoffel, O. G. Schmidt, T. H. Metzger, and R. Magalhães-Paniago, "X-ray study of atomic ordering in self-assembled Ge islands grown on $\text{Si}(001)$," *Phys. Rev. B*, vol. 72, p. 165315, 2005.
- [145] H. Cao, V. H. Schmidt, R. Zhang, W. Cao, and H. Luo, "Elastic, piezoelectric, and dielectric properties of $0.58\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.42PbTiO_3 single crystal," *J. Appl. Phys.*, vol. 96, no. 1, pp. 549–554, 2004.
- [146] E. Sun, S. Zhang, J. Luo, T. R. Shrout, and W. Cao, "Elastic, dielectric, and piezoelectric constants of $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ - $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 single crystal poled along $[011]_c$," *Appl. Phys. Lett.*, vol. 97, no. 3, p. 032902, 2010.
- [147] D. Dimos, W. L. Warren, M. B. Sinclair, B. A. Tuttle, and R. W. Schwartz, "Photoinduced hysteresis changes and optical storage in $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$ thin films and ceramics," *J. Appl. Phys.*, vol. 76, no. 7, pp. 4305–4315, Oct. 1994.
- [148] G. E. Pike, W. L. Warren, D. Dimos, B. A. Tuttle, R. Ramesh, J. Lee, V. G. Keramidas, and J. T. Evans, "Voltage offsets in $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$ thin films," *Appl. Phys. Lett.*, vol. 66, no. 4, pp. 484–486, Jan. 1995.
- [149] J. Lee, R. Ramesh, V. G. Keramidas, W. L. Warren, G. E. Pike, and J. T. Evans, "Imprint and oxygen deficiency in $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$ thin-film capacitors with La-Sr-Co-O electrodes," *Appl. Phys. Lett.*, vol. 66, no. 11, pp. 1337–1339, Mar. 1995.
- [150] B. H. Park, T. W. Noh, J. Lee, C. Y. Kim, and W. Jo, "Effects of interface charges on imprint of epitaxial $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films," *Appl. Phys. Lett.*, vol. 70, no. 9, pp. 1101–1103, Jun. 1997.
- [151] K. Abe, N. Yanase, T. Yasumoto, and T. Kawakubo, "Voltage shift phenomena in a heteroepitaxial BaTiO_3 thin film capacitor," *J. Appl. Phys.*, vol. 91, no. 1, pp. 323–330, Dec. 2002.
- [152] W. L. Warren, G. E. Pike, B. A. Tuttle, and D. Dimos, "Polarization-induced trapped charge in ferroelectrics," *Appl. Phys. Lett.*, vol. 70, no. 15, p. 2010, Jun. 1998.
- [153] W. Liu, J. Ko, and W. Zhu, "Asymmetric switching behavior of $\text{Ni}/\text{Pb}_{1.1}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3/\text{Pt}$ thin films," *Mater. Lett.*, vol. 49, no. 2, pp. 122–126, Jun. 2001.
- [154] S. Y. Hu, Y. L. Li, and L. Q. Chen, "Effect of interfacial dislocations on ferroelectric phase stability and domain morphology in a thin film—a phase-field model," *J. Appl. Phys.*, vol. 94, pp. 2542–2547, 2003.
- [155] W. Wu, Y. Wang, G. K. H. Pang, K. H. Wong, and C. L. Choy, "Effect of lattice-misfit strain on the process-induced imprint behavior in epitaxial $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ thin films," *Appl. Phys. Lett.*, vol. 85, no. 9, pp. 1583–1585, 2004.
- [156] C. K. Wong and F. G. Shin, "Modeling of anomalous shift and asymmetric hysteresis behavior of ferroelectric thin films," *J. Appl. Phys.*, vol. 96, no. 11, pp. 6648–6656, 2004.
- [157] K.-W. Lee, Y.-I. Kim, and W.-J. Lee, "Physical Modeling of the Effect of the Asymmetric Electrode Configuration on the Hysteresis Curves of Ferroelectric Film Capacitors,"

