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Ollscoil na hÉireann, Corcaigh
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**Synthesis and optimisation of Aurivillius phase
thin films for next generation data storage**

Thesis presented by

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for the degree of

Doctor of Philosophy

University College Cork

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Declaration

This is to certify that the work I am submitting is my own and has not been submitted for another degree, either at University College Cork or elsewhere. All external references and sources are clearly acknowledged and identified within the contents. I have read and understood the regulations of University College Cork concerning plagiarism and intellectual property.



Debismita Dutta

11th December, 2025

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List of Publications:

Under Review in *Advanced Science*: “Enhancing Vertical Ferroelectric Polarization Using Growth Spirals”

Debismita Dutta, Tigran Simonian, Joydipto Bhattacharya, Michael Schmidt, Sabir Hussain, Valeria Nicolosi, Lynette Keeney

Under preparation:

1. “Suppressing Crystal Twinning in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ Using Low Supersaturation”

Debismita Dutta, Tigran Simonian, Joydipto Bhattacharya, Michael Schmidt, Sabir Hussain, Valeria Nicolosi, Lynette Keeney

2. “X-Ray Diffraction Modelling of Growth Spirals”

Debismita Dutta, Roger Whatmore, Tigran Simonian, Michael Schmidt, Valeria Nicolosi, Lynette Keeney

Journal Publications:

1. “A model for out-of-phase boundary induced X-ray diffraction peak profile changes in Aurivillius oxide thin films” in *Journal of Applied Crystallography*
Roger Whatmore, Debismita Dutta, Lynette Keeney

2. “What lies beneath? Investigations of atomic force microscopy-based nanomachining to reveal sub-surface ferroelectric domain configurations in ultrathin films” in *Microstructures*
Keeney, L.; Colfer, L.; Dutta, D.; Schmidt, M.; Wei, G.

Abstract

Aurivillius phase oxides are well-established room-temperature ferroelectrics, whose high Curie temperatures and intrinsic fatigue resistance make them attractive candidates for emerging energy-efficient non-volatile memory and neuromorphic device concepts. However their integration in vertically oriented device architectures is limited by three interconnected challenges: (i) their spontaneous polarisation is predominantly in-plane, which is misaligned with the out-of-plane electric fields used in standard capacitor geometries; (ii) there is no predictive framework linking complex three-dimensional defect motifs to measurable X-ray diffraction (XRD) signatures; and (iii) crystal twinning frequently emerges during thin-film growth, reducing domain coherence and hindering reliable switching.

This thesis addresses these challenges through controlled thin-film synthesis, advanced structural characterisation, and analytical model development. Supersaturation, tuned through the precursor delivery kinetics and oxygen partial pressure of Direct Liquid Injection Chemical Vapour Deposition (DLI-CVD), serves as the unifying experimental variable across the three chapters, governing whether $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films grow via two-dimensional nucleation, dislocation-mediated spiral formation, or diffusion-limited single-variant epitaxy. This work identifies for the first time that films exhibiting spiral morphologies displayed a measurably enhanced vertical polarisation, with the required switching voltage reduced from ± 20 V to ± 5 V. Correlative piezoresponse force microscopy, density functional theory, and electron microscopy reveal a previously unrecognised mechanism by which inclined out-of-phase boundary defects generated by spiral growth alter local symmetry and strain environments, thereby stabilising an out-of-plane polarisation in a material class

normally constrained to in-plane orientation. To interpret the diffraction signatures of these non-planar defects, a new three-dimensional XRD model was developed. This framework extends the structure-factor formalism to incorporate both vertical registry offsets and angular boundary inclinations, enabling accurate simulation of the asymmetric peak splitting observed experimentally. The model provides a non-destructive estimation of defect density and orientation, establishing a predictive link between defect topology and reciprocal-space features.

Finally, the thesis demonstrates a previously unreported route to suppressing crystal twinning. By regulating supersaturation during metal–organic chemical vapour deposition, the twinning typically observed in Aurivillius films on epitaxially matched substrates can be effectively eliminated. Lower supersaturation enhances adatom mobility and promotes single-variant epitaxy, yielding films with improved structural coherence and spatially uniform ferroelectric switching. This approach provides an accessible, growth-parameter-based route to producing twin-free layered ferroelectrics without substrate modification or post-processing. Collectively, these findings provide new insight into the layered crystallography of Aurivillius phases and the growth mechanisms that modify their ferroelectric response. The thesis delivers three distinct advances: (i) a previously unrecognised mechanism by which spiral growth enhances out-of-plane polarisation; (ii) a new three-dimensional XRD framework that predicts diffraction signatures arising from complex defect geometries; and (iii) a previously unreported supersaturation-controlled route for eliminating twin variants in layered ferroelectric thin films. Together, these advances contribute a materials-centric foundation for integrating layered ferroelectrics into vertically oriented memory and neuromorphic device platforms, where controlled polarisation, structural coherence,

and engineered defect landscapes are essential for meeting key requirements for reliable operation at technologically relevant scales.

I. Introduction

1. Rising Data Demands and Storage Challenges

Published in 1992, and reprinted in 2000- Lyman and Varian's article- 'How much information'[1] provided detailed estimates of the amount of information being produced and stored digitally. They recognised that the amount of digital data was rapidly increasing and that managing this information was becoming a 'significant problem'. This was the start of a problem that would only grow with each passing year.

The exponential growth of data generation in the digital age has been unprecedented. With each passing year, we are producing more data than we can store, let alone process. With the onset of the pandemic, much of the world was pushed into online meetings, which in turn increased the demand for servers and hosting infrastructure, to the rise of artificial intelligence (AI), larger and larger volumes of data are being produced and stored. The volume of data generated is growing at an extremely fast pace, straining the capabilities of current storage technologies. Experts estimate that the world will store around 100 zettabytes of data in cloud environments by the end of 2025,[2], [3], [4] (**Figure 1.1**) representing roughly half of all data generated globally at that time (Figure 1).[5] The global data storage market is projected to expand from approximately US\$255 billion in 2025 to US\$774 billion by 2032,[6] reflecting a compound annual growth rate of approximately 17.2 percent. Meanwhile, data centres are experiencing surging power consumption: forecasts suggest that global demand for data centre electricity will increase by 50 percent by 2027 and could rise by as much as 165 percent by 2030[7] if current trends continue. Investment into these facilities is growing accordingly; in the United States alone, data centre power demand

may climb to around 130 GW by 2028, expanding at a compound annual growth rate of approximately 16 percent from 2023.[8] The increasing reliance on hyperscale data centre campuses is driven not only by enterprise workloads but also by the explosive demand from generative AI and large-language model training, which will represent a substantial portion of growth in compute and storage needs.[8]

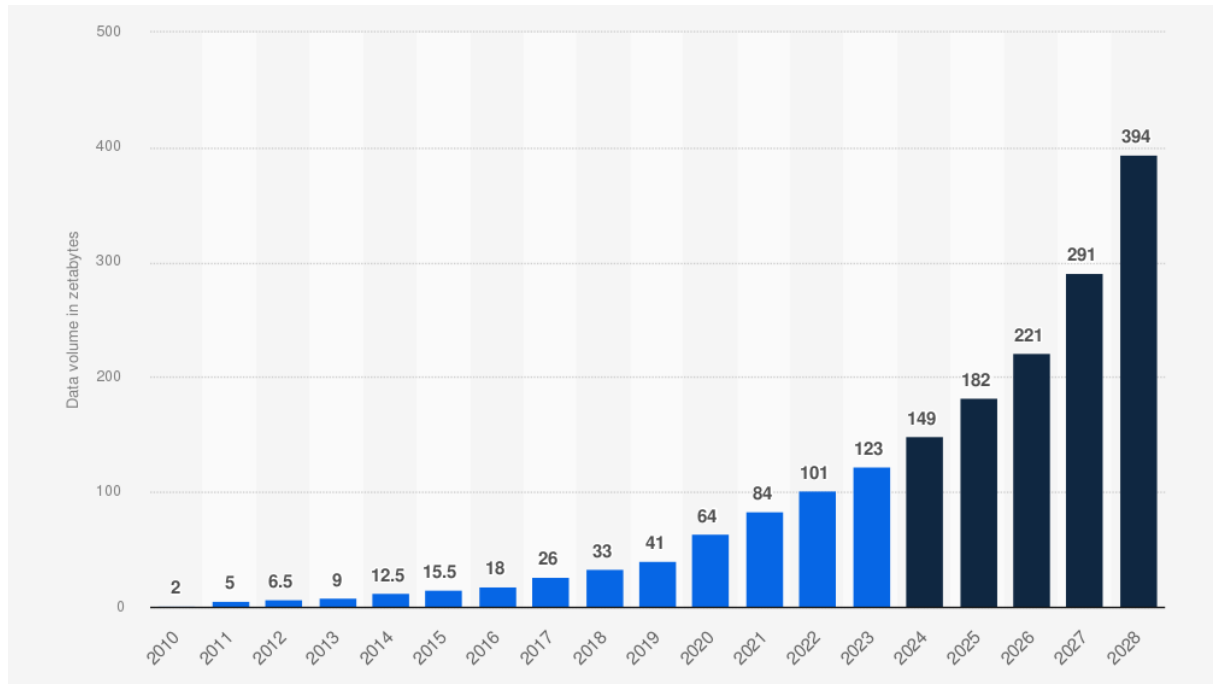


Figure 1.1: *Volume of data created and consumed worldwide from 2010 to 2023, with predictions from 2024 to 2028 by Statista.[9] Figure republished under enterprise/institutional copyright waiver.*

Supply-side strains are increasingly evident. Although improvements in energy efficiency and the adoption of renewable power have helped stabilise data centre's share of global electricity consumption at roughly 1 to 1.5 percent, the pressure on existing infrastructure remains intense.[10], [11] Industry responses reflect these concerns: Seagate's development of heat-assisted magnetic recording (HAMR) has pushed hard disk drive capacities beyond 30 terabytes today, with 36 terabytes and

higher on the near-term roadmap - critical for meeting the cost-per-terabyte demands of large-scale data storage deployments, even as solid-state drive adoption accelerates.[12] Yet, despite such advances, data generation continues to grow exponentially, while storage infrastructure and capacity struggle to scale at a comparable rate. This widening gap underscores the urgency of developing novel, high-capacity, efficient, and sustainable memory technologies.

2. The State-of-the-Art in Memory Storage

As digital systems contend with ever-growing data volumes, a range of non-volatile memory technologies have emerged to address the shortcomings of conventional DRAM (Dynamic Random-Access Memory).[13], [14] DRAM relies on capacitive charge-storage, refreshed continuously to retain data. It delivers high speed and high density, yet remains volatile and energy-intensive due to refresh cycles, which also limit scalability for high-performance or low-power systems.[15] The state-of-the-art in memory, which could address the shortcomings of DRAM are listed in the tables below, including their advantages, bottlenecks, and key applications. The most prominent of them, namely MRAM, DRAM, PCM and ReRAM are discussed in detail.

Table 1. Mainstream Memory

<i>Memory type</i>	<i>What it does (physical principle)</i>	<i>Advantages</i>	<i>Key limitations and bottlenecks</i>	<i>Best-fit use today</i>
<i>SRAM (Static Random Access Memory)</i>	Bistable cross-coupled CMOS inverters hold logic states while powered[16]. Read and write by accessing the cell through pass transistors.[17]	Fast random access with very low latency[18]; essentially unlimited write endurance[19]; robust for caches and register files.[17]	Large cell footprint limits density[16]; leakage grows with scaling; stability at low supply voltages requires circuit overheads and assist schemes.[17]	On-chip caches,[16]register files, small scratchpads, emerging[20] compute-in-SRAM macros.[21]
<i>DRAM (Dynamic Random Access Memory)</i>	Stores charge on a capacitor (1T-1C[22]). Sense amplifiers detect small voltage differences after charge sharing on bitlines. Periodic refresh maintains state. [23]	Highest density main-memory technology; mature manufacturing; low cost per bit relative to SRAM.[24]	Refresh energy and latency; scaling of capacitor and access device; read-disturb phenomena[25] (RowHammer and related effects[26], [27], [28]) threaten reliability and security; bank conflicts and activation limits throughput.[28]	System main memory (DIMMs, HBM stacks)[28]; accelerators where bandwidth per watt matters.
<i>NAND flash (2D/3D)</i>	Stores charge in floating-gate or charge-trap cells. Multilevel states via precise charge quantization. 3D stacks use vertical channels and charge-trap layers.[29]	High density and excellent cost per bit; nonvolatile; 3D integration scales capacity beyond planar limits.[30]	Endurance limited by interface traps and oxide damage; retention and read-disturb worsen with stacking and tighter pitches[31]; program-erase latency and variability require heavy ECC and wear levelling.[32]	Solid-state drives from client to hyperscale[33]; archival tiers with QLC/PLC; near-data storage for analytics. [34]
<i>Magnetic HDD (HAMR) (Heat-Assisted Magnetic Recording)</i>	Magnetic grains with very high anisotropy are locally heated by a plasmonic near-field transducer to lower coercivity, then written by the field from the head[35] [36].	Outstanding cost per terabyte; roadmap to multi-tens of TB per disk; continuous media reuse.[37]	Head-disk interface reliability at high temperature; thermal back-switching and write errors[38]; media and head materials integration[39]; optics and thermal management at nanoscale.	Cold to warm storage in data centres; streaming and backup where sequential throughput and cost dominate.[36]

The following table discusses the advances in the state-of-the-art non volatile memory technologies:

Table 2. Advanced Non-Volatile Memory

<i>Memory type</i>	What they do (device physics)	Advantages	Limitations and bottlenecks	Best-fit use today
<i>STT-MRAM (MTJ) (Spin-Transfer Torque Magnetic Random-Access Memory)</i>	Two ferromagnets separated by MgO tunnel barrier. Spin-polarized current switches the free layer via spin-transfer torque; resistance encodes state via TMR[40], [41].	Unlimited reads; very high endurance; nonvolatile; CMOS backend compatible; radiation hard[42].	Write current density and stochasticity; read disturb in small cells; thermal stability at sub-20 nm; cost per bit higher than flash and DRAM[41].	Embedded NVM in MCUs and caches; write buffers; last-level cache candidates[41].
<i>SOT-MRAM (Spin-orbit torque MRAM)</i>	In-plane current in a heavy metal or TI underlayer generates spin-orbit torque that switches a perpendicular MTJ, decoupling read and write paths.[43]	Faster writes and improved endurance; reduced read disturb; pathway to field-free switching and low-voltage operation[44].	Three-terminal footprint reduces density; requires high spin-Hall efficiency materials and careful stack engineering[44].	High-speed caches, embedded scratchpads where write bandwidth dominates[45].
<i>FeRAM (perovskite and hafnia-based)- (Ferroelectric RAM)</i>	Polarisation in a ferroelectric capacitor (perovskite PZT or fluorite HfO ₂ -based) encodes binary state[46]; non-destructive or destructive read depending on scheme.[47], [48]	Low-voltage, fast switching; excellent endurance[49]; CMOS-friendly materials with HfO ₂ enable scaling and BEOL integration[46].	Retention and imprint in legacy perovskites; wake-up and fatigue in hafnia films; variability of orthorhombic phase stabilization.	Embedded NVM, secure memory, ultralow-energy IoT; with HfO ₂ , dense FeFET and FeD arrays.
<i>FeFET (Ferroelectric Field-Effect Transistor)</i>	MOSFET with ferroelectric gate dielectric (often Hf _{0.5} Zr _{0.5} O ₂). Polarisation sets channel threshold for nonvolatile memory and analogue weight storage.[50], [51]	One-transistor cell, high density; analogue programmability for AI; low energy; CMOS compatibility.[52]	Threshold drift, retention at high temperature, endurance tied to ferroelectric fatigue; variability across arrays.[53]	Embedded NVM, AI accelerators with analogue compute-in-memory, reconfigurable logic.[50], [53]

PCM (Phase Change Memory)	Reversible switching between amorphous and crystalline phases in chalcogenides (for example GST). Resistance contrast stores data; threshold switching enables access.[54]	Fast SET/RESET; multilevel states; good endurance; mature for storage-class and in-memory computing.[55]	Drift and noise in amorphous phase; cycling induced material segregation; thermal crosstalk; selector integration.[55], [56], [57], [58]	Storage-class memory concepts, neuromorphic synapses and neurons, photonic-electronic hybrids.[54], [56]
ReRAM (memristive) (Resistive RAM)	Electric-field driven formation and rupture of nanoscale conductive filaments or interfacial redox at metal–insulator–metal stacks.[59]	High density in crossbars; analogue weights; low-energy writes; scalability.[60], [61]	Variability cycle-to-cycle and device-to-device; limited endurance in some oxides; sneak currents require selectors.[62], [63]	In-memory compute arrays, embedded NVM, low-power edge AI.[60], [61]
FTJ (Ferroelectric tunnel junction)	Two electrodes separated by a nanometre-scale ferroelectric barrier. Polarisation reversal modulates tunnelling barrier height and shape, producing tunnelling electroresistance.[64]	Non-destructive resistive readout; sub-10 nm scalable barrier; analogue conductance for synapses; potential for multifunctional MFTJs with spin filtering.[42], [65], [66]	Maintaining robust ferroelectricity at ultrathin thickness; interface dead layers; fatigue and retention at high fields; device-to-device variability.[67], [68], [69]	Selector-less crossbars for inference accelerators; secure IDs; niche NVM; hybrid magneto-electric memories.[65], [69], [70]
Magnetic Ferroelectric Tunnel Junction (MFTJ)	A ferroelectric barrier (e.g. BaTiO ₃ , BiFeO ₃ , Hf _{0.5} Zr _{0.5} O ₂) is sandwiched between two ferromagnetic electrodes. Tunneling current depends on both polarisation (TER) and magnetization (TMR), enabling four resistive states.[71], [72]	Non-volatile, low power, and multi-level storage; electric-field control of magnetism; scalable and CMOS compatible[42]	Interface quality and barrier thickness critically affect TER/TMR; fatigue, leakage, and limited endurance; complex integration and scaling challenges.[44], [72]	Multi-bit non-volatile memories; spintronic logic and neuromorphic devices.[44]

Magnetoresistive RAM (MRAM) stores data in magnetic domains within a magnetic tunnel junction (MTJ), where the relative orientation of magnetic layers (parallel or antiparallel) controls resistance.[40], [73] Spin-transfer-torque (STT) and spin-orbit-

torque (SOT) methods enable switching via spin-polarised currents. MRAM excels with near-zero standby power, fast read/write times, and endurance, yet it has notable drawbacks: reliability issues such as read disturbances (where reading can inadvertently alter data),[74] write failures, stochastic retention failures in idle states,[75] sensitivity to temperature fluctuations and manufacturing defects, larger cell area, higher write power than DRAM,[23] and elevated cost per bit. These factors collectively limit MRAM's potential to serve as a universal DRAM replacement.

Phase-Change Memory (PCM) operates based on reversible phase transitions between amorphous (high-resistance) and crystalline (low-resistance) states in materials like $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST), manipulated via localised heating pulses.[76] PCM achieves multilevel storage and relatively high density compared to DRAM.[77] However, it demands high programming currents, is prone to thermal crosstalk in dense arrays, shows resistance drift over time, and encounters retention and endurance issues as device dimensions are scaled down.[57]

Resistive RAM (ReRAM), or RRAM, encodes data through the formation and dissolution of conductive filaments, often involving oxygen vacancies, within oxide thin films under electrical stress.[62] ReRAM offers fast switching, low voltage operation, and potential sub-10 nm scaling. Yet it grapples with high variability due to the stochastic nature of filament formation,[78], [79] limited endurance, and sneak-path currents in crossbar architectures without reliable selectors.[80]

Along with the above memory architectures that have been in the research and development pipeline for a long time, there are a few emerging unconventional memory architectures. These are exploratory in nature, and present an exciting possibility for application as their development progresses.

Table 3. Unconventional and exploratory information media

<i>Concept</i>	<i>What it does</i>	<i>Advantages</i>	<i>Limitations and bottlenecks</i>	<i>Best-fit use envisioned</i>
<i>Racetrack (domain-wall) memory</i>	Stores bits as magnetic domains in nanowires. Spin-polarized currents shift domain walls past read/write elements.[81]	Nonvolatile; potential 3D density; no moving parts.[81], [82]	Pinning, stochastic DW motion; write energy; materials and fabrication complexity for vertical integration.[83]	High-density fast storage if reliable DW motion at low current is achieved.[81], [82], [83]
<i>Skymionics</i>	Encodes bits in topologically protected spin textures with ultralow current motion.[84]	Ultralow drive currents; topological stability; potential nanoscale bits.[84], [85]	Nucleation, detection, room-temperature stability in device-relevant materials; Hall effects. complicate readout.[85], [86]	Dense, low-energy logic and memory elements.[86]
<i>Topological-insulator driven SOT memories</i>	Uses extremely efficient charge-to-spin conversion of TIs to switch adjacent ferromagnets at very low energy.[43], [87]	Very low write energy; potential CMOS-compatible sputtered stacks.[87], [88]	TI materials integration, uniformity, oxidation control, and contact resistance; three-terminal area cost.[89], [90]	Ultralow-energy caches, cryogenic or edge systems where energy per write is pivotal.[88], [89], [90]
<i>Polar vortices and polar-skyrmion textures</i>	Uses topological polarisation textures in oxide superlattices as multistate or reconfigurable bits.[91]	Rich multilevel states; potential for ultrafast field control and new logic primitives.[92], [93]	Materials growth complexity; readout schemes; room-temperature robustness and endurance.[91], [92], [94]	Functional nanoelectronics, reconfigurable RF and logic if robust control is demonstrated.[92], [94]
<i>DNA data storage</i>	Encodes digital information into nucleotide sequences. Write via synthesis, read via sequencing; random access through primers.[95], [96], [97]	Astronomical volumetric density; archival longevity under proper conditions; energy-frugal at rest.[96]	Write and read latency; synthesis and sequencing cost; error management and standards.[98]	Ultra-long-term archival and cold storage with infrequent access.[98]

2. Ferroelectric Memories

In a ferroelectric capacitor used for **Ferroelectric RAM (FeRAM)**, binary information is encoded in antiparallel polarisation states of a thin ferroelectric film such as $\text{Pb}(\text{Zr,Ti})\text{O}_3$ or HfO_2 -based fluorite oxides.[99] A write operation applies a voltage pulse that switches the polarisation through domain nucleation and growth. A conventional read operation senses the displacement charge generated when the polarisation is forced to switch into a known reference direction, which means the read is destructive and must be followed by a rewrite to restore the original state.[47] FeRAM is attractive because polarisation reversal is intrinsically fast and requires low energy, and because the material can withstand very high cycle counts (up to 10^{16} cycles)[100] when interfaces are well engineered. The main scaling bottlenecks are the increasing depolarising fields a reduced thickness that destabilise polarisation,[101] fatigue and imprint driven by defect migration and charge trapping at the electrode interfaces, and the integration of high-quality ultrathin films with CMOS without incurring interfacial passive layers that suppress switchable polarisation.[102] The discovery and engineering of ferroelectricity in doped hafnium oxide have alleviated some of these issues[103] by enabling ferroelectricity at thicknesses of only a few nanometres with back-end compatibility. However retention, wake-up, and fatigue phenomena still require careful defect and interface control.[49], [104] Overall, while FeRAM surpasses DRAM with fast, low-power writes, non-volatility, and exceptional endurance, further scaling is constrained by depolarising fields, fatigue, and integrating challenged with advanced CMOS processes.

Classical von Neumann architectures, characterised by a clear separation between memory and processing units,[105], [106] are reaching fundamental limitations in power efficiency and speed due to the so-called “von Neumann bottleneck.” This performance bottleneck arises from the constant shuttling of data between memory and logic units, leading to high latency and energy costs. Neuromorphic computing, inspired by the architecture of the brain, integrates memory and computation within networks of artificial neurons connected via analogue-like synaptic elements.[107] These systems operate using event-driven, spiking communication, enabling massively parallel, low-power computation. Critical to these architectures are synaptic devices that are non-volatile, support multiple states or analogue weighting, consume minimal energy per event, and endure many write cycles.

Traditional memory candidates such as ReRAM, PCM, MRAM, have been investigated for neuromorphic applications, yet each present significant challenges: ReRAM suffers from variability and limited weight precision; PCM requires thermally intensive programming and is prone to resistance drift; and MRAM struggles with high write power and density scaling as noted above. Ferroelectric Tunnel Junctions (FTJs), by contrast, offer intrinsic advantages for synaptic roles: analogue-like resistance modulation, high ON/OFF ratio, non-destructive reading, low energy consumption. Moreover, ferroelectrics have the potential to be engineered for integration within semiconductor process flows, providing a scalable and versatile platform for neuromorphic hardware, although further work is required to address device variability and scaling.[108]

Ferroelectric Tunnel Junctions (FTJs) have an elegant fusion of ferroelectricity and quantum tunnelling. An FTJ consists of an ultrathin ferroelectric layer (a few

nanometres thick) sandwiched between conductive electrodes. Switching the ferroelectric polarisation reverses the interfacial potential profile, thereby modulating the tunnelling barrier height, yielding distinct high- and low-resistance states, a phenomenon known as the tunnelling electroresistance (TER) effect.[66] FTJs offer several advantages, including two-terminal device simplicity, fast and low-energy operation, non-destructive readout, large ON/OFF resistance ratios, compact footprint, and compatibility with CMOS back-end-of-line integration.[109] However, their practical realisation is impeded by the difficulty of preserving stable ferroelectric polarisation at ultra-thin film scales. As examples, interfacial passive “dead layers” can suppress switchable polarisation, while depolarising fields and leakage currents limit scalability.[67] Nevertheless, the intrinsic ability of FTJs to support analogue-like, multi-level resistance states makes them especially promising for neuromorphic applications, where synaptic weights must be tuned continuously rather than stored in binary form.

Realising this potential will require advances in the controlled growth of defect- and interface-engineered ultrathin ferroelectric films, improved understanding of polarisation dynamics at the nanoscale, and the development of reliable multi-level programming schemes that can be seamlessly integrated with CMOS technology.

This thesis aims to optimise and understand ferroelectric thin films for future memory storage applications, and to achieve this, it is essential to understand what ferroelectrics are, and how ferroelectricity manifests in materials.

3. Fundamentals of Ferroelectricity

Ferroelectricity is a property in which a spontaneous electric polarisation exists in the absence of an external electric field and can be reversed by applying an appropriate electric field. This reversibility distinguishes ferroelectrics from other polar materials that possess a permanent dipole moment but cannot have its direction switched. To understand how such a behaviour emerges, it is necessary to contrast ferroelectrics with ordinary dielectrics and polar dielectrics and to develop the thermodynamic description that governs their phase transitions.

3.1 Definition and Thermodynamic Framework

In a linear dielectric, the valence electrons and ions shift slightly in response to an applied electric field, producing a dipole moment proportional to the field:

$$P = \epsilon_0 \chi E \quad 1,$$

Where P is the polarisation, E the electric field, ϵ_0 the permittivity of free space, and χ the electric susceptibility. When the external field is removed, the ionic displacements relax back to equilibrium, and P returns to zero. The corresponding P – E characteristic is a straight line through the origin, indicating proportionality and reversibility.

Some dielectric crystals lack a centre of symmetry even without an applied field and carry a permanent built-in dipole moment. These are called polar dielectrics, and they form the base of a materials hierarchy. All polar dielectrics are pyroelectric (their spontaneous polarisation changes with temperature). All pyroelectrics are also piezoelectric (they develop a charge under mechanical stress). Ferroelectrics sit at the

top of this hierarchy: they are a subset of pyroelectrics in which the direction of the spontaneous polarisation can be reversed by an applied electric field.

Not all polar dielectrics make it to the top. Wurtzite ZnO, for example, has a well-defined polar axis and a permanent dipole moment, [110] but the energy barrier separating the two possible polarisation orientations is too large for any practical electric field to overcome. [111] The dipole exists, but it cannot be switched. ZnO is therefore pyroelectric and piezoelectric, but not ferroelectric.

The essential requirement for ferroelectricity is switchability: the material must have two or more energetically equivalent polarisation orientations that an electric field can drive between. These orientations arise from a structural phase transition in which the material cools from a high-symmetry parent phase into a lower-symmetry ferroelectric phase, breaking inversion symmetry in the process. A polar axis is necessary, but only a surmountable energy barrier between orientations makes a material truly ferroelectric.

3.2. Paraelectric to Ferroelectric Transition and the Role of the Order Parameter

At high temperature, many ferroelectrics exist in a paraelectric phase, where thermal fluctuations restore inversion symmetry and the average polarisation is zero. [112] Cooling through the Curie temperature, T_c , breaks inversion symmetry and yields a ferroelectric phase in which the ions adopt a displaced arrangement, lowering the free energy and creating spontaneous polarisation, P_s . This quantity acts as the order parameter for the transition. Whether P_s appears continuously or discontinuously upon cooling differentiates second-order (continuous) from first-order (discontinuous) transitions.

The evolution of the polar state near T_c can be described by Landau–Ginzburg–Devonshire theory, [113], [114] which expands the free energy F as a polynomial in P :

$$F = F_0 + \frac{1}{2}\alpha P^2 + \frac{1}{4}\beta P^4 + \frac{1}{6}\gamma P^6 - EP \quad 2,$$

Where:

F_0 is a reference energy, P is the polarisation, E is the applied electric field, $\alpha = \alpha_0(T - T_c)$ is a temperature-dependent coefficient, β and γ are higher-order coefficients that ensure stability.

For $T > T_c$, $\alpha > 0$ has a single minimum at $P = 0$, corresponding to the paraelectric phase. For $T < T_c$, $\alpha < 0$, and the free-energy profile transforms into a double-well potential (**Figure 1.2**), with minima at $\pm P_s$. These minima represent two equally favourable polar states.

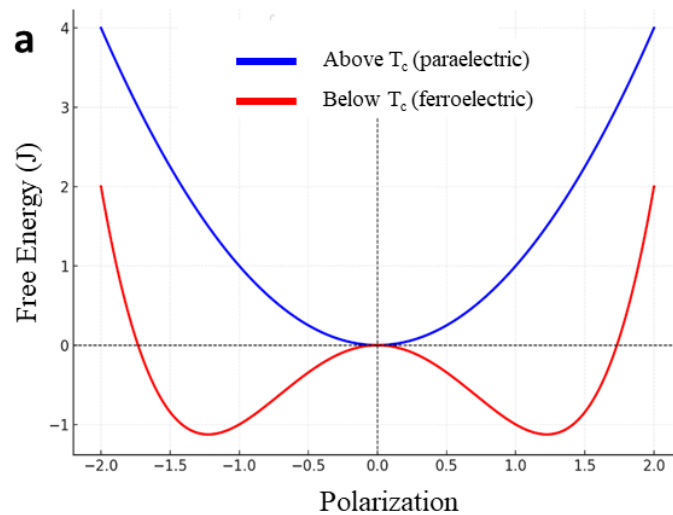


***Figure 1.2:** Free energy landscape of a proper ferroelectric, showing the emergence of a double-well potential below the Curie temperature*

3.2. Polarisation Switching and Hysteresis

When a ferroelectric material is subjected to an increasing electric field, the polarisation initially grows as domains aligned with the field expand at the expense of oppositely oriented ones (**Figure 1.3 a-b**). Once all domains are aligned, the polarisation reaches a maximum value known as the saturation polarisation P_{sat} . If the electric field is then reduced back toward zero, the polarisation does not return to the origin. Instead, a finite remanent polarisation P_r remains, arising from the fact that many domains remain aligned and the system remains in one of the free-energy minima (**Figure 1.3 d**). To reverse the polarisation, the applied field must not merely reach zero but exceed a critical negative value known as the coercive field E_c , which supplies sufficient energy to overcome the barrier between the two polar states. Beyond E_c , the polarisation switches direction, eventually saturating again as domains realign, thus completing the characteristic P–E hysteresis loop. [115]

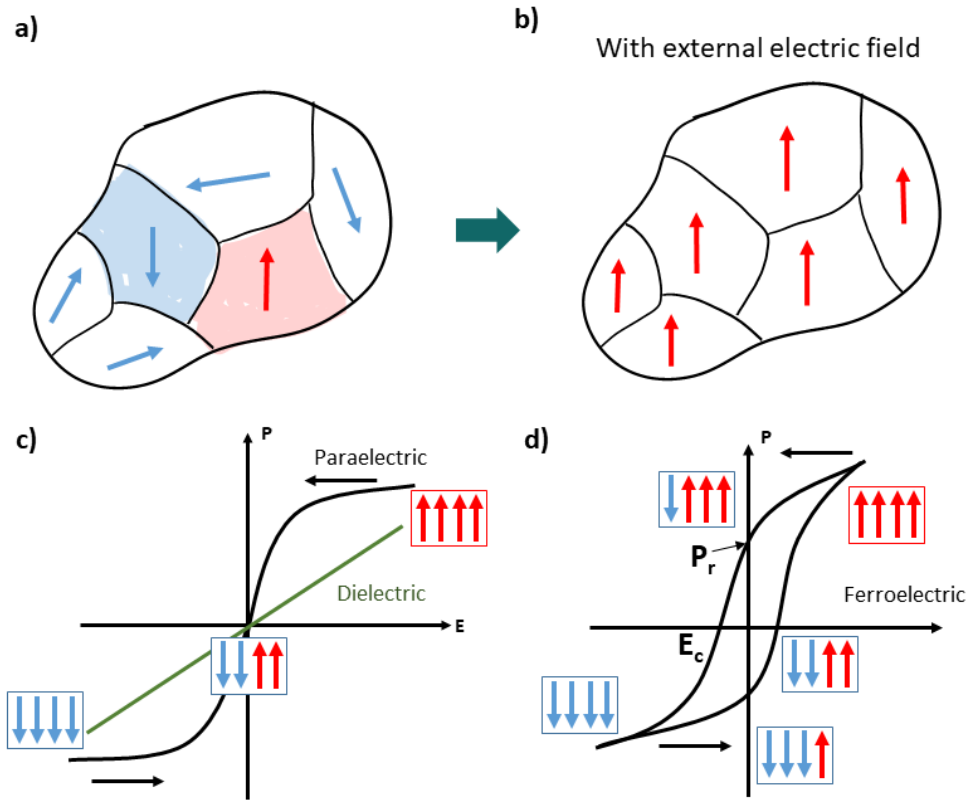


Figure 1.3: *a-b* Alignment of domains with an external electric field. *c-d* P-E Loops of paraelectric, dielectric and ferroelectric phases.

The shape of this loop reflects the underlying energy landscape: the existence of two stable polar states separated by an energy barrier gives rise to a history-dependent response in which the value of the polarisation at a given field depends on the path taken to reach it (**Figure 1.2**). This contrasts sharply with the behaviour of a linear dielectric (**Figure 1.3 c**), where polarisation is proportional to the applied field and returns to zero once the field is removed, producing a single-valued line through the origin, or a paraelectric, where the curve ‘saturates’, but doesn’t retain a remnant polarisation. Even linear dielectrics, which possess a built-in dipole, display a *non-hysteretic* response: although the P–E curve is offset from the origin due to the spontaneous polarisation, there is no coercive field and the original state is recovered

once the field is removed. In ferroelectrics, by comparison, the multivalued nature of the P–E curve and the presence of P_r , E_c , and P_{sat} arise from the ability of domains to switch direction under an applied field and remain in that switched state on removal of external stimulus.

It is this non-volatile retention of polarisation that distinguishes ferroelectrics from all other dielectric classes and lends them technological importance. The hysteresis loop is therefore not merely a graphical signature: it is a direct macroscopic manifestation of the bistable potential energy landscape that makes ferroelectrics suitable for logic, memory, and neuromorphic architectures where stable, electrically rewritable states are required.

3.3 Microscopic Origins of Ferroelectricity

While Landau theory provides a thermodynamic description of ferroelectricity at the macroscopic scale, it does not explain why spontaneous polarisation emerges at the microscopic level. The origin of ferroelectricity depends on how the material's internal degrees of freedom (such as lattice vibrations, electronic configuration, bonding geometry, and molecular motion) respond to changes in temperature and symmetry. Different classes of ferroelectric materials therefore exhibit distinct mechanisms that generate the polar state. These microscopic mechanisms strongly influence not only the magnitude and direction of polarisation, but also the switching kinetics, dielectric response, and coupling to external electric, magnetic, or mechanical fields.

3.3.1 Perovskite Ferroelectrics and Displacive Transitions

A large number of technologically important ferroelectrics adopt the perovskite ABO_3 structure, in which the A-site cations occupy the cube corners, the B-site cation is

located at the centre of an oxygen octahedron, and oxygen anions reside on the faces of the cube. In the high-temperature cubic paraelectric phase (space group $Pm\bar{3}m$), the B-site cation remains symmetrically coordinated and the crystal possesses inversion symmetry, resulting in no net electric dipole. Upon cooling below the Curie temperature T_c , many perovskites undergo a symmetry-lowering distortion in which the B-site cation shifts away from the centre of its octahedron (**Figure 1.4**). This displacement produces a dipole aligned along a crystallographic axis and gives rise to the spontaneous polarisation characteristic of the ferroelectric phase. Depending on the energetic balance of Coulombic, elastic, and short-range repulsive interactions, the distorted structure may adopt tetragonal ($BaTiO_3$, $PbTiO_3$), orthorhombic ($KNbO_3$), or rhombohedral ($BiFeO_3$) symmetry.

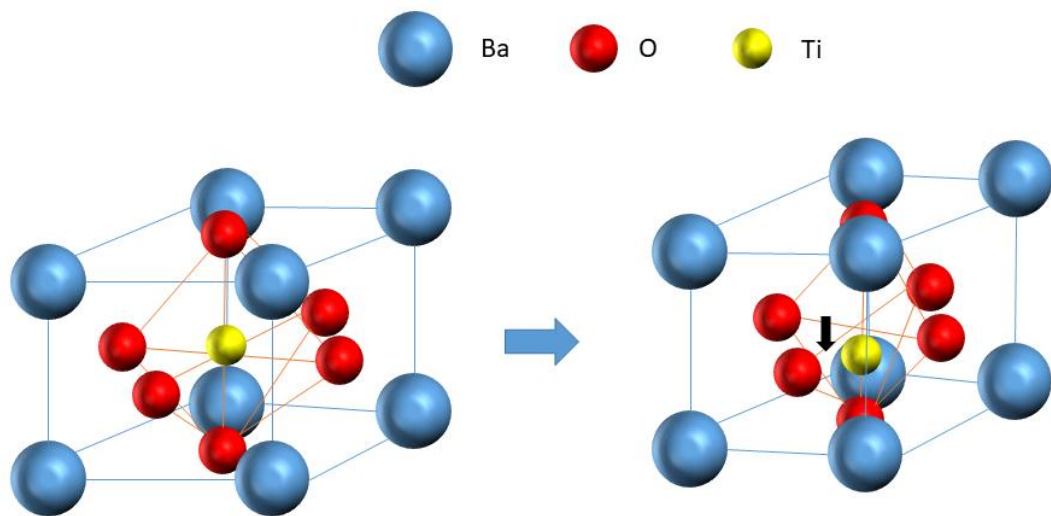


Figure 1.4: At the Curie temperature, $BaTiO_3$ undergoes a phase transition from the centrosymmetric cubic structure ($Pm\bar{3}m$) to the tetragonal structure ($P4mm$). Symmetry breaking involves anisotropic lattice distortion ($c \neq a$, $a=b=3.99\text{\AA}$, $c=4.03\text{\AA}$) and off-centring of the Ti^{4+} cation within the oxygen octahedron, leading to spontaneous polarisation along the c -axis and the onset of ferroelectricity.[116]

This behaviour is referred to as a displacive ferroelectric transition, since the polar state arises from collective ionic displacements. Slater (1950) [117] first interpreted this transition as a competition between long-range Coulomb forces, [118] which favour ionic off-centring, and short-range repulsive interactions, which oppose excessive displacement. Cochran (1959) [119] later reformulated this description in terms of lattice dynamics, demonstrating that a transverse optic phonon mode softens progressively as temperature approaches T_c , eventually exhibiting zero frequency at the transition point. This softening indicates an incipient structural instability whose condensation produces the polarised phase. Classical displacive ferroelectrics therefore exhibit a soft-mode whose frequency tends to zero at T_c , a continuous growth of spontaneous polarisation below the transition, under-damped polar excitations in the dielectric spectrum, and well-defined ionic displacements that can be directly observed using diffraction or microscopy. In such materials, switching involves coherent movement of ions between symmetry-equivalent minima of the double-well potential.

3.3.2 Order–Disorder Ferroelectrics

Not all ferroelectrics rely on ionic displacement to create dipoles. In order–disorder ferroelectrics, local dipoles already exist above T_c , but are dynamically disordered by thermal fluctuations, resulting in zero net polarisation in the paraelectric phase. As the material is cooled through T_c , these dipoles align cooperatively and a macroscopic polarisation appears. Prototypical examples include potassium dihydrogen phosphate (KH_2PO_4 or KDP), where hydrogen atoms can occupy two symmetry-related positions along $\text{O}-\text{H}\cdots\text{O}$ bonds, and triglycine sulphate (TGS), where polarisation arises from conformational ordering of glycine molecules. These materials typically display pronounced dielectric dispersion near the phase transition and are well described by

Ising-type models for dipole ordering. Unlike displacive systems, they do not exhibit a phonon mode that softens continuously to zero frequency; instead, they show overdamped dielectric responses associated with the progressive ordering of pre-existing dipoles. While displacive transitions create dipoles as ions move off-centre, order-disorder ferroelectrics simply arrange existing local dipoles into a coherent polar state. It is important to note that this distinction is not always clear-cut. Some materials, such as BaTiO_3 , display features of both mechanisms, demonstrating that ferroelectric transitions can involve mixed displacive and ordering contributions.

3.3.3 Lone-Pair and Second-Order Jahn–Teller Ferroelectricity in Bi-Based Oxides

A third microscopic route to ferroelectricity, particularly relevant to the Aurivillius phase studied in this thesis, involves stereochemically active lone-pair cations such as Bi^{3+} . [120] With its $6s^2$ electronic configuration, bismuth can undergo a second-order Jahn–Teller (SOJT) distortion in which mixing between the filled $6s$ orbital and empty $6p$ orbitals, mediated by O $2p$ states, lowers the energy of an off-centred cation position. [120] This process leads to an asymmetric electron density around the Bi ion, creating a local dipole that can couple across the lattice to produce macroscopic polarisation. In contrast to displacive ferroelectrics where the instability is primarily ionic, lone-pair-driven ferroelectrics derive their polarisation from electronic asymmetry. The SOJT mechanism explains why many Bi-containing oxides exhibit large spontaneous polarisations and pronounced anisotropy, and why ferroelectricity persists even in layered structures where conventional displacive criteria are not easily satisfied. Lone-pair activity often co-exists with other lattice instabilities, such as octahedral tilts or soft polar phonons, enabling hybrid or improper ferroelectric behaviour in layered or complex oxides.

3.3 Thin Film Effects and Boundary Conditions

In thin films, ferroelectric behaviour follows the same general principles as in bulk crystals, but is strongly modified by boundary conditions. Electrostatic constraints, substrate clamping, and interface effects can shift coercive fields, alter domain structures, and couple polarisation to defects and interfaces. In real thin films, switching is rarely homogeneous. Instead, it proceeds through domain nucleation and domain wall motion, often described by Merz's law.[121] Merz law relates switching time to the applied field and to deviations from ideal behaviour introduced by defects and interfaces. These microscopic mechanisms are central to device operation, because they set the coercive field, speed limits, and reliability in the nanometre regime where depolarising fields[122] and imperfect screening at electrodes become non-negligible. Ultrathin films are particularly sensitive to depolarising fields at the metal–ferroelectric interfaces, which can suppress the polar instability and give rise to a critical thickness for switchable polarisation. Compensation through formation of closure domains or enhanced screening can mitigate these effects.[101] First-principles calculations and phase-field modelling have established these principles as central scaling strategies in ferroelectric devices into the nanometre regime, where depolarisation fields, defect interactions, and interface quality critically affect stability and switching.

3.4. Domain Structures, Switching and Dynamics

3.4.1 Domains and Domain Walls

Ferroic domains form when a discrete symmetry is broken during a phase transition, causing dipole moments to organise into regions corresponding to different energy minima, each with distinct orientations and magnitudes. Classically, ferroelectric

materials segregate into uniform domains with differently oriented polarities, separated by neutral domain walls (**Figure 1.5 a**). Domain walls are the two-dimensional interfaces separating these domains, representing the boundaries between regions with differing dipole configurations. Ising-type domain walls are typical in ferroelectrics, where the polarisation magnitude decreases through the wall without rotation (**Figure 1.5 b**). It is widely acknowledged that ferroelectric domain structure is the primary factor governing polarisation switching[123], influencing domain wall motion[124], the evolution of existing domains, and the nucleation of new ones[125], [126]. In ferroelectric thin films, the equilibrium domain configuration resulting from the minimisation of elastic and electrostatic energies is affected by factors such as film composition, growth mechanism, growth and cooling temperatures, substrate, electrodes, and film thickness. Therefore, characterisation, understanding, and control of ferroelectric domain structures in ultrathin films are essential for tailoring electromechanical properties and optimising device performance.

The equilibrium domain pattern minimises the balance of depolarisation and wall energy, following scaling relations such as the Landau–Lifshitz–Kittel law, where stripe domain period scales approximately with the square root of film.[127]

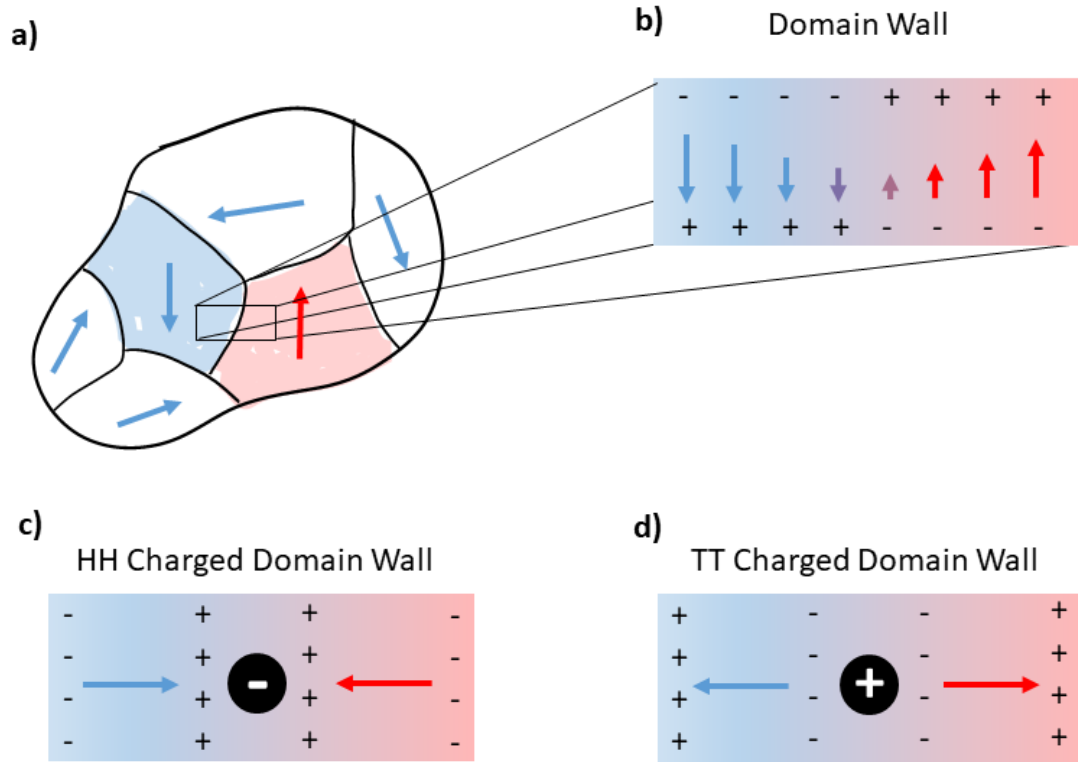


Figure 1.5: *a* Spontaneously polarized domains in the absence of an external electric field *b* Neutral Ising domain wall *c* Head to Head (negatively charged) domain wall *d* Tail to Tail (positively charged) domain wall.

3.4.2 Functional Domain Wall Phenomena

Deviations from ideal domain-scaling behaviour arise when coupling to additional order parameters or electrostatic boundary conditions contribute to roughening domain walls and modifies their dynamics. Notably, localised conduction at ferroelectric domain walls is observed in many oxide ferroelectrics. Such conduction can originate from charged domain walls, band bending effects, or local structural distortions that narrow the bandgap, and is now being actively explored for domain-wall-based nanoelectronic devices.[128] Charged domain walls, head-to-head (**Figure 1.5 c**) or tail-to-tail (**Figure 1.5 d**), are generally high-energy configurations but can

be stabilised through charge compensation or specific crystal chemistries. When stabilised, these walls can host enhanced conductivity or other emergent functionalities. While domain wall conduction (**Figure 1.5 (c and d)**) offers an additional degree of freedom, it also introduces leakage pathways and pinning centres that compromise device performance. Managing these effects is therefore crucial for reliable operation of nanoscale memories.

4. Types of Ferroelectrics

Proper ferroelectrics form the largest class in oxide ferroelectrics and are typified by perovskites such as BaTiO_3 , PbTiO_3 , and solid solutions like $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT). Polarisation arises from the unstable polar mode, so switching can be fast and strong with large remanent polarisation ($\sim 40\text{--}50 \mu\text{C}/\text{cm}^2$). Improper ferroelectrics include hexagonal manganites and many layered perovskites where the primary structural order induces polarisation.[118] These can show enhanced fatigue tolerance and unusual domain textures because the polar state is locked to a robust nonpolar lattice distortion.[129] Relaxor ferroelectrics are materials with chemical or structural disorder that produce polar nanoregions and diffuse phase transitions. They provide very high permittivity and electrostrictive response but are less suitable for deterministic binary memories because their hysteresis is broadened by disorder.[130]

The orientation of polarisation with respect to the film plane is also technologically important. Out-of-plane or vertical polarisation is favoured for one-transistor–one-capacitor and ferroelectric tunnel junction structures where the field is applied normal to the film.[64] In-plane or lateral polarisation is found in certain 2D or layered ferroelectrics and is relevant for planar devices, and for engineering charged domain

walls for nanoelectronic functionalities.[131] The choice between these cases influences depolarisation fields, domain configurations, and integration with electrodes and interconnects.

4.1. Most relevant oxide ferroelectrics for device candidature: merits and demerits

Lead zirconate titanate remains a benchmark proper ferroelectric with coercive field $\sim 3\text{-}5$ kV/mm[132], high Curie temperature $\sim 350\text{-}360$ deg C[133], and mature processing for thin films. The high endurance and rapid switching speed of PZT established it as the foundational workhorse material for early FeRAM devices.[134] The principal limitations are environmental restrictions associated with lead, difficulties integrating high-quality ultrathin films with modern back-end processes, and well known reliability issues such as fatigue and imprint when interfaces are not carefully engineered.[135]

Hafnia-based ferroelectrics have transformed the device landscape because they maintain switchable polarisation in films only a few nanometres thick and are compatible with atomic layer deposition and back-end thermal budgets[136]. However, they need very large coercive fields to switch ($\sim 100\text{-}270$ kV/mm).[137], [138] Modern perspectives and roadmaps document the stabilising role of dopants, stress, and electrode interfaces in favouring the polar orthorhombic phase of hafnia, and outline remaining reliability challenges that include wake-up, imprint, endurance, and retention trade-offs.[103] First-principles and data-driven studies now indicate that hafnia can behave as a proper ferroelectric, exhibiting a soft polar mode that supports fast polarisation switching, provided that the metastable orthorhombic phase is stabilised by factors such as doping, strain, or thin-film effects.[139]

The multiferroic BiFeO₃ provides room-temperature ferroelectricity with large polarisation and the added functionality of antiferromagnetism,[140] and has been a key model system for research in domain wall nanoelectronics because of its conductive domain walls.[128] The magnetic order in BiFeO₃ is primarily antiferromagnetic and displays only a weak ($\sim 2 \text{ emu/cm}^3$) residual moment from a canted spin structure. Superimposed on the antiferromagnetic ordering is a spiral spin structure, which suppresses the macroscopic magnetisation and prohibits linear magnetoelectric coupling between polarisation and magnetisation in BiFeO₃. This is incompatible with low-energy spintronics. Further integration challenges, leakage, and control of defect chemistry still limit widespread memory adoption for BiFeO₃, but it remains a valuable platform for understanding coupled order parameters.

Bismuth-layered Aurivillius phases such as SrBi₂Ta₂O₉ (SBT) and Bi₄Ti₃O₁₂ have historically offered excellent fatigue resistance($\sim 10^{13}$ cycles)[141], [142] because the fluorite-like Bi₂O₂ layers compensate charge and suppress oxygen vacancy formation[143], [144]. They have a long history of being commercialised in FeRAM devices[144] due to their high fatigue tolerance.[141] Their complex layered chemistry and relatively low remanent vertical polarisation per unit thickness complicate their modern device integration into tunnelling junctions, yet they remain attractive where cycling stability is paramount and will feature centrally in the later sections of this thesis. Another promising member of the Aurivillius family with room temperature multiferroicity is B6TFMO (Bi₆Ti_{2.8}Fe_{1.52}Mn_{0.68}O₁₈). It is a very promising Bi-based high-fatigue-resistant room temperature multiferroic wherein the ferroic order parameters are ferroelectricity and ferromagnetism - which is crucial to single-phase MFTJ device applications.[145]

The following section summarises the major material systems currently explored for ferroelectric memory applications, outlining their fundamental characteristics, advantages, limitations, and potential device implementations.

Table 4. Candidate material systems for ferroelectric devices

<i>Material system</i>	What it is and does	Merits for devices	Demerits and bottlenecks	Typical device usage
<i>HfO₂-based ferroelectrics</i> (<i>HfO₂, Hf_{0.5}Zr_{0.5}O₂ and doped variants such as Si, Y, Gd</i>)	Fluorite-derived oxide in which a metastable polar orthorhombic phase is stabilised at nanoscale by dopants, stress, interface, and kinetics. Switchable polarisation enables nonvolatile behaviour in ultrathin films suitable for CMOS back-end.[103], [146], [147]	Exceptional thickness scaling to 5–10 nm and below, full CMOS compatibility, low-voltage operation, high speed, potential for dense FeFET and FTJ arrays.[46], [136]	High coercive fields (~1-2.7MV/cm)[138], wake-up and fatigue phenomena, retention drift at temperature, variability of polar phase fraction and interface dead layers, reliability under high cycling requires engineering.[148], [149]	Embedded FeFET NVM, 1T-1C FeRAM refresh, selectorless or self-rectifying FTJs for neuromorphic weights, negative-capacitance transistors.[148], [149]
<i>PZT</i> (<i>Pb(Zr,Ti)O₃ near the MPB</i>)	Classic perovskite ferroelectric with large spontaneous polarisation (~88 $\mu\text{C}/\text{cm}^2$)[150] and fast switching used in discrete capacitors and early FeRAM.[151], [152]	High double remnant polarization (2Pr) (12-40 $\mu\text{C}/\text{cm}^2$) [133], [153], [154], [155] and strong piezoelectric response (~200-400pC/N)[156], mature deposition toolsets, well-understood processing windows.[152], [157], [158]	Lead toxicity, imprint and fatigue without proper electrodes, scaling limits for dense CMOS back-end, reliability at high temperature.[152], [159]	1T-1C FeRAM capacitors, piezo-MEMS actuators and sensors, discrete NVM elements.[157], [160]
<i>SBT</i> (<i>SrBi₂Ta₂O₉ (Aurivillius)</i>)	Layered [Bi ₂ O ₂] ²⁺ sheets alternating with perovskite-like slabs. Polarisation arises in the slabs; fluorite-like layers help manage point charge.[161]	Outstanding fatigue tolerance (10 ¹² cycles)[162] with proper electrodes, low imprint and	Smaller remanent polarisation (~5-16 $\mu\text{C}/\text{cm}^2$)[164], [165] than PZT, process complexity, careful Bi	FeRAM capacitors and endurance benchmarks, embedded NVM demonstrators.[161], [165]

		stable switching, good leakage characteristics. [144], [163]	stoichiometry control needed.[165], [166]	
<i>Bi₄Ti₃O₁₂</i> (<i>BiT</i> , <i>Aurivillius</i>) and <i>La-</i> or <i>Nd-</i> substituted derivatives	Layered Aurivillius phase with dominant in-plane polarisation. Lone-pair activity on Bi and Ti off-centring drive ferroelectricity.[167], [168]	Higher in-plane polarisation than SBT (50 $\mu\text{C}/\text{cm}^2$)[169], good thermal stability, compositional flexibility via A-site substitution to improve endurance.[170], [171]	Strong orientation dependence, potential leakage and Bi volatility during growth, lateral polarisation[172]	Thin-film FeRAM test vehicles, fatigue-resistant capacitors when oriented, FTJ barriers in specialised stacks.[142]
<i>BiFeO₃</i> (<i>BFO</i>)	Room-temperature multiferroic perovskite with large polarisation. Domain walls can be conductive and reconfigurable.[140]	Multiferroicity at room temperature, large 2Pr (~50-200 $\mu\text{C}/\text{cm}^2$)[173], [174], potential for magnetoelectric control, domain-wall nanoelectronics.[128], [140], [175], [176]	Leakage due to Fe redox and oxygen vacancies, antiferromagnetic (AFM) structure with a spiral spin arrangement that creates a small magnetisation ($\lesssim 10^{-2}$ μB) [177] and suppresses magnetoelectric coupling, making it unsuitable for low-energy spintronics.[178], [179]	FTJ barriers, MFTJs, domain-wall memory concepts, photovoltaic and spintronic elements.[180]
<i>BaTiO₃</i> (<i>BTO</i>)	Prototype perovskite ferroelectric with moderate 2Pr (10-260 C/cm^2)[181], [182]. Integrates into oxide heterostructures and on Si for photonics.[121], [183]	Negligible loss, fast switching (few nanoseconds)[184], strong electro-optic (~730-1300 pm/V)[185] and electrostrictive coefficients[186], compatibility with photonic modulators,	Deposition on Si requires buffer engineering, integration at sub-10 nm thickness needs careful interface control, retention and imprint depend on electrode and strain.[189]	Electro-optic modulators and RF tuners, energy-storage dielectrics, FTJ barriers in metal–ferroelectric–semiconductor stacks.[187], [190], [191]

		demonstrated FTJ barriers with giant TER when engineered.[187], [188]		
<i>SrBi₂Nb₂O₉</i> (SBN, <i>Aurivillius</i>)	Aurivillius analog of SBT with Nb on B-site. Similar layered mechanism of fatigue-free ferroelectricity.	Good fatigue characteristics (10 ⁶ switching cycles)[192], thermal stability, lower leakage than many perovskites (10 ⁻⁶ A/cm ²).[64],	Lateral Polarisation – which makes it incompatible with vertical architectures;[129], [172] Remanent polarisation modest, composition and texture control needed, Bi volatility.[172]	Endurance-focused FeRAM capacitors and test structures. [64]
<i>Ruddlesden–Popper hybrid-improper ferroelectrics</i> (for example <i>Ca₃Ti₂O₇</i> , <i>Ca₃Mn₂O₇</i>)	Polarisation arises from trilinear coupling between two nonpolar octahedral modes. Enables ferroic control by lattice-mode engineering.[193], [194]	Designable coupling of structure to polarisation, potential magnetoelectric coupling, rich domain topology for reconfigurable states.[195], [196]	Curie temperatures (34-300 K)[197] and leakage vary widely[198], thin-film integration is challenging, readout and endurance for memory still under exploration.[199]	Reconfigurable logic and neuromorphic elements using topological polar textures in superlattices and RP oxides.[199]

5. Aurivillius Phase Materials

Aurivillius phases are layered bismuth-based oxides composed of alternating fluorite-like [Bi₂O₂]²⁺ sheets and perovskite-like slabs, with general formula (Bi₂O₂)²⁺(A_{n-1}B_nO_{3n+1})²⁻ where “n” indicates the number of perovskite layers interleaved between consecutive fluorite-type layers (**Figure 1.6**)[200]. Their layered crystal structure and defect chemistry (particularly the tendency to accommodate oxygen vacancies within the [Bi₂O₂]²⁺ sheets rather than at switching interfaces) gave these oxides an early reputation for unusual cycling robustness in thin-film capacitors, which led to rapid adoption in prototype non-volatile FeRAM stacks during the

1990s.[201], [202] Capacitors based on $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and related layered perovskites could be made essentially fatigue-free with noble-metal electrodes ($\sim 10^{12}$ switching cycles),[162] addressing a central reliability problem that had limited earlier perovskite memories.[203] Subsequent analyses explored why Aurivillius films resisted classical fatigue mechanisms and how electrode choice, interface chemistry, and oxygen activity influenced endurance in SBT capacitors.[141], [203] Together these results established the class as a reference system for long-cycle ferroelectric operation, even though the relatively modest polarisation of some compositions and growth complexity slowed broader commercialisation compared with simpler perovskite.[167]

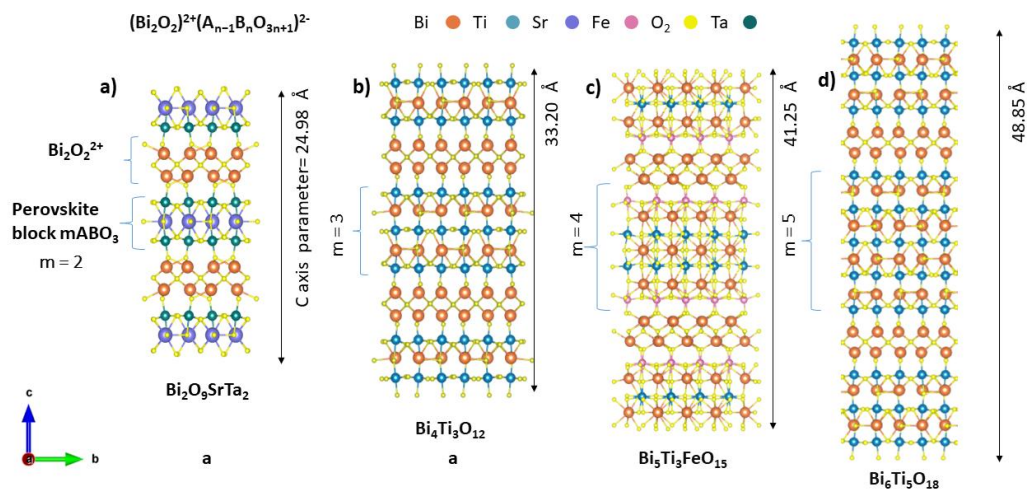


Figure 1.6: Half unit cell crystal structures of Aurivillius Phase compounds. The c-axis parameter is made up of two half-unit cell blocks

5.1. Odd–even Layer Effects and Polarisation Anisotropy

To understand ferroelectricity in Aurivillius compounds, one must begin with the high-symmetry, paraelectric parent structure.[169] Above the Curie temperature, the

structure is typically considered to adopt the tetragonal $I4/mmm$ symmetry,[204], [205] in which the perovskite subcells are undistorted and stacked coherently, and all cation and anion positions are centrosymmetric. In this phase, the overall polarisation vanishes because inversion symmetry is preserved, and the BO_6 octahedra are undistorted, with B-site cations placed at the centres of their octahedra.[205]

Upon cooling below the Curie temperature, Aurivillius compounds undergo various symmetry-lowering distortions. These include polar displacements of B-site cations (e.g. Ti^{4+} , Nb^{5+} , Ta^{5+}) within their octahedra, tilting and rotation of BO_6 octahedra, and displacements of Bi^{3+} ions, driven by their stereochemically active $6s^2$ lone pair electrons. Together, these distortions reduce the symmetry to various orthorhombic ferroelectric space groups, commonly indexed relative to the parent lattice as $\sqrt{2} a_t \times \sqrt{2} a_t \times c_t$ (where t refers to the tetragonal parent). For odd-layered Aurivillius compounds, space groups such as $B2cb$, $B2eb$, or $B1a1$ are often realised, whereas even-layered compounds frequently adopt the $A2_{1am}$ space group, due in part to retention of a mirror plane in the central Bi_2O_2 layer, as described by Newnham *et al.* [167]. Newnham[167] argued that in Aurivillius phases with an even number of m perovskite layers the crystal structure tends to retain a central mirror plane perpendicular to the c -axis. This mirror-plane symmetry suppresses out-of-plane polarisation, confining the spontaneous polarisation to the in-plane direction (typically along the a -axis). Breaking this symmetry to allow a c -axis component is energetically unfavourable. In contrast, Aurivillius phases with an odd number of perovskite layers cannot retain this central mirror plane without significant energetic penalty. As a result, they break the symmetry more readily. Rather than preserving the higher pseudo-tetragonal symmetry of the undistorted structure (with a fourfold axis along c), odd-layered Aurivillius phases (**Figure 1.6 b and d**) typically distort to lower-

symmetry orthorhombic space groups (e.g. $B2cb$), where a twofold rotation axis along a remains. This reduced symmetry allows a major in-plane polarisation along a axis, and a minor but symmetry-allowed out-of-plane (c -axis) component.

Colfer *et al.* [204] and Keeney *et al.* [144], [206] demonstrated through atomic-scale crystallographic and spectroscopic analysis of the five-layer Aurivillius phase $\text{Bi}_6\text{Ti}_3\text{Fe}_{1.5}\text{Mn}_{0.5}\text{O}_{18}$ that the octahedral framework exhibits distinct layer-dependent distortions. Specifically, they observed a progressive increase in octahedral tilting toward the central perovskite layers, which competes with the degree of tetragonal elongation of the TiO_6 octahedral- this tetragonal distortion being strongest near the outer perovskite layers adjacent to the $(\text{Bi}_2\text{O}_2)^{2+}$ sheets. Such competing distortions modify local symmetry and directly influence the spatial distribution of spontaneous polarisation and magnetic interactions across the layered structure. Atomic-resolution mapping of cation displacements confirmed that the polarisation magnitude is greatest in the outer perovskite slabs, where Ti-O bond elongation is most pronounced, and diminishes toward the interior layers where tilting dominates.

This gradient in local distortion has significant implications for the material's ferroelectric and multiferroic behaviour: the asymmetric distribution of polarisation and octahedral tilt governs how electric and magnetic order parameters couple, how switching pathways propagate through the layered lattice, and how the energy landscape for domain formation evolves. Understanding such non-uniform structural responses is therefore central to understanding polarisation behaviour in Aurivillius phases and motivates further inquiry into how lattice distortions interact with growth-induced features such as step and boundary defects.

5.2 Bismuth Titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$)

Among Aurivillius phase materials, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BiT, $n = 3$) has attracted sustained interest as both a model system for studying layered ferroelectric physics and a candidate material for non-volatile memory applications. Its three-layer perovskite structure (monoclinic, $a = 5.45 \text{ \AA}$, $b = 5.41 \text{ \AA}$, $c = 32.84 \text{ \AA}$) [318],[319] places it in the odd-layered category discussed above: the absence of a central mirror plane perpendicular to the c -axis permits a minor but symmetry-allowed out-of-plane polarisation component ($\sim 4 \text{ \mu C/cm}^2$ along c), alongside a dominant in-plane polarisation ($\sim 50 \text{ \mu C/cm}^2$ along a) [209], [235], [236]. The large polarisation anisotropy and relatively low Curie temperature ($\sim 675 \text{ }^\circ\text{C}$) make BiT tractable for thin-film growth and characterisation.

From a device perspective, BiT is notable for its fatigue resistance: thin-film capacitors based on BiT have demonstrated endurance exceeding 10^{13} switching cycles, attributed to the role of the $[\text{Bi}_2\text{O}_2]^{2+}$ layers in accommodating oxygen vacancies away from the switching interface. [203]

The principal challenge in using BiT for vertical device integration is its polarisation anisotropy. The dominant in-plane spontaneous polarisation is a direct consequence of the monoclinic symmetry and the twofold rotation axis along a , and efforts to enhance the c -axis component must therefore engage with the crystal's symmetry. [207] Strain engineering through substrate-induced lattice 3.837 and rare-earth A-site substitution have both been explored as routes to symmetry modification, but neither has yielded a reliable, scalable route to robust out-of-plane switching at low voltages. [208], [209], [210] This polarisation challenge, and the question of whether growth-

mode control can address it without chemical modifications like doping, motivates the experimental strategy of Chapter III.

Growth of phase-pure BiT thin films presents additional complications that are specific to its chemistry. Bismuth is highly volatile at the temperatures required for Aurivillius phase crystallisation (600–850 °C), and stoichiometric Bi loss during deposition leads to secondary phases, increased OPB density, and degraded ferroelectric properties. [211] Successful growth therefore requires either Bi-excess precursor delivery or an adsorption-controlled regime in which excess Bi re-evaporates, leaving the Ti flux to determine the final perovskite stoichiometry. [168], [172] The $n = 3$ stacking sequence (alternating $[\text{Bi}_2\text{O}_2]^{2+}$ fluorite layers and three-unit-cell-thick $[\text{BiTi}_2\text{O}_7]^{2-}$ perovskite slabs) also demands that the deposition process reproduce the correct layering order at each growth step, since steric offsets propagate as OPB defects. [212] Together, stoichiometric sensitivity, Bi volatility, and the structural complexity of the layered unit cell make BiT a demanding but instructive test case for the growth optimisation strategy developed in this thesis to get Aurivillius phase thin films to be closer to device application.

5.3. Origin of ferroelectricity and multiferroicity

Ferroelectricity in Aurivillius phases originates from the off-centring of B-site cations (e.g. Ti^{4+} , Nb^{5+} , Ta^{5+}) within BO_6 octahedra, combined with the stereochemically active $6s^2$ lone pair of Bi^{3+} , which enhances lattice asymmetry and stabilises the polar state. [213] The layered architecture supports strong in-plane polarisation while permitting chemical flexibility through A- and B-site substitution. Incorporation of magnetic ions such as Fe^{3+} or Mn^{3+} into the perovskite slabs introduces coupled magnetic order, giving rise to room-temperature multiferroicity in systems such as

$\text{Bi}_6\text{Ti}_3\text{Fe}_{1.5}\text{Mn}_{0.5}\text{O}_{18}$. [214], [215] Atomic-scale studies show that layer-dependent octahedral tilts and site-selective cation partitioning underpin this coupling, linking local distortions to the coexistence of switchable polarisation and weak ferromagnetism. [93], [204]. These mechanisms highlight how lattice distortions and cation chemistry jointly determine the balance between ferroelectric and magnetic order in layered bismuth oxides..

5.4. Origin of fatigue tolerance

The unusually high fatigue tolerance of Aurivillius phases is widely linked to how their layered chemistry manages bound charge and point defects. The $[\text{Bi}_2\text{O}_2]^{2+}$ sheets act as internal charge-compensating reservoirs that limit deleterious oxygen vacancy drift and reduce domain-wall pinning during repeated switching. [203] Experimental impedance and imprint studies on SBT found smaller voltage offsets and weaker defect-dipole contributions compared to classic PZT stacks with identical electrodes, consistent with a lower tendency for vacancy accumulation at the switching interface. [216] Comparative kinetic models of SBT, SBN and PZT (composition defined earlier) revealed distinct roles of ionic conductivity and interface barrier formation differ across the chemistries of these material systems, providing a rational basis for the superior cycling endurance of Aurivillius films under otherwise similar operating conditions. [217]

5.5. The need for growth optimisation in layered materials with volatile elements

Realising the intrinsic advantages of Aurivillius phase oxides requires growth strategies that account for the volatility of cations, particularly Bi, during

high-temperature deposition. Systematic studies across multiple deposition techniques have shown that Bi loss becomes significant even below 600 °C and is particularly acute in the 600 to 850 °C range typically used for epitaxy and crystallisation.[211] To counter this, successful growth protocols either introduce Bi excess into the precursor stream or operate under adsorption-controlled regimes with a sustained Bi overpressure, allowing the incoming Ti- or Ta-containing flux to determine the final stoichiometry while excess Bi re-evaporates.[168], [172] Recent studies on five-layer members has explicitly demonstrated the need for Bi excess (~50-100 %) [144], [204], [218] during growth in order to obtain phase-pure (for B6TFMO[144] and BTFO[129]), with reproducible ferroelectric switching[93]. These constraints do not act in isolation: oxygen partial pressure, heating profiles, and substrate selection all interact with Bi volatility, and the challenge is further compounded by the large unit cells and anisotropic thermal expansion inherent to layered materials.[144], [204] Consequently, careful optimisation of the growth-window is essential for device-grade films, where a narrow stoichiometry corridor yields the correct phase, suppresses out-of-phase boundary defects and intergrowths, and preserves the low vacancy concentrations that underpin the well-known cycling endurance of Aurivillius phases.

6. Synthesis of Aurivillius Phase Materials

Producing high-quality Aurivillius-phase thin films requires control over the earliest stages of nucleation and crystal growth, careful management of lattice mismatch and strain, and deposition strategies that guard against bismuth loss while stabilizing the desired layered architecture.[168], [172] A coherent synthesis strategy begins with a microscopic understanding of how adatoms arrive, diffuse, and aggregate on the

substrate surface, because these early events set the density of nuclei, the morphology of the first monolayers, and the propensity for defects that later propagate as stacking faults, out-of-phase boundaries, or intergrowths. Classic nucleation and growth theory links island densities and morphologies to adatom diffusivity, binding energies, and deposition flux through Arrhenius-type kinetics,[219] while the macroscopic growth “mode” that emerges reflects the balance between film–substrate and film–film interfacial energies as well as the evolving elastic energy from lattice mismatch.

The synthesis of Aurivillius phase thin films is complicated by their large unit cells, and the volatility of Bi. Achieving phase-pure, defect-minimised films requires a careful balance of thermodynamic and kinetic control during epitaxy, combined with deposition techniques that can maintain stoichiometry and structural integrity.

6.1. Growth modes and epitaxial processes

Epitaxial strain arises when a thin film is grown on a lattice-matched crystalline substrate and is constrained to adopt the substrate's in-plane lattice parameter rather than its own bulk equilibrium value. Hence, when an Aurivillius thin film is grown on a lattice-matched crystalline substrate, the film is constrained to adopt the in-plane lattice parameter of the substrate, provided the film thickness remains below a critical threshold. This constraint is termed epitaxial strain, and its magnitude is quantified by the misfit parameter:

$$f = \frac{a_s - a_f}{a_f} \quad 3,$$

where a_s and a_f are the in-plane lattice parameters of the substrate and the bulk film, respectively. Thin film growth generally proceeds through three classical epitaxial modes, first classified by Bauer (1958)[220]: Frank–van der Merwe (FM)[219] or

layer-by-layer growth, Volmer–Weber (VW)[219] or island growth, and Stranski–Krastanov (SK)[219] (**Figure 1.7**), which begins with layers but transitions to islands once strain energy exceeds a critical threshold.[220] The growth mode that emerges in a given experiment is governed by two interconnected variables, among many others: the epitaxial strain imposed by the substrate, and the supersaturation at the growth front. Both are introduced here because they recur throughout this thesis and underpin the experimental strategy of Chapters III–V. For Aurivillius oxides, FM growth is favoured when lattice mismatch with the substrate is small, producing atomically flat terraces and controlled layering. However, strain accumulation in thicker films or larger mismatches can trigger SK growth, leading to island formation, stacking faults, or intergrowths.

For $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BiT) grown on SrTiO_3 (STO, $a = 3.905 \text{ \AA}$), the positive misfit (+1.77% relative to the BiT pseudocubic parameter $a_p \approx 3.837 \text{ \AA}$) imposes a biaxial tensile strain in the film plane, partially accommodated by a compressive Poisson response out of plane. This coherent, pseudomorphic state is thermodynamically metastable: as the film thickens, accumulated elastic strain energy eventually exceeds the cost of introducing misfit dislocations at the film–substrate interface.

The Matthews–Blakeslee model provides a criterion for the critical thickness at which misfit dislocations form to relieve strain.[221] In Aurivillius phases, such strain relaxation often couples to structural anisotropy, promoting out-of-phase boundaries (OPBs) and secondary phases.[222]

In addition, step-flow growth represents a distinct kinetic pathway, particularly relevant when ad-atom diffusion lengths exceed terrace widths at elevated substrate temperatures.[223] Here, atoms attach preferentially to step edges rather than

nucleating islands on terraces, enabling continuous advancement of atomic steps across the surface. Such growth minimises defect densities and promotes highly ordered terraces. Under certain conditions, step-flow can give rise to spiral growth,[224] which arise when a screw dislocation intersects the film surface, producing continuously advancing steps that rotate around the dislocation core and propagate according to the Burgers vector. This mechanism was first described by Burton, Cabrera, and Frank (BCF theory) [225] where screw dislocations act as persistent step sources- eliminating the need for repeated two-dimensional nucleation. As shown in **Figure 1.7 (g–k)**, as adatoms diffuse across the surface, they attach preferentially to the edges of these continuously generated steps, producing a helical or spiral growth front that propagates outward from the dislocation core. The resulting surface morphology consists of concentric terraces that maintain a constant step height but gradually decrease in radius, oriented along crystallographic directions such as [100] or [110].

Step-flow growth, in which adatoms migrate across terraces and incorporate at existing step edges rather than nucleating new islands, is one of the principal growth modes relevant to Aurivillius phase thin films under near-equilibrium deposition conditions. While step-flow produces smooth, layer-by-layer advance of the growth front in the ideal case, real surfaces are susceptible to lateral instabilities that distort step morphology over time. The most significant of these is the Bales–Zangwill instability, [223] which arises from an asymmetry in adatom attachment kinetics at step edges. When adatoms arriving on a terrace preferentially attach to the ascending (upper) side of a step rather than descending to the terrace below, small perturbations in step-edge geometry (unavoidable at any real surface) are amplified rather than smoothed. A slightly protruding section of a step edge captures more adatoms from

the surrounding terrace than a recessed section, causing the protrusion to advance faster and the perturbation to grow. Over time, initially straight steps become progressively meandered.

This uphill adatom flux is sustained by the Schwoebel–Ehrlich barrier,[226], [227] an additional energy barrier that adatoms must surmount to descend from one terrace to the one below. In the absence of this barrier, adatoms would equilibrate freely across the surface and perturbations would be damped. The barrier effectively creates a directional preference: adatoms stay on the terrace on which they land, attach preferentially at ascending step edges, and reinforce the Bales–Zangwill mechanism. The result is a characteristic meandered step morphology in which step edges develop lateral undulations on a length scale determined by the ratio of adatom diffusivity to deposition flux and the magnitude of the Schwoebel–Ehrlich barrier.

In Aurivillius phase systems, where the layered unit cell imposes a large step height ($\sim 0.5 \times c$, corresponding to half a unit cell) and where Bi volatility and anisotropic surface diffusion introduce additional kinetic complexity, these instabilities are particularly relevant. The morphology of the growing surface: whether steps are straight, meandered, or disrupted by spiral growth at dislocation cores, has direct consequences for defect formation, OPB density, and the distribution of polarisation in the final film. Understanding step-flow instabilities therefore provides the mechanistic context for interpreting how deposition conditions translate into the structural and functional properties of Aurivillius thin films.

This hence combined with the higher surface energy of stepped substrates allow steady-state growth even under conditions of low supersaturation ($\alpha = P/P_{eq}$, where P is the local precursor partial pressure and P_{eq} its equilibrium vapour pressure; see

Section 6.5 for a full explanation) [224], as the dislocation supplies an uninterrupted source of new step edges. Consequently, spiral growth plays a crucial role in controlling surface morphology and defect evolution in oxide thin films.

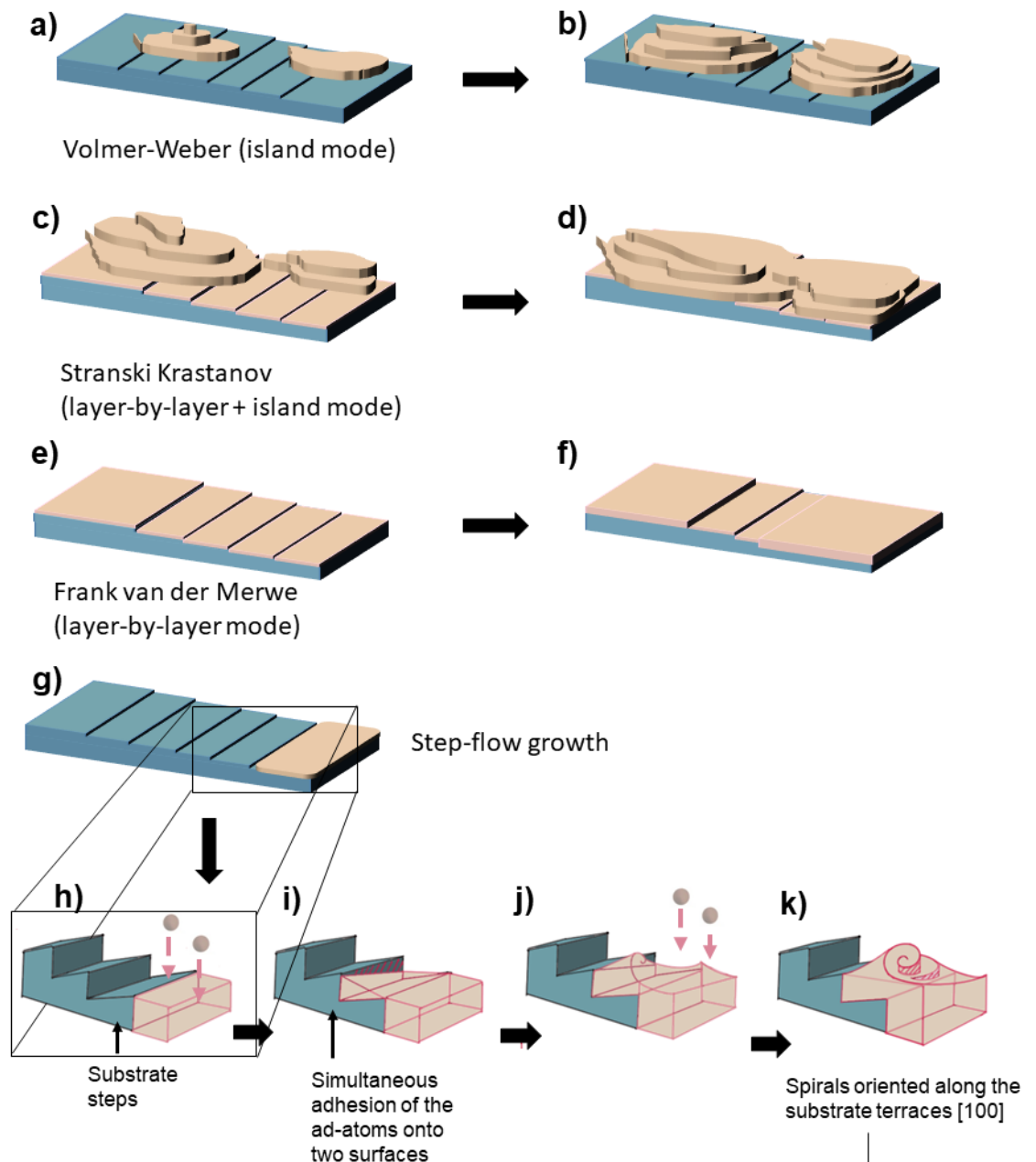


Figure 1.7: a-f) Schematic showing three classical epitaxial growth modes: Volmer–Weber island mode (a–b), Stranski–Krastanov layer-plus-island mode (c–d), and Frank–van der Merwe layer-by-layer mode (e–f), as described by Bauer[220] and

Venables[219]. h-k) Schematic showing the process of step flow growth leading to spiral formation.

6.2. Direct Liquid Injection Chemical Vapour Deposition (DLI-CVD)

DLI-CVD has emerged as a particularly effective method for growing Aurivillius thin films due to its ability to deliver precise stoichiometry in multi-cation systems. In this process, organometallic precursors (like Bi, Ti, Fe, and Mn) are dissolved in a solvent, injected into a vapouriser, and transported by carrier gas to a heated substrate, where decomposition and crystallisation occur (**Figure 1.8**). [228]

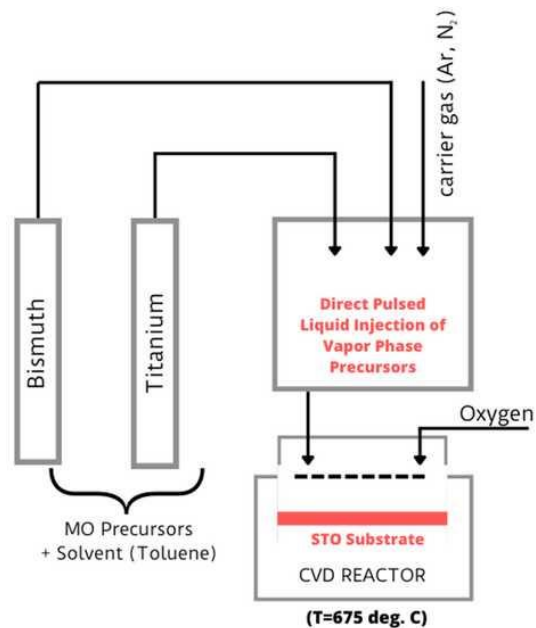


Figure 1.8: Schematic of the DLI-CVD system used for industrially-compatible thin film deposition

The method enables accurate Bi overpressure control, which is essential for suppressing Bi volatility and minimising secondary phases. Keeney *et al.* (2022,

2023)[222], [229] demonstrated that sequential DLI-CVD growth of multiferroic $\text{Bi}_6\text{Ti}_{2.9}\text{Fe}_{1.5}\text{Mn}_{0.6}\text{O}_{18}$ (B6TFMO) with Bi-rich pulses suppressed intergrowths and preserved switchable ferroelectric polarisation down to ~ 8 nm thickness. Compared to Molecular Beam Epitaxy (MBE) and Pulse Laser Deposition (PLD), DLI-CVD offers superior scalability and defect control without ultra-high vacuum, although it provides slightly lower crystalline perfection than MBE and is more sensitive to precursor stability than PLD.[230]

6.3. Parameters Governing the Growth Window

Out of all the parameters that govern film growth, the following are identified as both controllable and critical to the successful synthesis of phase-pure Aurivillius films:

- Bismuth excess: Due to the high volatility of Bi at elevated growth temperatures, a deliberate Bi overstoichiometry is required to maintain compositional balance. Studies have shown that incorporating a Bi excess of $\sim 40\text{--}50\%$ effectively compensates for Bi loss, reducing impurity phase formation to below 0.5% and preserving ferroelectric behaviour even in ultrathin films. [222], [229]. The bismuth excess hence needs to be optimized per process.
- Kinetic control (precursor flow rate): The precursor flow rate determines the rate of adatom arrival at the substrate surface and hence the effective supersaturation (which is the ratio of local partial pressure during deposition and equilibrium partial pressure (See Section 6.5)). High flow rates increase supersaturation and promote rapid nucleation, often leading to three-dimensional islanding and surface roughness. Conversely, excessively low flow rates can result in insufficient nucleation density and incomplete surface

coverage. Sequential or pulsed injection strategies, where Bi and B-site precursors are alternately delivered, help maintain kinetic balance and promote ordered Aurivillius stacking. [204], [231]

- Supersaturation and precursor concentration: Supersaturation (α), is a state where a solution contains more dissolved solute than it could normally hold under equilibrium conditions. It's a highly unstable temporary condition that occurs past normal saturation. Mathematically, it is defined as the ratio of partial pressure of depositing species (P) to their equilibrium vapour pressure (P_{eq}), [232] governs nucleation and growth dynamics:

$$\alpha = \frac{P}{P_{eq}}$$

1

The degree of supersaturation, dictated by the local precursor concentration and temperature, is one of the primary parameters that dictates the rate and morphology of the growth modes: layer-by-layer, step-flow, or island modes. [219], [233]

- Substrate influence: The choice of substrate strongly impacts lattice matching, strain accommodation, and overall epitaxial quality. Perovskite-based substrates such as SrTiO₃ (STO) or (La,Sr)(Al,Ta)O₃ (LSAT) offer close lattice compatibility and thermal expansion matching with Aurivillius phases, promoting coherent epitaxy. Additionally, the substrate's surface termination and miscut angle influence step density and dislocation formation, which in turn govern domain orientation, twinning, and the likelihood of spiral growth initiation. [234]

6.4. Kinetic Considerations and Avrami's Model

Beyond the fundamental thermodynamic parameters of temperature, pressure, and chemical potential, which govern supersaturation, phase stability, and interfacial strain, factors such as lattice mismatch and kinetic barriers also critically influence film growth in chemical vapour deposition. While thermodynamics sets the driving force for nucleation and growth, the kinetics of how nuclei form and evolve strongly determines Aurivillius film quality. These kinetics have long been described by the Johnson–Mehl–Avrami–Kolmogorov (JMAK) framework, first formalised by Avrami in a series of papers (1939–1941).[235], [236], [237] The model expresses the transformed volume fraction $X(t)$ as:

$$X(t) = 1 - e^{-kt^n} \quad 2$$

where k is a temperature-dependent rate constant and n (the Avrami exponent) reflects the dimensionality of growth and the nucleation mechanism (continuous vs. site-saturated). In thin film epitaxy, values of n provide qualitative insight into whether growth proceeds via island nucleation, two-dimensional layer advance, or a mixture of both[238]. In Aurivillius films, the Avrami model is particularly relevant because their layered structure and anisotropy often bias growth toward two-dimensional step-flow rather than fully three-dimensional nucleation. For example, high Bi supersaturation can increase nucleation density, leading to rapid island formation (analogous to Volmer–Weber), whereas optimised Bi overpressure and oxygen partial pressure suppresses nucleation density, reducing n toward values consistent with layer-by-layer advance.[219] Experimental Avrami analyses of oxide thin films has

shown that adjusting growth temperature and precursor supply shifts the kinetics between these competing modes, ultimately determining which type of defects dominate.[239]

Thus, Avrami's framework complements epitaxial growth models: while Bauer's classification distinguishes equilibrium growth morphologies (FM, VW, SK), Avrami kinetics quantify the pathways and timescales by which films evolve toward these regimes. It should be noted, however, that the classical JMAK framework assumes homogeneous nucleation and isotropic growth in bulk systems. Epitaxial thin films often deviate from these assumptions due to anisotropy, surface/interface effects, and substrate-induced constraints. Consequently, Avrami exponents in thin films are best interpreted qualitatively, as indicators of relative growth modes rather than as strict dimensionalities.