- Ferroelectrics*, vol. 271, no. 1, pp. 179–185, Jan. 2002.
- [158] A. Matavž, J. Kovač, M. Čekada, B. Malič, and V. Bobnar, “Enhanced electrical response in ferroelectric thin film capacitors with inkjet-printed LaNiO_3 electrodes,” *Appl. Phys. Lett.*, vol. 113, p. 12904, 2018.
 - [159] I. Lubomirsky, D. T. Chang, and O. M. Stafsudd, “Observation of self poling in BaTiO_3 thin films,” *J. Appl. Phys.*, vol. 85, no. 9, pp. 6690–6694, Apr. 1999.
 - [160] C. Beekman, W. Siemons, M. Chi, N. Balke, J. Y. Howe, T. Z. Ward, P. Maksymovych, J. D. Budai, J. Z. Tischler, R. Xu, W. Liu, and H. M. Christen, “Ferroelectric Self-Poling, Switching, and Monoclinic Domain Configuration in BiFeO_3 Thin Films,” *Adv. Funct. Mater.*, vol. 26, no. 28, pp. 5166–5173, Jul. 2016.
 - [161] E. Khomyakova, M. Sadl, H. Ursic, J. Daniels, B. Malic, A. Bencan, D. Damjanovic, and T. Rojac, “Self-Poling of BiFeO_3 Thick Films,” *ACS Appl. Mater. Interfaces*, vol. 8, no. 30, pp. 19626–19634, Aug. 2016.
 - [162] V. V. Osipov, E. Y. Kaptelov, S. V. Senkevich, D. A. Kiselev, and I. P. Pronin, “The study of self-poled PZT thin films under variation of lead excess,” *Ferroelectrics*, vol. 525, no. 1, pp. 76–82, Mar. 2018.
 - [163] M. Mtebwa, L. Feigl, and N. Setter, “PLD growth and PFM study of self-poled, monocrystalline PZT thin films,” in *2013 Joint IEEE International Symposium on Applications of Ferroelectric and Workshop on Piezoresponse Force Microscopy (ISAF/PFM)*, 2013, pp. 73–75.
 - [164] S. Sun, L. Liu, P. A. Fuierer, and B. A. Tuttle, “Depolarization and hysteresis loop asymmetry in PZT thin films with self polarization,” *Ferroelectrics*, vol. 152, no. 1, pp. 187–193, Feb. 1994.
 - [165] J. Chen, Y. Luo, X. Ou, G. Yuan, Y. Wang, Y. Yang, J. Yin, and Z. Liu, “Upward ferroelectric self-polarization induced by compressive epitaxial strain in (001) BaTiO_3 films,” *J. Appl. Phys.*, vol. 113, no. 20, p. 204105, May 2013.
 - [166] R. G. Polcawich and S. Trolier-McKinstry, “Piezoelectric and dielectric reliability of lead zirconate titanate thin films,” *J. Mater. Res.*, vol. 15, no. 11, pp. 2505–2513, Nov. 2000.