7. Defects in Layered Aurivillius Phases: Structure, Consequences, and Control

In layered Aurivillius ferroelectrics, defects such as stacking faults, out-of-phase boundary (OPB) defects (**Figure 1.9**), and intergrowths critically influence polarisation switching, domain stability, and leakage.[163], [212], [246] Stacking faults, which are planar defects in crystals that occur when the repeating sequence of atomic layers is disrupted, arise from deviations in the regular sequence of perovskite and $(\text{Bi}_2\text{O}_2)^{2+}$ fluorite layers, disrupting *c*-axis periodicity.

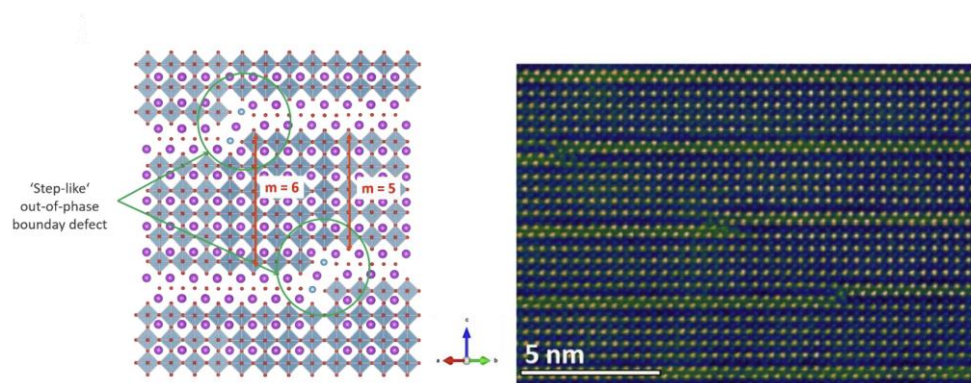


Figure 1.9. Left: Schematic of an OPB defect in Aurivillius phase thin films where ‘*m*’ refers to the number of perovskite blocks within the bismuth oxide layer. Right: Transmission Electron Microscopy showing OPB defects in $\text{Bi}_6\text{Ti}_3\text{Fe}_{1.5}\text{Mn}_{0.5}\text{O}_{18}$. Figure reproduced from L. Colfer ‘Multiferroic investigations of Aurivillius phase thin films’ with permission.[234]

An out-of-phase boundary (OPB) defect (sometimes also called an anti-phase boundary (APB) in related materials) is a planar defect that occurs in layered or ordered crystalline structures when there is a translational shift in the stacking sequence between two adjacent regions of the crystal. During thin-film growth, a local steric offset can occur, leading to a displacement of one Aurivillius block relative to its neighbour. OPBs are especially significant because they couple directly to ferroic properties. In earlier work, Keeney *et al.* showed that OPBs act as preferential sites for Fe and Mn partitioning in multiferroic $\text{Bi}_6\text{Ti}_3\text{Fe}_{1.5}\text{Mn}_{0.5}\text{O}_{18}$, thereby modifying local exchange interactions and stabilising magnetic order. In later work[93] it was demonstrated that OPBs can also nucleate charged domain walls and polar vortex states. The lattice discontinuity at an OPB introduces local polar mismatches, which under strain and electrostatic constraints stabilise otherwise unstable head-to-head or tail-to-tail walls, and in some cases closed-loop polarisation textures.[93] This

highlights the necessity to model such defects when assessing crystalline quality and functional performance in these materials.

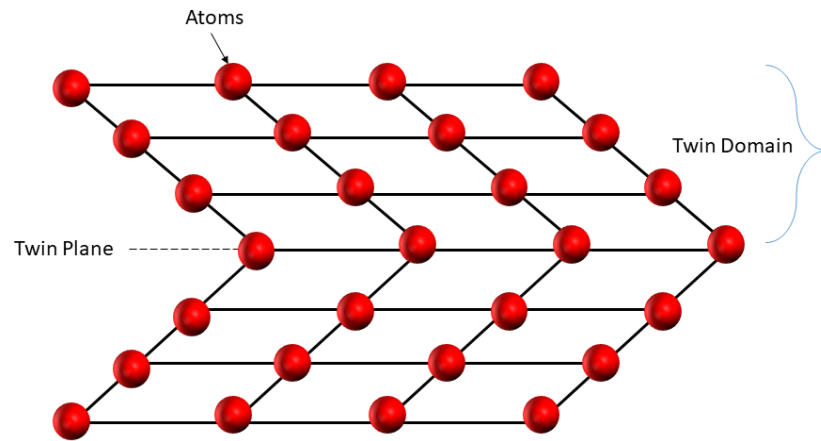


Figure 1.10: Schematic showing crystal twinning

Crystal twinning (**Figure 1.10**) is another pervasive defect in Aurivillius thin films, arising when symmetrically related domain orientations nucleate and propagate during growth. Nanotwinned (NT) materials have attracted attention across diverse fields for their enhanced conductivity, mechanical robustness, and unique structural characteristics.[247] In layered ferroelectrics such as $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{SrBi}_2\text{Ta}_2\text{O}_9$, twinning arises from the small energy differences between equivalent domain orientations, stabilised by the pseudo-tetragonal or orthorhombic unit cell symmetry.[248], [249] For instance, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films on SrTiO_3 often exhibit 90° rotated domains around the c-axis (a- versus b-axis alignment), reflecting symmetry relations between the film and substrate surface planes.[250] Twin domains introduce additional domain walls that strongly affect polarisation behaviour: they can modify switching pathways,[251] alter coercive fields[252] and contribute to fatigue by pinning or impeding domain wall motion.[253] Structurally, twinning is often visible

in TEM as alternating lamellae of mirror-related domains (**Figure 1.10**).[254] From a device perspective, twinning is generally detrimental, as it disrupts long-range ferroelectric coherence and complicates integration into capacitor and tunnel junction structures.[247] In Aurivillius films grown by DLI-CVD, the propensity for twin formation depends on factors such as supersaturation, substrate step morphology, and bismuth volatility. Careful tuning of these parameters can suppress twin nucleation and improve epitaxial quality.

7.1 Experimental Characterisation of Structural Defects

A precise understanding of the structure–property relationships in Aurivillius phase thin films requires not only control over synthesis parameters but also reliable characterisation of structural defects that inevitably arise during growth. Defects such as stacking faults, out-of-phase boundaries (OPBs), intergrowths, and twin domains play a decisive role in determining ferroelectric and multiferroic behaviour, influencing domain wall motion, leakage pathways, and overall polarisation stability. Therefore, a detailed structural analysis is indispensable for correlating microstructural features with macroscopic functional properties.

A variety of experimental techniques are employed to probe such defects at different length scales. Transmission electron microscopy (TEM) and scanning TEM (STEM) provide direct real-space imaging of atomic stacking sequences, dislocations, and interface terminations, often coupled with electron diffraction or energy-dispersive X-ray spectroscopy (EDS) to assess local chemistry. High-resolution atomic force microscopy (AFM) can reveal step-flow features, growth spirals, and terrace morphology, which indirectly reflect the presence of screw dislocations or step bunching phenomena.

However, while real-space imaging offers direct visualisation, it is inherently limited by sampling volume and field of view. In contrast, X-ray diffraction (XRD) enables the statistical characterisation of structural coherence and defect distributions over macroscopic sample volumes. Subtle features in XRD patterns- such as peak broadening, asymmetry, or splitting-can reveal the presence of strain fields, lattice distortions, stacking disorder, or the emergence of OPBs. For instance, anisotropic peak broadening in Aurivillius phase reflections has been directly linked to planar faults and intergrowths disrupting the periodic stacking of perovskite and Bi_2O_2 layers.[246]

Thus, XRD serves as a powerful, non-destructive probe for quantifying defect-induced structural variations, complementing high-resolution microscopy. As the following section demonstrates, the modelling of XRD peak shapes provides not only a diagnostic tool for identifying defect types but also a predictive framework to interpret how specific structural irregularities- such as OPBs or stacking faults- manifest in reciprocal space. This quantitative approach bridges atomic-scale disorder with diffraction observables, enabling a deeper understanding of defect formation and its consequences for ferroelectric functionality.

7.2. Modeling Defect-Induced Broadening and Splitting of XRD Peaks

The modelling of defects in layered systems using X-ray diffraction (XRD) has an evolving history, beginning with early statistical treatments and progressing toward modern analytical and computational frameworks tailored to complex oxides (Table 5). The first systematic approach was the Hendricks–Teller statistical layer-lattice model (1942)[255], which introduced transition probabilities between stacking states to describe diffraction from one-dimensional disordered sequences . This framework

showed how random stacking faults affect diffraction, but its applicability was limited to nearest-neighbour statistics and simple chemistries, making it less suitable for complex layered oxides. In parallel, Warren's work (1959)[256] offered a means of connecting XRD peak broadening to defect densities, dislocations, and microstrain in both layered and non-layered crystals. While this remains a standard baseline method for interpreting powder profiles, it does not distinguish between different types of planar disorder, as multiple defect mechanisms can produce similar broadening effects.

The Hendricks–Teller model was later applied directly to graphite intercalation compounds (1985),[257] where it successfully captured disorder in stacked graphite layers. This marked an important milestone in adapting classical models to layered systems, though the treatment still relied on simple staging probabilities and could not accommodate chemically complex oxides. Around the same time, new attention was given to artificial heterostructures: the Locquet superlattice disorder model (1989)[258] developed a general diffraction model for multilayers that incorporated both discrete thickness fluctuations and interface roughness. This model explained the linewidth increase of satellite peaks at high scattering angles, but it was designed for periodic superlattices and was less capable of handling natural non-periodic stacking faults.

A key breakthrough came with the recursion method of Treacy (1991),[259] implemented in the widely used program DIFFaX, which enabled efficient simulation of diffraction from crystals containing planar faults, stacking disorder, and intergrowths. DIFFaX became a workhorse software for simulating XRD of faulted layered systems ranging from oxides to clays, zeolites, and graphite. Nevertheless, it

remains a kinematic method, and while powerful for forward simulations, it is prone to parameter degeneracy where different disorder models can generate nearly identical diffraction patterns, requiring independent constraints for reliable fits. Moreover, the stacking faults in this model would have to continue throughout each layer, with no way to simulate parallel faults of varying degrees in a block of film. Building on this foundation, Fullerton (1992)[260] extended diffraction refinement to metallic and oxide superlattices, offering a quantitative method for extracting interface widths and thickness fluctuations from high-resolution XRD. Yet this method was most effective in nearly periodic systems and was not well-suited to the real-life irregular defects.

In the early 2000s, stochastic approaches gained momentum. Varn and Crutchfield (2002)[261] applied hidden Markov models (HMMs) to diffraction from close-packed structures such as ZnS, enabling the inference of richer sequence statistics beyond simple stacking-fault fractions. Later work[262] extended this to derive diffraction patterns directly from HMM parameters, demonstrating the theoretical power of information-theoretic approaches but also highlighting their computational intensity and limited application to complex oxides. At the same time, DIFFaX was applied to real systems such as layered double hydroxides (2005)[263] and Li_2MnO_3 -based cathodes,[264] where it successfully reproduced mixed stacking fault fractions and quantified stacking-fault frequencies in combination with complementary probes like solid-state NMR. These studies reinforced both the utility and the limitations of DIFFaX: while versatile, it required careful external validation to avoid overfitting. It also highlighted that DIFFaX could simulate stacking faults to some degree, but there was still no solid proof of it handling other types of faults or unique parallel faults in a system.

Alternative models emerged in the 2020s- the Debye scattering equation (2020)[265] was applied to nanocrystalline layered systems such as kaolinite and clays, explicitly separating stacking disorder from finite-size effects in powder profiles. Although rigorous, the Debye approach is computationally demanding for large layered systems and requires realistic particle size distributions for reliable modelling. In parallel, FAULTS and TOPAS workflows (2020)[266], [267] embedded DIFFaX-style recursion within Rietveld refinement, providing a practical way to co-refine stacking disorder alongside the underlying crystal structure in layered oxides .

For Aurivillius oxides, connections between structural defect density and XRD peak splitting was made, however specific defect modelling began to appear later. Zurbuchen *et al.* [212] were among the first to quantitatively examine how defect populations, particularly stacking irregularities and local misorientations, influence both the broadening and asymmetric splitting of (00 ℓ) reflections in layered oxide thin films. Their work demonstrated that increasing defect density led to a systematic evolution in peak shape and intensity distribution, reflecting a direct structural–diffraction link rather than purely instrumental broadening. Building upon this, a later study on Bi-titanate derivatives (2015)[268] reported that out-of-phase boundaries (OPBs) selectively split certain 00 ℓ reflections, such as 004 and 0012, while others like 006 remained unsplit. This established a case-specific connection between OPBs and diffraction features, but it lacked a predictive, generalisable framework. The first such general framework was introduced by Whatmore *et al.* (2025)[269], who proposed an analytical OPB model parameterised by three physically meaningful variables: the step size, the OPB tilt angle, and the OPB spacing distribution. This model not only reproduced observed splitting in systems such as Bi₄Ti₃O₁₂ and SrBi₂Ta₂O₉ but also predicted in advance which 00 ℓ peaks would split and by how

much. Unlike earlier empirical reports, it provided a rigorous quantitative basis for linking XRD signatures to defect structures, marking a decisive advance in the analysis of non-stacking fault defects in layered systems.

Taken together, these developments chart a trajectory from the early statistical models of Hendricks–Teller, through recursion-based and superlattice approaches like DIFFaX and Locquet, to advanced stochastic and Debye scattering methods, and finally to OPB-specific analytical models such as Whatmore’s. Each approach contributes unique insights: while early methods captured the essence of planar disorder, modern frameworks provide predictive capacity tailored to layered oxides.

Despite these advances, most existing XRD defect-modelling approaches either treat disorder statistically or restrict analysis to simple stacking-fault sequences. The unique morphologies of layered oxides, particularly those that generate out-of-phase boundaries through step-flow and spiral growth, remain largely unmodelled, despite their morphology arising from these defects (making their understanding all the more crucial). No current framework fully models the diffraction of 3-D growth spirals in layered thin films, leaving a critical gap that motivates the development of new models tailored to defect-driven morphologies in layered thin films. **Table 5** below presents a summarized version of the literature survey described above.

Table 5: Overview of XRD Models

<i>Reference and approach</i>	Layered system focus	Defect type captured	What the model or tool does	Main drawbacks or limits
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Hendricks–Teller statistical layer-lattice model J. (1942)[255]	Close-packed and layered lattices with 1D sequence disorder	Random stacking faults, layer probability chains	Analytic treatment of X-ray interference from partially ordered layer lattices using transition probabilities between stacking states. Canonical starting point for planar disorder analysis.	Assumes 1D disorder and simple nearest-neighbour statistics; cannot easily accommodate complex layer chemistries or finite domain distributions without extensions.
Warren line-broadening and defect analysis (1959)[256]	Layered and non-layered crystals	Dislocations, size strain, stacking faults	Connects peak breadth and moments to defect densities and microstrain in powder XRD; widely used baseline for defect broadening.	Not specific to layered stacking sequences; conflates multiple broadening sources without explicit stacking statistics.
Hendricks–Teller in intercalated graphite (1985)[257]	Stage-n graphite intercalation compounds	Random stacking in stage structures	Applies Hendricks–Teller to model out-of-plane profiles of staged graphite, a canonical layered system.	Effective for quasi-1D stacking but not chemistry-complex oxides; relies on simple stage probabilities.
Locquet superlattice disorder model (1989)[258]	Artificial superlattices and multilayers	Discrete layer-thickness fluctuations, interface roughness	General diffraction relation for superlattices with discrete and continuous fluctuations; explains peak linewidth increases at large q.	Designed for periodic multilayers rather than natural polytypism; focuses on thickness fluctuations more than faulted layer sequences.
Treacy recursion method and DIFFaX (1991); DIFFaX manual[270]	Broad layered materials including oxides, zeolites, LDHs, graphite	Coherent planar faults, stacking disorder, intergrowths	Recursion algorithm to compute diffracted intensities from crystals containing planar faults; implemented in DIFFaX for kinematic XRD and NPD simulations of stacking-faulted structures.	Kinematic scattering only; parameter degeneracy can occur; forward simulation rather than unique inversion; quality depends on accurate layer structure factors.
Fullerton quantitative superlattice refinement (1992)[260]	Metallic and oxide superlattices	Interface roughness, layer-thickness error	Refinement procedure to extract periodic layering parameters from HRXRD, including interface widths.	Assumes near-periodicity; less suited to nonperiodic stacking faults such as OPBs in natural layered oxides.

<i>Varn–Crutchfield inverse methods</i> (2002)[261]	Close-packed layer sequences (e.g., ZnS)	Planar disorder beyond simple fault models	Infers hidden Markov processes that generate stacking from XRD, moving beyond simple fault fractions to richer sequence statistics.	Computationally intensive; best suited to close-packed systems; extension to complex oxide chemistries is nontrivial.
<i>DIFFaX applications to layered double hydroxides</i> (2005)[263]	LDHs and related lamellar compounds	Mixed polytypes, stacking faults	Shows DIFFaX can reproduce mixed 3R1/2H1 motifs and quantify stacking disorder chosen by hydrogen bonding interactions.	Sensitivity to assumed stacking probabilities; still kinematic; uniqueness of fit not guaranteed without complementary probes.
<i>DIFFaX for layered cathodes</i> (2005)[271]	Layered Li_2MnO_3 -based oxides	Fault frequency along c, stacking disorder	Combines DIFFaX with HR-XRD and solid-state NMR to quantify stacking-fault frequency in layered oxides.	Requires independent constraints from NMR or TEM to avoid overfitting; assumes kinematic scattering.
<i>Hidden-Markov diffraction of layered CPS</i> (2013)[262]	CPS like ZnS	Disorder via HMMs	Derives diffraction patterns directly from HMM parameters for layered stacks, with examples.	Method development paper; application to complex oxides not demonstrated; requires careful model selection.
<i>Debye scattering equation for layered defects</i> (2020)[265]	Kaolinite and clays	Stacking faults, finite size, turbostratic disorder	Solves the Debye scattering equation for nanocrystals to separate contributions of stacking defects and size to powder profiles.	DSE is computationally heavy for large systems; inversion can be non-unique; requires realistic particle size distributions.
<i>FAULTS and TOPAS recursion workflows</i> (2020) [266]	Battery layered oxides and faulted precursors	DIFFaX-like recursion within Rietveld	Implements DIFFaX-style recursion inside TOPAS to co-refine stacking disorder with crystal structure from lab XRD.	Model choice strongly affects results; still kinematic; requires high-quality data and careful restraints.
<i>OPB-induced splitting in Bi-layered films</i> (2015)[268]	Aurivillius Bi-titanate derivatives	OPB-driven splitting of 004 and 00 12	Reports that 004 and 00 12 split with OPB formation while 006 remains single; ties splitting to OPB emergence under modified growth.	Does not provide a general predictive model; relies on case-by-case assignment.

**General OPB
XRD model for
Aurivillius
(2025)[269]**

Aurivillius BiT, SBTN; extendable to RP	Out-of-phase boundaries with finite spacing and angle	Analytical model predicting which 00 l peaks split and the magnitude of splitting from three physical parameters: OPB step δ , OPB angle α , and OPB spacing distribution; validated on SBTN and BiT.	Kinematic and 1D along c ; other defects like intergrowths need additional terms; instrumental broadening not intrinsic to the closed- form.
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7.3. A recent analytical model for OPB defect induced XRD peak profile changes in Aurivillius phase thin films

The latest model considered the state-of-the-art in modelling OPB defects is Whatmore *et. al.*[269] Hence, it is necessary to understand the state- of-the-art model to be able to expand upon it and be able to address its limitations:

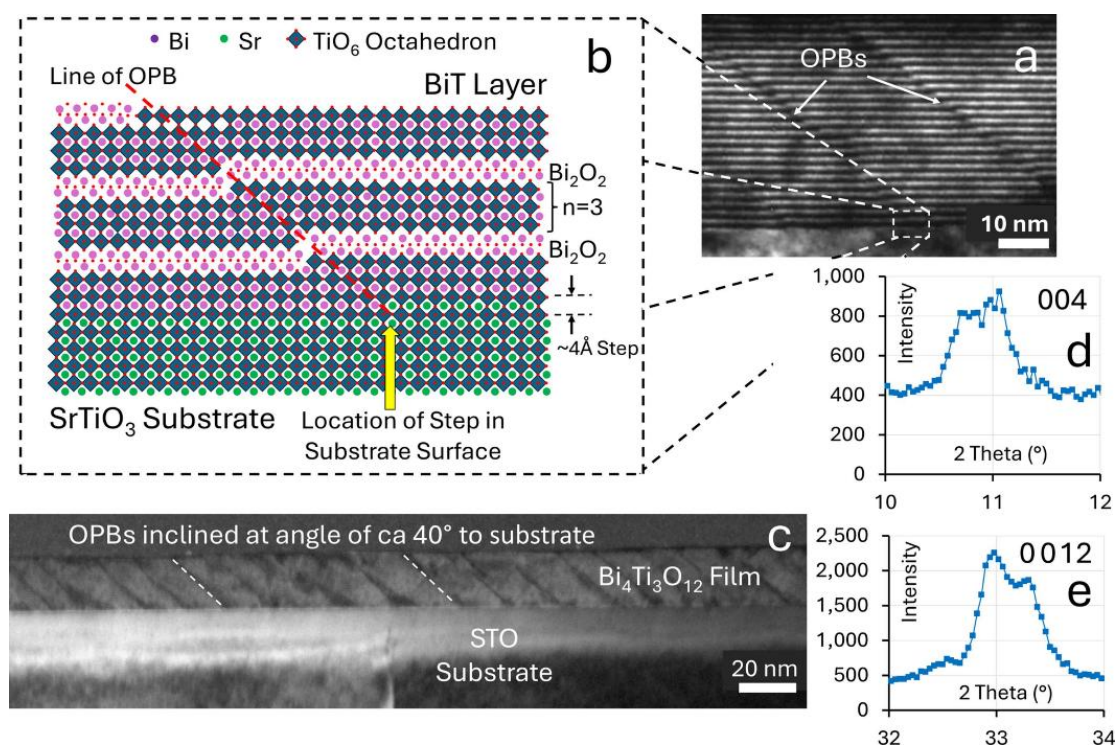


Figure 1.11: *a* A side-view TEM image of a BiT thin film grown on an STO substrate using atomic vapour deposition. The bright horizontal lines represent Bi_2O_2 layers in the material's layered structure. *b* A diagram showing how a small step at the interface between the STO and BiT layers can trigger the formation of an OPB. This causes a shift in the atomic arrangement, about 4 angstroms along the c -axis. These boundaries may also appear in areas with more layers. *c* A zoomed-in TEM image reveals that OPBs form a regularly spaced pattern, tilted roughly 40° from the surface of the substrate. *d* & *e* RD graphs showing split peaks for specific crystal reflections (004 and 0012), which indicate the presence of OPBs in the film.

7.3.1. Scope, motivation, and contribution

The model develops an analytical diffraction mathematical framework that links specific features in θ - 2θ X-ray diffraction line profiles of layered oxides to the presence of OPB defects, in epitaxial thin films.

In this work, for BiT on SrTiO_3 , the authors show TEM images where bright Bi_2O_2 layers are displaced across boundaries that lie at roughly 40 degrees to the substrate, and corresponding θ - 2θ scans reveal clear splitting in the 004 and 0012 reflections, while 006 remains a single peak (**Figure 1.11**). This empirical pairing motivates the model: a periodic sequence of phases along c , caused by OPB defects, imposes a modulation on the structure factor of 00ℓ lines. Depending on the OPB defect displacement and boundary angle, the interference at a given reciprocal-space position either suppresses the original Bragg maximum and redistributes intensity symmetrically into two side peaks, which appears as a split reflection, or it reinforces the central maximum, which remains single.

7.3.2. Model construction: geometry, parameters, and the layered building block

To construct the model, the film is decomposed into identical rectangular blocks ABCD that tile the lateral dimension with period L , each block containing a single OPB that divides it into an undisplaced region and a region displaced by δ along $+c$. The number of layers in a block is $N = 2n + 1$ so its height is $H = 2nc + \delta$ (**Figure 1.12**). The OPB line is inclined by an angle ϕ to the substrate. The key model parameters are: the c -axis lattice parameter c , the displacement at the OPB $\delta = 2\epsilon$ (**Figure 1.12**), the average inter-OPB spacing L , and the OPB inclination ϕ . For convenience the authors define an OPB density $\rho = 1/L$. Crucially, the block size is taken to be smaller than the X-ray coherence length so that scattering from the undisplaced and displaced halves can be summed coherently within each block. This construction is general and independent of the layer count m in the Aurivillius stack.

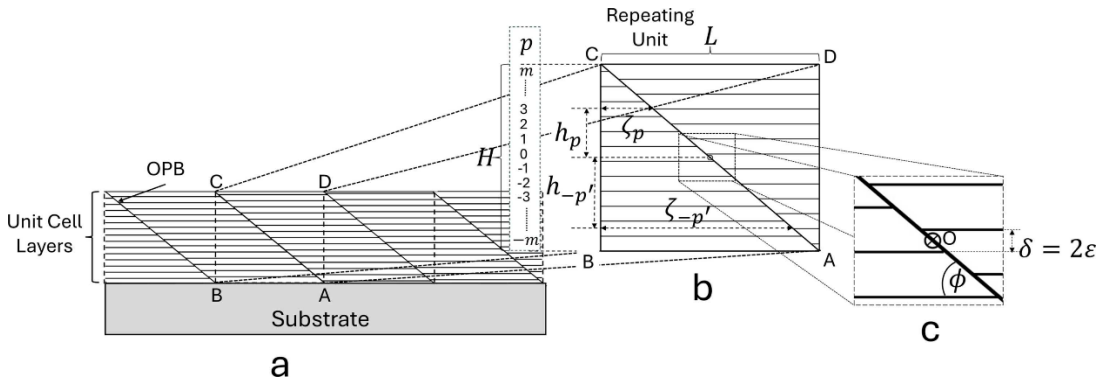


Figure 1.12: *a* A diagram showing an array of OPBs within a thin film grown on a substrate. The film is organised into identical repeating sections. *b* A close-up of one repeating section, highlighting the dimensions used for the modelling discussed in the main text. *c*. Illustration of the angle ϕ between the OPB and line AB (which runs parallel to the material's layers), along with the central point O of the defined region ABCD.

7.3.3. Scattering framework and the core equations

Let s denote the scattering variable used by the authors, with 00ℓ reciprocal-lattice positions occurring at $s = \frac{\ell}{c}$ for the 00ℓ series. The scattering from the block is written as the sum of contributions from the undisplaced and displaced halves, $F_{ABC}(s)$ and $F_{CDA}(s)$. The unit-cell structure factor is $\Phi(s)$, and the total block scattering is

$$F(s) = \Phi(s) \cdot \Gamma_N(s) \quad 4,$$

where

$$F(s) = F_{ABC}(s) + F_{CDA}(s) \quad 5,$$

the displaced half contributes a phase factor, and the sum over the $2n + 1$ layers on either side leads to the compact form

$$F_{CDA}(s) = \Phi(s) \sum_{p=-n}^{p=+n} \frac{\zeta_p}{L} \exp(2\pi i \cdot -h_p s) \quad 6,$$

And

hence,

$$\Gamma_N(s) = \frac{2}{L} \{ \sum_{p=-n}^{p=+n} \zeta_p \cos(2\pi h_p s) \} \quad 7,$$

where the weights ζ_p encode the geometry on the two sides of the OPB. The model then gives the explicit analytical expression for $\Gamma_N(s)$,

$$\Gamma_N(s) = 2 \left[\begin{aligned} & (1 + Z\delta) \cos(\pi\delta s) \frac{\sin(2n\pi cs)}{2\sin(\pi cs)} \\ & - Zc \cdot \sin(\pi\delta s) \left\{ \frac{\cot(\pi cs) \sin(2n\pi cs)}{2\sin(\pi cs)} - \frac{m \cos(2n\pi cs)}{\sin(\pi cs)} \right\} \end{aligned} \right] +$$

$$(1 - Z\{L\tan\phi - \delta\})\cos(\pi\{L\tan\phi - \delta\}s) \quad 8,$$

For $s > 0$, where

$$n = \frac{N - 1}{2} \quad 9,$$

which depends only on the inter-OPB spacing L through N , the OPB inclination ϕ , and the displacement δ . Substitution into the standard expression for the diffracted intensity gives

$$I(s) = |F(s)|^2 q L_P(s) = |\Phi(s)\Gamma_N(s)|^2 q L_P(s) \quad 10,$$

q = Multiplicity (=2 for the $00l$ reflections)

$L_P(s)$ = Lorenz-Polarisation Factor

Note that this predicts the intensity $I(s)$ continuously as a function of s (or 2θ) rather than solely at the $(00l)$ diffraction peaks.

The key idea is that the OPBs introduce an extra “envelope” factor into the scattering, given by the terms involving $\cos(\pi\delta s)$ and $\sin(\pi\delta s)$. When $\cos(\pi\delta s) \approx 0$, the contribution from $\Gamma_N(s)$ is suppressed. In this case, $\Gamma_N(s)$ dominates, and instead of a single diffraction peak, the intensity splits into two maxima positioned on either side of the Bragg peak. When $\sin(\pi\delta s)$ is small but $\cos(\pi\delta s)$ is still significant, $\Gamma_N(s)$ remains strong. In this situation, the peak does not split and stays as a single maximum.

Applying this rule to $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films explains the experimental observations: the 004 and 0 0 12 reflections split into double peaks, while the 006 reflection remains single.

This happens because the “zeros” of $\cos(\pi\delta s)$ coincide with the Bragg positions for $\ell = 4$ and 12, but not for $\ell = 6$ under the measured geometry.

While the analytical framework proposed by Whatmore et al. (2025)[269] represents a major step forward in connecting out-of-phase boundary (OPB) geometry with measurable diffraction features, it has a few limitations. The model’s principal strength lies in its predictive accuracy for well-defined, periodically spaced OPBs- it captures the essential physics of how discrete step heights and tilts influence 00ℓ peak splitting, enabling direct extraction of OPB parameters such as step size and inclination from XRD data. This capability marked the first instance where diffraction could be used not merely to detect defects, but to quantitatively reconstruct their geometric characteristics in layered oxides.

However, the model’s scope is limited to idealised systems, where OPBs are relatively uniform, linear, and propagate continuously through the film thickness. As highlighted in the paper[269], the real defect landscape in higher- m Aurivillius phases is considerably more complex. In such systems, multiple defect classes- including stacking faults, intergrowths with mixed layer numbers ($m > 3$), and non-parallel OPB arrays- coexist and interact, producing both peak splitting and significant line broadening.[234], [272], [273]The model does not yet incorporate these contributions or their statistical distributions, nor does it treat the coexistence and annihilation of OPBs that terminate mid-film or merge with others at varying inclination angles.

Furthermore, because the model is fundamentally two-dimensional, it describes diffraction from planar arrays of OPBs but cannot yet simulate three-dimensional defect networks or non-uniform OPB morphologies, such as those formed during spiral growth or at intersecting step fronts. These morphologies introduce local

curvature, finite domain boundaries, and angular variations in phase offset that break the periodic assumptions of the existing formulation. As a result, while the current model elegantly rationalises OPB-driven splitting, it cannot yet account for the full 3D defect topology that develops in real Aurivillius thin films grown under kinetically complex conditions.

Addressing these limitations is therefore essential for advancing the predictive power of diffraction analysis in layered ferroelectrics. The present work extends this understanding by developing a three-dimensional diffraction model capable of describing OPBs of arbitrary orientation and termination, including those arising within spiral-growth morphologies. By capturing the interactions between OPBs, stacking faults, and intergrowths, this new approach provides a more complete description of the defect landscape in high-quality Aurivillius thin films and offers a direct route to correlating structural disorder with ferroelectric functionality.

8. Research Questions for this thesis

The preceding discussion highlights the urgent need for materials-level innovation in ferroelectric thin films, particularly in layered Aurivillius phases, if they are to become viable candidates for integration into next-generation memory and neuromorphic devices. Three interrelated challenges emerge from this context, each motivating the investigations pursued in the following technical thesis chapters.

1. How can vertical polarisation of laterally-polarised Aurivillius phase films be enhanced, to optimise future vertical device integration?

Despite excellent fatigue tolerance of $\sim 10^{13}$ switching cycles, most Aurivillius compounds, such as $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, exhibit a spontaneous polarisation vector lying

primarily within the crystallographic *a*-axis. This intrinsic anisotropy severely limits their compatibility with vertical device architectures, including ferroelectric tunnel junctions, where out-of-plane switching is required. Achieving a stable *c*-axis polarisation demands an understanding of how crystal symmetry, growth orientation, and lattice distortions can be manipulated to favour vertical dipole components without destabilising the layered structure. Answering this question is essential for bridging the gap in practical device implementation in layered oxides.

2. Is there is a way to predictively model the XRD spectra of non-linear OPB defects geometries?

Despite the availability of an existing XRD model[269] that successfully predicts diffraction peak splitting associated with linear or parallel out-of-phase boundary defects, its applicability remains limited to a specific subset of defect geometries. The current framework assumes OPB defects that extend continuously from the substrate to the film surface, maintaining parallel alignment across the film thickness. In practice, however, OPB defects in Aurivillius thin films often exhibit far more complex morphologies. Many terminate within the film before reaching the surface, while others curve or form pyramidal configurations characteristic of growth spirals. Such three-dimensional defect architectures cannot be fully captured within the current two-dimensional approximation. Consequently, extending diffraction modelling into a three-dimensional regime is essential to accurately represent the structural realities of these films and to achieve a more predictive understanding of defect-driven diffraction behaviour.

3. How can crystal twinning in layered-structured thin films be overcome without changing substrate orientation?

Crystal twinning is another pervasive defect in epitaxial Aurivillius thin films, arising from symmetry-equivalent nucleation during growth. Twinned domains interrupt long-range polarisation coherence and complicate domain switching, thereby reducing device reliability and yield. Currently, the most common method of overcoming twin defects is changing the substrate orientation[274], [275] or increasing the temperature.[276] However, changing either could push the system out of the optimal growth condition, given that growth heavily relies on substrate orientation and temperature. Hence, there is a need to find an alternative route to overcome crystal twinning such that the optimal growth window is not compromised. This is critical for establishing predictive control over thin-film growth and for enabling the fabrication of ferroelectric architectures with consistent switching behaviour.

What unifies these three questions, and what distinguishes this work from prior investigations into individual aspects of Aurivillius phase behaviour, is that they are not pursued independently. They emerge organically in a sequence from a single line of investigation: the systematic reduction of supersaturation during DLI-CVD growth, combined with deliberate exploitation of epitaxial strain and substrate geometry. The framework established in Section 6.1 provides the conceptual foundation. At low supersaturation, sequential precursor injection lowers the instantaneous nucleation density at the growth front, enabling screw dislocations, whose formation is itself a consequence of strain relaxation at the film–substrate interface, to act as persistent step sources on the terraced STO(100) surface. The spiral growth morphology encodes a specific defect architecture within the film interior, one whose structural and

functional consequences are the subject of Chapter III. Those same defects produce characteristic, analytically tractable signatures in reciprocal space, motivating the development of the XRD framework in Chapter IV. And the nucleation physics responsible for variant selection under high supersaturation, which Chapter III uses as a baseline, is the root cause of the twinning that Chapter V eliminates by pushing the system further still toward the diffusion-limited regime. Each chapter therefore builds on the structural vocabulary introduced by its predecessor, and the three research questions, read in sequence, trace a single arc from growth-mode control, through defect decoding, to the suppression of a structurally disruptive consequence of nucleation-dominated epitaxy.

II. Methods

2.1 Direct Liquid Injection Chemical Vapour Deposition (DLI-CVD)

Chemical vapour deposition (CVD) is a vapour-phase thin film growth technique in which volatile precursor species are transported to a heated substrate, where they undergo chemical reactions that ultimately form a solid film.[277] For oxide materials, this process relies on the thermal decomposition and oxidation of gaseous metalorganic fragments at the substrate surface, resulting in the formation of an extended crystalline network, while the ligands and reaction by-products remain volatile and are continually removed from the reaction chamber. [278] The CVD process thus separates precursor delivery, gas-phase transport, surface reaction, and film formation into coupled dynamic events that take place under well-defined thermodynamic and kinetic constraints. The technique is especially suited to the synthesis of complex oxide thin films because it allows high deposition temperatures,

good control over oxygen partial pressure, and uniform coverage over large substrates, conditions that are often difficult to attain in physical vapour deposition methods.

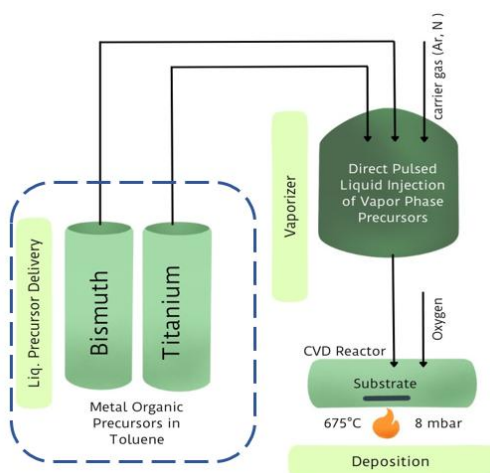


Figure 2.1: Schematic of the DLI-CVD process in AIXTRON AIX 200/4FE DLI-CVD

In this work, **Direct Liquid Injection Chemical Vapour Deposition (DLI-CVD)** was used to deposit bismuth titanate thin films. DLI-CVD extends conventional CVD by enabling the use of liquid precursor solutions rather than relying on solid precursors with insufficient intrinsic vapour pressure. The process flow diagram is in **Figure 2.1**. The precursors employed were bismuth tris(2,2,6,6-tetramethyl-3,5-heptanedionate), $\text{Bi}(\text{thd})_3$, and titanium bis(isopropoxide) bis(2,2,6,6-tetramethyl-3,5-heptanedionate), $\text{Ti}(\text{O-iPr})_2(\text{thd})_2$, both dissolved in toluene to form homogeneous solutions of controlled molarity. The liquid state of the precursor reservoir is essential, as these complexes do not exhibit sufficiently high vapour pressures to allow direct evaporation without decomposition. The process begins with the precursor solutions, which are held in stainless steel containers. The precise delivery of these liquid precursors is managed by flow meters that control the volume injected into the vaporizer. The system utilizes an advanced TriJet™ evaporation unit, a key feature designed for non-contact evaporation. In this unit, a continuous flow of nitrogen gas

is directed along the walls, effectively preventing the liquid precursors from physically contacting the vaporizer surface. This step minimizes the occurrence of undesirable parasitic reactions that could otherwise take place on the hot walls, ensuring the purity of the precursor vapour. Once vaporized, the gaseous flow is directed toward the reaction chamber, with all transport lines maintained at an elevated temperature to prevent condensation and subsequent blockage.

Upon entering the TriJet™ evaporation unit region, which is maintained at 220 °C, the solution undergoes **nebulisation**, producing a vapour phase that contains all metalorganic components in precisely the same stoichiometric ratio as in the liquid phase.

The principal advantage of DLI-CVD is that the **relative cation fluxes** are not determined by vapour pressure differences but instead by the **valve opening time** and injection frequency of each precursor line. Because the mass of precursor delivered per pulse is proportional to the injection duration, the Bi:Ti ratio in the gas phase can be controlled digitally, allowing compositional tuning with no modification of physical hardware. This capability is of particular relevance to bismuth titanate systems, where the volatility of bismuth oxides can lead to Bi loss and subsequent formation of secondary phases if the gas-phase chemical potential of Bi is not sufficiently high.

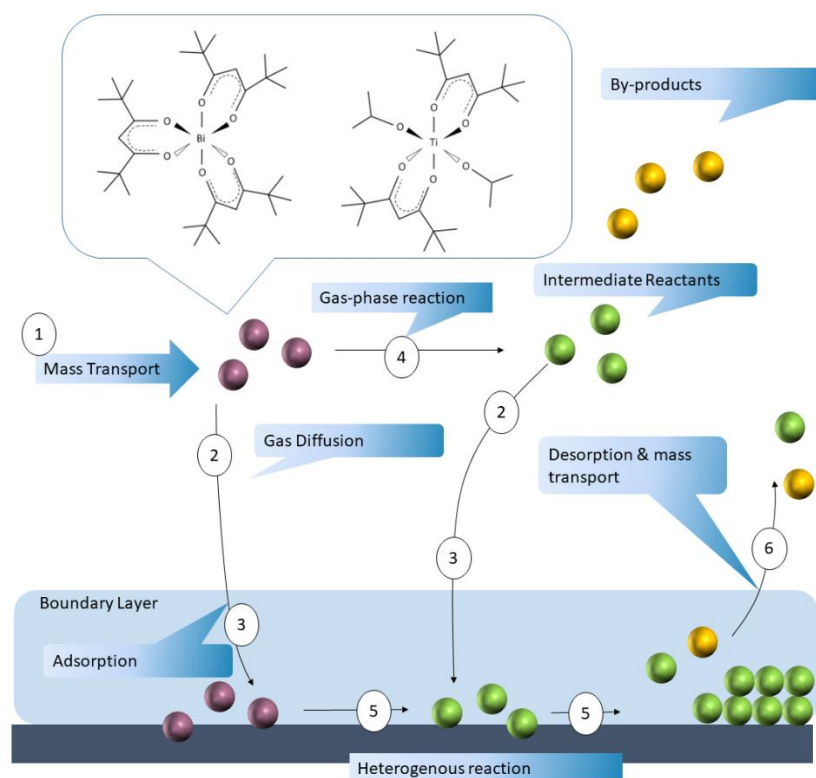


Figure 2.2: Schematic of the growth process inside the CVD reactor. The elementary physicochemical steps of a typical CVD process begin with the transport of gaseous precursors into the reaction chamber via the main gas flow. As these gases approach the substrate, several phenomena can occur: precursors may adsorb directly to the surface or, alternatively, react in the gas phase to form intermediate species that then adsorb. Once adsorbed, heterogeneous surface reactions take place, accompanied by surface diffusion of adatoms across the substrate. This surface activity ultimately leads to the nucleation and growth of the thin film. The process concludes as volatile reaction by-products desorb from the surface and are subsequently carried out of the reaction chamber by the gas flow.