 - [167] F. Johann, A. Morelli, D. Biggemann, M. Arredondo, and I. Vrejoiu, “Epitaxial strain and electric boundary condition effects on the structural and ferroelectric properties of BiFeO_3 films,” *Phys. Rev. B*, vol. 84, no. 8, p. 084105, 2011.
 - [168] Y. H. Chu, Q. He, C. H. Yang, P. Yu, L. W. Martin, P. Shafer, and R. Ramesh, “Nanoscale control of domain architectures in BiFeO_3 thin films,” *Nano Lett.*, vol. 9, no. 4, pp. 1726–1730, Apr. 2009.
 - [169] V. Shelke, D. Mazumdar, G. Srinivasan, and A. Gupta, “The role of SrRuO_3 bottom layer in strain relaxation of BiFeO_3 thin films deposited on lattice mismatched substrates,” *J. Appl. Phys.*, vol. 109, no. 7, p. 07D914, Apr. 2011.
 - [170] J. Peräntie, M. S. Stratulat, J. Hannu, H. Jantunen, and M. Tyunina, “Enhancing polarization by electrode-controlled strain relaxation in PbTiO_3 heterostructures,” *APL Mater.*, vol. 4, p. 016104, 2016.
 - [171] S. P. Alpay, V. Nagarajan, L. A. Bendersky, M. D. Vaudin, S. Aggarwal, R. Ramesh, and A. L. Roytburd, “Effect of the electrode layer on the polydomain structure of epitaxial $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ thin films,” *J. Appl. Phys.*, vol. 85, no. 6, p. 3271, 1999.
 - [172] N. Chaban, M. Weber, S. Pignard, and J. Kreisel, “Phonon Raman scattering of perovskite thin films,” *Appl. Phys. Lett.*, vol. 97, p. 31915, 2010.
 - [173] C. Guerrero, F. Sánchez, C. Ferrater, J. Roldán, M. V. García-Cuenca, and M. Varela, “Pulsed laser deposition of epitaxial $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ ferroelectric capacitors with LaNiO_3 and SrRuO_3 electrodes,” *Appl. Surf. Sci.*, vol. 168, no. 1–4, pp. 219–222, 2000.
 - [174] J. Hwang, J. Son, J. Y. Zhang, A. Janotti, C. G. Van De Walle, and S. Stemmer, “Structural origins of the properties of rare earth nickelate superlattices,” *Phys. Rev. B*, vol. 87, no. 6, p. 060101, 2013.
 - [175] P. M. McBride, A. Janotti, C. E. Dreyer, B. Himmetoglu, and C. G. Van De Walle, “Effects