Once in the reaction chamber, the gaseous precursors flow over the heated substrate in a laminar regime, producing a concentration gradient between the bulk of the gas stream and the surface of the film (**Figure 2.2**) The resulting stagnant boundary layer

plays a decisive role in determining growth kinetics: precursor species must diffuse across this layer and adsorb onto the hot substrate before decomposition can take place. Film growth occurs through a sequence of events that include precursor adsorption, ligand dissociation, formation of metal-oxygen bonds, and desorption of volatile reaction by-products.[278], [279] These steps initiate nucleation of the film, where small clusters of Bi-O and Ti-O species aggregate into stable nuclei once a critical size is achieved. The structure and energy landscape of the substrate strongly influence this nucleation stage.[219], [280] Substrates with atomically smooth terraces, such as SrTiO₃ or other perovskite-type oxides, provide low-energy nucleation sites that promote epitaxial ordering. At sufficiently high temperatures, adatom surface mobility is enhanced, enabling atoms to reorganise into extended ordered layers that reflect the underlying substrate symmetry.

The nucleation mode adopted during CVD dictates the resultant microstructure and is broadly described by classical thin-film growth models. In layered systems, growth often proceeds via a two-dimensional, step-mediated mechanism, in which the film extends laterally from the nucleation sites and forms layers before vertical growth dominates. Such behaviour is favoured when the surface energy of the film is lower than that of the substrate, and when deposition occurs under conditions that support high surface diffusion. The high temperatures and oxygen-rich atmosphere available in CVD enable this regime by promoting both adatom mobility and ligand removal, resulting in films that often crystallise directly during deposition rather than requiring a post-annealing step.

CVD offers several advantages when compared to other thin film deposition techniques. Relative to Molecular Beam Epitaxy (MBE),[281] which relies on ultra-

high vacuum and physically evaporated atomic beams, CVD provides a chemically rich and oxidising environment that is better suited to the synthesis of complex oxides containing highly volatile species such as bismuth. MBE growth of bismuth titanate requires additional oxide sources to stabilise Bi valence states, whereas CVD inherently supplies oxygen at pressures compatible with maintaining Bi-O bonding throughout growth. In contrast to Atomic Layer Deposition (ALD), [282] which achieves atomic-scale thickness control through self-limiting surface reactions, CVD does not require step-wise precursor saturation and therefore supports higher growth rates, making it more suitable for depositing films with thicknesses relevant to functional ferroelectric devices. Although ALD can achieve unrivalled interface sharpness, its process chemistry is often more restrictive, and suitable bismuth precursors for self-limiting reactions are far less common than those compatible with CVD.

Nevertheless, DLI-CVD is not without limitations. The complexity of its parameter space, encompassing temperature, precursor concentration, injection timing, chamber pressure, carrier gas flow, and oxygen supply, means that optimisation can be non-trivial, and small deviations in process conditions may lead to measurable changes in stoichiometry or defect formation. In addition, the hot-wall reactor geometry encourages deposition on the chamber walls and quartz liner, necessitating regular cleaning to avoid parasitic reactions and particulate contamination. Despite these constraints, the combination of vapour-phase chemistry, digital control of precursor flux, and compatibility with Bi-rich oxide growth renders DLI-CVD uniquely suited to the deposition of layered Aurivillius titanates, providing a balance between compositional control, crystalline quality, and industrial scalability that is not readily achieved by alternative deposition methods.

2.2 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) arises from the interaction between incident X-rays and the periodically arranged electrons in a crystalline solid. Because the X-rays interact primarily with the electron density surrounding atomic nuclei, they can be scattered by the electrons within a crystal. Although X-rays may undergo both elastic and inelastic scattering, it is the elastically scattered component that can interfere constructively when the electrons are arranged in a periodic lattice, giving rise to the diffraction patterns observed in X-ray diffraction (XRD). When the X-ray wavelength is comparable to the spacing between the scattering centres, the resulting interference maxima occur at angular positions that are experimentally accessible and well resolved, enabling direct measurement of crystal structure. The cumulative interference of these scattered waves gives rise to the diffraction patterns recorded in XRD experiments (**Figure 2.3**). The intensity, position, and shape of diffraction peaks depend not only on the geometric conditions described by Bragg's Law,

$$n\lambda = 2d \sin \theta \quad 11,$$

but also on the electronic structure of the constituent atoms, the arrangement of atoms within the unit cell, and instrumental factors that affect scattered beam intensity.[283]

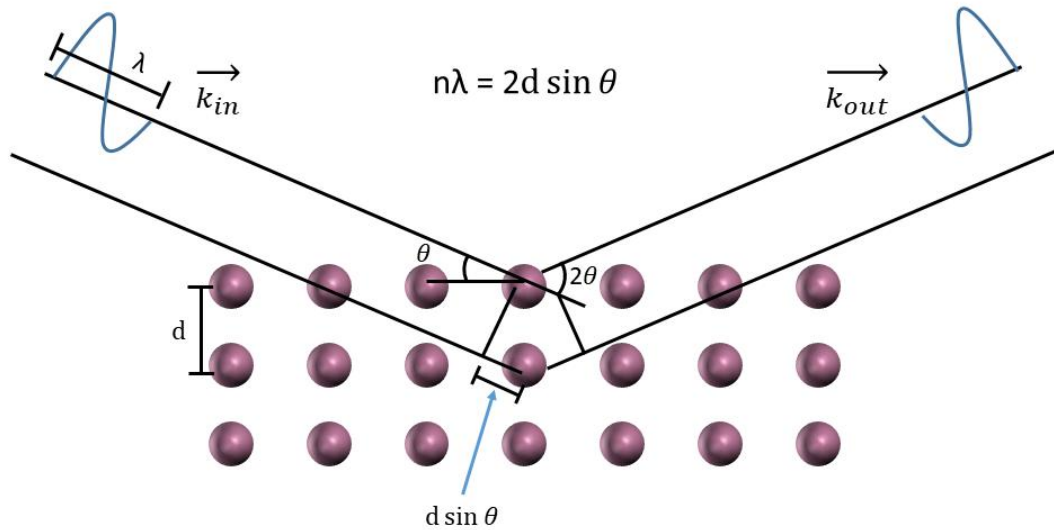


Figure 2.3 Diagram explaining the diffraction of X-Rays through atomic spaces following the Bragg Law.

2.2.1. Atomic Scattering and the Atomic Form Factor

At the most fundamental level, diffraction originates from the scattering of a beam of X-ray photons by individual electrons. For a single free electron, the amplitude of scattered radiation can be described by Thomson scattering. However, in real crystals, X-rays interact with atoms composed of multiple electrons distributed around the nucleus. The efficiency with which an atom scatters X-rays depends on its atomic scattering factor, also known as the atomic form factor, f . [283], [284]

The atomic form factor quantifies how the scattering amplitude of an atom differs from that of a single free electron and is defined as the Fourier transform of the atom's electron density distribution. [285] Mathematically, it can be expressed as:

$$f(Q) = \int \rho(r) e^{iQr} dr \quad 12,$$

where $\rho(r)$ is the electron density and Q is the scattering vector. It is defined as the difference between the incident and scattered wavevectors,

$$Q = k_{\text{out}} - k_{\text{in}} \quad 13,$$

and has magnitude

$$|Q| = \frac{4\pi}{\lambda} \sin \theta \quad 14,$$

where λ is the X-ray wavelength and θ is half the scattering angle. The vector Q therefore identifies which lattice planes satisfy the diffraction condition, and each point in reciprocal space corresponds to a specific set of interplanar spacings in the crystal.

The value of f decreases as the scattering angle increases, because higher-angle scattering probes finer details of the electron density, to which atoms contribute less efficiently.[285] Heavy atoms, possessing more electrons, have larger scattering factors, meaning that compounds with high-Z elements (such as Bi in bismuth titanate) produce stronger diffraction peaks than those composed of lighter elements. This behaviour explains why peaks associated with oxygen positions are often weaker and more difficult to resolve than those originating from metal cations.

2.2.2. Structure Factor and Unit Cell Interference

Although atomic scattering factors describe the response of isolated atoms, diffraction from a real crystal depends on the collective scattering from all atoms within the repeating unit cell. The interference of waves scattered by different atoms leads to constructive or destructive interference, and the resultant diffracted intensity is captured by the structure factor, F_{hkl} -

$$F_{hkl} = \sum_{j=1}^N f_j e^{2\pi i(hx_j + ky_j + lz_j)} \quad 15,$$

Where f_j is the atomic form factor of the j^{th} atom, (x_j, y_j, z_j) are its fractional coordinates within the unit cell, and hkl are the Miller indices of the diffracting plane. The exponential term encodes the path difference between waves scattered from different atoms. If the sum yields a non-zero amplitude, constructive interference occurs and the corresponding reflection is observable. If the sum cancels, the reflection becomes systematically absent. Such extinctions are signatures of crystal symmetry and enable space-group determination.[284]

The experimentally measured diffracted intensity of a given reflection is proportional to $|F_{hkl}|^2$, meaning that both the types and positions of atoms influence diffraction intensities. This is why substitutions or vacancies produce measurable changes in peak intensities even when peak positions remain nearly unchanged.

2.2.3. Lorentz–Polarisation Factor

Raw diffracted intensities cannot be interpreted directly without correcting for geometrical and instrumental effects. Two such corrections are combined in the Lorentz–polarisation (LP) factor, which adjusts measured intensities according to (i) the probability of satisfying the diffraction condition and (ii) the polarisation state of the incident X-ray beam.[283]

The Lorentz correction arises from the fact that crystals in a diffractometer pass through the diffraction condition at different speeds depending on the geometry. In a powder diffractometer, only a fraction of crystallites is correctly oriented at any moment, and the likelihood of satisfying the Bragg condition varies with 2θ .

Reflections at low angles persist longer in the diffracting position and hence appear artificially more intense unless corrected.

The polarisation correction addresses the fact that X-rays are partially polarized during generation and further modified by interactions with monochromators and slits. Scattering efficiencies depend on the angle between the electric field vector and the scattering plane, meaning that the observed intensity must be corrected to reflect the actual polarisation state.

The combined Lorentz–polarisation factor is often written as:

$$L_p = \frac{1 + \cos^2(2\theta)}{2 \sin^2 \theta \cos \theta} \quad 16,$$

for conventional θ – 2θ laboratory diffractometers. This factor is applied multiplicatively to raw data so that intensities can be compared quantitatively, particularly in Rietveld refinement or when attempting to extract occupancy factors or thermal parameters. Without this correction, low-angle reflections would appear exaggerated and comparisons between reflections at different angles would be physically meaningless.

2.2.4. Debye–Waller Factor and Thermal Motion

X-ray diffraction is fundamentally a probe of the *time-averaged* electron density within a crystal. At finite temperatures, atoms undergo thermal vibrations about their equilibrium lattice sites. These oscillations reduce the coherence of scattered X-rays, attenuating high-angle reflections more severely than low-angle ones.[283] This effect is captured by the Debye–Waller factor, sometimes called the temperature factor, which modifies the structure factor as:

$$F_{hkl} = \sum_j f_j \exp \left[-8\pi^2 U_j \frac{\sin^2 \theta}{\lambda^2} \right] \exp[2\pi i(hk_j + ky_j + lz_j)] \quad 17$$

where U_j is the mean-squared displacement of atom j . The exponential decay reflects the fact that higher-order reflections, which probe finer lattice periodicities, are more sensitive to thermal disorder. The Debye–Waller factor therefore provides microscopic insight into lattice dynamics and can differentiate between heavy elements, whose thermal vibrations are small due to large atomic mass (e.g., Bi^{3+} in Aurivillius phases), and light elements, such as oxygen, which exhibit larger vibrational amplitudes. In quantitative refinements such as Rietveld analysis, these temperature factors are indispensable for accurately modelling electron density and validating cation positions in complex oxides.

2.2.5. Multiplicity and Reflection Degeneracy

Each diffraction peak corresponds to a set of crystallographic planes indexed by Miller indices. The multiplicity of a reflection, the number of symmetrically equivalent planes with the same (hkl) , contributes linearly to its measured intensity:

$$I_{hkl} \propto m_{hkl} |F_{hkl}|^2 \quad 18$$

Multiplicity is a geometric consequence of the crystal's space group. Cubic crystals have higher multiplicities than lower-symmetry systems, whereas highly oriented thin films- such as epitaxial Aurivillius titanates- often display drastically reduced multiplicities because only a subset of reflections is accessible in a θ – 2θ geometry. Understanding multiplicity is essential when comparing intensities between reflections or inferring atomic occupancies, since uncorrected multiplicity can mask structural changes or lead to erroneous conclusions about site occupancies.[283]

2.2.6. Peak Shapes and Broadening Mechanisms

Real diffraction peaks exhibit finite widths rather than appearing as ideal delta functions. This peak broadening contains valuable physical information. The observed profile is a convolution of the instrumental resolution function and sample-dependent broadening mechanisms. Sample contributions arise from:

1. **Finite crystallite size:** Small grains produce peak broadening via the Scherrer effect, where peak width is inversely proportional to crystallite size.
2. **Microstrain:** Spatial variations in lattice spacing induce peak broadening that increases with diffraction angle.
3. **Defects and stacking faults:** Disruptions in periodicity smear reciprocal lattice points into finite distributions, modifying both peak shape and position. Aurivillius oxides frequently develop out-of-phase boundary defects, which introduce anisotropic broadening along specific crystallographic directions.
4. **Disorder in layered structures:** Fluctuations in the stacking of perovskite blocks generate diffuse tails or streaks, especially along the c-axis repeat direction.

Instrumental factors include monochromator bandwidth, slit divergence, and detector geometry, and are independent of the sample. To extract meaningful microstructural parameters, these instrumental contributions must first be deconvolved. Advanced diffraction studies distinguish Lorentzian broadening (size effects) from Gaussian broadening (strain effects), enabling quantitative separation of crystallite size and microstrain via Williamson–Hall analysis or whole-pattern refinement.

2.3 Atomic Force Microscopy (AFM)

Atomic Force Microscopy is a scanning probe technique that enables the quantitative measurement of surface topography and local mechanical interactions at nanometre and even sub-nanometre length scales. Unlike optical or electron microscopy, which form images using propagating beams, AFM generates contrast by monitoring the interaction forces between a sharp tip and the sample surface. The probe consists of a microfabricated cantilever with a nanoscale tip at its free end. A laser beam is focused on the back of the cantilever, and its reflection onto a position-sensitive photodiode converts cantilever bending into a measurable electrical signal. As the tip is raster-scanned across the surface, the intrinsic forces between the tip apex and the sample induce deflections that are detected with picometre precision, allowing AFM to reconstruct the sample's three-dimensional surface topography.

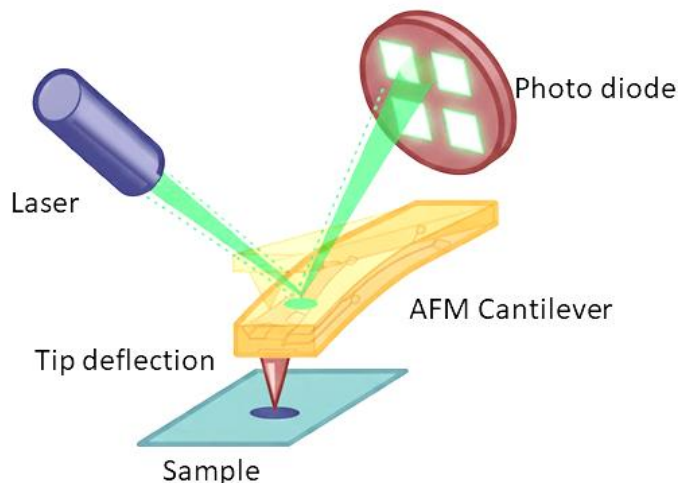


Figure 2.4. Schematic showing the process of Atomic Force Microscopy

The physical basis of AFM operation lies in the collective action of intermolecular and interatomic forces that act over different distance ranges. When the tip is far from the surface, attractive van der Waals forces dominate, arising from correlated fluctuations

of electronic charge (London dispersion). As the tip approaches closer, electrostatic and capillary forces begin to contribute, leading to adhesion, where the tip deflection leads to movement of the laser pointer position in the photodiode (**Figure 2.4**). [286] At contact, Pauli repulsion between overlapping electron clouds produces a steep increase in force with decreasing tip–surface distance. The total tip–sample force F_{ts} can be formally expressed as the sum of these contributions, and within the elastic deformation regime, the cantilever deflection follows Hooke’s law,

$$F = -k\Delta z \quad 19,$$

where k is the cantilever spring constant and Δz is the deflection. Accordingly, AFM is not merely an imaging tool but a force transducer capable of quantifying nanoscale material interactions.[286]

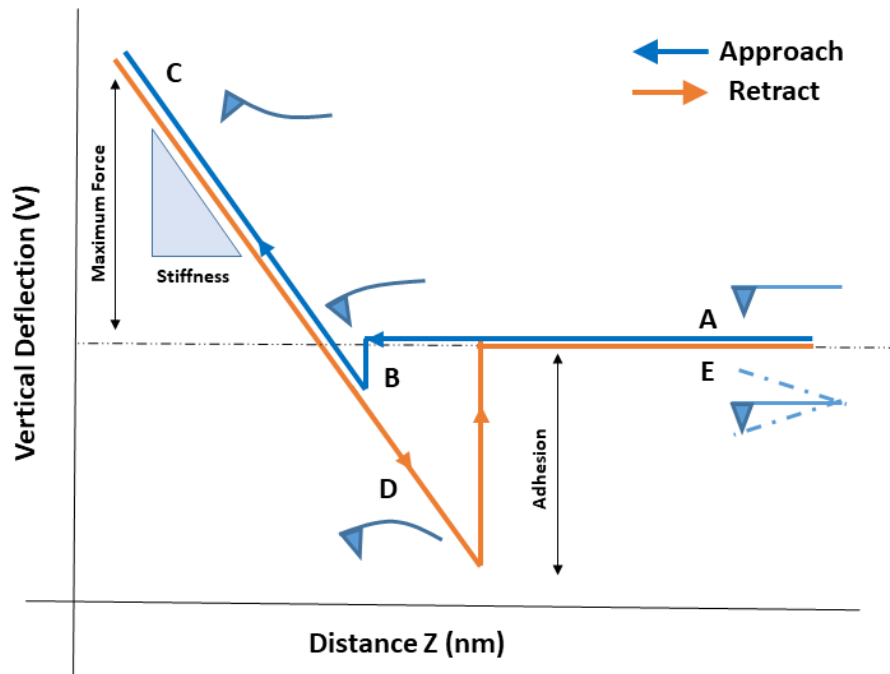


Figure 2.5. *The Force Distance Curve*

A central concept underpinning AFM interpretation is the force–distance curve (**Figure 2.5**), which plots the measured cantilever deflection as the tip approaches and retracts from the surface. The curve is typically split into an approach phase and a retract phase. As the tip approaches the surface from a distance, it is initially subjected to weak attractive forces (like Van der Waals), causing the cantilever to bend slightly until it "snaps-in" to contact due to a rapid increase in attraction. Once the tip is in contact, further movement of the scanner pushes the tip against the sample, causing the cantilever to bend dramatically due to repulsive forces (the contact region), with the slope in this region providing information on the sample's stiffness (Young's Modulus). As the tip is retracted, it sticks to the surface due to adhesion forces (the pull-off force), and the cantilever bends downward into a negative force region before the tip finally "snaps-off" the surface to return to its initial non-contact position. The adhesion force is quantified by the maximum negative deflection observed during retraction. This entire curve provides critical quantitative data on both the mechanical properties (stiffness, elasticity) and surface interactions (adhesion) of the sample at the nanoscale. The shape of this curve encodes information about surface adhesion, stiffness, and elasticity, and forms the theoretical basis for AFM imaging modes.[287]

In contact mode, the tip remains in the repulsive regime, continuously deforming the surface. In tapping and non-contact modes, the cantilever oscillates near its resonance frequency, sensing long-range forces without damaging the sample. Across all modes, changes in tip–surface interaction are converted into deflection signals that trace the surface profile with atomic-scale sensitivity.[287]

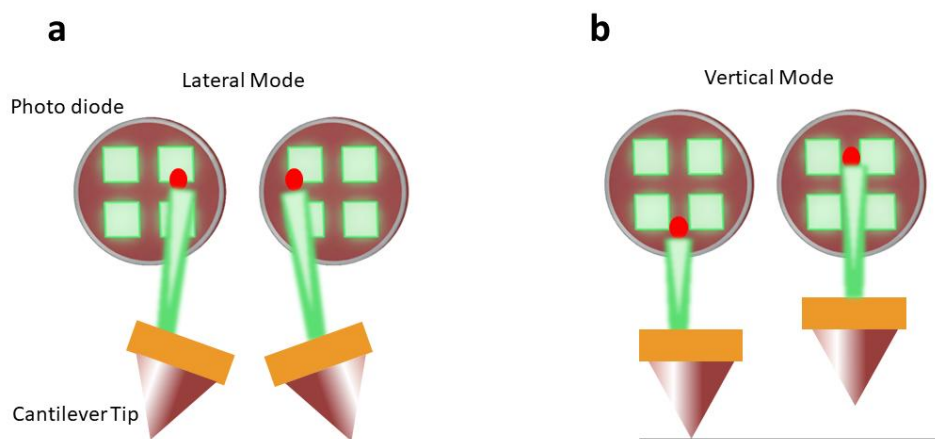


Figure 2.6. *Lateral and Vertical modes of images corresponding to their tip movements.*

The AFM photodetector architecture allows simultaneous measurement of both vertical and lateral cantilever motion (**Figure 2.6**). Vertical deflection corresponds to bending of the cantilever orthogonal to the sample, producing a shift in the laser spot along one axis of the detector. This deflection forms the basis for height measurements in conventional AFM topography. Lateral or torsional motion arises when the cantilever twists as the tip experiences shear forces parallel to the surface. Such lateral signals reflect friction, viscoelasticity, and shear stiffness at the nanoscale. Vertical and lateral channels therefore separate normal and tangential force components, enabling AFM to probe not only morphology but also tribological and mechanical properties with unparalleled spatial resolution.[286]

Although Atomic Force Microscopy (AFM) enables quantitative measurement of nanoscale surface features, this capability is not absolute and must be interpreted with care. The accuracy of AFM data depends critically on the condition and calibration of the probe, as the measured signal reflects not only true surface topography but also the

convolution of the tip geometry with the sample. A finite tip radius can artificially broaden sharp features, while tip wear during scanning progressively degrades resolution and introduces systematic errors that may be mistaken for real surface changes. In addition, AFM probes experience a range of stray forces (van der Waals interactions, capillary forces from ambient humidity, electrostatic contributions, and frictional drag) that can distort height measurements if not properly controlled. These effects are especially pronounced when imaging soft, rough, or chemically heterogeneous materials, where the feedback loop may misinterpret surface compliance as height variation. Scan artefacts, such as streaking, line skipping, or thermal drift, further complicate interpretation unless corrected through careful calibration, environmental stabilisation, and repeated measurements.

AFM is therefore best viewed as a powerful surface-imaging tool with quantitative potential, but one whose precision relies on rigorous experimental practice. To obtain a complete structural picture, AFM is frequently complemented by techniques such as Scanning Electron Microscopy (SEM), which provides larger-area morphological context, and Transmission Electron Microscopy (TEM), which reveals internal interfaces and lattice defects that lie beyond AFM's surface sensitivity. In this way, AFM contributes essential nanoscale topographic information, but its measurements must be embedded within a broader microscopy framework for reliable structure–property correlations.

2.4 Piezoresponse Force Microscopy (PFM)

Piezoresponse Force Microscopy is an extension of AFM specifically designed to probe ferroelectric and piezoelectric behaviour at the nanoscale. Whereas conventional AFM detects mechanical forces induced by tip–surface interactions,

PFM introduces an external AC electric field through a conductive AFM tip, stimulating electromechanical deformation in materials that exhibit the converse piezoelectric effect. In response to an applied voltage

$$V(t) = V_{AC} \cos(\omega t) \quad 20,$$

a piezoelectric surface undergoes a periodic displacement

$$u(t) = d_{33} V_{AC} \cos(\omega t + \phi) \quad 21,$$

where d_{33} is the longitudinal piezoelectric coefficient and ϕ is the phase of the induced deformation. This oscillatory motion is transferred to the cantilever, causing a modulation of the reflected laser signal.[288] The amplitude of the detected signal reflects the magnitude of the local piezoelectric response, whereas the phase indicates the orientation of the ferroelectric polarisation. Domains aligned parallel and antiparallel to the applied field differ by 180° , enabling PFM to reveal not only domain morphology but also their switching directionality.

PFM provides two complementary imaging geometries that distinguish vector components of polarisation. Vertical PFM measures normal cantilever deflection and is sensitive to out-of-plane electromechanical deformation associated with the d_{33} and d_{31} tensor elements. Lateral PFM measures torsional cantilever motion that arises from shear strains linked to the d_{15} coefficient, enabling access to in-plane polarisation.[288] Through simultaneous acquisition of vertical and lateral responses, PFM reconstructs the full polarisation vector field, an essential capability for layered oxides such as Aurivillius titanates, where ferroelastic and ferroelectric distortions coexist.

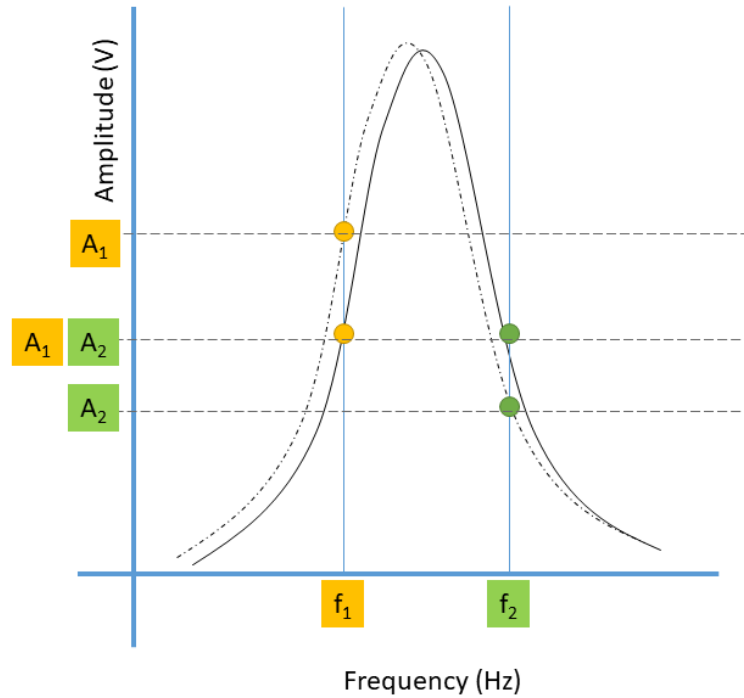


Figure 2.7 Mechanism of frequency adaptation of DART-SS-PFM to modulate the frequency according to the changing topography to maximise the sensitivity to the piezoresponse.

The PFM signal is greatly enhanced when the applied excitation frequency approaches the mechanical resonance of the cantilever–sample system, a condition that increases sensitivity to sub-picometre displacements. Advanced modes such as Dual AC Resonance Tracking (DART-PFM) and Switching Spectroscopy PFM (SS-PFM) automatically track this resonance and separate tip–sample nonlinearities from genuine piezoelectric responses (**Figure 2.7**). [289] In particular, SS-PFM allows measurement of nanoscale hysteresis loops by sweeping a DC bias while monitoring the local amplitude and phase response, yielding coercive voltages and nucleation energies at the level of individual ferroelectric domains. These capabilities transform PFM into a nanoscale analogue of macroscopic ferroelectric characterisation

techniques, bridging structural, electrical, and functional information on a length scale inaccessible by bulk measurements.

A key challenge in standard single-frequency PFM is that the measured cantilever response contains contributions from both the intrinsic electromechanical deformation of the sample and non-contact electrostatic forces acting between the tip and the sample surface. These electrostatic contributions arise from capacitive coupling between the tip and underlying charges including surface adsorbates, space-charge layers, and any unscreened depolarisation field and they produce a signal at the same drive frequency as the genuine piezoelectric response, making them indistinguishable in amplitude or phase images acquired at a fixed frequency. DART-PFM mitigates this by tracking the contact resonance of the cantilever-sample system at two frequencies simultaneously, one on either side of the resonance peak, and using the difference signal to lock onto and stabilise the resonance frequency as it shifts with local contact stiffness across the surface. Because the genuine piezoelectric response is mechanically mediated it acts through direct deformation of the surface and is therefore amplified at contact resonance whereas the electrostatic contribution acts through a non-contact force that does not shift the contact resonance frequency, operating at resonance preferentially amplifies the piezoelectric signal while suppressing the relative contribution of electrostatic background. [289] The result is an improvement in signal-to-noise ratio of typically one to two orders of magnitude relative to off-resonance acquisition, enabling reliable detection of sub-picometre piezoelectric displacements in thin films where the electrostatic background would otherwise dominate. It should be noted, however, that DART reduces rather than

eliminates electrostatic artefacts, and residual contributions from long-range capacitive forces- particularly pronounced in films with significant leakage or at high DC bias- cannot be entirely excluded without complementary off-field imaging or dual-harmonic measurements.

While Piezoresponse Force Microscopy (PFM) is a powerful extension of AFM that enables nanoscale mapping of ferroelectric domains and switching behaviour, its interpretation carries important caveats. PFM does not measure polarisation directly; rather, it infers electromechanical activity from the local piezoresponse induced by an applied AC voltage at the tip. This makes the technique sensitive to tip-sample contact mechanics, electrostatic forces, and substrate compliance, all of which can generate signals that mimic or obscure genuine ferroelectric switching. Variations in contact stiffness or surface chemistry can produce apparent contrast unrelated to domain orientation, while electrostatic artefacts may dominate the response in leaky or poorly screened films. Tip wear, calibration uncertainties, and frequency-dependent resonance effects further complicate quantitative interpretation. As a result, PFM measurements are inherently local and may not represent the collective switching behaviour of the entire film.

In contrast, bulk ferroelectric characterisation techniques such as Sawyer-Tower circuits, P-E hysteresis loops, and switching current measurements probe the integrated response of the material, providing an unambiguous measure of switchable polarisation but lacking the spatial resolution to identify domain configurations or local heterogeneity. PFM and bulk measurements are therefore complementary rather than interchangeable: PFM reveals where switching occurs and how domain walls evolve at the nanoscale, while bulk techniques confirm whether the material exhibits

true macroscopic ferroelectricity. A rigorous interpretation of nanoscale phenomena thus requires correlating local PFM contrast with independently verified bulk switching behaviour to distinguish genuine ferroelectricity from electromechanical or electrostatic artefacts. This balanced approach is essential, particularly in thin films where defects, strain gradients, and local chemistry can cause nanoscale responses that do not scale straightforwardly to device-level performance.

The measurements in this thesis were performed in PFM only, without a patterned capacitor stack, for two reasons that reflect the scope of the work. First, the films examined here were grown and characterised as part of a structural study aimed at establishing the relationship between growth mode, defect topology, and polar response; fabricating capacitor structures with defined electrode geometries was beyond the scope of this investigation and would have required an additional process development stage. Second, and more fundamentally, tip-only PFM is well suited to the specific questions asked here: whether spiral growth modifies the local polar response relative to 2D-grown films, and whether twin suppression yields spatially coherent domain switching. These are comparative and spatial questions, and PFM answers them directly the relative contrast between growth conditions, the domain alignment with substrate terraces, and the lateral uniformity of switching are all accessible in tip geometry and are not contingent on having a bottom electrode. What tip-only geometry does not provide is a quantitative measure of switchable polarisation in $\mu\text{C}/\text{cm}^2$ or a coercive field in kV/cm comparable to literature values from capacitor-based studies; the apparent switching voltages reported here reflect local domain nucleation thresholds under a hemispherically distributed field and should be interpreted as relative indicators rather than absolute material parameters. Macroscopic P–E hysteresis, PUND pulse measurements, and endurance and retention

testing, all of which require lithographically defined capacitor structures- constitute the primary electrical characterisation step needed to translate the structural findings of this thesis into a device context, and are identified as immediate future work in the Conclusions.

2.5 Transmission Electron Microscopy (TEM):

Transmission electron microscopy is a high-resolution characterisation technique that employs a beam of high-energy electrons, typically accelerated between 80 and 300 keV, to probe the internal structure of materials at atomic length scales. [290] The spatial resolution of TEM surpasses that of optical microscopy because the resolving power of an imaging system is fundamentally constrained by the wavelength of the radiation used. According to the de Broglie relation, $\lambda=h/p$, the wavelength of an electron decreases with increasing momentum, and electrons accelerated to typical TEM voltages (80–300 kV) possess wavelengths on the order of a few picometres. These wavelengths are several orders of magnitude smaller than those of visible light, which range from approximately 400 to 700 nanometres and set the diffraction-limited resolution of conventional optical microscopy at roughly 200–300 nm. Although the intrinsic electron wavelength is sufficiently short to, in principle, permit picometre-scale resolution, practical TEMs do not achieve this theoretical limit. Instead, their resolution is restricted by spherical and chromatic aberrations in the electromagnetic lenses, mechanical instabilities, and residual specimen-induced scattering effects. Modern aberration-corrected instruments mitigate many of these limitations and can routinely achieve sub-ångström resolution, enabling direct imaging of atomic columns, but they still fall short of the picometre wavelengths implied by the de Broglie relation.

Figure 2.8 illustrates the basic ray path and component arrangement of a conventional Transmission Electron Microscope (TEM). The electron source generates a coherent electron beam that is shaped and controlled by a series of condenser lenses before interacting with the specimen in the objective lens; the transmitted electrons are then magnified and projected onto detectors or cameras by a sequence of intermediate and projector lenses to form an image. As the electron beam reaches the specimen, some electrons are transmitted through regions of lower atomic number or thickness, while others are scattered by interactions with the electrostatic potential of the atomic nuclei and surrounding electrons. The balance between transmitted and scattered electrons forms the basis of image and diffraction contrast in TEM. The objective lens system forms an image and a diffraction pattern, with the diffraction information visible at the objective back focal plane. Subsequent magnification are achieved by the intermediate lens, projecting the image onto the image plane, which can then be viewed directly on a camera. This setup allows for high-resolution imaging and structural analysis of the specimen.[290]

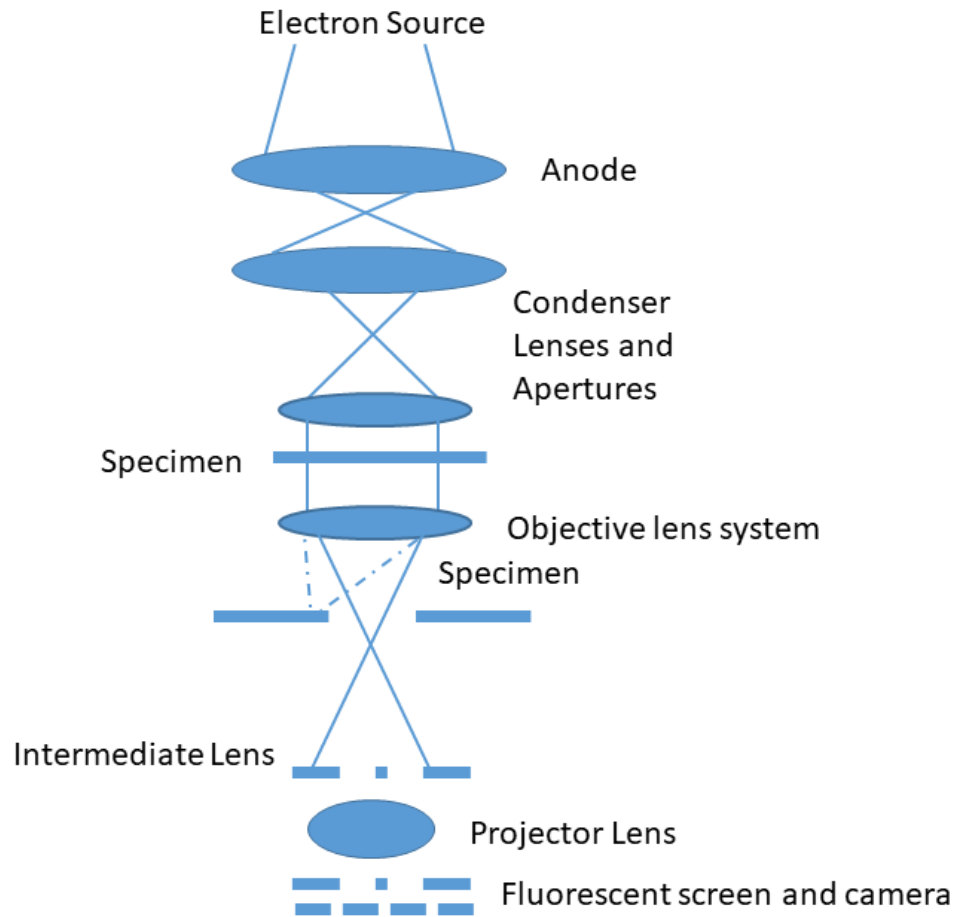


Figure 2.8. *Schematic of the process of Transmission Electron Microscopy*

As the electron beam interacts with the sample, it undergoes elastic and inelastic scattering events due to Coulombic interactions with the electrostatic potential arising from atomic nuclei and surrounding electron clouds.[290]

Elastic scattering occurs when the incident electrons are scattered with negligible energy loss. Coherent elastic scattering events give rise to diffraction patterns, and high-resolution TEM (HRTEM) images, where lattice fringes emerge from the interference of transmitted and scattered waves.

Scanning Transmission Electron Microscopy (STEM) represents an alternative imaging mode of the TEM in which a finely focused electron probe is rastered across

the specimen, and scattered electrons are collected point-by-point to form an image. Unlike conventional TEM, which forms images using the parallel illumination of a broad region, STEM allows spatially localised interrogation of structure and chemistry, making contrast directly interpretable in terms of scattering mechanisms at each probe position. Depending on the detector geometry, STEM can produce bright-field, annular dark-field, or high-angle annular dark-field (HAADF) images, each sensitive to different sample properties. In contrast, high-angle annular dark field scanning TEM (HAADF-STEM) employs an annular detector placed at large scattering angles, collecting incoherent elastically scattered electrons. The contrast of the image is based on mass-thickness, which is approximately proportional to Z^2 , where Z is the atomic number.[291] In Aurivillius oxides and related layered perovskites, this capability allows the direct visualization of A- and B-site cation columns, displacements of which form the structural basis of ferroelectric polarisation.

2.5.1 Electron Energy Loss Spectroscopy (EELS): Inelastic Scattering and Electronic Structure

Electron energy loss spectroscopy, exploits the inelastic interaction between the incident electron beam and the sample to reveal information about the chemical composition, oxidation states, coordination environments, and electronic structure.[292] As electrons scatter through the sample, some undergoes inelastic scattering by exciting collective or individual electronic states. These electrons emerge with a reduced kinetic energy, and the magnitude of this energy loss ($\Delta E = E_0 - E_f$) constitutes the measured EEL spectrum.

The underlying physics of EELS is governed by quantised electron-matter interactions. Low-energy losses correspond to plasmon excitations that reflect the

dielectric response of the material,[293], [294] whereas core-loss edges arise from electronic transitions between deep core levels and unoccupied states above the Fermi level. [295] Each edge has a characteristic onset energy determined by the binding energy of the core shell; thus, the EEL spectrum acts as a fingerprint for specific atomic species. [292] Fine structure oscillations, known as Extended Energy Loss Fine Structure (EXELFS) and Energy Loss Near Edge Structure (ELNES), encode information analogously to X-ray absorption spectroscopy, providing insights into valence states, coordination geometry, and hybridisation. Because the energy resolution of modern monochromated TEM instruments can reach the sub-10 meV range, [296], [297], [298] EELS can allow for the probing of subtle electronic changes associated with oxygen octahedral distortions, cation ordering, and defect chemistry, all of which play central roles in determining the functional behaviour of ferroelectric oxides.[299]

The combined capabilities of atomic-resolution STEM imaging and EELS enable simultaneous structural and electronic characterisation at the unit-cell scale. Whereas HAADF-STEM reveals atomic column positions via Z-contrast, EELS assigns chemical identity and oxidation states to the same columns, allowing correlation between structural displacements and electronic modifications. In ferroelectric materials, this coupling is particularly significant because the spontaneous polarisation originates from off-centring displacements of B-site cations and redistribution of electron density along covalent bonds. [300] EELS thereby complements structural imaging by confirming changes in bonding and charge localisation that accompany polarisation switching, domain wall formation, and compositional gradients.

2.5.2 Atomistic Polarisation Vector Mapping Using Atomap

To quantify polarisation directly from atomic structure, it is necessary to resolve site-specific cation displacements with picometre accuracy. In perovskite-derived ferroelectrics, the spontaneous polarisation vector P may be approximated as a sum of dipole moments arising from the displacement of B-site cations relative to the centrosymmetric positions defined by their surrounding oxygen octahedra. In a simplified form, the local polarisation can be expressed as:

$$P = \frac{1}{V} \sum_i q_i \Delta r_i \quad 22,$$

where q_i denotes the nominal ionic charge and Δr_i the displacement of atom i from its reference position within the unit cell volume V . Extracting Δr_i experimentally requires sub-Angström precision, which is now achievable through HAADF-STEM imaging combined with computational analysis pipelines such as the Atomap Python package[301].

In this thesis, this package and the TEMUL Toolkit[302], [303] were employed to perform atomic displacement analysis on HAADF-STEM images. Atomap identifies atomic columns by locating intensity maxima corresponding to the A- and B-site cations, refines their positions using two-dimensional Gaussian fitting routines, and constructs sublattice models that retain crystallographic geometry. Because HAADF-STEM intensities are approximately proportional to Z^2 , the brighter A-site cations are identified first, and their centroid positions establish the parent sublattice. The fainter B-sites are then reconstructed relative to this lattice using nearest-neighbour triangulation. If necessary, atomic positions are interactively corrected before Gaussian refinement ensures statistically robust localisation.

Once both A- and B-site sublattices have been established, the TopoTEM module[302] of the TEMUL Toolkit computes local polarisation vectors by comparing the B-cation displacements relative to a centrosymmetric reference. The function “get_polarisation_from_second_sublattice” evaluates the vector field, and “plot_polarisation_vectors” visualizes it as arrow maps superimposed on the atomic lattice. These polarisation vector maps reveal the directionality and magnitude of ferroelectric dipoles, enabling direct correlation between domain patterns, structural distortions, and microstructural features such as domain walls, intergrowths, and octahedral tilting.

By converting experimental atomic coordinates into spatially resolved polarisation fields, Atomap transforms HAADF-STEM from a qualitative imaging modality into a quantitative tool capable of interrogating the fundamental order parameter of ferroelectricity. The resulting vector fields provide insights into polarisation rotation phenomena, domain connectivity, and nanoscale polarisation configurations relevant to switching, aspects that cannot be inferred from conventional diffraction or electrical measurements alone. Thus, polarisation vector mapping bridges the gap between atomic structure and macroscopic ferroelectric response, offering a powerful platform for understanding how processing routes, strain, and defects govern the performance of complex oxide thin films.