- of biaxial stress and layer thickness on octahedral tilts in LaNiO_3 ," *Appl. Phys. Lett.*, vol. 107, p. 261901, 2015.
- [176] S. Rakshit and P. S. Gopalakrishnan, "Oxygen nonstoichiometry and its effect on the structure of LaNiO_3 ," *Journal of Solid State Chemistry*, vol. 110, no. 1, pp. 28–31, 1994.
 - [177] J. M. Rondinelli and N. A. Spaldin, "Structure and properties of functional oxide thin films: Insights from electronic-structure calculations," *Adv. Mater.*, vol. 23, no. 30, pp. 3363–3381, 2011.
 - [178] C. L. Jia, J. R. Contreras, U. Poppe, H. Kohlstedt, R. Waser, and K. Urban, "Lattice strain and lattice expansion of the SrRuO_3 layers in $\text{SrRuO}_3/\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3/\text{SrRuO}_3$ multilayer thin films," *J. Appl. Phys.*, vol. 92, no. 1, pp. 101–105, 2002.
 - [179] D. Lavric, R. A. Rao, Q. Gan, J. J. Krajewski, and C. B. Eom, "Epitaxial thin film heterostructures of relaxor ferroelectric $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$," *Integr. Ferroelectr.*, vol. 21, no. 1–4, pp. 499–509, Sep. 1998.
 - [180] J. Wang, K. H. Wong, H. L. W. Chan, and C. L. Choy, "Composition control and electrical properties of PMN-PT thin films around the morphotropic boundary," *Appl. Phys. A Mater. Sci. Process.*, vol. 79, no. 3, pp. 551–556, 2004.
 - [181] K. Saito, R. Europe, T. Kurosawa, T. Akai, S. Yokoyama, H. Morioka, T. Oikawa, and H. Funakubo, "Characterization of Epitaxial $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ Thin Films with Composition Near the Morphotropic Phase Boundary," *Mat. Res. Soc. Symp. Proc.*, vol. 748, p. U13.4.1, 2011.
 - [182] H. Morioka, S. Yokoyama, T. Oikawa, K. Saito, and H. Funakubo, "Growth of epitaxial tetragonal $\text{Pb}(\text{Zr,Ti})\text{O}_3$ thin films with 100% polar-axis-orientation and their electrical properties," *MRS Proc.*, vol. 784, no. 100, p. C6.2, 2011.
 - [183] C. E. Seo and D. Y. Yoon, "The effect of MgO addition on grain growth in PMN-35PT," *J. Am. Ceram. Soc.*, vol. 88, no. 4, pp. 963–967, 2005.
 - [184] J. P. Guha, "Effect of compositional modifications on microstructure development and dielectric properties of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ solid solutions," *J. Eur. Ceram. Soc.*, vol. 23, no. 1, pp. 133–139, 2003.
 - [185] J. C. Frederick, T. H. Kim, W. Maeng, A. A. Brewer, J. P. Podkaminer, W. Saenrang, V. Vaithyanathan, F. Li, L. Q. Chen, D. G. Schlom, S. Trolier-Mckinstry, M. S. Rzchowski, and C. B. Eom, "Visualization of dielectric constant-electric field-temperature phase maps for imprinted relaxor ferroelectric thin films," *Appl. Phys. Lett.*, vol. 108, no. 13, 2016.
 - [186] O. Noblanc, P. Gaucher, and G. Calvarin, "Structural and dielectric studies of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ ferroelectric solid solutions around the morphotropic boundary," *J. Appl. Phys.*, vol. 79, no. 8, p. 4291, 1996.
 - [187] F. Li, S. Zhang, Z. Xu, X. Wei, J. Luo, and T. R. Shrout, "Composition and phase dependence of the intrinsic and extrinsic piezoelectric activity of domain engineered $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-xPbTiO}_3$ crystals," *J. Appl. Phys.*, vol. 108, no. 3, 2010.
 - [188] N. Sama, R. Herdier, D. Jenkins, C. Soyer, D. Remiens, M. Detalle, and R. Bouregba, "On the influence of the top and bottom electrodes-A comparative study between Pt and LNO electrodes for PZT thin films," *J. Cryst. Growth*, vol. 310, no. 14, pp. 3299–3302, 2008.
 - [189] R. Zhang, B. Jiang, and W. Cao, "Elastic, piezoelectric, and dielectric properties of multidomain $0.67\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.33\text{PbTiO}_3$ single crystals," *J. Appl. Phys.*, vol. 90, no. 7, pp. 3471–3475, 2001.
 - [190] V. Nagarajan, A. Stanishevsky, L. Chen, T. Zhao, B.-T. Liu, J. Melngailis, A. L. Roytburd, R. Ramesh, J. Finder, Z. Yu, R. Droopad, and K. Eisenbeiser, "Realizing intrinsic piezoresponse in epitaxial submicron lead zirconate titanate capacitors on Si," *Appl. Phys. Lett.*, vol. 81, no. 22, pp. 4215–4217, Nov. 2002.
 - [191] M. Wallace, R. L. Johnson-Wilke, G. Esteves, C. M. Fancher, R. H. T. Wilke, J. L. Jones, and S. Trolier-McKinstry, "In situ measurement of increased ferroelectric/ferroelastic domain wall motion in declamped tetragonal lead