III. Enhancing Vertical Ferroelectric Polarisation Using Growth Spirals

In this chapter, all research is the work of the author, with the exception of the following contributions from collaborators: M. Schmidt (Tyndall-UCC) prepared cross-section lamella of the samples. T. Simonian (Imperial College London) carried out scanning transmission electron microscopy (STEM), high resolution TEM (HRTEM), electron energy loss spectroscopy (EELS) and polarisation simulation. J. Bhattacharya (Tyndall-UCC) carried out the density functional theory calculations and the interpretation of the results. S. Hussain carried out the Kelvin Probe Force Microscopy (KPFM) measurements.

3.1. Introduction

Section 6.1 of the Introduction introduced that supersaturation, controlled through the precursor injection sequence during DLI-CVD, acts a key selector of growth mode in Aurivillius thin films, and that the growth mode in turn determines the nature and geometry of the defect landscape encoded within the film. For $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, a material whose spontaneous polarisation is overwhelmingly confined to the in-plane direction by its crystal symmetry, this raises a question that has not previously been addressed experimentally: can the defect topology generated under a particular growth regime locally perturb the polar energy landscape sufficiently to modify the out-of-plane polarisation response? Answering this requires first establishing how supersaturation and oxygen partial pressure together govern grain morphology and defect formation in DLI-CVD-grown BiT, and then determining whether any resulting structural

changes carry measurable functional consequences. This chapter pursues both questions through systematic variation of the growth parameters.

Ferroelectric thin films, characterized by a spontaneous polarisation that can be switched by an external electric field and sustained after its removal, are technologically important non-volatile memory materials for low-power ferroelectric (FE) random access memory (RAM) devices. These devices find widespread applications in smart cards, ticketless transportation and contactless electronic payment systems.[49], [304], [305] Emerging system-on-chip FE-RAM technologies offer ultra-low energy operation (~ 10 femtojoules per bit), fast write speeds (≤ 14 ns), and excellent scalability to sub-10 nm dimensions,[306], [307] outperforming magnetoresistive RAM, phase change RAM, and oxide-based RAM in energy efficiency and overall performance. Ferroelectric-based memory systems such as ferroelectric field effect transistors (FE-FETs) and ferroelectric tunnel junctions (FTJs), show significant promise for advancing energy-efficient, ‘brain-inspired’ neuromorphic computing devices.[64] FTJs comprise a nanometer-scale ferroelectric layer sandwiched between metallic electrodes with differing screening lengths, creating an asymmetric potential profile for opposite polarisation directions. When an electric field is applied, the polarisation switches, modulating the electron tunneling barrier height and enabling ON:OFF tunneling current ratios spanning 2 to 3 orders of magnitude.[64], [65], [308], [309], [310], [311] Additionally, precise control over ferroelectric domain nucleation during switching allows FTJs to achieve multi-level resistance states, increasing storage density and versatility, thereby broadening their applicability in neuromorphic computing.[312][313], [314], [315] In 2019, the concept of lateral FTJs based on in-plane polarisation was introduced.[131] These devices have the advantage of avoiding competing depolarisation fields when scaled

down to miniaturized, ultra-thin dimensions. However, devices based on lateral architectures encounter fabrication challenges, including lithography of sub-10 nm horizontal tunnel layers and integration with suitable electrodes. Therefore, most of the industry focus involves integration of ferroelectrics displaying vertical polarisation.[304]

Aurivillius phase crystals (**Figure 3.1 a**) are an established class of lead-free ferroelectrics displaying high Curie temperatures ($>600\text{ }^{\circ}\text{C}$),[316] with materials such as $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ($n = 2$) and $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ ($n = 3$)[49], [161], [305], [317] finding commercial use in FE-RAM devices. Aurivillius phases are described by the formula: $(\text{Bi}_2\text{O}_2)(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})$ and are composed of alternating layers of fluorite-type bismuth oxide $(\text{Bi}_2\text{O}_2)^{2-}$ interface layers and perovskite-type blocks $(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2+}$, as shown within the schematic within **Figure 3.1 a**. ‘ n ’ is the number of perovskite layers per half-unit cell. The charge compensating role of the bismuth oxide layers provides significant fatigue tolerance (10^{12} switching cycles).[162] The flexibility of their layered structure allows the value of n to be varied and enables the tunability of ferroelectric behaviour through A/B site cation substitution. Via charge-mediated synthetic routes,[318] Aurivillius phase crystals can be modified to display room temperature multiferroic properties on substitution of magnetic Fe and Mn cations,[145] [272] and have been synthesized epitaxially via industry-compatible Direct Liquid Injection Chemical Vapour Deposition (DLI-CVD) methods.[144], [145] In addition to, stable and switchable ferroelectricity persists in sub-10 nm Aurivillius phase thin films, indicating their potential relevance for miniaturized architectures and ultrathin tunnel junction concepts.[129], [144], [222], [229], [242]

Despite their advantageous characteristics, integrating Aurivillius phase materials into future miniaturized functional devices remains challenging, primarily due to the system's polarisation direction.[200] Aurivillius phase thin films predominantly exhibit a preferential c -axis (00 l) crystal orientation. However, even-layered Aurivillius phases are restricted to in-plane polarisation along the b -axis because of a mirror plane perpendicular to the c -axis, which prevents out-of-plane polarisation. Achieving purely vertical b -axis (010) orientated thin films using orientated substrates is particularly difficult, as this orientation often competes with the (118) orientation.[319], [320], [321], [322] This limitation poses significant problems in an industry that predominantly relies on out-of-plane polarized thin films for compatibility with conventional vertical device architectures. Odd-layered variants, such as $n = 3$ bismuth titanate (Bi₄Ti₃O₁₂, BiT; monoclinic, $a = 5.45$ Å, $b = 5.41$ Å, $c = 32.84$ Å)[324], [325] illustrated in **Figure 3.1 a**, provide a potential solution. These phases exhibit a minor out-of-plane polarisation along the c -axis (~ 4 $\mu\text{C}/\text{cm}^2$) while maintaining a dominant in-plane polarisation (~ 50 $\mu\text{C}/\text{cm}^2$).[215], [242], [243] This behaviour arises from the absence of the energetically unfavorable horizontal mirror plane below the ferroelectric transition temperature, alongside the retention of a more energetically favorable twofold rotation axis along the a -axis.[207] The modest c -axis polarisation in odd-layered Aurivillius phases highlights their potential relevance for vertical architectures, provided strategies are developed to enhance this out-of-plane response.

Prior efforts to enhance the c -axis polarisation of bismuth titanate have primarily focused on strain engineering, through rare-earth doping (e.g. La and Nd) and substrate induced lattice mismatch, with the aim of altering crystal symmetry to

promote polarisation along the desired direction.[208], [209], [210] Notably, Chon *et al.*[326] reported an unusually high *c*-axis polarisation of approximately 100 $\mu\text{C}/\text{cm}^2$ in $\sim 280\text{nm}$ thick Nd-doped BiT films, attributing this enhancement to Nd doping influencing Ti ion displacement and a symmetry shift from orthorhombic to pseudo-tetragonal. Upon reducing film thickness to $\sim 100\text{nm}$, however, it was found that the *c*-axis polarisation reduces to $\sim 6\text{--}12 \mu\text{C}/\text{cm}^2$. [169], [322], [327] Moreover, subsequent investigations by Garg *et al.*[322] and Roy *et al.*[169] disagreed with Chon *et al.*'s [326] interpretation, prompting further research into how subtle variations in sample preparation affect crystal symmetry and ferroelectric behaviour. Giddings *et al.*[328] further emphasize that the functional properties of Aurivillius phase oxyfluorides are tightly linked to their crystal structure and symmetry, both of which are sensitive to synthesis conditions, cooling rates, and strain. Collectively, these studies highlight the intrinsic complexity of tailoring Aurivillius phase materials for potential technological applications.

This study introduces a new approach to enhancing vertical ferroelectric polarisation in epitaxial bismuth titanate thin films by actively controlling the growth mechanism through precise adjustment of supersaturation and oxygen partial pressure during industrially relevant DLI-CVD. By steering the process between two-dimensional nucleation and growth, which favors in-plane polarisation, and dislocation-mediated spiral growth, which promotes vertical polarisation, the microstructural morphology and defect topology of Aurivillius phase BiT can be deliberately engineered. While spiral growth has previously been observed in layered ferroelectrics deposited by high-vacuum methods such as pulsed laser deposition (PLD) and molecular beam epitaxy (MBE), its direct influence on polarisation behaviour has not been experimentally established. Here, we demonstrate for the first

time that spiral-mediated growth enhances out-of-plane polarisation by introducing ordered networks of out-of-phase boundary (OPB) defects that locally influence sub-unit cell modifications in elastic strain, localized electron densities and local symmetry-lowering distortions. Atomic-resolution electron microscopy and density functional theory studies reveal that these effects induce polarisation discontinuities and shifts in polarisation direction, effectively enhancing vertical polarisation. This approach lowers the local switching barrier and stabilizes vertical polarisation, significantly reducing the minimum vertical switching voltage from ± 20 V to ± 5 V. This combined mechanistic and process-level understanding establishes a scalable, atomically informed route to controlling ferroelectric functionality in layered oxides, linking growth optimization, defect structure, and polarisation behaviour relevant to emerging low-power electronic technologies. Accordingly, this study aims to elucidate how controlled spiral growth in DLI-CVD-derived Aurivillius thin films can be harnessed to enhance vertical ferroelectric polarisation through atomic-scale defect engineering and mechanistic design.

3.2. Results and discussion

3.2.1. Optimizing grain morphology via tunable growth parameters

Recognizing the critical role of supersaturation in crystallization during thin film deposition, this study investigates how varying supersaturation levels and oxygen partial pressure impact the microstructure and properties of BiT thin films grown by DLI-CVD. Supersaturation (α), defined as the ratio of partial pressure of depositing species (P) to their equilibrium vapour pressure (P_{eq}), [232] governs nucleation and growth dynamics:

$$\alpha = \frac{P}{P_{eq}}$$

High supersaturation levels ($\sim < 50\%$) typically promote two-dimensional nucleation of new islands on terraces, whereas even low supersaturation ($\sim 1\%$) can sustain step-growth at existing step edges due to their lower kinetic and energetic barriers.[233] While nucleation requires a relatively high degree of supersaturation to overcome the associated energy barrier, continued lateral growth along step edges can proceed at much lower supersaturation levels if such energetically favorable sites are present. Film growth can follow one of three primary modes: layer-by-layer (Frank–van der Merwe), island (Volmer–Weber), or a mixed mode (Stranski–Krastanov).[219] At low supersaturation, growth rates dominate over nucleation, leading to the formation of larger grains.[329] In contrast, high supersaturation enhances nucleation rates, resulting in smaller grains.[330] This section therefore compares high and low supersaturation regimes, and also examines how oxygen partial pressure modulates grain morphology and out-of-phase boundary (OPB) defect density.

3.2.1.1. Supersaturation Control

a. High Supersaturation CVD Growth: Simultaneous Precursor Injections

In conventional DLI-CVD growth, simultaneous injection of Bi and Ti precursors ([Supplementary Figure S 3.1 a](#)) creates high supersaturation conditions. Deposited at one injection per second on [100] SrTiO₃ (STO) substrates, this method yields rapid film growth (~ 1.47 nm/min) via a Frank–van der Merwe layer-by-layer mechanism

([Supplementary Figure S 3.1 c, Figure S 3.2 a, b](#)). Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM) imaging reveal the presence of two-dimensional islands and pits with heights corresponding to multiples of the half-unit cell c -axis parameter (~ 5 nm)[213][331] indicating layer-by-layer nucleation.

TEM images ([Supplementary Figure S 3.2 c](#)) reveal pronounced sub-unit cell OPB defects,[93], [144], [206] which are attributed to bismuth volatility and migration at 675 °C.[172] OPB defects are commonly observed in Aurivillius phase materials with high structural anisotropy and are characterized by a fractional lattice parameter shift (c/x) between adjacent regions along the c -axis.[269] These shifts manifest as distinct “steps” within the film, clearly visible in the TEM micrographs ([Supplementary Figure S 3.2 c](#)). The combination of a limited activation energy to suppress bismuth diffusion, high crystalline anisotropy, and unidirectional growth fronts confines structural rearrangement to the surface layers, thereby exacerbating OPB defect formation.[212][332] X-ray diffraction reciprocal space mapping ([Supplementary Figure S 3.2 d](#)) confirms the epitaxial relationship between the BiT film and the STO substrate.

b. Low Supersaturation CVD Growth: Sequential Precursor Injections

To precisely control supersaturation during DLI-CVD growth of BiT, bismuth and titanium precursors were injected sequentially, with a 5-second purge between each cycle (**Figure 3.1 a**). This method, repeated over 20 cycles, produces ~ 25 nm thick BiT films while mimicking the layered atomic structure of the Aurivillius phase.[168] The epitaxial nature of the film is confirmed by Aberration-corrected high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM)

(**Figure 3.1 c**). Spectral mapping acquired by scanning transmission electron microscopy-electron energy loss spectroscopy (STEM-EELS) clearly resolves the periodic arrangement of $(\text{Bi}_2\text{O}_2)^{2+}$ interface layers alternating with perovskite units within the Aurivillius phase structure (**Figure 3.1 b**). The elemental distribution maps show titanium (red) localized at the B-sites of the perovskite blocks, while bismuth (green) predominantly occupies the A-sites of the perovskite blocks as well as the $(\text{Bi}_2\text{O}_2)^{2+}$ layers, highlighting the well-defined atomic-scale layering.

By reducing the instantaneous concentration of reactive species, sequential precursor injection lowers supersaturation, preventing excessive nucleation. The calculated supersaturation ratio (α) between high and low supersaturation conditions in this study is 5.4:1 ([Appendix IV Section I](#)). At high supersaturation, rapid nucleation drives two-dimensional, layer-by-layer growth. In contrast, under low-supersaturation conditions, where step-flow crystal growth dominates over nucleation, BiT thin films grown on [100] STO substrates exhibit a distinct spiral growth morphology (**Figure 3.1 d**, **Figure 3.2 e**) and enlarged grain sizes, in agreement with the Burton–Cabrera–Frank (BCF) theory.[225] AFM confirms spiral step heights of ~ 1.7 nm, corresponding to half the c-axis unit cell parameter of the $n = 3$ Aurivillius phase (**Figure 3.1 e**).[213]

[S 3.3](#)), rather than appearing as symmetric, random, or mirror-balanced step configurations. This handedness is a direct fingerprint of screw-dislocation-driven spiral growth, where the sign of the Burgers vector fixes the rotational sense of step propagation[334]. Importantly, the absence of counter-rotating (left-handed) spirals indicates that the dislocation nucleation is not stochastic, rather, it is deterministically biased by the interfacial step geometry and local misfit strain fields[335]. The growth spiral's chirality (handedness of the screw dislocation) is fundamentally useful in ferroelectric memories because it provides topological control over the domain structure[336]. By governing the local lattice strain and atomic displacements around the spiral core, chirality enables the engineering of chiral domain walls. They serve as nanoscale functional elements for high-density domain wall memory and potentially enabling stable multi-state or topological memory based on structural orientation rather than just bulk charge[337].

These growth conditions for spirals are consistent with reports of other bismuth-based systems, such as Bi_2Te_3 growth spirals.[338] Sequential precursor injection plays a key role in maintaining the low deposition rate necessary for promoting spiral growth. In contrast, simultaneous injection results in a higher deposition rate (~ 1.47 nm/min) and a significantly elevated supersaturation ratio of 5.4:1 ([Appendix IV Section I](#)), which instead favors two-dimensional nucleation and layer-by-layer growth ([Supplementary Figure S 3.1 and S 3.2](#)). This transition in growth mode aligns with the crystal growth predictions proposed by Lovette *et al.*[339]. The differentiation between the 2D growth under high and low supersaturation is described in [Appendix I](#).

Two key defects arise from the spiral growth process. The first is the screw dislocation itself, characterized by a cylindrically symmetric stress field and a highly distorted core (**Figure 3.1 d**).[340] The second is the prevalence of OPB defects (**Figure 3.2 (d, e)**), which form at low-angle grain boundaries where adjacent growth spirals merge.[212] These OPB defects define the edges of growth pyramids, consistent with the Burton–Cabrera–Frank (BCF) model.[225]

3.2.1.2. Tuning of Grain Morphology with Oxygen Partial Pressure

An important advantage of DLI-CVD, an industrially relevant method for synthesizing layered perovskites, is its ability to precisely control the oxygen partial pressure across a wide operational range, thereby minimizing Bi_2O_3 re-evaporation compared to high-vacuum techniques.[341] In this study, the oxygen partial pressure was systematically varied from 13.2 Pa to 26.6 Pa by adjusting the $\text{N}_2\text{g}:\text{O}_2\text{g}$ ratio from 2:1 to 1:2 during sequential precursor injection (see [Appendix IV Section II](#)), enabling investigation of its effect on grain morphology and defect density.

X-Ray Diffraction analysis reveals that films grown under lower oxygen partial pressure (13.2 Pa; $\text{N}_2:\text{O}_2 = 2:1$) exhibit pronounced peak splitting, with separations of 1.96° and 1.46° in the 004 and 00 10 reflections, respectively (**Figure 3.2 a**, [Supplementary Figure S 3.4](#)). This splitting, accompanied by a broader full width at half maximum (FWHM) of the 004 peak (2.15°), is indicative of OPB defects and local structural disorder.[168], [212], [269] As the oxygen partial pressure increases to 26.6 Pa ($\text{N}_2:\text{O}_2 = 1:2$), the diffraction peaks converge and sharpen, and the FWHM narrows to 1.33° ([Supplementary Figure S 3.5](#), [Supplementary Table S 3.2](#)), reflecting enhanced structural coherence and a reduction in OPB defects. This structural evolution is corroborated by AFM and TEM analyses ([Supplementary](#)

[Figure S 3.6](#)). For growth under lower oxygen partial pressure (13.2 Pa), AFM imaging **Figure 3.2 (b (v))** reveals a high density of spiral growth features (~ 2.6 spirals/ μm^2), consistent with dislocation-driven growth in OPB-rich regions.[212] [225] As the oxygen partial pressure increases, the surface morphology transitions from spiral-dominated to smoother, step-meandering, two-dimensional growth (**Figure 3.2 (b i)**). The spiral density decreases accordingly, dropping to ~ 1.3 spirals/ μm^2 under an oxygen partial pressure of 17.2 Pa (**Figure 3.2 (b (iii))**), and becoming nearly absent under an oxygen partial pressure of 26.6 Pa (**Figure 3.2 (b i)**). The trends establish a clear link between oxygen deficiency, spiral formation, and OPB defect generation, as further supported by the broader XRD peaks and peak splitting observed at lower oxygen pressures ([Supplementary Table S 3.2](#))[269]. Similar behaviour has been reported in other bismuth oxides,[342], [343] as well as in BaSnO_3 ,[344] and indium tin oxide,[345] where increased oxygen partial pressure suppresses defect formation and promotes film coalescence. Unless otherwise stated, FWHM values quoted in this chapter refer to the full width at half maximum extracted from θ - 2θ scans at the 00ℓ reflections; rocking curve (ω -scan) widths, which reflect mosaicity and tilt distribution independently of d-spacing variation, are quoted separately and identified as such where reported.

In the present study, the transition from spiral growth to 2D meandered step-flow growth is corroborated by XRD analysis of BiT films, which shows the disappearance of peak splitting under an oxygen partial pressure of 26.6 Pa (**Figure 3.2 a**), indicative of improved crystallographic coherence. Corresponding AFM and TEM imaging (**Figure 3.2 (b–e)**) reveal that previously distinct growth spirals coalesce into more continuous, uniform films, providing direct evidence for the suppression of dislocation-driven growth under oxygen-rich conditions.

The degree of coalescence (D_c), defined as:

$$D_c = \frac{\text{Area of coalesced regions}}{\text{Total area of the image}} \quad 25,$$

increases significantly from ~0.4 at 13.2 Pa to ~0.75 at 26.6 Pa, indicating an ~87.5% improvement in surface coalescence. This trend is consistent with observations other layered systems like $\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (SmBCO) films,[346] where increasing oxygen pressure reduces defect densities and promotes two-dimensional growth. The step heights of the spiral islands successively decrease (from ~1.7 nm to ~1 nm) with increasing oxygen partial pressure ([Supplementary Figure S 3.6](#)), aligning with the trend observed with the degree of coalescence and the degree of XRD peak splitting. Moreover, tuning oxygen partial pressure during the cooling phase provides further control over morphology and defects. Oxygenated cooling at a constant flow rate of 1200 sccm reduces peak splitting ([Supplementary Figure S 3.7](#)), which is attributed to the suppression of bismuth volatilization (a key factor in OPB defect formation) under an oxygen-rich atmosphere during post-deposition cooling to room temperature.

Evidence indicates that the additional shoulders/split features in the (00l) reflections arise from OPB-induced peak splitting and broadening, not from a crystalline secondary phase. First, with increasing O_2 partial pressure the XRD peaks sharpen and converge (**Figure 3.2 a**, [Supplementary Table S 3.2](#)) while AFM/TEM independently show a reduction in spiral/OPB density (**Figure 3.2 (b, c, d)**) establishing a one-to-one process–structure–diffraction correlation. Second, HAADF-STEM and EELS confirm uninterrupted Aurivillius layering across the film thickness, and STEM-EELS maps show no extended regions of a distinct composition, which argues against a bulk impurity phase. Third, the intensity and spacing of the extra

features track the oxygen-pressure-dependent spiral density and OPB signatures seen in TEM ([Supplementary Figures S 3.5 –S 3.6](#)). This behaviour is consistent with OPB-driven splitting of (001) peaks and additional microstrain/finite-domain broadening expected for translational faults, whereas a true secondary phase would produce composition-specific reflections whose positions and relative intensities would not systematically collapse with OPB suppression.

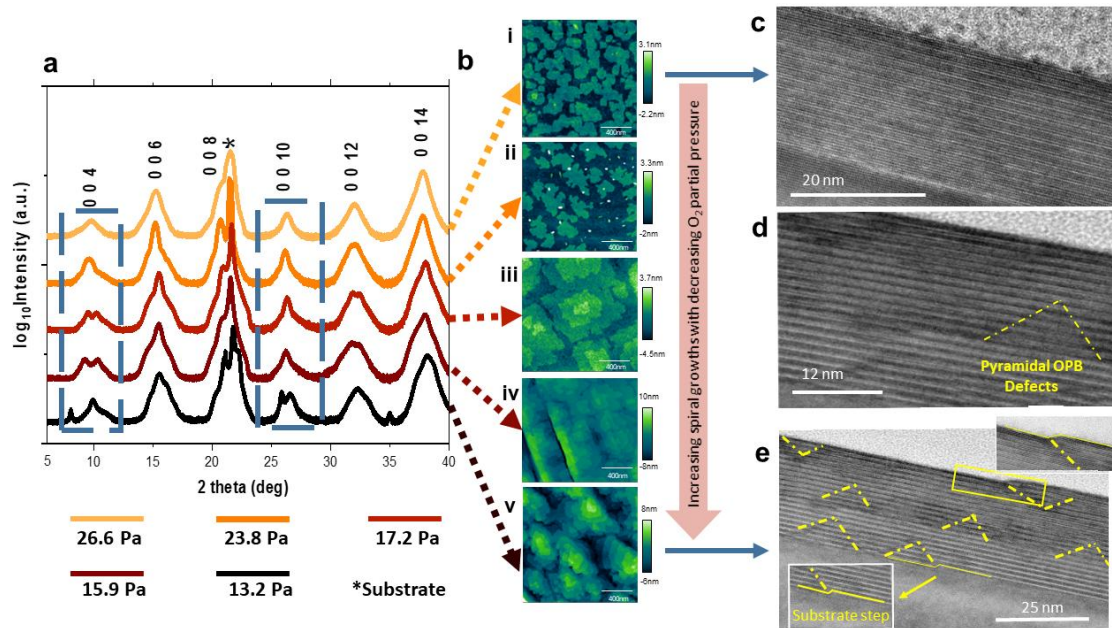


Figure 3.2: *a* XRD patterns of thin films grown under low supersaturation and varying $N_2:O_2$ ratios from 1:2 to 2:1 (26.6 Pa to 13.2 Pa). *b* AFM topography images of $2\ \mu\text{m} \times 2\ \mu\text{m}$ thin film areas (*i* - *v*) reveal a clear correlation with XRD trends, where increased peak splitting and broadening-attributed to OPB defects-result in denser spiral growth as the O_2 partial pressure decreases from 26.6 Pa to 13.2 Pa. (*c-e*) TEM cross sectional images reveal an increased defect density with decreasing O_2 partial pressure, with *c* corresponding to 26.6 Pa and (*d & e*) corresponding to 13.2 Pa. OPB defects, indicated by dashed yellow lines, delineate the edges of the growth pyramids. **Insets in e:** **Top:** The height of each growth spiral step corresponds to approximately half of the *c*-axis unit cell parameter of BiT. **Bottom:** STO substrate-BiT film interface.

3.2.2. Influence of grain morphology on ferroelectric properties

We investigate the influence of grain morphology on ferroelectric properties by comparing films exhibiting growth spirals with those formed via two-dimensional

meandered step-flow growth. Both morphologies arise under low supersaturation conditions but differ based on the applied oxygen partial pressure. Through detailed analysis of domain structures, lateral and vertical piezoresponse signals, and piezoresponse force microscopy (PFM) hysteresis loops, we examine how these distinct growth modes affect polarisation behaviour. Additionally, poling studies reveal the samples' responses to external fields, offering further insight into their switching dynamics.

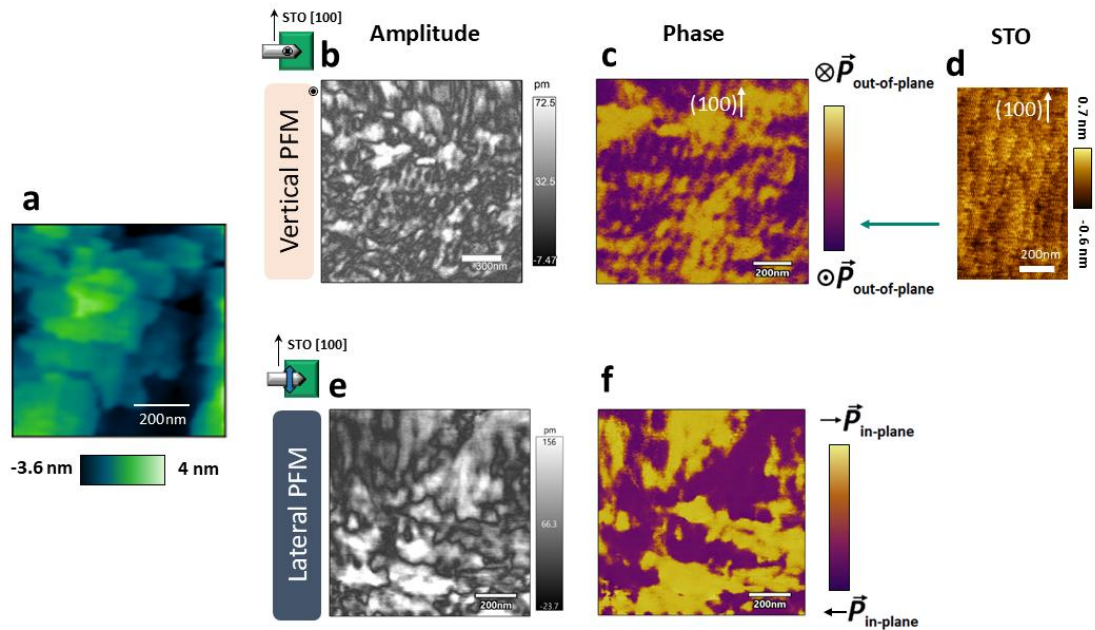


Figure 3.3: *a* AFM topography image of a BiT thin film exhibiting spirals (*b, c*) Vertical PFM (VPFM) amplitude and phase images revealing ferroelectric domain alignment along the [100] direction, consistent with the underlying substrate step orientation. *d* AFM topography image of the bare [100]-orientated STO substrate, showing well-defined step-terrace features that guide the domain orientation in the overlying film. (*e, f*) Lateral PFM (LPFM) amplitude and phase images of the growth spiral sample.

3.2.2.1. Ferroelectric domain morphology

Aurivillius phase thin films, such as the $n = 3$ BiT, exhibit dominant ferroelectric polarisation along the b-axis (lateral direction, $\sim 50 \mu\text{C}/\text{cm}^2$) with significantly weaker

polarisation along the c-axis (vertical direction, $\sim 4 \mu\text{C}/\text{cm}^2$). [242], [243] Consequently, the lateral piezoresponse consistently exceeds the vertical response across all BiT thin films (**Figure 3.3 (b, c, e, f), [Supplementary Figure S 3.8](#)**). Lateral ferroelectric domains formed within spiral-mediated growth structures are substantially larger ($\sim 4,250 \text{ nm}^2$; standard deviation: $26,200 \text{ nm}^2$) (**Figure 3.3 f**) compared to those in films exhibiting two-dimensional meandered step-flow growth ($\sim 421 \text{ nm}^2$; standard deviation: $2,460 \text{ nm}^2$) (**[Supplementary Figure S 3.8 e](#)**). BiT films grown under two-dimensional meandered step-flow conditions show only weak vertical piezoresponse (**[Supplementary Figure S 3.8 b](#)**), whereas films grown under low supersaturation and low oxygen partial pressures, (conditions favoring spiral growth), exhibit a pronounced vertical piezoresponse (**Figure 3.3 b**). While lateral domains in both growth modes show no preferential in-plane alignment (**Figure 3.3 (e, f), [Supplementary Figure S 3.8 \(d, e\)](#)**), vertically polarized domains in spiral-grown films align with the [100]-oriented terraces of the underlying STO substrate (**Figure 3.3 (b–d)**). In contrast, films grown via two-dimensional meandered step-flow do not exhibit comparable vertical domain alignment or piezoresponse (**[Supplementary Figure S 3.8 \(b, c\)](#)**). Alignment of ferroelectric domains with substrate-induced features has been reported for Aurivillius phases grown on vicinal surfaces, where substrate miscut angles influence domain orientation.[347] However, in this study, the alignment specifically pertains to vertical domain response, strongly templated by the substrate terraces. The combination of low supersaturation conditions, a slow deposition rate ($\sim 0.74 \text{ nm}/\text{min}$), and limited oxygen availability promotes spiral-mediated step-flow growth, initiated at terrace kinks ($\sim 0.5 \text{ nm}$ in height). This growth mode gives rise to steric OPB defects at low-angle grain

boundaries (**Figure 3.2 e**), which in turn appear to align vertically polarized domains and enhance the vertical piezoelectric response.

AFM nanomachining ([Supplementary Figure S 3.9](#)) confirms that this substrate-induced alignment of vertical domains persists throughout the film thickness. The surface was machined to a depth of ~ 21 nm (approximately 3–4 unit cells) using a diamond probe, and subsequent vertical PFM imaging revealed that vertical domain alignment remained consistent along the $[100]$ substrate direction in sub-surface layers ([Supplementary Figure S 3.9 c](#)).

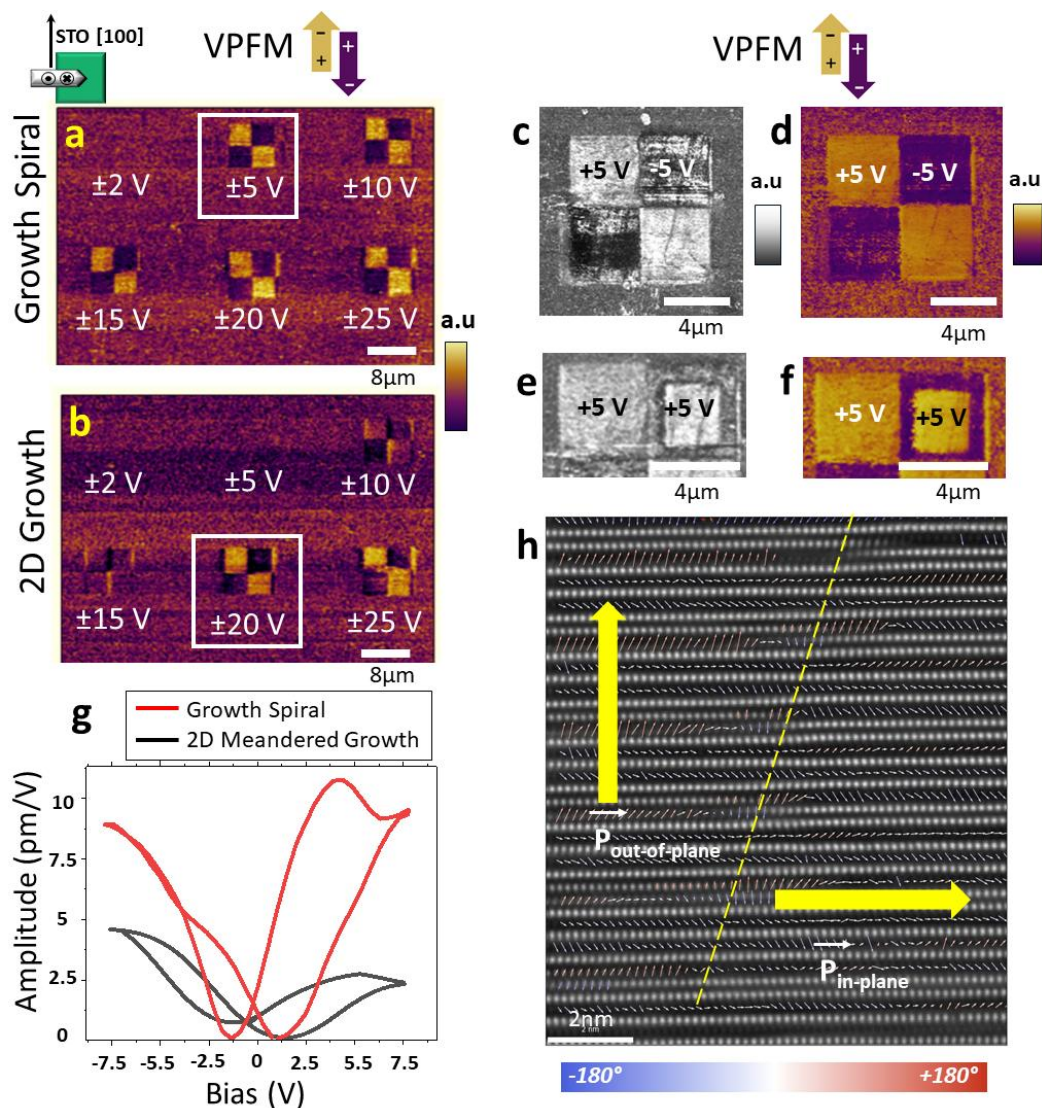


Figure 3.4: ***a** VPFM phase image of a BiT film exhibiting growth spirals, demonstrating up and down switched regions, with vertical switching achieved at ± 5 V. **b** VPFM phase image showing the minimum bias required for vertical poling of BiT films from two-dimensional meandered step-flow growth is ± 20 V. (c-f) VPFM amplitude (c, d) and phase images (d, f): Initially, $4\ \mu\text{m} \times 4\ \mu\text{m}$ regions were poled with either $+5$ V or -5 V. Subsequently, a $3\ \mu\text{m} \times 3\ \mu\text{m}$ region within a -5 V poled area was reverse poled using a $+5$ V DC bias. **g** PFM displacement amplitude loop measurements in the ‘off’ state, showing higher piezoresponse (~ 8.7 pm/V) for the BiT films exhibiting growth spirals (red) compared to films from two-dimensional meandered step-flow growth (black) (~ 3.7 pm/V). **h** HAADF-STEM image of a BiT growth spiral sample overlaid with a reverse B-site displacement polarisation map of each perovskite cell. The vector lengths indicate the relative magnitude of the B-site displacement, reflecting the corresponding polarisation strength. Approximate positions of OPB defects are indicated by the dashed yellow line. The larger yellow arrows represent the net polarisation vectors.*

3.2.2.2. Ferroelectric Switching Behaviour

Through PFM imaging of electrically poled regions, we reveal that dense spiral growth structures of BiT on [100]-oriented STO substrates act to dramatically lower the voltage required for vertical switching. Spiral-grown BiT films exhibit effective vertical switching at ± 5 V (**Figure 3.4 a**, [Supplementary Figure S 3.10 & S 3.11](#)), whereas two-dimensional meandered step-flow grown films require a higher bias of ± 20 V (**Figure 3.4 b**). **Figure 3.4 (c–f)** demonstrates the reversibility of vertical ferroelectric switching. Initially, selected regions of the film were poled using a negative DC bias (**Figure 3.4 (c–d)**). Subsequently, smaller subregions within the negatively poled areas were reverse-poled using a positive DC bias (**Figure 3.4 (e–f)**). The ability to reversibly switch ferroelectric domains with high spatial precision demonstrates stable and repeatable polarisation control, for a key step toward non-volatile memory and reconfigurable logic technologies. It is important to note that the switching voltages reported here (± 5 V and ± 20 V) are derived from local PFM lithography experiments, where the conductive tip is used to pole and erase ferroelectric domains by applying a localized bias. In this electrode-free configuration,

the electric field is confined to a nanometer-scale contact area, producing artificially high local field intensities to overcome the lack of uniform charge screening and strong depolarisation fields at the free surface. As a result, the voltages required for PFM-based switching are necessarily higher than those needed in a conventional capacitor stack, where continuous top and bottom electrodes ensure uniform field distribution and efficient charge compensation. Hence, when translated to macroscopic capacitor geometries with continuous top and bottom electrodes, the effective switching voltage is expected to be substantially lower due to the uniform field distribution, improved charge compensation, and reduced depolarisation effects.

Vertical ferroelectric hysteresis and butterfly loops, obtained using PFM with a stepped triangular bias waveform (0.2 Hz frequency, 500 mV AC read voltage), confirm this enhanced out-of-plane switching behaviour in spiral-grown films. Under a DC bias of ± 7.5 V applied via the PFM tip, the spiral-grown films show a measured remnant out-of-plane displacement of ~ 8.7 pm/V. Compared to two-dimensional meandered step-flow films (~ 3.7 pm/V under the same bias), spiral-grown film deliver a $\sim 135\%$ greater piezoresponse amplitude (**Figure 3.4 g**), highlighting its superior out-of-plane electromechanical performance. The slight asymmetry in the hysteresis loops is attributed to an intrinsic built-in bias, likely caused by minor domain population imbalances, common in ferroelectric thin films.[348] The coexistence of persistent PFM and SKPFM signals over multiple days ([Supplementary Figure S 3.12](#)) rules out transient artefacts such as tip-induced charging, and instead provides compelling evidence of true, remanent ferroelectric switching, supported by effective charge compensation at the surface. Such temporal stability is a key prerequisite for future non-volatile ferroelectric memory concepts.

Whereas spiral growth structures favor low voltage vertical switching, lateral polarisation switching is markedly more efficient in two-dimensional meandered step-flow grown films synthesized under higher oxygen partial pressures (26.6 Pa), a result attributed to enhanced film continuity along the a-b plane and higher coalescence ($D_c \sim 0.75$). These two-dimensional films achieve lateral switching at reduced voltages of ± 5 V ([Supplementary Figure S11 h](#)) whereas, spiral-grown films require higher lateral poling voltages of ± 15 V ([Supplementary Figure S11 d](#)).

The depth-dependent switching behaviour of spiral-grown BiT films was further investigated by nano-machining the films to ~ 10 nm using an AFM diamond cantilever ([Supplementary Figure S 3.9](#)), followed by PFM lithography with an applied voltage of ± 20 V ([Supplementary Figure S 3.13](#)). The results show no degradation in ferroelectric switching characteristics with reduced thickness ([Supplementary Figure S 3.13](#)), indicating that polarisation switching originates from bulk properties rather than surface effects. This confirms that spiral-grown films maintain robust ferroelectric behaviour down to nanoscale dimensions, a characteristic highly relevant for future miniaturized ferroelectric architectures.

To investigate vertical polarisation changes at the sub-unit cell scale in spiral-grown films, HAADF-STEM imaging was employed to visualize atomic-scale displacements[93]. Given the distinct bond lengths in the outer and central perovskite layers (**Figure 3.5 a**), we compared displacement and polarisation behaviour in regions with and without OPB defects (**Figures 3.5 (b-e)**). Local polarisation vectors were then extracted from these regions (**Figures 3.5 (f-g) and Figure 3.4 h**), with red and blue arrows indicating both the direction and magnitude of cation displacements. The resulting net polarisation directions are summarized by the large yellow arrows in

Figure 3.4 h. The approximate position of the domain wall, marked by the dashed yellow line (**Figure 3.4 h**), corresponds with the locations of the OPB defects. The domain on the right exhibits an overall net in-plane polarisation, characteristic of the bulk BiT film. In contrast, for the domain on the left of the OPB, the polarisation magnitudes result in a net vertical, *c*-axis polarisation. These findings offer direct atomic-scale evidence that spiral-mediated growth, via its associated OPB defects, governs vertical ferroelectric ordering and polar orientation.

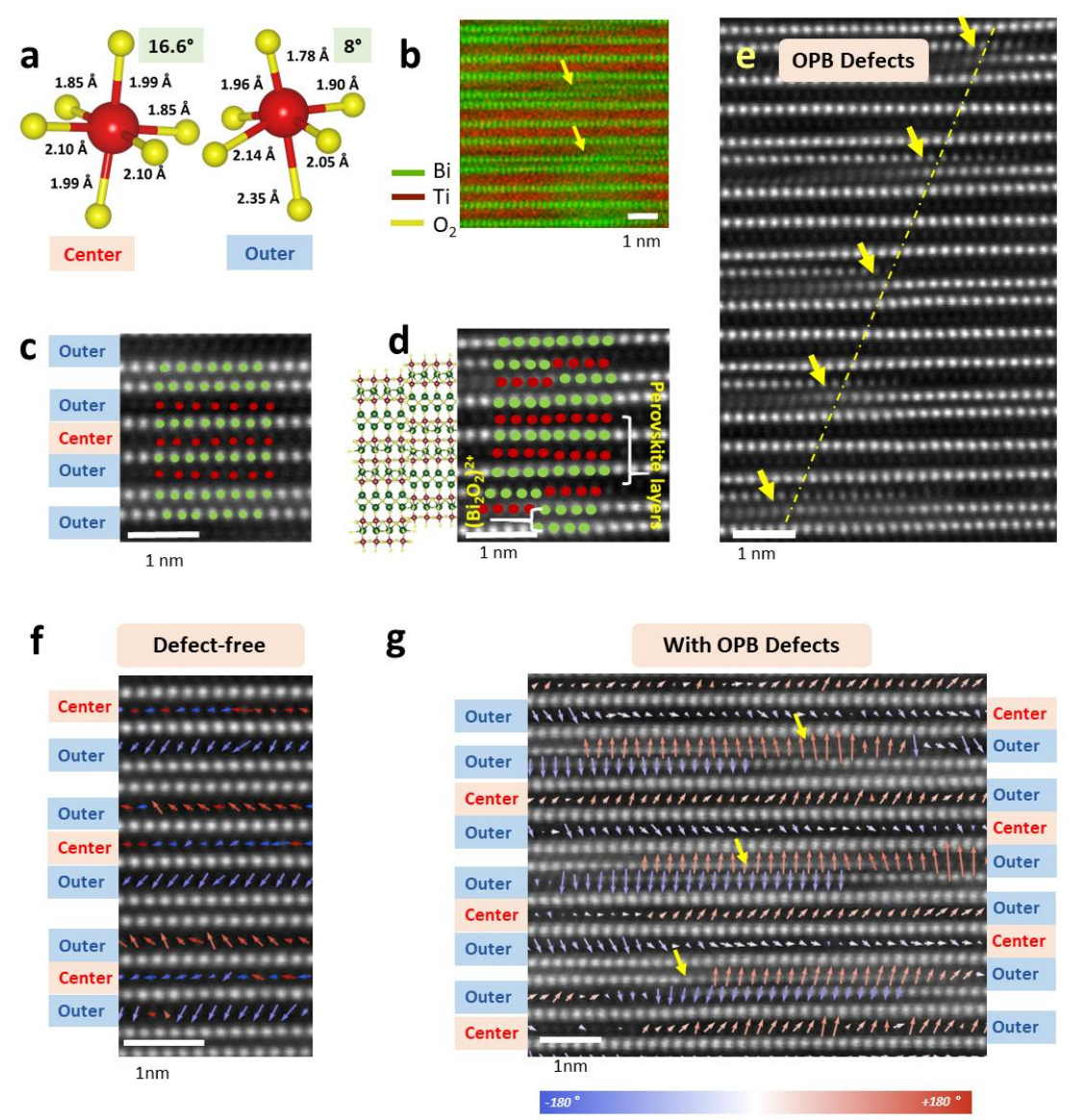


Figure 3.5: *a* Comparison of Ti-O bond lengths in central and outer perovskite layers of BiT as well as their octahedral tilt angles in the absence of OPB defects (adapted from DFT simulations in

[Supplementary Figure S 3.14](#)). **b** STEM-EELS map of a BiT growth spiral sample showing positions of Bi and Ti at the OPBs. **(c, d)** HAADF- STEM images showing the separation between bismuth and titanium layers. Atomic positions of BiT overlaid onto the TEM images to compare a defect free region **c** with a region containing OPB defects **d**. **e** HAADF- STEM image of a growth spiral sample showing OPB defects propagating along low-angle grain boundaries. Approximate positions of OPB defects are indicated by yellow arrows. **f** Polarisation map from HAADF-STEM data showing polarisation vectors in defect-free region of BiT. **g** OPB defects create polar discontinuities, where polarisation vectors visibly re-orient vertically.

The atomic-scale comparison between defect-free and defect regions offers crucial insights into how structural discontinuities influence polarisation. In the defect-free region shown in **Figure 3.5 f**, polar vectors are well-ordered along the lateral direction, while the opposing out-of-plane components at the top and bottom (antipolar) effectively cancel, producing a net lateral polarisation. In contrast, **Figure 3.5 g** highlights an OPB defect, indicated by a yellow line, where atomic planes are shifted. The yellow arrows point to disruptions in atomic alignment. At OPB defects, polarisation discontinuities and reorientations occur. STEM imaging reveals that OPB defects are not strictly confined along the *c*-axis but exhibit a subtle twisting, suggesting local distortions of the crystal structure affecting the lattice parameters along the *a*- and *b*-axes (**Figure 3.5 g**). This "screw-like" character likely arises from the spiral-driven growth mechanism, where screw dislocations at the film-substrate interface serve as step sources, enabling continuous, cylindrical step expansion. OPB defects form at the low-angle grain boundaries where adjacent growth spirals merge, defining edges of the BCF growth pyramids.[225] The mapped local displacement fields occasionally appear to coincide with bismuth columns; however, this apparent

overlap results from the projection of multiple atomic columns along the electron beam direction. At OPB locations, the Ti (B-site) positions are slightly shifted within the perovskite block. However, when viewed in projection, on some occasions these displacements overlap with the brighter bismuth (A-site) columns, assigning polar vectors over Bi sites. This demonstrates how OPB defects perturb both the atomic arrangements of the perovskite blocks and bismuth oxide fluorite-type layers, creating complex, three-dimensional distortions that couple vertical polarisation with lateral shear components. Such twisting also reinforces the notion that OPB defects serve as both structural discontinuities and rotational mismatch centres within the crystal structure, contributing local disruptions in crystal periodicity, lowering symmetry and affecting polarisation continuity.

Such three-dimensional, defect-mediated lattice distortions not only modify the local symmetry landscape but also have direct implications for switchable ferroelectric behaviour. In this context, it is important to emphasize that PFM probes local electromechanical switching at the nanoscale, and thus the measured coercive bias does not directly equate to a macroscopic switching voltage in capacitor geometry. Nevertheless, several lines of evidence confirm genuine, remanent vertical ferroelectric switching in the spiral-grown films: i well-defined hysteresis loops in off-state PFM switching (**Figure 3.4 g**); (ii) stable domain contrast persisting for more than three days ([Supplementary Fig. S 3.12](#)); (iii) reversible vertical domain writing/erasure across multiple cycles without amplitude fatigue (**Figure 3.4(c-f)**); and (iv) correlated atomic-scale displacement of Bi/Ti columns near OPBs observed by HAADF-STEM (**Figure 3.5**). Together, these findings demonstrate that the local polarisation reversal is not electrochemical or ionic in origin but corresponds to a true ferroelectric response stabilized by the spiral-induced defect topology.

3.2.3. Atomic-Scale Mechanism of OPB-Mediated Polarisation Enhancement

The observed reduction in vertical switching voltage and the enhanced vertical piezoresponse in spiral-grown films can be attributed to four key mechanisms arising from sub-unit cell structural distortions:

a. Local symmetry-lowering distortions

Recognizing that OPB defects can induce local symmetry-lowering distortions, we used density functional theory (DFT) simulations to probe their effect on vertical polarisation in BiT. Conducted on a 304-atom supercell containing a single OPB defect (**Figure 3.6 a**), these simulations complement the HAADF-STEM polarisation mapping to establish direct structure–property correlations. The Ti–O bond lengths in both the central and outer perovskite blocks are analyzed, with comparisons made between regions proximate to and distant from the OPB defect, as well as pristine perovskite blocks lacking OPB defects ([Supplementary Figure S 3.14](#)). In BiT structures devoid of OPB defects, the central perovskite octahedra exhibit minimal distortion (**Figure 3.5 a** resulting in negligible in-plane polar displacements (**Figure 3.5 f**).^[349] Conversely, the outer perovskite octahedra, adjacent to fluorite-type $(\text{Bi}_2\text{O}_2)^{2+}$ interface layers, undergo more significant tetragonal distortions (**Figure 3.5 a**). These distortions arise from bonding interactions between Bi atoms in the $(\text{Bi}_2\text{O}_2)^{2+}$ interface layer and apex oxygens of the outer perovskite TiO_6 octahedra.^[204] In the outer blocks, Ti displace toward the adjacent $(\text{Bi}_2\text{O}_2)^{2+}$ interface layers, inducing asymmetric distortions within the TiO_6 octahedra and modified axial Ti–O bond lengths. Because the top and bottom outer octahedra displace in opposite directions, these distortions result in antiparallel Ti shifts along the c-axis, characteristic of anti-polar behaviour.

Figure 3.6 b illustrates the calculated B-site displacements and octahedral tilts for the structure containing an OPB defect. Notably, within Perovskite Block 3, located at the OPB defect, the Ti-O displacements along the *c*-axis are aligned in the same direction. Along the positive *c*-axis, the Ti-O bond length increases (+0.19 Å) from a value of 1.78 Å for the defect-free outer perovskite block (**Figure 5 a/ [Supplementary Figure S 3.14](#)**) to 1.97 Å in Perovskite Block 3 near the OPB (**Figure 3.6 b**). Conversely, along the negative *c*-axis, the Ti-O bond shortens (-0.38 Å) from a value of 2.35 Å (without an OPB defect) (**Figure 3.5 a**), to 1.97 Å (with an OPB defect) (**Figure 3.6 b**). In contrast, other outer perovskite blocks neighboring the OPB (Perovskite Blocks 1, 2, and 4) display Ti–O bond distortions similar to those in defect-free regions ([Supplementary Figure S 3.14](#)/**Figure 3.5 a**), with B-site cations displacing in opposite directions along the *c*-axis, resulting in characteristic asymmetric Ti–O bond lengths, one short and one long (**Figure 3.6 b**). Near the defect, however, the top and bottom outer octahedra no longer oppose each other, disrupting the usual antipolar arrangement. This symmetry lowering at the OPB gives rise to distinct behaviours among the outer perovskite blocks, particularly Perovskite Blocks 1 and 3, producing differing local dipole magnitudes. As a result, the typical cancellation of antipolar displacements between the top and bottom outer perovskite blocks is prevented, resulting in a net *c*-axis dipole moment.

Octahedral tilting plays a crucial role in defining the local structure and ferroelectric properties of Aurivillius phases. Variations in tilt angles can modulate symmetry and polarisation, particularly near structural defects such as OPB sites. Understanding how these tilting patterns evolve around OPB defects is therefore key to deciphering their influence on polarisation behaviour.

Enhanced octahedral tilting ($+5^\circ$) is observed at the OPB defect, particularly in the outer Perovskite Block 3, where the tilt angle reaches 13° (**Figure 3.6 b**, left). This contrasts with outer regions farther from the defect, where tilting ranges from 6° in Perovskite Block 4 to 9° in Perovskite Block 2 (**Figure 3.6 b**, right), and is also higher than the 8° tilt measured in a perovskite block without an OPB defect (**Figure 3.5 a**). These differences indicate a localized structural response induced by the OPB defect. Similarly, in the ab-plane, Ti–O bond distortions are more pronounced in Perovskite Block 3 compared to more distant blocks such as Perovskite Block 4.

More strikingly, the central perovskite blocks (Blocks 5 and 6) exhibit even greater octahedral tilting: 19° near the OPB defect (Block 5) and 14° further away (Block 6) (**Figure 3.6 b**, bottom), surpassing the tilting observed in outer blocks (6° to 13° , **Figure 3.6 b**, centre). This trend is consistent with our previous observations in a five-layered multiferroic Aurivillius phase.[204] Within these central blocks, octahedral tilting competes with tetragonal distortion: where tetragonal distortion is minimised, octahedral tilting is maximized. This behaviour mirrors that seen in central layers without OPB defects ([Supplementary Figure S 3.14](#)). Consequently, although outer perovskite blocks generally display less tilting and greater tetragonal distortion, and central blocks show the opposite, this pattern can be disrupted at OPB defects due to an additional reduction in structural symmetry. Notably, Perovskite Block 3 at the OPB defect exhibits increased tilting (13°) and reduced distortion compared to defect-free regions (**Figure 3.6 b**). In BiT films devoid of OPB defects, anti-polar displacements in the top and bottom outer perovskite blocks tend to cancel each other, resulting in no net polarisation. However, the enhanced octahedral tilting and distortions near OPB defects disrupt this cancellation. The reduced symmetry at OPB sites causes Ti–O bond displacements within specific perovskite blocks to align

coherently, generating a net out-of-plane dipole moment (**Figure 3.6 b**). Together, these results demonstrate that OPB defects induce localized structural modifications that lower symmetry and promote net vertical polarisation, providing crucial insight into defect-mediated ferroelectric behaviour in Aurivillius thin films.

This effect is experimentally corroborated by HAADF-STEM polarisation mapping. At OPB defect sites, the local coordination environment is notably disrupted. In contrast to defect-free regions, where outer Ti atoms form Ti–O–Ti linkages across octahedral layers, these Ti atoms instead bond with oxygen atoms associated with adjacent Bi atoms in the fluorite-like $(\text{Bi}_2\text{O}_2)^{2+}$ layers (**Figure 3.5 (d, e)** and [Supplementary Figure S 3.15](#)). This altered bonding configuration reduces the local symmetry and introduces polar discontinuities, manifested as vertical reorientations of the polarisation vectors (**Figure 3.5 g**).

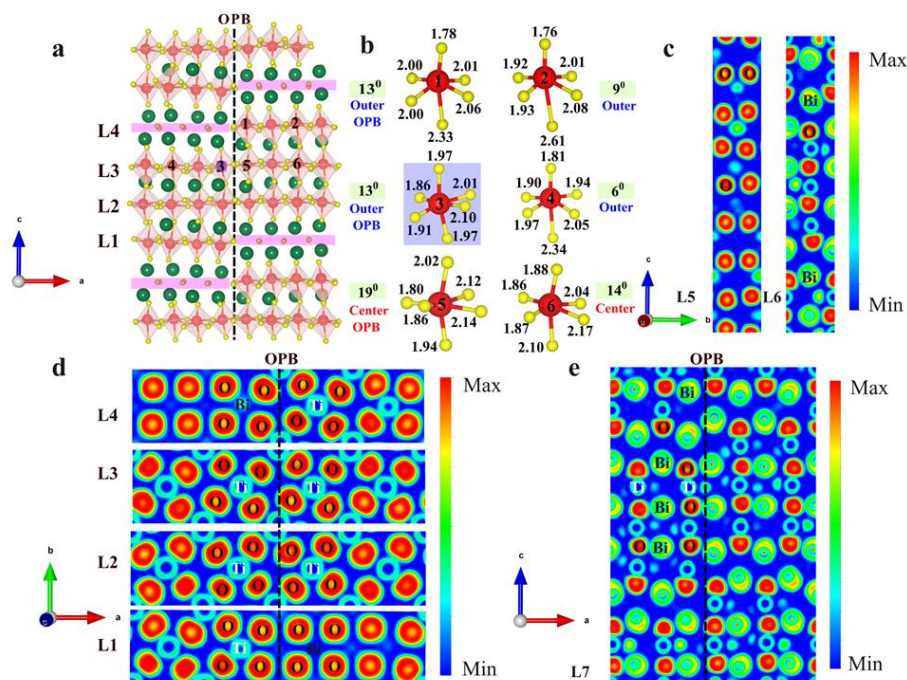


Figure 3.6: Theoretical model of Aurivillius BiT with an OPB defect: *a* Optimized atomic structure of BiT at the OPB, calculated using DFT. The layer numbers of different horizontal sections of the modelled structure are denoted L1–L4 *b* Ti–O bond lengths in the perovskite blocks near and away

from the OPB (in Å). Numbers 1–6 represent Ti atoms, where 1–4 belong to the outer perovskite blocks near the $(\text{Bi}_2\text{O}_2)^{2+}$ interface layer, and 5–6 are in the central perovskite blocks. The O–Ti–O tilt angles along the vertical Ti–O bonds in each perovskite block are shown within the green shaded region. Electron localization function (ELF) showing charge transfer across different layers and surfaces **c** projection onto the ZY planes, **d** projection onto the XY planes, and **e** projection onto the ZX plane. The maximum and minimum ELF values are 0.97 and 0.097, respectively.

b. Modifications to localized electron densities

When an OPB defect forms in BiT, it disrupts the atomic registry across the boundary, shifting the positions of Bi^{3+} and Ti^{4+} ions and altering the local electrostatic potential. To probe how these changes affect chemical bonding and lone pair behaviour, we calculated the electron localization function (ELF), as shown in **Figure 3.6 (c–e)**. The ELF visualizes regions of high electron localization (yellow-red) and low localization (blue), providing insights into local bonding environments.

In the XY plane (**Figure 3.6 d**), the Bi–O bonds within the $(\text{Bi}_2\text{O}_2)^{2+}$ fluorite-type interfacial layers (**L4 (left), L1 (right)**) show nearly uniform, symmetric ELF distributions around the O atoms, consistent with ionic bonding. By contrast, the Ti–O bonds in the outer perovskite layers (**L1 (left), L2 (right), L3 (left), L4 (right)**) exhibit more localized and directional ELF features near the O atoms, reflecting distortions in the local charge density, particularly close to the OPB. These Ti–O distortions become even more pronounced in the central perovskite blocks (**L2 and L3, Figure 3.6 d**), contributing to the in-plane polarisation.

The ELF slice along the O–O plane at the OPB (**L5, Figure 3.6 c**) reveals a distinct lone pair attractor basin between Bi and O atoms, pointing to p–p interactions between Bi 6p and O 2p orbitals. In the ZY plane (**L6, Figure 3.6 c**), which includes

both Ti–O and Bi–O bonds, the ELF shows strong localization near Bi atoms, with charge extension toward neighboring O atoms, indicating interlayer electronic coupling.

Finally, the ZX plane projection (**L7, Figure 3.6 e**) highlights increased tilting of Ti–O bonds at the OPB, consistent with the larger Ti–O–Ti tilt angles measured in **Figure 3.6 b**. Additionally, we observe directional ELF features along Bi–O bonds in the out-of-plane (c-axis) direction, which contributes to an enhanced out-of-plane polarisation, supplementing the dominant in-plane polarisation.

c. Elastic Strain Differences

Elastic strain gradients between the perovskite blocks (under compressive strain) and bismuth oxide layers (under tensile strain) play a critical role in determining polarisation behaviour. The outer perovskite blocks ($a_p = 3.837$ Å) adjacent to the $(\text{Bi}_2\text{O}_2)^{2+}$ layers ($a_B = 3.80$ Å), experience relatively greater compressive strain due to lattice mismatch, while central blocks remain comparatively stress-relaxed.[350] DFT calculations (**Figure 3.6 b**) reveal pronounced Ti–O bond distortions and reduced octahedral tilting in the compressively strained outer layers, in contrast to the central perovskite blocks.

At OPB defect sites, lattice misalignment between $(\text{Bi}_2\text{O}_2)^{2+}$ interface layers and perovskite layers relieves vertical stress. DFT models (**Figure 3.6 b**) show reduced out-of-plane Ti–O bond distortions at OPBs compared to defect-free layers, confirming the role of OPB defects as strain-relief points. Enhanced octahedral tilts and in-plane distortions near OPB defects redistribute strain across the octahedron, helping to minimize net out-of-plane stress in the crystal framework. This local

vertical stress relaxation reduces the energy barrier for *c*-axis polarisation switching, facilitating low-voltage switching. The effect aligns with predictions from Landau–Ginzburg–Devonshire theory[113]:

$$P_i = P_{i^o} + Q_{ijkl}\sigma_{jk} \quad 26,$$

where *P* is induced polarisation, *P_{i^o}*

 is spontaneous polarisation, *Q_{ijkl}* is the electrostrictive tensor coefficient, and *σ_{jk}* is the stress tensor. ZX projections of the Ti displacement vectors reveal reduced local stress in octahedral (σ) adjacent to OPB defects, characterized by smaller vertical displacements and diminished strain (**Figure 3.6 c**). This local strain relaxation correlates with enhanced switchability of vertical polarisation.

d. Pyramidal Arrangement of OPB Defects

Polar vector mapping (**Figure 3.5 g**) reveals that defect-mediated modifications to local symmetry-lowering distortions, electron density distributions, and elastic strain within the crystal structure framework give rise to vertically reoriented dipoles. The characteristic pyramidal arrangement of OPB defects at growth-spiral grain boundaries (**Figure 3.2 d**) prevents cancellation of these local vertical dipole contributions. Instead, their spatial configuration promotes constructive alignment of vertical dipole moments (**Figure 3.4 g**), effectively enhancing the net out-of-plane polarisation and reducing the voltage required for vertical ferroelectric switching, as shown in **Figure 3.4**.

To summarize the atomic-scale mechanism of OPB-mediated vertical polarisation enhancement, DFT calculations elucidate how the atomic structure of OPB defects modifies local bonding and polarisation in BiT. The screw-dislocation geometry

associated with spiral growth introduces a periodic lattice shear that locally disrupts the stacking of the $(\text{Bi}_2\text{O}_2)^{2+}$ layers and perovskite-like slabs, producing measurable off-centring of Ti cations and Bi displacement along the c-axis. The optimized structures indicate that Ti–O bond lengths and octahedral tilts are significantly altered near the OPB, leading to symmetry-lowering distortions and enhanced local polarisation along the vertical direction. The corresponding ELF maps reveal localized redistribution of charge density and strengthened Bi–O covalency, consistent with a defect-stabilized polar distortion (**Figure 3.6**).

The causal chain can thus be summarized as follows: *screw dislocations* → *growth spirals* → *OPB lattice shear* → *octahedral tilt / Ti–O bond reconfiguration* → *modified local electron density* → *reduced activation energy for c-axis switching*. This sequence is supported experimentally by HAADF-STEM imaging, which shows systematic displacement of Bi columns adjacent to OPBs (**Figure 3.5**), confirming that spiral-induced defects directly alter the local symmetry and energetics governing vertical polarisation switching, as corroborated by local electromechanical switching observed in PFM measurements (**Figure 3.4**).

Growth spirals have previously been reported in layered Aurivillius and related ferroelectric thin films grown by high-vacuum techniques such as PLD and MBE[163], [172], [318], where they typically arise from screw dislocations generated during epitaxial relaxation. However, these earlier reports[163], [172], [318] did not establish a direct correlation between spiral formation and ferroelectric polarisation response. In contrast, the present work provides the first explicit demonstration that spiral-mediated growth can enhance out-of-plane ferroelectric polarisation in Aurivillius phase BiT thin films. This conclusion is supported by complementary nanoscale PFM switching (**Figure 3.4**), atomic-resolution HAADF-STEM evidence

of tetragonal distortion at OPBs (**Figure 3.5**), and DFT analysis of local dipole reorientation (**Figure 3.6**). It is also important to note that the earlier studies[163], [172], [318] reported the presence of spiral growth but did not demonstrate any deliberate control over the spiral density or degree of coalescence. In contrast, the present work systematically tunes these parameters, establishing a direct link between growth conditions (**Figure 3.3 a**), spiral-mediated defect density (**Figure 3.3 b**), and vertical polarisation enhancement (**Figure 3.4**, [Supplementary Figure S 3.11](#)). Furthermore, by inducing such spirals through controlled supersaturation and oxygen partial pressure in an industrially scalable DLI-CVD process, this study extends the phenomenon from descriptive observation to deliberate, reproducible growth engineering with tunable ferroelectric functionality.

The mechanistic understanding developed here provides a framework for tailoring Aurivillius ferroelectric thin films toward specific functional requirements. By correlating screw-dislocation-driven OPBs with local lattice shear, octahedral tilt modification, and enhanced c-axis polarisation, this work establishes a direct link between structural defects and polarisation behaviour. Such atomic-level insight enables rational control of growth parameters: supersaturation, oxygen partial pressure, and substrate miscut, to engineer defect densities that tune ferroelectric behaviour for different functional contexts. Promoting controlled spiral formation may be advantageous in low-voltage capacitors or ferroelectric tunnel junctions where enhanced out-of-plane polarisation is essential[351], [352], [353], whereas minimizing defect density could be preferred in contexts where endurance and retention[354], [355] are critical. This deeper understanding advances spiral-mediated

growth from an empirical observation toward a predictive framework for tuning ferroelectric functionality in materials relevant to emerging low-power architectures.

Building on these mechanistic insights, the following section outlines practical considerations for translating spiral-engineered BiT films toward device-relevant architectures, where substrate design, growth control, and electrical reliability become critical determinants of performance. Although such investigations lie beyond the present manuscript's scope, they represent logical next steps for realizing functional integration of spiral-mediated ferroelectrics.

3.2.4. Device Integration Considerations

Translating spiral-engineered BiT films into practical devices requires substrates and electrode layers that maintain both electronic compatibility and the structural cues necessary for spiral nucleation. The 0.2° miscut STO substrates used here provide single-unit-cell terraces that act as initiation sites for screw-dislocation-driven growth. Preliminary studies indicate that conductive SrRuO_3 layers grown on similar vicinal surfaces on STO can inherit this step-terrace morphology while offering excellent lattice matching and work-function alignment for capacitor structures. In contrast, polycrystalline electrodes such as Pt(111) or LaNiO_3 [356], although providing suitable work-function alignment with BiT and thermal stability under DLI-CVD conditions, would likely require templating or the use of vicinal substrates to replicate the step–terrace landscape necessary for spiral growth.

At the device scale, controlling step density, supersaturation, and oxygen partial pressure allows the spiral density and film morphology to be tuned for specific architectures. This work demonstrates that increasing oxygen partial pressure or precursor supersaturation during DLI-CVD promotes lateral step propagation and

island coalescence (~ 0.4 to ~ 0.75 (equation 2)), thereby reducing surface roughness and filling voids between spirals (**Figure 3.2 b (i-iv)**). Moderate spiral densities promote enhanced out-of-plane polarisation and low switching voltage, ideal for capacitor or ferroelectric tunnel-junction configurations, whereas smoother, nearly coalesced films may be preferred for transistor channels requiring planar interfaces.[357] Partial coalescence, combined with mild chemical-mechanical polishing or a thin conformal cap, could yield surfaces suitable for device integration while preserving the subsurface spiral network that stabilizes vertical polarisation.

The demonstrated local switching voltage of ± 5 V suggests that fully processed capacitors with top and bottom electrodes could operate below ± 3 V after accounting for uniform field distribution and reduced depolarisation fields in continuous films of ≤ 25 nm thickness. Such a voltage range lies within the regime typically considered compatible with CMOS-based ferroelectric field-effect transistors (FeFETs).[358], [359], [360] Moreover, recent demonstrations of sub-10 nm Aurivillius phase films grown by DLI-CVD, confirm that this deposition route remains stable and stoichiometric at the few-nanometer limit.[144], [222], [229] These reports, combined with the present spiral-growth strategy, highlight the scalability of the DLI-CVD method for integrating complex ferroelectrics into nanoscale capacitor and transistor stacks, where switching voltages approaching 1 to 2 V are feasible.

The functional relevance of the spiral-mediated growth strategy is quantitatively validated against established ferroelectric benchmarks (**Supplementary Table S 3.1**). By exploiting controlled spiral nucleation rather than conventional 2D step-flow, this approach achieves a four-fold reduction in vertical switching voltage relative to step-meandered BiT grown under high supersaturation, enabling low-voltage operation at ± 5 V in a 25 nm, lead-free film. Importantly, the

out-of-plane piezoelectric response of 8.7 pm/V exceeds the ~2–6 pm/V measured in CMOS-compatible hafnia systems (e.g. $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$) (**Table S 3.1**), positioning this material above the performance ceiling of current logic-integrated ferroelectrics.

While >100nm BLT and SBT thin films exhibit OOP responses when grown in tilted orientations such as (116) for SBT and (118)/(104) for BLT (**Table S 3.1**), their intrinsic polarisation lies strictly in-plane, meaning that any vertical switching arises only from geometrical projection rather than a native c-axis. Similarly, $\text{Nd-Bi}_4\text{Ti}_3\text{O}_{12}$ (NBT) achieves higher OOP values ~6-12 $\mu\text{C cm}^{-2}$ but only when both rare-earth substitution and non-(001) orientations (104) are employed, and still requires >100 nm thickness for reliable switching (**Table S 3.1**). This dependence on orientation engineering is a major integration drawback, as (118)/(104) epitaxial growth demands single-crystal lattice-matched substrates and is not directly transferable to polycrystalline Si or BEoL CMOS platforms. By contrast, the present spiral-engineered $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is inherently (001)-oriented, with native out-of-plane polarisation and no need for chemical modification or orientation tuning, and further demonstrates stable domain switching down to 10 nm thickness ([Supplementary Figure S 3.13](#)).

Taken together, the combination of low switching voltage, lead-free chemistry, sub-100 nm scalability, and intrinsically enhanced OOP coupling establishes spiral-engineered BiT as a credible pathway toward vertical device integration.

Reliable operation will ultimately depend on establishing quantitative electrical benchmarks. While PFM confirms stable nanoscale switching, macroscopic capacitor measurements of polarisation-electric-field hysteresis, retention, and endurance will be needed to verify long-term stability. Optimizing spiral and defect

densities to balance low-voltage switching with minimal leakage will be important for advancing these films toward integration in low-power ferroelectric and neuromorphic technologies. The DLI-CVD approach demonstrated here thus provides both the process control and scalability necessary to meet these requirements, positioning spiral-engineered Aurivillius films as promising candidates for future energy-efficient electronic systems.

3.3.Conclusion

Fabrication-compatible ferroelectric technologies require materials that exhibit strong vertical polarisation, a property typically limited in Aurivillius phases and other predominantly laterally polarized thin films. This study addresses this challenge by achieving a substantial reduction in vertical switching voltage (from ± 20 V to ± 5 V) and by enhancing the *c*-axis polarisation response in Aurivillius phase $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films through spirals-mediated growth. The observed enhancement in vertical polarisation is attributed to the pyramidal arrangements of OPB defects generated during spiral formation. These defects disrupt local elastic strain energy and electron density distributions, inducing symmetry-lowering distortions that tilt the polarisation vector away from the lateral plane, strengthening the vertical polarisation response. By coupling atomic-scale simulations with high-resolution structural and functional characterisation, we establish a direct and mechanistically grounded link between growth mode, defect architecture, and vertical ferroelectric response in Aurivillius thin films. Beyond elucidating this fundamental defect–structure–property relationship, the study demonstrates a scalable thin-film synthesis strategy that unites atomic-level mechanism with process-level functionality. By optimizing synthesis parameters, including supersaturation levels, oxygen partial pressure during nucleation, and

oxygenated cooling environments, precise control over both ferroelectric domain configuration and polarisation magnitude were achieved. While spiral growth in this material system has previously been reported for high-vacuum techniques such as molecular beam epitaxy[212] and pulsed laser deposition[361], this work achieves its deliberate induction and control in BiT using an industrially scalable chemical deposition route, linking growth optimization, defect topology, and polarisation enhancement within a manufacturable framework.. While the films in this study were ~25 nm thick, our earlier work showed that chemical vapour deposition can reliably produce Aurivillius phase films as thin as 5 nm,[144] demonstrating the scalability and potential suitability of this approach for integration into miniaturized vertical device architectures. Collectively, these findings establish a process-informed and mechanistic pathway for tuning ferroelectric properties in layered oxides, advancing their potential relevance for emerging low-power electronic and memory technologies. Overall, this work establishes spiral-mediated growth control as a scalable and mechanistically grounded strategy for engineering ferroelectric behaviour in layered oxides, offering a pathway toward energy-efficient materials for future electronic systems.

The pyramidal OPB arrays characterised here produce a diagnostic structural fingerprint that extends beyond the functional measurements of this chapter. Their three-dimensional, inclined geometry gives rise to asymmetric features in symmetric 00 ℓ X-ray diffraction profiles, order-selective peak splitting and broadening (notably the 004 and 00 10 peaks), that the existing parallel-OPB model cannot reproduce due to its planar geometry assumption.[269] Decoding these signatures quantitatively, and establishing what defect statistics they encode, is the subject of Chapter IV, which develops the pyramidal model extension. This raises a critical question for Chapter

V: can the same supersaturation conditions that generate spiral OPB defects be tuned further to eliminate orientation variants entirely, producing the cleanest diffraction profiles and most coherent ferroelectric response?

Table 3.1. Growth conditions and structural and functional outcomes for BiT thin films grown by sequential DLI-CVD on STO(100). FWHM values are from $\theta-2\theta$ scans at the 004 reflection. Piezoresponse and switching voltage refer to vertical (out-of-plane) PFM measurements.

pO ₂ (Pa)	N ₂ :O ₂	Growth rate (nm/min)	004 FWHM (°)	Spiral density (μm^{-2})	Coalescence degree (D _s)	Out-of-plane piezoresponse (pm/V)	Min. vertical switching voltage (V)
13.2	2:1	~0.74	2.15	~2.6	~0.40	~8.7	±5
26.6	1:2	~0.74	1.33	~0	~0.75	~3.7	±20

Experimental Section / Methods: Refer to [Appendix V. Experiments and Methods](#) for detailed description of experimental and theoretical methods

IV. X-Ray Diffraction Model for Detecting Growth Spiral-Driven 3D Defects in Layered Thin Films

In this chapter, all research is the work of the author, with the exception of the following contributions from collaborators: M. Schmidt (Tyndall-UCC) prepared cross-section lamella of the samples. T. Simonian (Imperial College London) carried out scanning transmission electron microscopy (STEM), high resolution TEM (HRTEM), electron energy loss spectroscopy (EELS) and polarisation simulation.

Table 4.1. Symbol notation for Chapter IV.

Symbol	Definition	Units	First appears in
Defect geometry			
δ	c-axis steric offset at the OPB defect (lattice displacement parallel to the crystallographic z-axis); $\delta = 2\varepsilon$	Å	Eq. 28
ε	Half-offset: $\varepsilon = \delta/2$, applied symmetrically to each face of the pyramidal OPB	Å	Eq. 30
φ_1	Inclination angle of the left-hand OPB face (line AE) to the plane perpendicular to the crystallographic c-axis	°	Eq. 30
φ_2	Inclination angle of the right-hand OPB face (line BE) to the plane perpendicular to the crystallographic c-axis; related to φ_1 via Eq. 33	°	Eq. 30
L	Mean lateral spacing between adjacent OPB pairs (base width of the pyramidal ABCD unit block); $L = \Delta^{-1}$	nm	Eq. 31
H	Vertical height of the pyramidal unit block ABCD	nm	Eq. 28
Δ	OPB density (number of OPB pairs per unit length); $\Delta = 1/L$	nm ⁻¹	Eq. 32
Layer indexing			

Symbol	Definition	Units	First appears in
m	Integer layer index within the pyramidal block, measured from the central reference plane O. Runs from $-m$ to $+m$. Distinct from the Miller index h, k, l	dimensionless	Eq. 28
p	Summation index over layers within the pyramidal block; runs from $-m$ to $+m$ in the ζ_p and $\Gamma(s)$ sums	dimensionless	Eq. 35
h_p	Height of the p -th layer relative to the central reference plane O; $h_p = (p + \frac{1}{2})c - \varepsilon$	nm	Eq. 30 / 40
ζ_p	Lateral length of the p -th layer between the two OPB boundary lines (BC–AD projection)	nm	Eq. 35
a	Horizontal distance from the left boundary B to the apex E of the pyramidal cross-section (i.e. BF in Fig. 4.3g)	nm	Eq. 47
Crystallographic parameters			
a, b, c	Lattice parameters along the a -, b -, and c -axes of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$	Å	Eq. 28
h, k, l	Miller indices of the reflection 00ℓ . Note: l is the diffraction index; distinct from the layer height h_p	dimensionless	Eq. 38
u, v, w	Fractional atomic coordinates: $u = x/a$, $v = y/b$, $w = z/c$ (from VESTA)	dimensionless	Eq. 37
Scattering and diffraction			
s	Scattering vector magnitude; $s = 2\sin\theta/\lambda$	Å ⁻¹	Eq. 27
θ	Bragg diffraction angle	°	Eq. 27
λ	X-ray wavelength (Cu K α 1: 1.54051 Å)	Å	Eq. 34
$\Delta\lambda$	Linewidth of the radiation source; $\Delta\lambda = 0.000461$ Å for Cu K α 1	Å	Eq. 34
ξ	X-ray coherence length; $\xi = (\lambda/2)/(\lambda/\Delta\lambda)^2 \approx 500$ nm	nm	Eq. 34

Symbol	Definition	Units	First appears in
$I(s)$	Diffracted intensity as a function of scattering vector	arb. units	Eq. 27
$F(s)$	Total structure factor of the pyramidal OPB unit; $F(s) = \Phi(s)\Gamma(s)$	arb. units	Eq. 43
$\Phi(s)$	Unit-cell structure factor (capital Φ); sum of atomic scattering contributions over N_a atoms. Distinct from the scattering phase φ	arb. units	Eq. 27 / 29
$\varphi(s)$	Scattering phase for one unit cell (lowercase φ); $\varphi = 2\pi(hu + kv + lw)$. Distinct from the OPB inclination angles φ_1, φ_2	rad	Eq. 36
$\Gamma(s)$	Geometric interference factor encoding the OPB spatial distribution; $\Gamma(s) = (2/L)\sum_p \zeta_p \cos(2\pi h_p s)$	arb. units	Eq. 44
$\Gamma_{N(s)}$	Interference factor in the parallel model (Whatmore et al.) for N coherently scattering blocks	arb. units	Eq. 27
q	Multiplicity factor ($q = 2$ for 00ℓ reflections)	dimensionless	Eq. 27
$L_p(s)$	Lorentz–polarisation factor; $L_p = (1 + \cos^2 2\theta)/(\sin^2 \theta \cos \theta)$	dimensionless	Eq. 27
$f_j(s)$	Atomic form factor for the j -th atom	electrons	Eq. 29
$T_j(s)$	Debye–Waller (temperature) factor for the j -th atom; $T_j = \exp(-B_j(\sin \theta/\lambda)^2)$	dimensionless	Eq. 29 / 50
B_j	Isotropic temperature factor for the j -th atom; $B_j = 8\pi^2 \langle u_j^2 \rangle$	$\text{\AA}^2$	Eq. 50
U_j	Mean-square atomic displacement for the j -th atom; $U_j = \langle u_j^2 \rangle$	$\text{\AA}^2$	Eq. 50

Note: φ_1 and φ_2 (OPB inclination angles, lowercase italic) and $\Phi(s)$ (unit-cell structure factor, uppercase) are typographically distinct. Similarly, p (layer summation index) and q (multiplicity) are distinct from each other and from the Miller indices h, k, l . The parameter ε is not listed in the original parameter definitions in §4.2; it should be understood as $\varepsilon = \delta/2$ wherever it appears.

4.1. Introduction

Chapter III demonstrated that the growth mode accessible under low supersaturation in DLI-CVD-grown $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ generates a defect landscape whose functional consequences are measurable and significant. The OPB arrays formed at spiral coalescence fronts adopt a pyramidal, three-dimensional geometry whose inclination and spatial distribution through the film thickness are visible in cross-section electron microscopy and reflected in the asymmetric features of the 00ℓ X-ray diffraction profiles (notably the 004 and 00 10 peaks). Those diffraction signatures are characteristic and reproducible, but they currently lack a predictive analytical framework capable of connecting defect geometry to statistically-relevant reciprocal-space observables such as step height. The existing parallel model for OPB-induced XRD peak modification, developed for planar OPB configurations,[269] is not equipped to describe pyramidal defects whose inclination varies with depth. This chapter addresses that gap by developing a pyramidal extension that extracts defect statistics from routine θ - 2θ scans.

Spiral growth is a mode of crystal addition in layered oxides and 2D materials: screw dislocations generate persistent step sources, producing helical terraces that knit together into winding mesoscale mounds of consistent step height. This mechanism shapes topography: where advancing spiral fronts from different origins merge, they can seed translation boundaries that displace the stacking sequence by a fraction of a lattice spacing. These structures are called out-of-phase boundary (OPB) defects, as detailed in the Introduction Section 7.[212] Within the context of spiral growth, OPB defects can be viewed as growth-encoded microstructural features whose geometry reflects the kinematics of spiral advance and the underlying step-terrace landscape.[241], [362], [363] Their broader significance is evident across different

material classes. In ferroelectric layered oxides, OPB defects can locally bias domain nucleation and influence the stability of otherwise unfavourable polarisation configurations (e.g. head-tail distortions, vortex/flux-closure variants, non-Ising rotations), with their effects determined by the immediate defect environment.[347] In layered perovskite superconductors such as Sr_2RuO_4 , OPB defects/antiphase boundaries can disrupt the registry of conducting planes. When their density is comparable to or less than the in-plane superconducting coherence length, such defects can strongly suppress (or even destroy) superconductivity. For example, the suppression of OPB defects has been shown as a key requirement to recover superconductivity in epitaxial Sr_2RuO_4 thin films.[364] In photonic and semiconductor heterostructures, stacking faults,[365] a class of planar phase-shift defects related to OPBs, introduce band-structure perturbations that shift and broaden optical resonances and modify radiative recombination in quantum wells, highlighting the sensitivity of light-matter responses to translational defects.[366] Because OPB defects can introduce localised strain gradients, they can couple to polarisation through flexoelectricity, providing a mechanism to cant dipoles out-of-the film plane, even in systems with nominally in-plane spontaneous polarisation.[367] Recent electron-microscopy studies of Aurivillius phases show that OPB defects and associated domain topologies (including charged walls and vortex-like structures) can be manipulated through growth conditions and directly modify ferroic behaviour, reinforcing that defect landscapes constitute a powerful lever for property control.[93]

Aurivillius phases provide a natural testbed for studying spiral-mediated-growth OPB defects. Their structures consists of perovskite block layers sandwiched by $[\text{Bi}_2\text{O}_2]^{2+}$ layers (general formula $\text{Bi}_2\text{O}_2(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})$)[200]. Many members, ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BiT)) among them, are ferroelectric with well-documented thin-film

applications.[368], [369] The layered architecture readily accommodates fractional c-axis offsets and often hosts OPB defects that run at a definite angle to the substrate plane. Such boundaries have been imaged directly in BiT and related Aurivillius films and correlate with split (00 ℓ) reflections.[212] Aurivillius thin films often exhibit spiral growth,[168] and spiral-mediated OPB defects produce characteristic splitting and asymmetry of 00 ℓ X-ray diffraction (XRD) pattern peaks.[333], [362]

Although the influence of OPB defects on diffraction signatures, most notably the splitting of 00 ℓ reflections, was evident, there was a lack of a compact, predictive framework to connect an OPB's geometry to *which* XRD peaks split, and *by how much*. Early defect-diffraction approaches were not well suited to this task and either targeted different problems (e.g., statistical models for high- T_c thin films) or modelled themselves on stacking fault defects instead of OPBs, such as DIFFaX/FAULTS[267], [271], [370] or faster matrix schemes like ClayStrat[371], which was useful for predefined stacking sequences, rather than the discrete registry shifts characteristic of OPB defects. There have also been defect models that use atomistic Debye-scattering approaches, [265] which are powerful but computationally heavy and not predictive for OPB-driven, order-selective splitting in epitaxial layered thin films. Because OPB defects had not previously been modelled in a comprehensive way for layered systems, this gap motivated the analytical OPB defect diffraction model developed by Whatmore *et al.*[269] Without relying on *ad hoc* peak functions, the model correctly predicted which 00 ℓ reflections should split and reproduced the experimental trends. This provided, for the first time, a direct, non-destructive route to extract OPB defect statistics from routine θ -2 θ scans.

Overview of the parallel OPB model by Whatmore et. al.[269] (henceforth referred to as the ‘parallel model’)

The model gave an analytical way to predict how OPB defects split and reshape 00 ℓ X-ray diffraction peaks in layered thin films. The film is tiled into parallel blocks on either side of a single, planar OPB that is inclined by an angle ϕ to the substrate; the two sides are shifted along $\mathbf{c}$ by a displacement δ , and neighbouring OPBs are separated on average by a spacing L . The total diffracted amplitude is written as the unit-cell structure factor times a closed-form interference term that depends only on $\{\delta, \phi, L\}$; intensity then follows with the usual Lorentz–polarisation and multiplicity ($q = 2$ for 00 ℓ).

From this form, three clear predictions follow: (i) which specific diffraction orders are split is defined by the step height δ in relation to the unit cell height c ; (ii) the amount of splitting scales with the OPB defect density ($\propto 1/L$); and (iii) the relative intensity weights within the split peaks are controlled by ϕ . The model assumes a pure c -axis translation fault, a planar OPB defect, and with coherently scattering blocks much smaller than the X-ray coherence length. Under these conditions, it captures the far-field interference effects without requiring an explicit atomic-scale description of the boundary. It was validated on $\text{SrBi}_2(\text{Ta,Nb})_2\text{O}_9$ (SBTN), where peak split grows linearly with $1/L$, and on $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BiT), where the observed pattern: 004 and 00 12 peaks split while the 006 peak does not, and a measured OPB-spacing distribution. This parallel, three-parameter backbone (δ, ϕ, L) is extended in the present work to pyramidal OPB arrangements associated with spiral growth. We retain the same crystallographic framework as the parallel-fault model, but allow the OPB inclination to vary with height, reflecting the stacked triangular geometry observed in the experimental TEM data. Importantly, the pyramidal features themselves arise from the

spiral growth morphology, while the OPBs running along their edges constitute the actual defects captured in the model.

The final intensity equation of the Whatmore *et al.*[269] model is as follows:

$$I(s) = |F(s)|^2 q L_P(s) = |\Phi(s) \Gamma_N(s)|^2 q L_P(s) \quad 27,$$

where $F(s)$ is the form factor, q is the multiplicity (2 for 00ℓ), and $L_P(s) =$ Lorenz-Polarisation Factor.

The approach presented here unifies several threads spanning decades of work: early foundations on the structural basis and anisotropy of Bi-layered ferroelectrics,[167], [350] the identification of spiral growth and OPB defect nucleation routes in Aurivillius films,[163] and, most recently, analytical treatments that quantify how OPB defects sculpt peak positions and shapes[269] By placing growth spirals at the centre of the narrative and using OPB defects as the bridge between microstructure and functional response, the results here show that OPB defect modelling permits the routine interpretation of Aurivillius thin-film diffraction and, more broadly, why understanding these defects is a viable route to tuning polarisation states in layered ferroelectrics.[93], [347]

This approach is applied here to $\text{Bi}_4\text{Ti}_3\text{O}_{12}/\text{SrTiO}_3(100)$ thin films. Atomic force microscopy (AFM) shows spiral hillocks on the growth surface (**Figure 4.1 a**), while cross-section TEM reveals a repeating triangular/pyramidal OPB motif extending through the film thickness. High-resolution TEM resolves the c-axis registry offset (δ) at successive OPBs; because the OPBs are inclined, these offsets appear as an oblique, quasi-periodic “train” across the film. The spacing of this train (L) corresponds to the real-space periodicity whose Fourier counterpart produces the

split and oscillatory features in the (00 ℓ) XRD profiles- δ determines the phase of the splitting, while L sets the characteristic spacing/width of the envelope. Simulated XRD profiles calculated using our model based on the relationship between the pyramidal OPB array structure and the resulting experimental XRD patterns accurately reproduce the asymmetric splitting and broadening of the 004 and 0010 reflections, in a similar way to the model derived for parallel OPBs.[269] Once XRD profile fitting has been undertaken, the model provides a non-destructive path to extract OPB density ($\sim 1/L$) and angle statistics $\{\varphi_1, \varphi_2\}$, reconciling the diffraction behaviour with the OPB microstructure observed by microscopy.