- zirconate titanate thin films," *J. Appl. Phys.*, vol. 117, no. 5, p. 054103, Feb. 2015.
- [192] R. Keech, L. Ye, J. L. Bosse, G. Esteves, J. Guerrier, J. L. Jones, M. A. Kuroda, B. D. Huey, and S. Trolier-McKinstry, "Declamped Piezoelectric Coefficients in Patterned 70/30 Lead Magnesium Niobate-Lead Titanate Thin Films," *Adv. Funct. Mater.*, vol. 27, no. 9, 2017.
- [193] J. M. Huijbregtse, J. H. Rector, and B. Dam, "Effect of the two (100) SrTiO_3 substrate terminations on the nucleation and growth of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ thin films," *Phys. C Supercond. its Appl.*, vol. 351, no. 3, pp. 183–199, 2001.
- [194] D. Pesquera, G. Herranz, A. Barla, E. Pellegrin, F. Bondino, E. Magnano, F. Sánchez, and J. Fontcuberta, "Surface symmetry-breaking and strain effects on orbital occupancy in transition metal perovskite epitaxial films," *Nat. Commun.*, vol. 3, no. 1, p. 1189, Jan. 2012.
- [195] A. Solmaz, M. Huijben, B. Noheda, and G. Rijnders, "Influence of substrate–film interface engineering on the multiferroic BiFeO_3 ," in *Advanced Characterization Method*, 2013, p. ISAF-P1A-3.
- [196] G. Rijnders, D. H. A. Blank, J. Choi, and C. B. Eom, "Enhanced surface diffusion through termination conversion during epitaxial SrRuO_3 growth," *Appl. Phys. Lett.*, vol. 84, no. 4, pp. 505–507, 2004.
- [197] R. Keech, C. Morandi, M. Wallace, G. Esteves, L. Denis, J. Guerrier, R. L. Johnson-Wilke, C. M. Fancher, J. L. Jones, and S. Trolier-McKinstry, "Thickness-dependent domain wall reorientation in 70/30 lead magnesium niobate- lead titanate thin films," *J. Am. Ceram. Soc.*, vol. 100, no. 9, pp. 3961–3972, 2017.
- [198] S. S. Kim, T. S. Kang, and J. H. Je, "Structural evolution of epitaxial SrRuO_3 thin films grown on SrTiO_3 (001)," *J. Appl. Phys.*, vol. 90, no. 9, pp. 4407–4410, 2001.
- [199] J. Choi, C. B. Eom, G. Rijnders, H. Rogalla, and D. H. A. Blank, "Growth mode transition from layer by layer to step flow during the growth of heteroepitaxial SrRuO_3 on (001) SrTiO_3 ," *Appl. Phys. Lett.*, vol. 79, no. 10, pp. 1447–1449, 2001.
- [200] M. B. Kelman, P. C. McIntyre, A. Gruverman, B. C. Hendrix, S. M. Bilodeau, and J. F. Roeder, "Origin and implications of the observed rhombohedral phase in nominally tetragonal $\text{Pb}(\text{Zr}_{0.35}\text{Ti}_{0.65})\text{O}_3$ thin films," *J. Appl. Phys.*, vol. 94, no. 8, pp. 5210–5219, 2003.
- [201] I. Rafalovskyi, "Lead-based relaxor ferroelectrics by Raman scattering," Czech Academy of Sciences, 2017.
- [202] I. Rafalovskyi, I. Gregora, and J. Hlinka, "Electric-field-induced tetragonal phase in $[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]_{0.68}-[\text{PbTiO}_3]_{0.32}$ by Raman scattering," *Phase Transitions*, vol. 89, no. 7–8, pp. 816–822, 2016.
- [203] W. L. Warren, D. Dimos, B. A. Tuttle, R. D. Nasby, and G. E. Pike, "Electronic domain pinning in $\text{Pb}(\text{Zr,Ti})\text{O}_3$ thin films and its role in fatigue," *Appl. Phys. Lett.*, vol. 65, no. 8, pp. 1018–1020, 1994.
- [204] W. L. Warren, D. Dimos, B. A. Tuttle, and D. M. Smyth, "Electronic and Ionic Trapping at Domain Walls in BaTiO_3 ," *J. Am. Ceram. Soc.*, vol. 77, no. 10, pp. 2753–2757, Oct. 1994.
- [205] K. Carl and K. H. Hardtl, "Electrical After-Effects In $\text{Pb}(\text{Ti,Zr})\text{O}_3$ Ceramics," *Ferroelectrics*, vol. 17, no. 1, pp. 473–486, Jan. 1977.
- [206] A. Matavz, J. Kovač, M. Cekada, B. Malič, and V. Bobnar, "Enhanced electrical response in ferroelectric thin film capacitors with inkjet-printed LaNiO_3 electrodes," *Appl. Phys. Lett.*, vol. 113, p. 12904, 2018.