4.2. Results and Discussion

4.2.1 Defect Gradients in Growth Spirals

In the Bi₄Ti₃O₁₂/SrTiO₃(STO)(100) thin films studied here, AFM imaging reveals a film surface dominated by screw-dislocation–driven growth spirals (**Figure 4.1 a**). Height profiling across an individual spiral shows a step of ~ 1.7 nm along the c -axis (**Figure 4.1 b**), consistent with a half-unit-cell displacement, and annotated as ~ 0.5 u.c. This is characteristic of OPB defects in Aurivillius phases.[212] The STO(100) substrate exhibits atomically stepped terraces with a uniform step height of ~ 0.4 nm $\pm$ 0.10 nm and terrace widths on the order of ~ 100 nm $\pm$ 36 nm (**Figure 4.1 c**). The step height is similar to the cubic c -axis of one STO unit cell (0.391 nm).[372] Within a 2 μ m x 2 μ m region, 56 measurements were taken for terrace width and 20 measurements were taken for step height. Such a regular step-terrace landscape provides persistent step sources and stabilises local adatom fluxes, favouring spiral nucleation (as detailed in Chapter 1 Section 2) during chemical vapour deposition-conditions well-known to promote spiral-dislocation-mediated spiral growth in layered oxides under low-to-moderate supersaturation.[339], [373], [374] In

Aurivillius systems, OPB defects frequently emerge from where spiral growth fronts merge, as shown in **Figure 4.1d-g**, introducing fractional c-axis misregistries that produce characteristic modifications in the X-ray diffraction patterns.[172], [212]

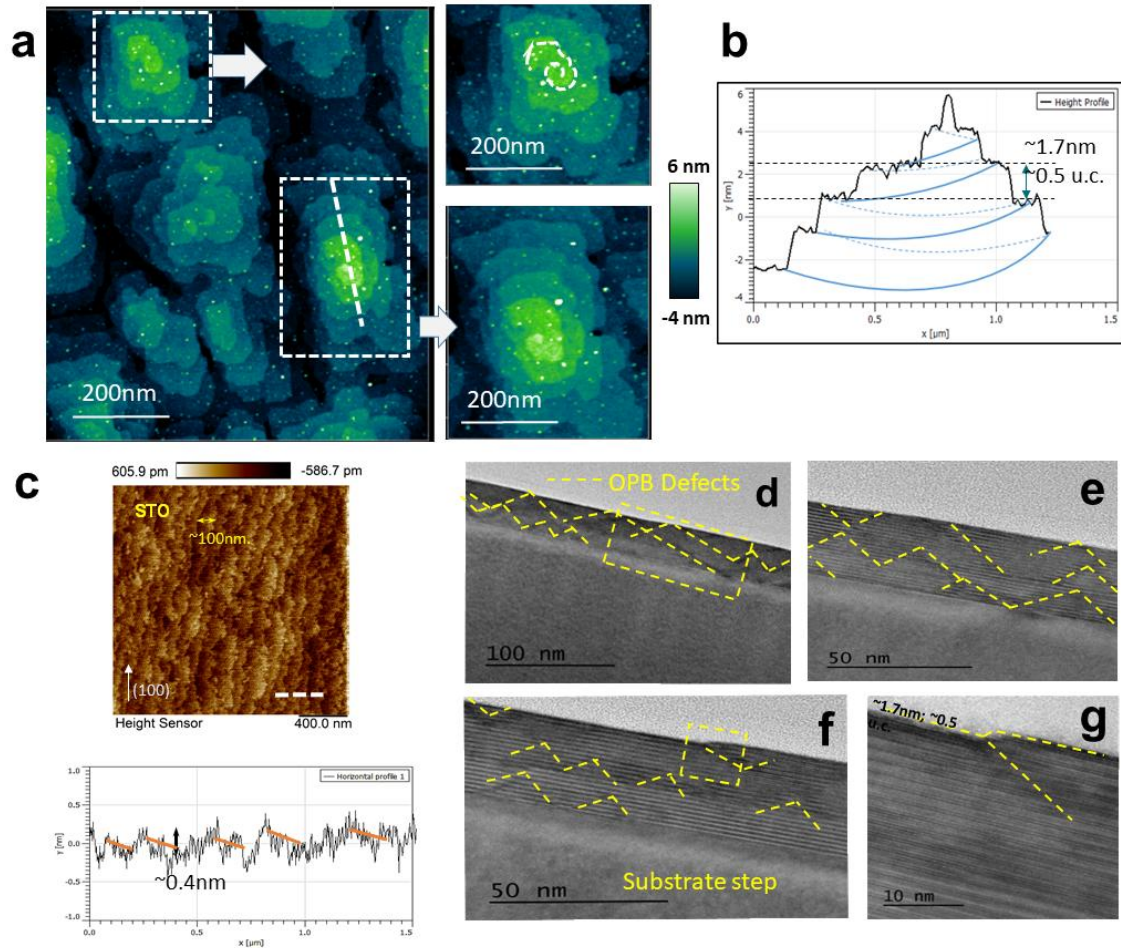


Figure 4.1: **a-** AFM image of growth spirals in a $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ film. **b-** Height profile of an individual growth spiral extracted from the AFM image in **a**). **c-** STO (100) substrate surface with uniform 4 steps. **c-** AFM image of an STO substrate showing $\sim 100 \text{ nm} \pm 36 \text{ nm}$ terraces and $\sim 0.4 \text{ nm} \pm 0.1 \text{ nm}$ height. (56 sample points considered for measurement of terrace width, and 20 sample points considered for measurement of step height in a $2 \mu\text{m} \times 2 \mu\text{m}$ area respectively). **d-g** TEM images showing OPB defects (indicated by dashed yellow lines), marking the boundaries of the pyramidal growth motifs that extend throughout the thin film thickness.

These defects also perturb the local ferroelectric polarisation. A polarisation map measured across one such inclined boundary (**Figure 4.2 a**) demonstrates a reorientation at the OPB line as shown in the TEM image (**Figure 4.2 b**), i.e., a vertical polarisation component emerges where the symmetry and strain state change. This observation underscores that these defects are active ingredients in the ferroic response rather than an inactive background microstructure. The broader picture aligns with early observations that $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ can grow by spiral-driven kinetics under adsorption-controlled conditions, where the resulting step-terrace geometries promote fractional lattice-translation offsets when spiral fronts merge. Subsequent studies across layered oxides have further established clear links between morphology and OPB density.[212], [375]

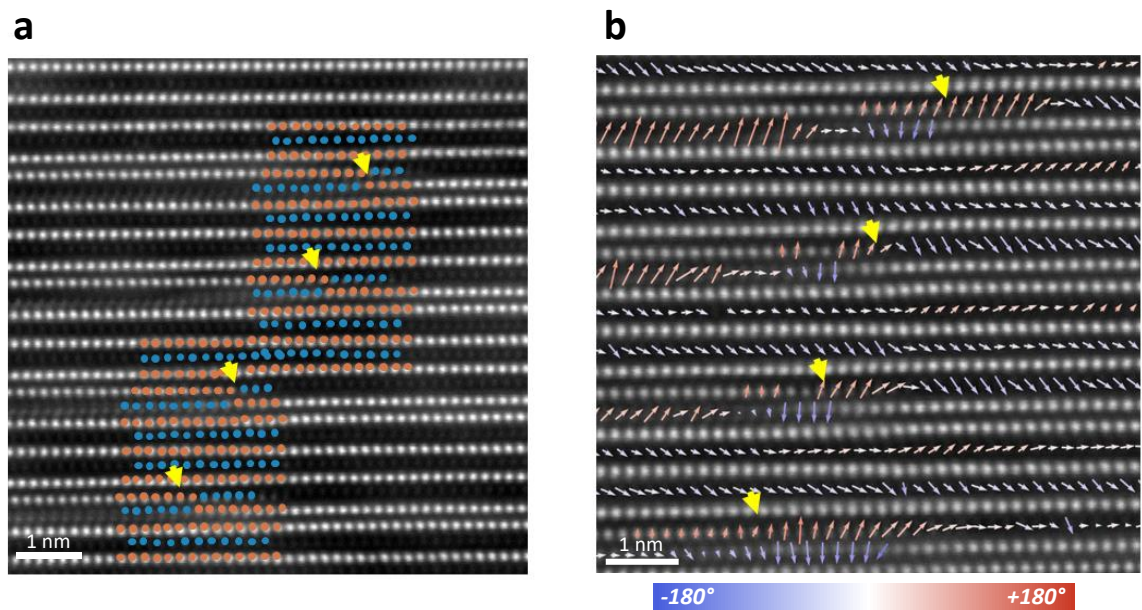


Figure 4.2: *a-* Cross-section HAADF-STEM image of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ growth spiral sample along the $[110]$ projection, showing OPB defects coincident with alternating Aurivillius fluorite and perovskite layers (Bi in orange, Ti in blue). *b-* Polarisation map illustrating the reorientation at the local polarisation at the OPB defect.

Experimental TEM images (**Figure 4.1 d-f**, **Figure 4.3 d–e**) reveal that OPBs (**Figure 4.3 a, c**) formed at the junctions of merging spirals adopt a pyramidal geometry, where the pyramids are arrayed with differing heights through the film thickness. This added structural complexity demands a refined diffraction model capable of describing both the angular asymmetry and the vertical displacement gradients generated by stacked pyramidal OPB boundaries throughout the film's thickness. The earlier parallel-OPB defect model[269], which assumes a simplified defect geometry, does not capture the repeating pyramidal arrangement characteristic of spiral-mediated growth.

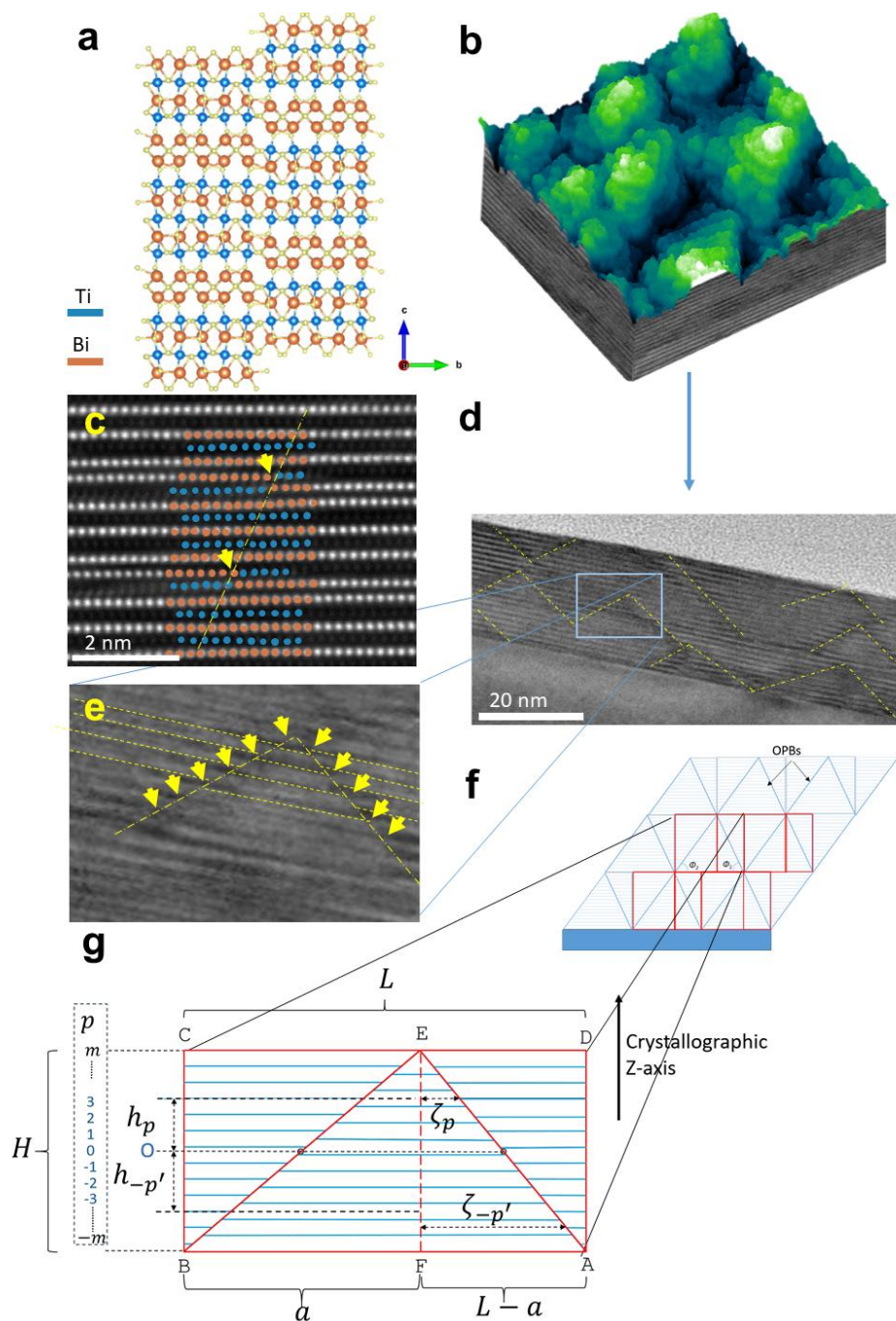


Figure 4.3: *a-* Schematic of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ structure indicating the location of the OPB defect. *b-* 3D-AFM image showing the surface spiral growth hillocks. *c-* HAADF-STEM image providing a magnified view of the OPB defect region. *d-* Cross-section HR-TEM image showing the repeating pyramidal growth geometries formed where spiral growth fronts merge. *e-* Enlarged HR-TEM view along the $[110]$ projection of an individual pyramidal growth feature, highlighting the opposing OPB defects that

run along its edges. **f-g-** Representation of the repeating OPB-bounded pyramidal arrangement used in the analytical XRD model, which is constructed to follow the experimentally observed OPB geometry. A detailed schematic of this geometry is shown in **Figure 4.4.**

Both the parallel model discussed above as well as the pyramidal model detailed below in the work defines the vertical position of the m^{th} layer, relative to a central reference as:

$$H = 2mc + \delta \quad 28,$$

where c is the lattice parameter along the c -axis, ϕ_1 is the OPB inclination angle, and m is the layer index. The structure factor $\Phi(s)$ is evaluated by summing the scattering contributions from displaced and undisplaced regions:

$$\Phi(s) = \sum_{j=1}^{N_a} f_j(s) T_j(s) \exp(2\pi i \cdot z_j c s) \quad 29 ,$$

where $f_j(s)$ is the form factor $T_j(s)$ is the Debye-Waller factor or atomic displacement parameter for the j^{th} atom, z_j is the z coordinate of the j^{th} atom. While effective for planar OPBs, this model cannot represent the angular and spatial variability of spiral-driven defects.

4.2.2. Pyramidal OPB Diffraction Model

In pyramidal geometry, OPBs form 2 inclined boundaries instead of one. The diagram shown in **Figure 4.3 g** and **Figure 4.4** represents this. In the pyramidal model, the step height δ is not just indicative of the height of the substrate step that produces the cascading parallel defect lines shown in the TEM images of Whatmore *et al.*, [269]. Instead, δ is primarily represents the atomic steric offset value at the OPB defect, because each pyramidal feature arises from the coalescence of adjacent growth fronts rather than substrate steps alone. These pyramidal features appear in a repeating sequence in the cross-section TEM (**Figure 4.3 d,f**), not because they are physically stacked through the film thickness, but because the TEM image represents a projection through the lamella. OPB segments from the spiral being imaged, together with contributions from neighbouring spirals located at different c-axis heights within the projection volume, overlap to produce an apparent quasi-periodic pyramidal pattern.

Consider a unit block ABCD (**Figure 4.4**) of height H and base L . H is given by equation 2. The “undisplaced” lattice is represented by the region ABE, while there are two regions ADE and BCE that are both displaced relative to ABCD by an amount $\delta = 2\varepsilon$ parallel to the crystallographic z-axis. $\varepsilon = \delta/2$, i.e. the half-offset applied symmetrically to each face of the pyramidal OPB. ' δ ' is assumed to be the same across both sides of the pyramidal geometry (as in, the δ in block ADEF is the same, and in the same direction as the offset δ in the block FECB in **Figure 4.3 a**). Within block ABCD, the height h_p parallel to the z-axis

$$h_p = \left\{ \left(p + \frac{1}{2} \right) c - \varepsilon \right\} \quad 30,$$

The two displaced regions ADE and BCE are separated from the block ABE by OPBs represented by the lines AE and BE that are respectively at angles ϕ_1 and ϕ_2 with the plane perpendicular to the crystallographic c-axis (see **Figure 4.4 a**).

The ABCD block has a width , given by:

$$L = \cot(\phi_1) * (2mc + \delta) + \cot(\phi_2) * (2mc + \delta) \quad 31,$$

and

$$L = \Delta^{-1} \quad 32,$$

where the OPB density is Δ .

As the model developed here describes XRD splitting particularly for growth spiral morphology, the cross section has a pyramidal arrangement of OPB defects, with the OPB angles at the base of the triangular face being ϕ_1 and ϕ_2 .

In **Figure 4.3 g**, the perpendicular line EF will be equal to H and will divide the line into two sections BF and FA with lengths a and $L - a$ respectively. The inclination angles of the two OPBs are related to each other through the following equation:

$$\phi_2 = \tan^{-1} \left(\frac{\tan(\phi_1)}{\frac{L}{H} \{ \tan(\phi_1) - 1 \}} \right) \quad 33 ,$$

The various parameters are defined as follows:

c = c-axis lattice parameter

δ = Displacement of the lattice at the OPB in the direction of the c-axis. In this case we set $\delta = 2\varepsilon$

m = Layers of perovskite in the Aurivillius phase bismuth titanate, with the point of reference being O. As both the blocks are rotationally symmetric about O, layer m in the undisplaced region ABC is identical to the layer $-m$ in the displaced region.

h_p = Height of each layer relative to O

ζ_p = Length of each layer between OPB lines and BC and AD.

λ = Wavelength of X rays

ξ = coherence length of radiation

$$\xi = \frac{\left(\frac{\lambda}{2}\right)}{(\lambda/\Delta\lambda)^2} \quad 34,$$

$\Delta\lambda$ = linewidth of the radiation source being used

The value of $\Delta\lambda$ for Cu $K\alpha_1$ radiation (wavelength $1.54051\text{\AA}$) is $0.000461\text{\AA}$. This gives $\xi \approx 500\text{nm}$, which is much larger than the regions being considered.

$F_{ADE}(s)$ = Scattering Factor

s = Scattering vector, where

$$s = \frac{2\sin\theta}{\lambda} \quad ; \quad \theta = \text{diffraction angle.}$$

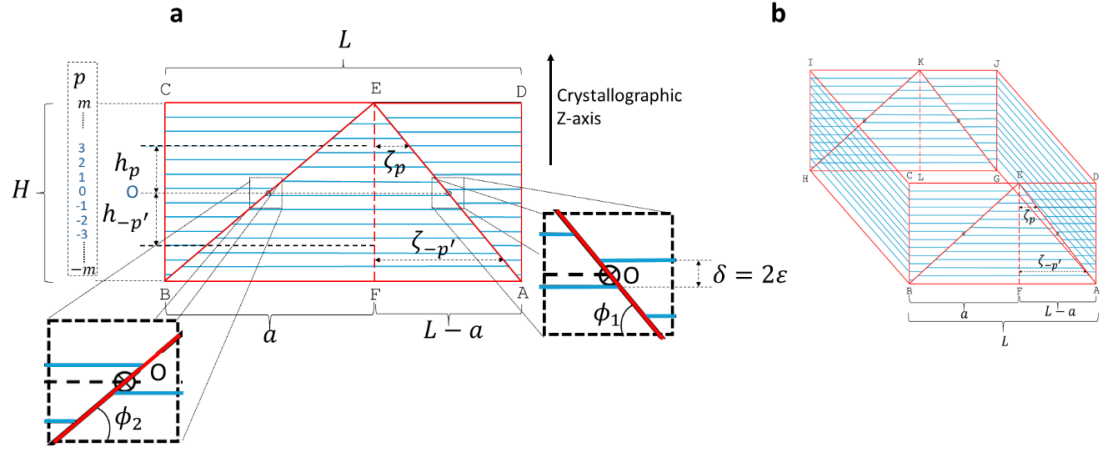


Figure 4.4: **a-** Illustration of the geometric parameters used to describe the triangular face of the pyramidal arrangement of OPB defects. ζ_p across m layers from the centre. L is the lateral distance between B and A , and h_p is the vertical height of the unit cell relative to the reference ' m ' layer ($m=0$). Each h_p corresponds to either h_m or h_{-m} depending on the layer index ' m '. **b-** 3D representation of the pyramidal OPB defect arrangement extending through the depth of the thin film along the b -axis.

We can now build the form factor equation for the new model, accounting for the phase shift in each layer, where $\phi(s)$ is the scattering factor for one unit cell:

$$F_{ALE}(s) = \phi(s) \sum_{p=-m}^{p=m} \frac{\zeta_p}{L} e^{(2\pi i h_p s)} \quad 35,$$

Where scattering factor for this system is:

$$\phi = 2\pi(hu + kv + lw) \quad 36,$$

Where

$$u = \frac{x}{a}; v = \frac{y}{b}; w = \frac{z}{c} \quad 37,$$

Here a , b , and c are lattice parameters and x, y , and z are position coordinates accessible from VESTA. The model hence is transformed from **Figure 4.4 a** to **Figure 4.4 b**.

Therefore,

$$\phi = 2\pi i h \left(\frac{x}{a} \right) + k \left(\frac{y}{b} \right) + l \left(\frac{z}{c} \right) \quad 38,$$

Instead of calculating h_p with only the c axis parameter, inclusion of the 3 dimensional equation of scattering factor with all three lattice parameters can help make the model 3D to get the model closer to the true geometry of a growth spiral. Hence, such a form factor equation will look like this:

$$F_{hkl} = \phi(s) \sum_{p=m}^{p=-m} \frac{\zeta_p}{L} e^{\{2\pi i(hu_p + kv_p + lw_p)(s)\}} \quad 39,$$

Here, as per the previous parallel model

$$h_p = \left\{ \left(m + \frac{1}{2} \right) c - \varepsilon \right\} \quad 40,$$

Where h_p corresponds to the c -axis calculation and hence is equivalent to the lw_p term in this equation where $w = \frac{z}{c}$. Hence, upon adding the a and b lattice parameters to the equation along with the x and y positions (from VESTA) it should get the model closer to 3 dimensions, which is necessary for capturing the true defect geometry of a 3D growth spiral, as shown in **Figure 4.3** and **Figure 4.4**:

$$F_{ALE}(s) = \phi(s) \sum_{p=-m}^{p=m} \frac{\zeta_p}{L} e^{(2\pi i(hu_p+kv_p+lw_p)(s))} \quad 41,$$

$$F_{ADE}(s) = \phi(s) \sum_{p=-m}^{p=m} \frac{\zeta_p}{L} e^{(2\pi i.-(hu_p+kv_p+lw_p)(s))} \quad 42,$$

For accurate calculation of gamma in 3D (**Figure 4.4 b**), $F_{ADE}+F_{ALE}$ and $F_{BCE}+F_{BLE}$ are done assuming that $\delta=2\epsilon$ is true for both BCE and ALE triangles, i.e. the phase shift in both the sides of the triangle ABD in **Figure 4.4 a** are equal (which from the experimental data in **Figure 4.3 e**, is an accurate assumption).

$$F(s) = \phi(s) \sum_{p=-m}^{p=m} \frac{\zeta_p}{L} e^{(2\pi i(hu_p+kv_p+lw_p)s)} + \phi(s) \sum_{p=-m}^{p=m} \frac{\zeta_p}{L} e^{(2\pi i.-(hu_p+kv_p+lw_p)s)} = \Phi(s). \Gamma(s) \quad 43,$$

From the previous model by Whatmore *et al.*[269]

$$\Gamma(s) = \frac{1}{L} \left\{ \sum_{p=-m}^{p=+m} \zeta_p [\exp(2\pi i-h_p s) + \exp(2\pi i-h_p s)] \right\} \quad 44,$$

Recognising that: $e^{-ix} + e^{-ix} = 2\cos x$, we can write:

$$\Gamma(s) = \frac{2}{L} \left\{ \sum_{p=-m}^{p=+m} \zeta_p \cos(2\pi h_p s) \right\} \quad 45,$$

Remodelling the gamma equation (45) for the pyramidal model, we get:

$$\Gamma(s) = \frac{2}{L} \left(\sum_{p=m}^{p=m} \zeta_p \cos \left(2\pi i(s) h \left(\frac{x}{a} \right)_p + k \left(\frac{y}{b} \right)_p + l \left(\frac{z}{c} \right)_p \right) \right) \quad 46,$$

Where $l \left(\frac{z}{c} \right)_p$ is the same as h_p in equation 40

4.2.3 Full Modelling of the Pyramidal OPB Defect Array

Now calculating ζ_p in 1 dimension from the **Figure 4.4 a**:

$$\zeta_p = \left(\frac{a}{2} - h_p \cot(\phi_1) + \left(\frac{(L-a)}{2} - h_p \cot(\phi_2) \right) \right) \quad 47,$$

Substituting ϕ_2 from equation 33:

$$\zeta_p = \left(\frac{a}{2} - h_p \cot(\phi_1) + \left(\frac{(L-a)}{2} - h_p \cot \left(\tan^{-1} \left(\frac{a \cdot \tan(\phi_1)}{L-a} \right) \right) \right) \right) \quad 48,$$

Substituting h_p from equation 40:

$$\zeta_p = \left(\left(\frac{a}{2} - \left(c \left(p + \frac{1}{2} \right) - \varepsilon \right) \cot(\phi_1) + \left(\frac{(L-a)}{2} - \left(c \left(p + \frac{1}{2} \right) - \varepsilon \right) \cot \left(\tan^{-1} \left(\frac{a \cdot \tan(\phi_1)}{L-a} \right) \right) \right) \right) \right) \quad 49,$$

Now substituting equations 49 into equation 46 gives us the 3D gamma value with 1D ζ_p calculation because ζ_p doesn't exist in x and y direction (as the phase shift is only along c-axis)

$$\Gamma(s) = \frac{2}{L} \left(\sum_{p=-m}^{p=m} \left(\left(\frac{\frac{a}{2} - \left(c \left(p + \frac{1}{2} \right) - \varepsilon \right) \cot(\phi_1) + \left(\frac{(L-a)}{2} - \left(c \left(p + \frac{1}{2} \right) - \varepsilon \right) \cot \left(\tan^{-1} \left(\frac{\tan(\phi_1)}{\frac{L}{H} \times \{\tan(\phi_1) - 1\}} \right)} \right) \right) \right) \cos \left(\begin{matrix} 2\pi(s)h \left(\frac{x}{a} \right)_p + \\ k \left(\frac{y}{b} \right)_p + \\ l \left(\frac{z}{c} \right)_p \end{matrix} \right) \right) \right) \quad 50,$$

This is the equation for three dimensional $\Gamma(s)$ where a triangular OPB continuity is assumed in one LxH unit block $\{(\phi(s) \text{ and } T_j(s) \text{ (Debye-Waller or Temperature factor for the } i^{\text{th}} \text{ atom are the same as the earlier model} \} T_j(s) = \exp \left(-B_j \left(\frac{\sin \theta}{\lambda} \right)^2 \right)$; and $B_j = 8\pi^2 \overline{u_j^2}$ = Isotropic temperature factor for the j 'th atom. $\overline{u_j^2}$ is the average mean square displacement of the j 'th atom in a direction normal to the (hkl) plane. Sometimes, we are given the U_j factors for the atoms, where $U_j = \overline{u_j^2}$.

Once we have the $\Gamma(s)$ from equation 50, we can calculate the intensity as a function of 2θ using the expression:

$$I(s) = |F(s)|^2 p \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) \quad 51,$$

Where:

p = Multiplicity (=2 for 00 l the reflections)

$\left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right)$ = Lorenz-Polarisation Factor

4.2.4. Predictive Capability and Experimental Validation

The calculated model produces different simulated XRD intensity patterns for different values of δ (step height/steric offset value). The peak split in the model outputs were compared to the peak splitting in the experimental XRD pattern (**Figure 4.5 a and d**). Upon input of various values of δ , 4 Å produced a pattern whose convoluted fit matched the Full Width Half Maximum (FWHM) of the experimental 004 peak split. The experimental 004 reflection splits into two distinct peaks, which, after Gaussian deconvolution, exhibit FWHM values of 1.21 and 1.98 (**Figure 4.5 a**). The pyramidal model output provides a convolution whose FWHM is 1.15° (-4.96% difference) and 1.99° (+0.51% difference) respectively, closely matching the experimental values (**Figure 4.5 b**). The experimental 004 scan (**Figure 5a**) exhibits a broad, asymmetric envelope (FWHM = 1.21°) with a resolvable low-angle shoulder near 12°. The pyramidal-OPB defect model reproduces both the overall breadth and the two-component character of the peak after instrument convolution is applied. Importantly, the simulated shoulder appears at 13.3° in **Figure 4.5 b**. This ~1° offset arises naturally in the model once the discrete kinematic scattering sub-components from the individual pyramidal blocks are summed and subsequently convolved with the Cu K α 1 emission profile and the Lorentz–polarisation factor: the convolution redistributes intensity toward the main maximum while retaining a secondary maximum one to two degrees lower in 2θ . The resulting line shape therefore matches both the asymmetric tail and the shoulder observed experimentally. The parallel model (**Figure 4.5 c**) cannot generate this behaviour; after the same convolution, it remains nearly symmetric and orders of magnitude too ‘narrow’, where upon keeping the same input values in the parallel model, the output convolution has a peak split in the 004 peak, which has an FWHM value of 0.03°. The overall convolution doesn’t match

with the experimental XRD pattern. Moreover, the ‘ripples’ or oscillations in the pyramidal model output is markedly higher than those in the parallel model output, because for a coherent vertical height H , the Laue/shape term gives fringe spacing $\Delta q_z \approx \frac{2\pi}{H}$ where $q_z = \frac{4\pi}{\lambda} \sin \theta$ near the Bragg angle θ_B , that converts to an angular spacing of $\Delta(2\theta) = \frac{\lambda}{H \cos \theta_B}$ (Cu K α_1 ; $\lambda=1.5406$ Å) . If the projected pyramidal OPB features display an effective repeat spacing L along the projection direction (**Figure 4.3 d**), arising from the overlap of OPB segments within the TEM projection, the diffraction pattern acquires a second fringe scale of $\Delta q_z \approx \frac{2\pi}{L}$.

Finally, in the pyramidal model the OPB unit geometry is applied repeatedly across the simulated film thickness (**Figure 4.1 d-f and Figure 4.3 f**), consistent with the quasi-periodic OPB arrangement observed in TEM projections. The inclusion of the full 3D geometric input (**Figure 4.4 b**) increases the number of OPB segments that must be accounted for in the diffraction calculation. As a result, the oscillations are understandably higher in the pyramidal model as it is accounting for a defect density closer to that of the experimental thin film.

It is important to note the criterion for comparing experiment and simulation in this work differs from that used in the parallel model of Whatmore *et al.*[269] In the previous model, the magnitude of the peak splitting was the appropriate comparison metric , whereas in the present study the relevant features arise from the asymmetric envelope and multi-component line shape produced by the pyramidal OPB geometry. Since the defects in this growth spiral model have a higher defect density, oscillations in the output XRD pattern are a necessary signature of the film’s characteristics. This makes peak split a redundant metric of comparison since the value

of the peak split cannot be accurately measured in degrees, and would depend too much on post-simulation fitting, making an honest comparison difficult. Hence, a convolution overlay connecting the maxima of the oscillations is a more reliable and intuitive indication of the model's comparison to the experimental data. The present model represents the film using a repeated pyramidal OPB unit rather than a single planar fault, capturing the quasi-periodic OPB geometry observed in TEM projections. This introduces an additional characteristic length scale (the base L) which gives rise to corresponding interference fringes in reciprocal space. That residual oscillatory structure, attenuated but not erased by convolution, is a distinguishing fingerprint of a periodically stacked pyramidal OPB defect network. It also explains why the present model reproduces the observed shoulders and peak skewness that the earlier parallel model could not capture.

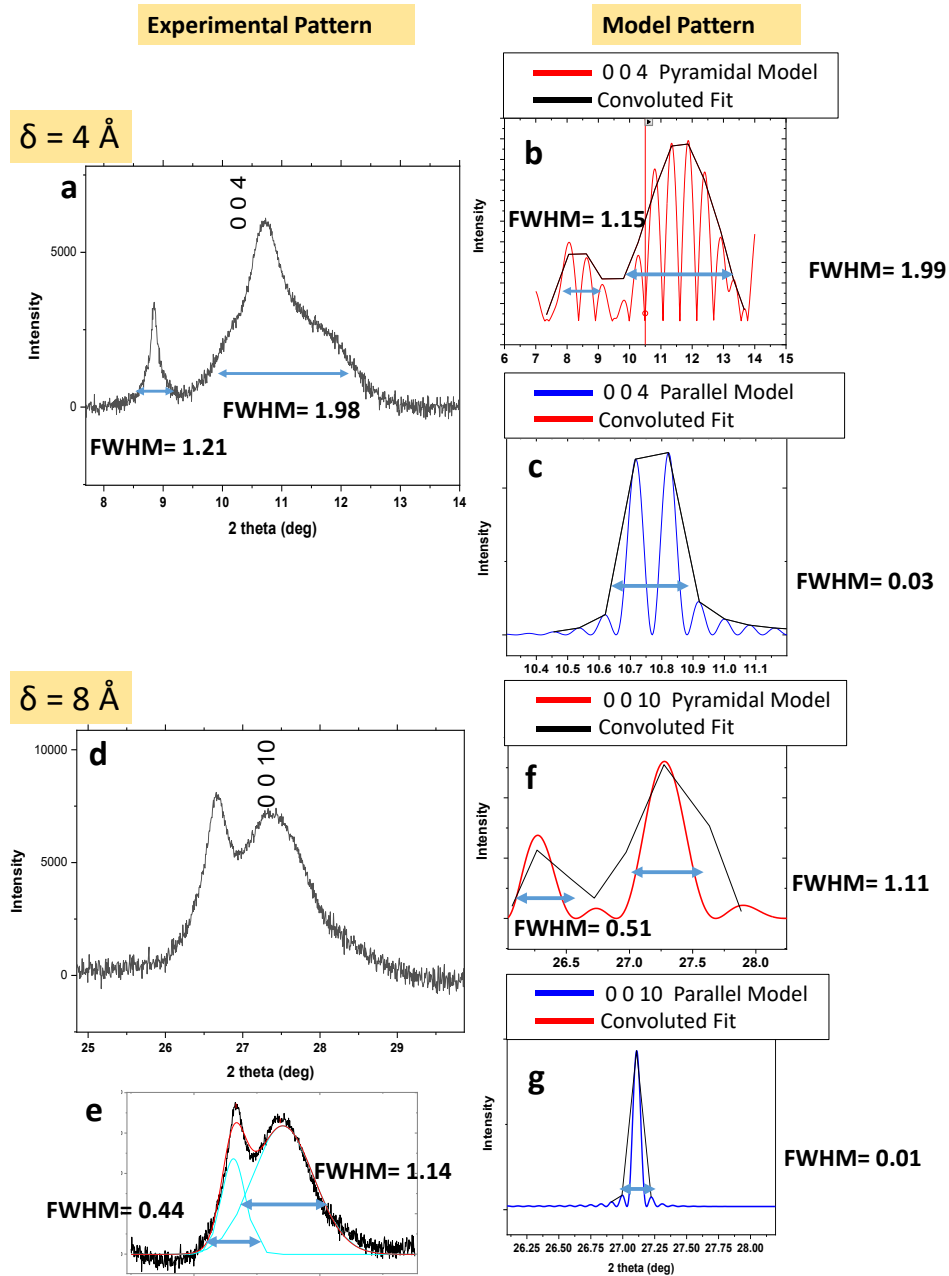


Figure 4.5: Comparison of the experimental XRD patterns with the simulated patterns generated using the pyramidal OPB model (red) and the parallel OPB model (blue) for two 00l reflection -(004 and 00 10). All FWHM values are in degrees (°)

a- Experimental XRD pattern of the 004 reflection. **b-** Simulated 004 reflection from the pyramidal OPB model developed in this work, using a step height ' δ ' = 4 Å. **c-** Simulated 004 reflection (blue) and its convoluted fit (red) from the previous parallel OPB model of Whatmore et al.[269] using the same step height. **d-** Experimental XRD

pattern of the 0010 reflection. e- Gaussian deconvolution of the split 00 10 peak, showing convergence to two distinct components. f- Simulated 0010 reflection from the pyramidal model with step height ' δ ' = 8 Å. g- Simulated 00 10 reflection from the parallel OPB model with step height ' δ ' = 8 Å. All Full Width Half Maximum (FWHM) values are calculated through a standard Gaussian fit, with a standard uncertainty of ± 0.895 . The instrumental resolution function of the PANalytical MRD under the measurement geometry used was modelled as a Gaussian with FWHM $\approx 0.05^\circ$ at the 004 reflection, consistent with typical laboratory diffractometer resolution at this angle for a Cu K α source with Soller slits. This function was convolved numerically with the model-calculated intensity profiles before comparison with experimental data, ensuring that the simulated line shapes reflect both the intrinsic defect distribution and the finite instrumental resolution.

In the experiment (**Figure 4.5 d-e**), the 00 10 reflection is clearly not a single symmetric Bragg peak. A two-component envelope is resolved by Gaussian deconvolution (**Figure 4.5 e**; component FWHMs $\approx 0.44^\circ$ and $\approx 1.14^\circ$), i.e., there is genuine order-dependent splitting at 00 10. The pyramidal model reproduces the existence of this split: when the OPB steric offset is set to $\delta = 8$ Å (double the value that fits 004), the simulated 00 10 profile becomes two-lobed after convolution (**Figure 4.5 f**; envelope FWHM $\approx 0.51^\circ$ and 1.11°). By contrast, the parallel OPB model with the same δ remains essentially unresolved and unrealistically narrow (**Figure 4.5 g**; FWHM $\approx 0.01^\circ$). The difference stems from how the two models generate the phase field along c . In the parallel model the OPB inclination is depth-independent, so the phase increment is a single constant gradient; even at $\delta = 8$ Å the interference at 00 10 is too coherent to broaden or split the line significantly. In the pyramidal model, the OPB faces are inclined and the inclination varies with depth

across each unit (two faces with angles φ_1 and φ_2 , repeated with spacing L). This produces a height-dependent c-axis phase, so different layers contribute different phase increments to the 00 10 structure factor. When the input variables approach a destructive-interference condition, this depth dispersion resolves into two maxima after convolution, hence the split observed for 00 10 only in the pyramidal case. This order-selective behaviour reflects the different sensitivities of the $00l$ reflections to the underlying c-axis phase field. Lower order reflections (e.g. 004) are predominantly influenced by the smaller OPB step height and are best reproduced using $\delta \approx 4$ Å, whereas higher order-reflections (e.g. 00 10) require an effective $\delta \approx 8$ Å to capture the observed two-lobed profile.

These fitted values lie squarely within the 4-8 Å range of OPB offsets measured directly by HRTEM (**Figure 4.6 a**), confirming that the XRD response represents a coherent average over the film's real δ -distribution (**Figure 4.6 b**). Importantly, the pyramidal model is capable of predicting the actual distribution of δ step heights (with comparatively more global statistical relevance, something the TEM cannot do). Because higher-order $00l$ reflections are intrinsically more sensitive to c-axis phase increments, they preferentially amplify the larger ~ 8 Å offsets: the 004-line shape is governed by the 4 Å steps, while the 00 10 profile reveals the influence of the 8 Å steps. Thus, the order-selective behaviour arises from the combined effect of (i) two physically present OPB step heights and (ii) the l -dependent sensitivity of the structure factor to the depth-varying phase field generated by the pyramidal OPB geometry. In the simulations we approximated each defect set as a rectangular-base pyramid (**Figure 4.4 b**). This choice follows from the crystallography of the model: the OPB is treated as a pure c-axis translation fault, so the phase term can be written unambiguously on a c-a triangular face and then extruded along b to form a 3D object

with two well-defined faces (angles φ_1, φ_2). This gives a consistent surface on which the c-axis misregistry δ is applied symmetrically and makes the structure-factor sum tractable. In the real film, however, spiral coalescence is expected to generate defects that are closer to a cone or frustum rather than a perfect pyramid, i.e., with defects turning around the spiral core. ^[229] A truly conical defect would not have a single crystallographic face with constant δ ; the misregistry would vary around the circumference, complicating the 3D phase field and smearing the interference. HRTEM (**Figure 4.6 a,b**) shows precisely this reality: multiple inclined OPBs arranged diagonally across the cross-section, with discrete c-axis offsets of ~ 4 Å and ~ 8 Å measured at different boundaries. We therefore use the rectangular-pyramid geometry as a controlled approximation that (i) preserves the correct c-axis phase shift, (ii) provides a pair of fixed faces on which δ can be applied, and (iii) accurately predicts two observed δ “quanta” (4 Å and 8 Å) that appear in the HRTEM (**Figure 4.6 a**). The residual differences between the simulated and experimental line shapes: e.g. peak split, lobe FWHM, and small 2θ shifts, are consistent with the more conical, azimuthally varying defects present in the film, which our pyramid model intentionally simplifies.

In this work we set $N = 5$ ($N = 2m + 1$) for the pyramidal OPB arrangement unit, whereas the earlier parallel model used $N \approx 35$ to span the full film thickness. The change reflects the difference in geometry. In the parallel model, a single planar OPB traverses the entire film, so the kinematic sum must include all (00ℓ) planes within the thickness to capture the full phase ramp. By contrast, the OPB features in our case form a pyramidal arrangement whose apparent repetition does not represent a defect sequence extending through the entire film thickness. Instead, the cross-section TEM

reveals a quasi-periodic series of finite-height OPB segments, arising from the projection of spiral-related OPB boundaries within the lamella. We therefore evaluate the structure-factor sum over a local block ($N = 5$ layers) that represents one pyramid's height H , and then tile these units through thickness and laterally with spacing L . This keeps the OPB defect phase field faithful to the stacked, finite geometry while avoiding an artificial thickness average that would dilute the depth-dependent phase responsible for the observed split and asymmetry.