Bibliography

Publications Related to the Thesis

Journal Articles

- Z. Jovanović, M. Spreitzer, U. Gabor, D. Suvorov, "Control of SrO buffer-layer formation on Si(001) using the pulsed-laser deposition technique", *RSC Advances*, vol. 6, no.85, pp. 82150-82156, 2016.
- U. Gabor, M. Spreitzer, H. Uršič, E. Tchernychova, Z. Samardžija, W. J. Wu, D. Suvorov, "Structural peculiarities of $0.67\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.33PbTiO_3 thin films grown directly on SrTiO_3 substrates", *Journal of the European Ceramic Society*, vol. 38, pp. 4453-4462, 2018.

Published scientific conference contribution abstract (invited talk)

- M. Spreitzer, D. Díaz-Fernandez, T. Parkelj, U. Gabor, D. Suvorov, "Tailoring epitaxial oxide thin film on Si(001) using pulsed-laser deposition", *Nineteenth Annual Conference YUCOMAT 2017*, Herceg Novi, Montenegro, August 31 - September 4-8, 2017. Belgrade: Materials Research Society of Serbia. 2017, p. 41. (plenary talk)
- M. Spreitzer, U. Gabor, H. Uršič, E. Tchernychova, Z. Samardžija, W. J. Wu, D. Suvorov. Structural characteristics of pulsed-laser deposited $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 epitaxial thin films for energy-harvesting devices. *2018 ISAF-AMF-AMEC-PFM*, Danvers: IEEE, 2018.

Published scientific conference contribution abstract

- U. Gabor, M. Spreitzer, D. Suvorov, "Pulsed-laser deposition of heterostructured oxide thin films for piezoelectric MEMS applications", *23rd International Conference on Materials and Technology*, September 28-30 2015, Portorož, Slovenia. Ljubljana: Inštitut za kovinske materiale in tehnologije. 2015, p. 50.
- U. Gabor, M. Spreitzer, D. Suvorov, "Avoiding lead loss in PLD growth of PMN-PT thin films", *COST TO-BE Fall Meeting*, Ljubljana, Slovenia, September 28-30 2016. Ljubljana: Jožef Stefan Institute. 2016, p. 55.
- U. Gabor, M. Spreitzer, D. Suvorov, "Different approaches to avoiding lead deficiency in PMN-PT thin films", *24th International Conference on Materials and Technology*, September 28-30 2016, Portorož, Slovenia. Ljubljana: Inštitut za kovinske materiale in tehnologije, 2016, p. 76.
- U. Gabor, M. Spreitzer, D. Suvorov, "Influence of Pb-enriched targets on PLD growth of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 thin films", *2016 joint IEEE ISAF-ECAPD-PMF 2016, International Symposium on Applications of Ferroelectrics (ISAF), European Conference on the Applications of Polar Dielectrics (ECAPD), Workshop on*

Piezoresponse Force Microscopy (PMF), August 21-25, 2016, Darmstadt, Germany. Darmstadt: Technische Universität. 2016.

- U. Gabor, M. Spreitzer, D. Suvorov, "Structural and electrical properties of PMN-PT thin films prepared with pulsed-laser deposition", *10th Young researchers' day*, March 31 2016, Ljubljana, Jožef Stefan Institute, 2016, p. 21.
- U. Gabor, M. Spreitzer, D. Suvorov, "Pulsed-laser deposition of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ thin films on SrTiO_3 ", *25th International Conference on Materials and Technology*, October 16-19 2017, Portorož, Slovenia. Ljubljana: Inštitut za kovinske materiale in tehnologije. 2017, p. 60.
- U. Gabor, M. Spreitzer, D. Suvorov, "Formation mechanism of PLD-derived $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ thin films", *15th Conference of the European Ceramic Society, ECerS 2017*, July 9-13, Budapest, Hungary. Budapest: Akadémiai Kiadó. 2017, p. 718-719.

Biography

Urška Gabor obtained her bachelor's degree from the Faculty of Chemistry and Chemical Engineering, University of Maribor (FKKT-UM), in 2012. In 2014, she finished her master studies at FKKT-UM, and enrolled in the Nanosciences and Nanotechnologies third-level study program at the Jožef Stefan International Postgraduate School in Ljubljana, and started working as a Young Researcher at the Advanced Materials Department (K9) at the Jožef Stefan Institute in Ljubljana. She received the Dean's Award for the best B. Sc. and M. Sc. thesis at FKKT-UM. In 2016, she was awarded for the best oral presentation at the 24th International Conference on Materials and Technologies in Portorož. She was the winner of the Student Speech Contest at the 15th International Conference and Exhibition of the European Ceramic Society in 2017.