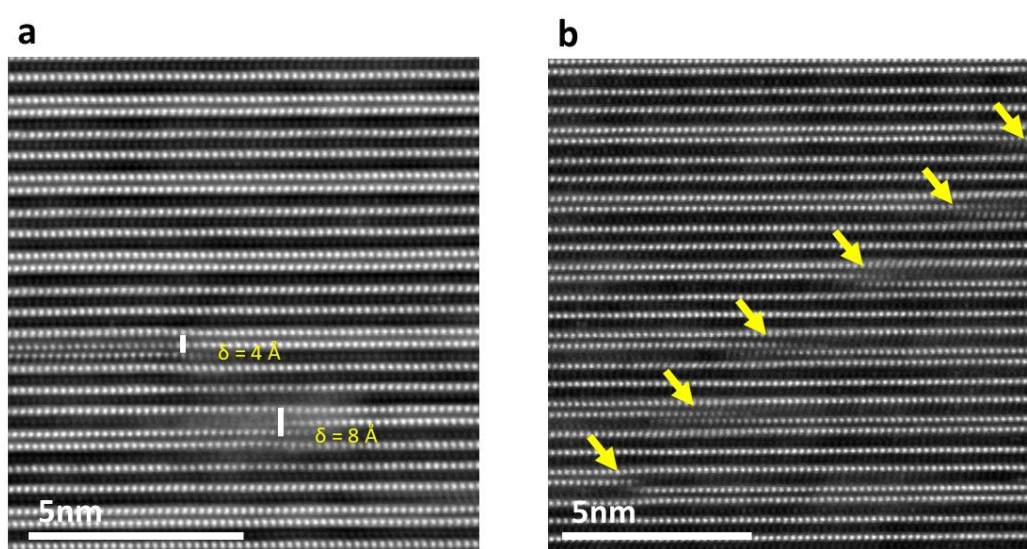


Figure 4.6: *a-* Cross-sectional HRTEM image showing the OPB-induced ‘ δ ’ offset values fall within the range of $4\text{\AA}$ and $8\text{\AA}$. *b-* Cross-sectional view showing the spatial distribution and repeating pattern of OPBs throughout the film.

A practical advantage of the pyramidal-OPB model is that it predicts the entire 00ℓ peak shape, not just whether a split occurs. Because the structure factor is evaluated and then convolved, the model reproduces the observed broadening and asymmetric envelopes as well as the split/shoulder positions. For instance, the $00\ 12$ peak shows broadening but no visible splitting ([Supplementary Figure S 4.1](#)). Here, the pyramidal model is able to capture a comparable FWHM (experimental FWHM =

1.84° and the pyramidal model FWHM is 1.80°, yielding a % difference of -2.22%). Whereas the parallel model produces a peak split whose convolution produces an FWHM of 0.08°, which is -95.65% difference. A current limitation is that each calculated pattern corresponds to a single steric offset δ , whereas the film exhibits a distribution of δ values (e.g., 4–8 Å in **Figure 4.6**). Consequently, the simulated envelope can be sharper or differently weighted compared to experiment, which averages coherently over many OPBs with varying δ (and L , $\phi_{1,2}$). In principle this can be addressed by mixture averaging, i.e., summing patterns over a probability density $P(\delta)$ (and, if desired, $P(L)$, $P(\phi_{1,2})$). But here we report single- δ fits to keep the parameter space controlled and to highlight the order-dependent selection of δ (~ 4 Å for 004; ~ 8 Å for 00 10) that predicts and aligns with HRTEM results.

[Supplementary Figure S 4.2](#) shows the full θ – 2θ pattern from 5° to 42°. For clarity, each trace is multiplied by an arbitrary scaling factor, so weaker reflections are visible on the same axis; this rescaling affects apparent intensities but not peak positions or line shapes. Because such visualisation can make some reflections look disproportionately large or small, we compare the key peaks individually in **Figure 4.5**, each on its own intensity scale to enable a fair assessment of shape, width, and splitting.

The remaining differences are expected consequences of model simplifications that we kept to preserve analytic tractability. i The simulation uses a single “family” of pyramids (one δ , one pair $\{\phi_1, \phi_2\}$, one L) for each output pattern, while TEM shows a distribution of offsets (4–8 Å), face angles and spacings through the thickness. A real distribution broadens the envelope and changes the relative lobe intensities, whereas a single-family model inevitably over- or under-weights one lobe. (ii) We

assume a symmetric δ on both OPB faces and a 1D phase shift only along c ; any asymmetry of δ on the two faces or small in-plane components will skew the intensity differently than our symmetric construction. (iii) The current convolution uses a fixed instrumental line shape and coherence length; modest misestimation of either (or background subtraction) changes the apparent depth of the central minimum and the shoulder height. All three effects soften the simulated oscillations and adjust the lobe ratio in the experiment relative to **Figure 4.5 f**, without undermining the key result that a pyramidal, depth-varying phase field is required to resolve the split.

4.3. Conclusion

In this work, a generalised X-ray diffraction (XRD) model was developed and analysed to describe the impact of pyramidal arrangements of out-of-phase boundary (OPB) defects formed during spiral-driven growth in layered thin films. By building upon the previous parallel OPB model,[269] our pyramidal model accounts for meeting growth-fronts, three-dimensional lattice displacements, and angular asymmetries that emerge during screw dislocation-mediated growth. Simulated XRD patterns show excellent agreement with experimental data, successfully capturing asymmetric peak broadening and splitting, while accurately predicting the atomic offset at the defect, as confirmed by HRTEM. Furthermore, correlative electron microscopy and piezoresponse measurements confirm that the pyramidal arrangements of OPB defects influence the local polar structure: they impose vertical lattice offsets that modify the out-of-plane-polarisation continuity and act as preferential sites for domain wall pinning or nucleation. This demonstrates that OPB defects are not merely structural irregularities but participate in shaping the functional ferroelectric response. This work not only provides the first predictive framework for

understanding diffraction signatures of spiral-driven OPB defects, but also is the first three-dimensional XRD model in this context.

The pyramidal OPB model developed here quantifies the diffraction consequences of one specific defect type — the inclined, three-dimensional OPB arrays that spiral growth encodes in BiT films on STO. A structurally distinct class of defect arises under high-supersaturation conditions on orthorhombic NGO substrates: 45°-rotated twin boundaries, where the near-degenerate in-plane lattice parameters of NGO make multiple film orientations energetically accessible during nucleation.[ref] Twin boundaries produce their own characteristic diffraction signature — incoherent, broadened reflections that differ qualitatively from the order-selective peak splitting modelled here — and their suppression is a prerequisite for achieving the structural coherence that device integration requires. Chapter V asks whether that suppression is possible: can supersaturation be tuned further to eliminate twin-variant nucleation entirely, or will substrate-driven orientation variants persist regardless of growth conditions?

For detailed description of the Experimental Methodology, refer to the [Appendix V](#).

5. Suppressing Crystal Twinning in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ via Supersaturation Control

In this chapter, all research is the work of the author, with the exception of the following contributions from collaborators: M. Schmidt (Tyndall-UCC) prepared cross-section lamella of the samples. T. Simonian (Imperial College London) carried out scanning transmission electron microscopy (STEM), high resolution TEM (HRTEM), electron energy loss spectroscopy (EELS) and polarisation simulation. S. Hussain supported the nano-machining studies and PFM analysis.

5.1. Introduction

Chapters III and IV examined the structural and functional consequences of a specific growth regime: the spiral morphology that develops in BiT when supersaturation is reduced below the two-dimensional nucleation threshold through sequential precursor injection. That regime was characterised in terms of its defect geometry, its diffraction signatures, and its influence on the out-of-plane polarisation response. This chapter examines whether the same supersaturation lever that controlled morphology in Chapters III and IV can be used to address them. Crystal twinning represents a major obstacle to the development of high-performance ferroelectric thin films, particularly in layered oxide systems with strong crystallographic anisotropy such as the Aurivillius $((\text{Bi}_2\text{O}_2)(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1}))$ phases. Twinning occurs when two or more regions within a crystal adopt specific orientational relationships, typically through mirror or rotational symmetry.[376] In epitaxial thin films, these twinned domains originate from the atomic-scale processes governing nucleation and growth, especially when films are deposition occurs on anisotropic substrates.[377], [378] In Aurivillius

oxides such as $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, epitaxial growth on lattice matched but anisotropic substrates like NdGaO_3 (NGO) readily induces such orientation variants due to directional strain fields established during nucleation.

The presence of twin boundaries locally disrupt polarisation continuity,[378] and act as pinning centres for domain walls, thereby impeding ferroelectric switching.[252], [379] Consequently, understanding and controlling the formation of twinned domains is critical for integrating Aurivillius ferroelectrics into non-volatile memory and logic devices, where uniform and reversible polarisation is essential for reliable operation.

To overcome this, several strategies have been explored. One approach has been to use substrates with reduced in-plane anisotropy,[380] such as cubic or pseudocubic SrTiO_3 (STO), which do not themselves promote twinning. However, changing the substrate is not always ideal if a specific lattice mismatch is needed to induce epitaxial strain or to stabilize the desired orientation or phase. Other methods include increasing the substrate temperature to enhance surface diffusion,[276], [381] which can promote step-flow growth and reduces the density of structural defects such as twin boundaries.[253], [377] While effective in some cases, high temperatures can compromise phase purity and stoichiometry, particularly in bismuth-based materials where volatile Bi species are prone to re-evaporation.

Post-deposition annealing has also been employed to relax strain and promote grain coarsening,[276], [382], [383] though this is often insufficient to eliminate twin boundaries once formed and may impact interfacial sharpness. Some studies have investigated buffer layers or seed templates to influence nucleation behaviour,^[13] but these add complexity to the growth stack and can compromise interface quality or

introduce additional defects.[386] Each of these methods offers partial solutions but tends to be material, or substrate-specific, or insufficiently robust to guarantee twin-free growth under diverse conditions.

Despite significant advances in oxide epitaxy, a broadly applicable, energy-efficient, and process-compatible strategy for eliminating crystallographic twinning in layered Aurivillius thin films has remained elusive. In this work, we employ a supersaturation-controlled growth method using direct liquid injection chemical vapour deposition (DLI-CVD), a precursor-delivery variant of MOCVD. In DLI-CVD, liquid precursor solutions are metred and flash-vapourised at the injector, enabling stable control of precursor flux. By tuning delivery kinetics and the ambient oxygen partial pressure, we indirectly modulate the effective supersaturation at the growth front. This enables control over nucleation and orientation selection without the need for high substrate miscut angles, sacrificial buffer layers, or post-growth annealing. Unlike conventional high-temperature methods that rely on enhanced adatom mobility to suppress twinning,[276], [387], [388] this strategy achieves control through thermodynamic tuning of the growth driving force via precursor chemistry and ambient conditions. Because the core principle of supersaturation modulation is compatible with vapour-phase techniques that permit control over precursor flux and oxidizing environment, including atomic layer deposition, Low Pressure Chemical Vapour Deposition (LPCVD), and sputtering, this approach offers a general and scalable framework for twin defect suppression across a wide range of complex oxide systems.

We demonstrate that this supersaturation-controlled growth approach completely suppresses twinning in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films grown on (001) NGO substrates.

In contrast, twinned films exhibit weakened X-Ray Diffraction features due to incoherent scattering from multiple orientation variants, which diminishes the intensity and definition of Bragg reflections. Under low supersaturation conditions, the resulting films exhibit sharp X-ray diffraction peaks with well-defined Laue fringes, atomically abrupt interfaces in scanning transmission electron microscopy (STEM), and spatially coherent polarisation switching across uniformly oriented domains, as revealed by piezoresponse force microscopy (PFM). These results establish that precise kinetic regulation of supersaturation during MOCVD growth directly governs orientation selectivity, enabling deterministic control over structural coherence and functional response in layered ferroelectric oxides.

5.2. Results and Discussion

5.2.1. Thermodynamic–Kinetic Framework for Twin Formation in Layered $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ Thin Films

Crystal twinning in epitaxial thin films arises from the coupled influence of thermodynamic driving forces and kinetic growth constraints. Supersaturation, defined by the chemical potential difference between the vapour phase and the crystal surface, governs this interplay by setting the thermodynamic driving force for nucleation and growth.[389] Although not a kinetic parameter itself, supersaturation controls how strongly the system is driven from equilibrium, while the resulting growth behaviour depends on how precursor decomposition, adatom diffusion, and surface incorporation respond to this force. In MOCVD, the effective degree of supersaturation can be tuned experimentally through the control of precursor flux and oxygen partial pressure, which together modulate the balance between adatom arrival and incorporation kinetics. Under high supersaturation conditions, the large chemical potential gradient accelerates nucleation beyond the rate of adatom diffusion and

equilibration. This imbalance promotes the simultaneous stabilization of multiple in-plane orientation variants, increasing the probability of mirror-related twin-related domains. In contrast, lowering supersaturation reduces the nucleation rate and enhances adatom mobility, shifting the growth regime from nucleation-limited to diffusion-limited. Adatoms then selectively occupy energetically favourable lattice sites, enabling single-orientation nucleation and suppressing twin boundary formation.[390], [391]

Twinning is particularly prevalent in layered oxide systems such as the Aurivillius phases, $(\text{Bi}_2\text{O}_2)(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})$, which are intrinsically two-dimensionally nanostructured with large c -axis lattice parameters, where the number of perovskite-like ABO_3 units per half-cell is denoted by m . The pronounced crystallographic anisotropy and modular stacking of alternating perovskite-like and fluorite-type layers introduce shear planes and direction-dependent strain fields during epitaxial growth, making these systems especially susceptible to twin formation. On anisotropic substrates such as (001) NGO, nearly degenerate in-plane lattice parameters make multiple orientation variants energetically accessible.[129] The unequal in-plane lattice constants of NGO generate directional strain fields during nucleation. To minimize strain energy, the film adopts multiple orientation variants, leading to the formation of twin boundaries.[229], [392] In contrast, cubic or pseudocubic perovskites exhibit more isotropic elastic and structural symmetry, favouring uniform epitaxy in which strain is accommodated by octahedral tilting or dislocation formation rather than twinning.

Figures 5.1 and 5.2 illustrate the structural relationship in $m = 3$ Aurivillius phase $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BiT) films grown epitaxially on NGO (001) substrates. STEM-EELS

imaging (**Figure 5.1 (a-b)**) confirms coherent heteroepitaxial growth with sharp interfacial contrast. Despite NGO's orthorhombic symmetry ($a = 5.47 \text{ \AA}$, $b = 5.62 \text{ \AA}$), a close pseudo-cubic lattice match exists along the diagonal of the ab -plane, with an effective pseudo-cubic parameter of $a_p \sim 3.86 \text{ \AA}$, closely aligning with the pseudo-cubic perovskite lattice of BiT ($\sim 3.837 \text{ \AA}$), as depicted in **Figures 5.1 (c-d)**. This diagonal alignment results in a 45° in-plane rotation of BiT grains along the NGO $[110]$ direction to minimize interfacial strain, as shown in the atomistic simulation in **Figure 5.2 a**.

Together, these observations establish that the interplay between supersaturation, adatom kinetics, and crystallographic anisotropy provides a coherent framework for understanding and controlling twin formation in layered oxide thin films. To experimentally validate this model, we examined the structural evolution of BiT films grown under distinct supersaturation regimes.

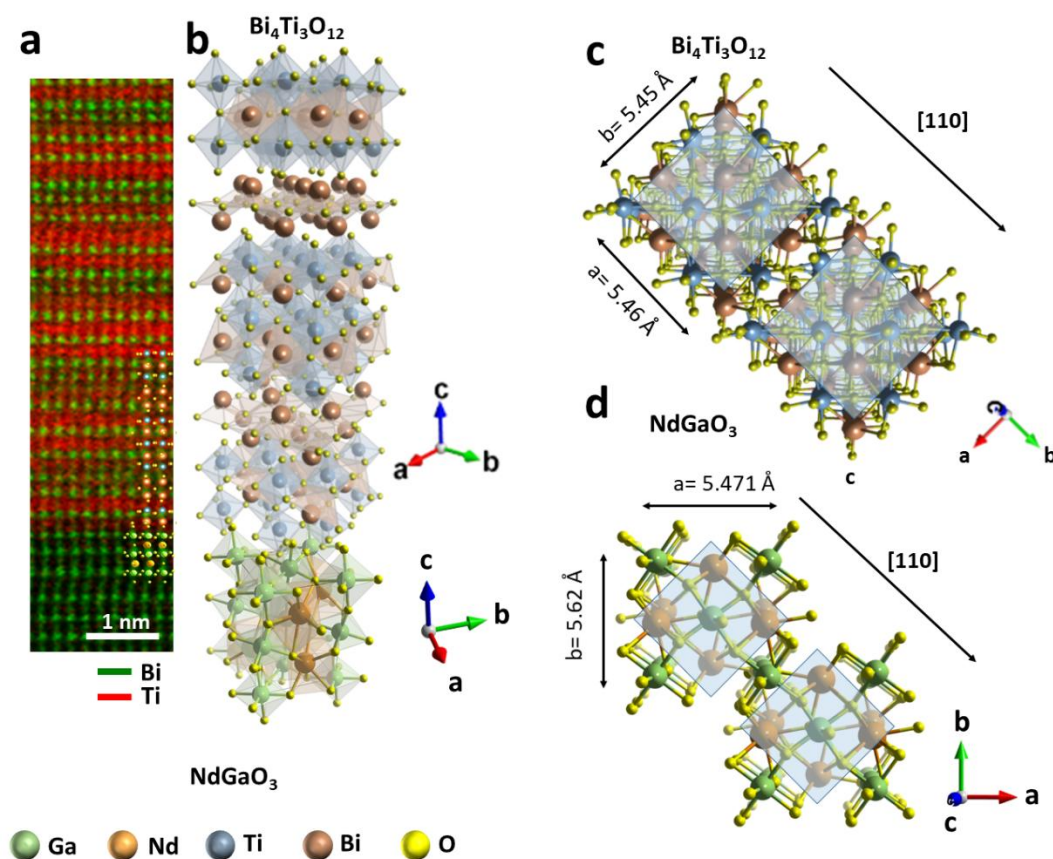


Figure 5.1. STEM–EELS imaging and atomistic simulations illustrating the epitaxial alignment and lattice relationship between BiT and (001)-oriented NGO. **a)** Cross-sectional STEM-EELS elemental map acquired along the $[100]$ projection of BiT grown epitaxially on (001) NGO. **b)** Atomistic model of the lattice-matched BiT/NGO interface. **c-d)** Simulated top-view crystal structures depicting the pseudocubic lattice relationship between BiT ($a_p \sim 3.837 \text{ \AA}$) and NGO ($a_p \sim 3.86 \text{ \AA}$), illustrating the 45° in-plane rotation of the BiT lattice along the $[110]$ direction relative to the substrate.

5.2.2. Structural Evolution under High Supersaturation: Nucleation-Limited Growth and Twinning

Supersaturation (α) quantifies the thermodynamic driving force for nucleation and is defined by the ratio of precursor partial pressure (P) to the equilibrium pressure for solid-phase deposition (P_{eq}):

$$\alpha = \frac{P}{P_{eq}} \quad 24,$$

A high value of α indicates a strong departure from equilibrium, resulting in a large chemical potential gradient that accelerates nucleation. Under such conditions adatoms have insufficient time to diffuse and equilibrate, promoting random, polyvariant nucleation and the development of twin-related domains. In contrast, reducing α decreases the thermodynamic driving force and enhances surface diffusion, favouring selective, layer-by-layer epitaxy with a single orientation variant. The calculated supersaturation ratio (α) between the high- and low- supersaturation regimes in this study is approximately 5.4:1 (see in **Appendix IV Section I**).

During concurrent precursor injections at a rate of one pulse per second on (001)-oriented NGO substrates, the high supersaturation regime produces a rapid film growth rate of ~ 1.47 nm/min ([Supplementary Figure S 5.1](#)). Under these conditions, BiT growth transitions into a nucleation-limited regime, where rapid precursor decomposition and adatom arrival rates far exceed surface diffusion and equilibration. This imbalance between deposition flux and surface mobility leads to the formation of numerous small, misoriented nuclei, that subsequently coalesce into twin-related domains. Such behaviour is emblematic of kinetically dominated growth, in which the system is driven far from equilibrium and lacks the opportunity to stabilize a single orientation variant.

As shown in the AFM images in **Figure 5.2 b**, films grown under high supersaturation conditions exhibit in-plane rotation of BiT grains relative to the NGO substrate, forming elongated, twin-related domains separated by distinct boundaries along the [110] planes. These features correspond to $\sim 45^\circ$ in-plane rotations of BiT grains with respect to the NGO lattice, consistent with the epitaxial alignment expected from the pseudocubic lattice match between the two systems.

Among the Aurivillius phases studied, this pronounced twinning tendency appears most severe in the $m = 3$ Aurivillius phase $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. In contrast, higher-order members such as $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ (BTFO) ($m = 4$)[129] and B6TFMO ($m = 5$)[144] remain largely twin-free under identical substrate conditions. BiT possesses a shorter c -axis lattice parameter ($\sim 32.8 \text{ \AA}$) compared to BTFO ($c \approx 41.2 \text{ \AA}$) and B6TFMO ($c \approx 49.3 \text{ \AA}$), both of which exhibit extended out-of-plane periods ($c > 40 \text{ \AA}$). Increased c -axis periodicity enhances vertical structural coherence and suppresses in-plane twinning by raising the nucleation barrier for twin formation along [110] mirror planes. Additionally, Fe/Mn substitution in BTFO and B6TFMO introduces greater chemical and structural complexity within the perovskite blocks, which likely imposes additional kinetic constraints that hinder the development of orientation variants.

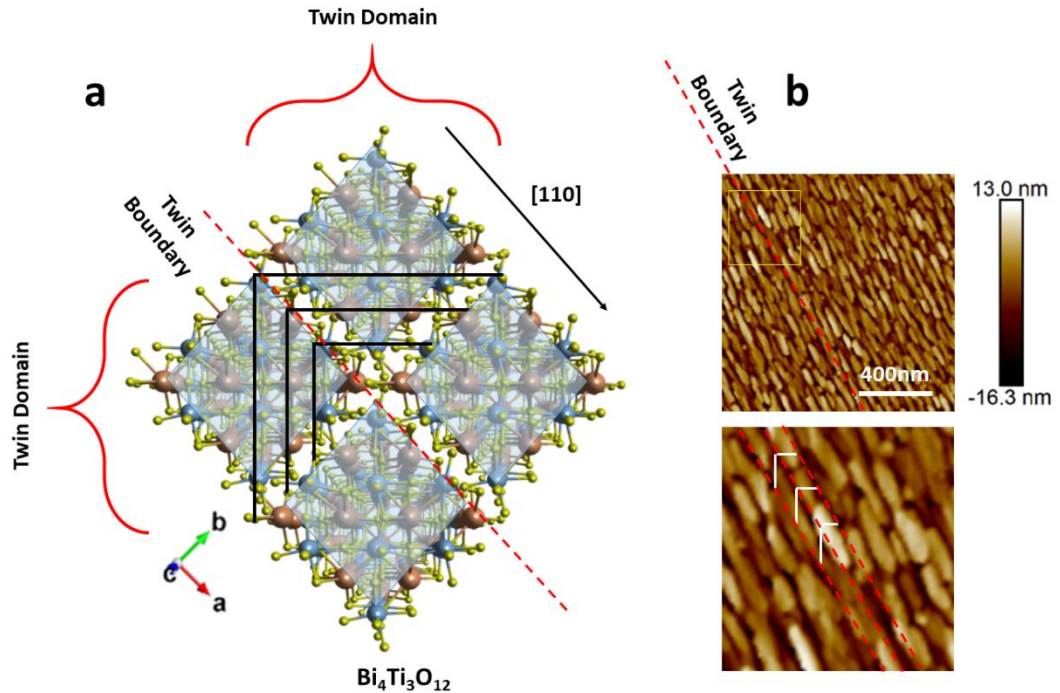


Figure 5.2. Visualization of twinned grain formation in BiT grown on (100) NGO under high supersaturation conditions. **a)** Atomistic representation showing the 45° in-plane rotation of BiT twin domains separated by [100] boundaries. **b)** AFM images illustrating elongated, twinned grains corresponding to these orientation variants under high supersaturation growth.

The structural manifestations of high supersaturation, namely, dense nucleation, in-plane rotation, and twin-related domain formation, have direct consequences for the ferroelectric behaviour of BiT films. Twin boundaries act as symmetry-breaking interfaces that disrupt polarisation continuity and hinder domain wall motion, thereby decoupling adjacent regions from coherent switching. A detailed clarification of the terminology used to distinguish crystallographic twin domains from ferroelectric domains is provided in the Supplementary Information (Section I). This distinction is essential for interpreting the subsequent piezoresponse force microscopy (PFM) results in **Figure 5.3**.

Figures 5.3 f and 5.3 g show lateral PFM amplitude and phase contrast images for twinned BiT films grown under high supersaturation conditions. The presence of a measurable piezoresponse confirms local ferroelectric activity across the sample surface, however, the irregular and discontinuous contrast similar to the surface topography reveals a lack of polarisation coherence. The relatively high root mean square (RMS) surface roughness of ~ 12 nm, likely contributes to topographic artifacts in the PFM phase signal,[393] an effect commonly observed when domain walls are pinned or when surface undulations interfere with PFM tip-sample contact mechanics.

More significantly, the PFM poling experiments shown in **Figures 5.3 h and 5.3 i** demonstrate a clear suppression of polarisation switching: despite biasing between ± 5 V to ± 45 V, no reversible phase inversion is observed, even after rotating the sample 90 degrees clockwise and anti-clockwise ([Supplementary Figure S 5.2](#)). This inability to pole the film is consistent with the influence of twin boundaries, which act as symmetry-breaking defects that locally rotate or reverse the polarisation vector.[394] Although each individual twin variant within $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ retains the crystallographic symmetry required for local ferroelectricity, the polarisation vectors in adjacent variants are rotated relative to one another, by 90° formed along the $[110]$ direction. As a result, the twin boundaries act as structural and electrostatic discontinuities that disrupt long-range polarisation coherence. These interfaces pin domain walls and inhibit polarisation reversal. Consequently, while twinned regions can exhibit localized ferroelectric response, the macroscopic film behaves as a collection of electrostatically decoupled domains with reduced switchability and stability.[379]

Crystallographically, twinning disrupts the in-plane lattice coherence by introducing multiple orientation variants, which gives rise to enhanced diffuse scattering and overlapping reflections in XRD patterns.[395], [396], [397], [398] In heavily twinned samples, the constructive interference required to generate well-defined Bragg peaks and Laue fringes is largely suppressed by incoherent scattering from disorientated domains, producing in broadened, weak, or even featureless diffraction profiles ([Supplementary Figure S 5.3](#)). The near absence of $(00l)$ reflections may appear counterintuitive, since out-of-plane peaks are typically retained even in partially textured films. However, this behaviour can be rationalized by considering the impact of severe in-plane orientation disorder.

Under high supersaturation conditions, rapid nucleation outpaces adatom diffusion, resulting in a dense mosaic of twin domains rotated by 45° or 90° , particularly along the $[110]$ twin planes. These misoriented variants scatter X-rays out of phase, causing destructive interference in the out-of-plane geometry and effectively cancelling the coherent $(00l)$ signal. . Similar effects have been reported in twinned oxide films with high mosaic spread and polyvariant microstructures.[399] Thus, the absence of distinct diffraction peaks is itself a signature of extensive twinning and orientation disorder, confirming the structural instability that arises under excessive supersaturation. Collectively, these results demonstrate that high supersaturation growth promotes twin formation that simultaneously degrades both crystallographic coherence and ferroelectric functionality. These findings define the characteristic microstructural signature of the high supersaturation growth regime, providing a basis for comparison with subsequent conditions explored in this study.

To disentangle the effects of precursor supply dynamics (supersaturation control) from those of ambient oxygen pressure (surface chemistry modulation), the following growth experiments were designed to vary each parameter independently. This approach enables a clear assessment of how kinetic and chemical factors contribute to twin suppression and overall film quality.

Atomic force microscopy provides direct insight into how oxygen partial pressure governs the evolution of film morphology and crystallinity. At low oxygen partial pressure, (13.2 Pa; Calculations provided in [Appendix IV Section II](#)), the BiT films exhibit small, elongated grains aligned along the [110] direction of the pseudocubic (001) NGO substrate (**Figure 5.3 a,e**). These grains show poor coalescence, consistent with rapid, high-density nucleation events.[219], [390] The limited adatom diffusion under such conditions promotes the simultaneous formation of multiple orientation variants, leading to the development of twin-related domains along the [110] mirror planes.[400].[330], [373] The resulting twin boundaries interrupt both lattice continuity and ferroelectric domain coherence, as reflected in the suppressed piezoresponse in **Figure 5.3**. While supersaturation is typically regarded as the dominant factor determining film morphology, the observed trend of increasing grain size on increasing oxygen partial pressure reveals an additional layer of kinetic complexity. As shown in **Figure 5.3 d**, increasing the oxygen partial pressure to 26.6 Pa results in markedly larger, more coalesced grains, indicating enhanced surface diffusion and improved crystalline order. This trend runs counter to the classical expectation from equilibrium thermodynamics: in principle, increasing the O₂ partial pressure lowers the equilibrium vapour pressure of Bi₂O₃ (P_{eq}) thereby increasing the effective supersaturation (P/P_{eq}) and favoring higher nucleation density and smaller grains.

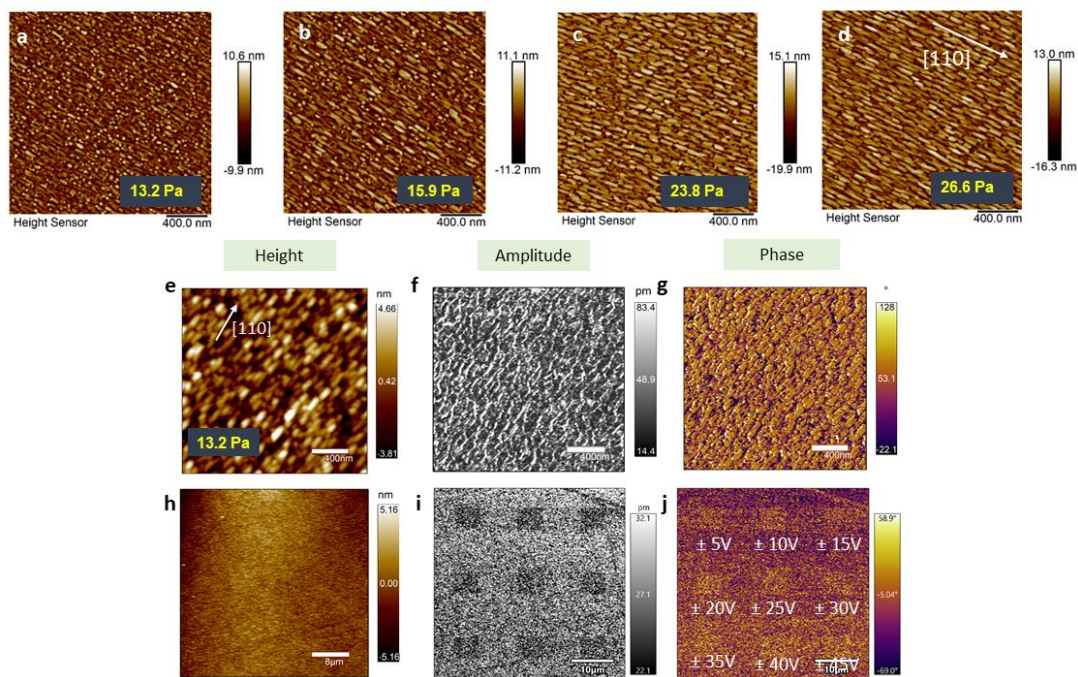


Figure 5.3. Morphological, ferroelectric, and structural characterisation of twinned BiT films grown on (100) NGO under varying oxygen partial pressures. **a-d)** AFM images of BiT films showing twinned surface morphology along the [110] direction, with grain size increasing as oxygen partial pressure increases. **e)** AFM image of a BiT film grown at 13.2 Pa oxygen partial pressure showing fine, elongated grains and pronounced twinning. **f-g)** Corresponding lateral piezoresponse force microscopy (LPFM), amplitude and phase images. **h-j)** Local poling studies performed under applied voltages ranging from ± 5 V to ± 45 V, showing limited polarisation switching in twinned samples.

The experimental observation of grain coarsening and improved crystallinity with higher oxygen pressure therefore points to a kinetic, rather than purely thermodynamic, origin. High O_2 flux likely induces surface passivation through adsorbed Bi_2O_3 species that saturate high-energy adsorption sites, reducing the density of active nucleation centres. This passivation, in turn, extends adatom migration lengths, allowing atoms to reach energetically favorable lattice sites and merge into

larger grains. Similar oxygen-mediated diffusion enhancement has been reported in several oxide systems, where excess oxygen suppresses spontaneous nucleation and promotes layer-by-layer growth modes.[401], [402]. Thus, the combined control of oxygen activity and supersaturation governs the delicate balance between nucleation density, adatom mobility, and twin suppression in BiT epitaxy.

5.2.3. Transition to Low Supersaturation Conditions: Diffusion-Limited Growth and Twin Suppression

When the degree of supersaturation is reduced, film growth transitions from a nucleation-limited to a diffusion-limited regime, where adatom mobility, rather than arrival rate, governs surface evolution. Under these conditions, adatoms possess sufficient time to migrate across the substrate, locate energetically favourable lattice sites, and incorporate coherently into the growing film. This kinetic relaxation suppresses the random formation of misoriented nuclei and promotes the propagation of a single crystallographic orientation.

Experimentally, low supersaturation growth was achieved through controlled sequential precursor injections. In contrast to conventional continuous-flow MOCVD, where Bi and Ti precursors react simultaneously at or near the substrate surface, the sequential mode temporally separates their arrival. This separation reduces the instantaneous local concentration of reactive species at the growth front and thereby lowers the effective supersaturation.

At high supersaturation, the growth rate is faster (~ 1.47 nm/min), but rapid nucleation and limited adatom diffusion result in numerous small nuclei, increased twin formation, and a relatively high twin defect density. Conversely, under sequential injection, precursor fluxes are temporally diluted, leading to reduced growth rates

(~0.74 nm/min), improved surface equilibration and lower supersaturation. The slower nucleation kinetics extend adatom residence times, enhancing lateral surface diffusion and promoting the coalescence of larger, well-oriented grains with fewer twin boundaries. These conditions favour layer-by-layer growth and epitaxial orientation selection- mechanisms that are critical for achieving twin-free high-quality Aurivillius phase films.[219]

Lowering the supersaturation through sequential precursor control eliminates twinning and dramatically enhances structural coherence, as demonstrated in **Figures 5.4 and 5.5**. Under optimized conditions, XRD patterns display sharp, well-defined (00l) reflections and distinct Laue fringes (**Figure 5.4 a**), indicating uniform film thickness and atomically smooth interfaces. Corresponding AFM images (**Figure 5.4 b**) reveal merged grains and smoother terraces. RMS roughness reduces significantly from ~12 nm to ~3 nm when switching from high to low supersaturation growth conditions at a constant pressure of 13.2 Pa, consistent with diffusion-mediated, layer-by-layer growth.

The role of oxygen partial pressure under diffusion-limited conditions provides further insight into kinetic control of film morphology. As oxygen partial pressures increases from 15.9 to 26.6 Pa ([Appendix IV Section II](#)), AFM images (**Figure 5.3 b to 3 d**) reveal progressively larger and more coalesced grains, indicative of reduced isolated nucleation events and improved lateral growth continuity. A similar trend is observed untwinned, low supersaturation BiT thin films (**Figure 5.4 b (i to iv)**), where increased oxygen partial pressure promotes grains coalescence and the eventual formation of continuous epitaxial layers. This morphological evolution is consistent

with a transition toward a layer-by-layer growth mode, characterized by smoother, well-ordered surfaces produced by diffusion-mediated adatom incorporation.[223]

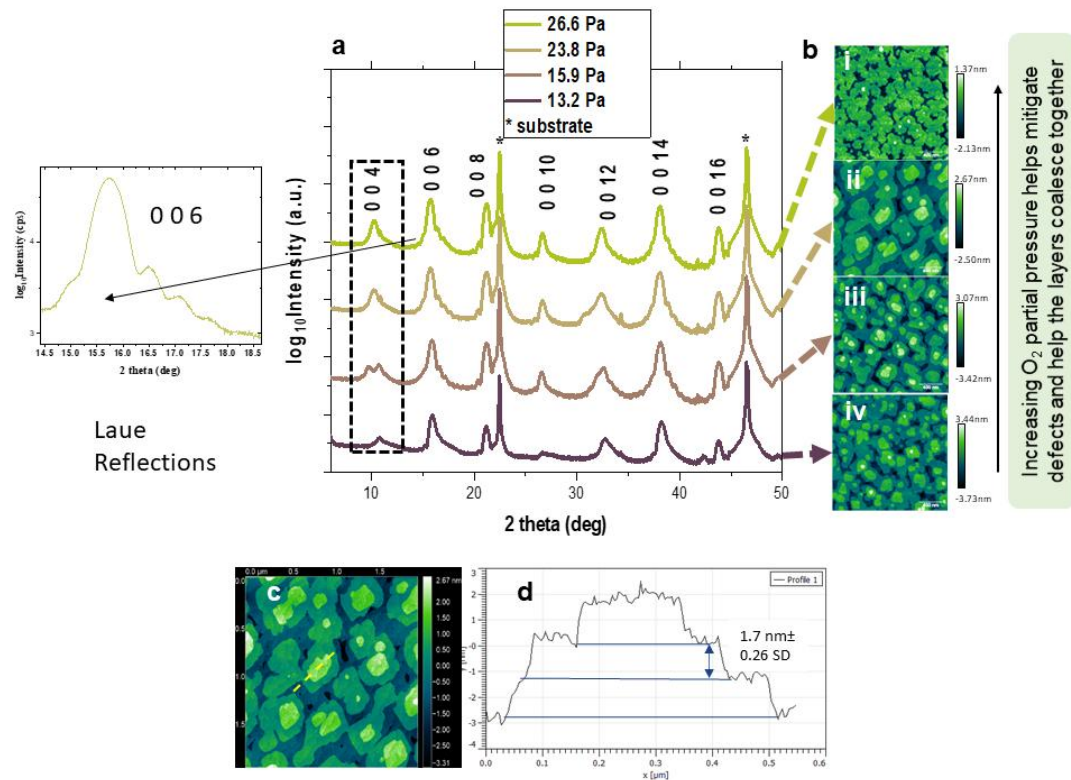


Figure 5.4. Evolution of crystallinity and surface morphology of BiT films with oxygen partial pressure. **a)** XRD patterns of untwinned BiT films showing progressive sharpening of (00l) reflections and emergence of Laue fringes, indicative of enhanced crystallinity and interfacial coherence. **b) (i-iv)** AFM images corroborating the XRD trend, revealing improved grain coalescence and surface smoothness as oxygen partial pressure increases. **c-d)** AFM topography and corresponding height profile for a film grown at 23.8 Pa oxygen partial pressure, showing discrete two-dimensional terrace ‘stacks’ with step heights of approximately 1.7 nm ($\pm 0.26 \text{ SD}$) ($\approx 1/2$ unit cell) consistent, with layer-by-layer growth.

The improvement in structural coherence with increasing oxygen partial pressure is clearly reflected in the XRD data. At the lowest pressure, the film exhibits broad and weak (00l) reflections, consistent with significant structural disorder and a high density of crystalline defects, including out-of-phase boundary (OPB) and stacking fault defects (described in **Chapter I** and **Chapter IV**).[269] The absence of Laue fringes in this sample further indicates interfacial roughness and non-uniform thickness across the film.

As the oxygen partial pressure increases to 26.6 Pa, the (00l) reflections sharpen markedly (FWHM of the (004) peak reduces to 0.47 (26.6 Pa) from 1.71 (13.2 Pa)) and distinct Laue fringes emerge (**Figure 5.4 a (inset)**), signifying near-atomically smooth interfaces, uniform film thickness, and coherent layer stacking over long lateral distances. Such diffraction features arise only when twin boundaries and in-plane disorder are largely suppressed. The improvement in XRD coherence accompanies enhanced oxidation completeness and stoichiometric balance at higher oxygen levels, which together reduce both twin and non-twin structural defects.

This trend is corroborated by AFM imaging (**Figure 5.4 b**), which shows progressively smoother, coalesced surfaces under the same conditions. The AFM topography in **Figure 5.4 c** highlights the two-dimensional terraced nature of the BiT surface. The corresponding height profile in **Figure 5.4 d** reveals discrete step heights of approximately 1.7 nm (± 0.26 standard deviation (SD)), consistent with the thickness of half a unit cell along the *c*-axis, confirming atomically smooth, layer-by-layer growth. Collectively, these improvements in crystallinity and surface morphology mark the transition from a high-supersaturation, nucleation-dominated

regime to a low-supersaturation, diffusion-limited growth mode, in which adatom mobility and lattice selectivity dictate the formation of coherent, twin-free BiT films.

5.2.4. Atomic-Scale Evidence of Twin Suppression and Chemical Coherence

High-resolution transmission electron microscopy (HR-TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) provide direct visualization of the atomic-scale organization and chemical uniformity in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films grown under different supersaturation regimes.

The cross-sectional HR-TEM comparison in Figure 5.5 highlights the profound influence of growth kinetics on structural order. Films grown under high supersaturation exhibit disrupted layer periodicity and diffuse image contrast (**Figure 5.5 a**), characteristic of twinned microstructures. When a $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ film containing [110]-type twins is imaged in STEM along the [100] projection, the overlapping of differently oriented domains produces a superposition of two distinct crystallographic lattices. Because the electron beam cannot simultaneously satisfy the Bragg condition for both orientations, the atomic columns appear blurred and streaked rather than discrete and periodic. This diffuse contrast is therefore not due to defocus but to the incoherent overlap of misoriented Aurivillius phase blocks, which obscures the regular fluorite-perovskite stacking sequence. Such contrast degradation is a defining feature of twinned systems, where 45° or 90° misorientation between domains leads to an incoherent superposition of lattice planes along the imaging axis and a corresponding loss of atomic registry in HR-TEM images.

In contrast, films grown under reduced supersaturation and optimized oxygen partial pressure (26.6 Pa) display the atomic-scale order expected for a single-

orientated $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ epitaxial film (**Figure 5.5 b**). The alternating $(\text{Bi}_2\text{O}_2)^{2+}$ fluorite-type and perovskite blocks are clearly resolved throughout the film thickness, with no evidence of mirror-related boundaries or rotational variants. The periodic lattice contrast remains sharp and continuous, reflecting coherent stacking and uniform orientation across the field of view. This high degree of structural order contrasts sharply with the diffuse, overlapping contrast observed in the twinned sample, confirming the elimination of orientation disorder. These features are consistent with the sharpened diffraction fringes observed in XRD and the smooth terraces revealed by AFM, together demonstrating that precise kinetic control, specifically the modulation of supersaturation, enables the growth of twin-free, single-oriented epitaxial Aurivillius phase films.

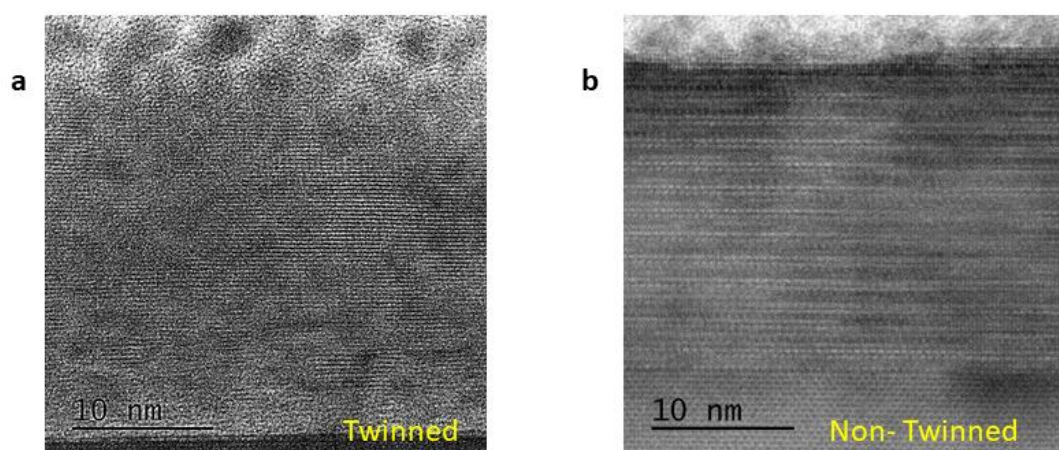


Figure 5.5 Cross-sectional HR-TEM comparison of twinned and untwinned BiT films.

a) Twinned film imaged along the $[100]$ direction, where overlapping $[110]$ -oriented twin variants produce streaked contrast and obscure the atomic-layer periodicity, consistent with disrupted lattice registry across the twin plane. **b)** Untwinned film imaged along the $[100]$ zone axis, showing the well-defined alternating fluorite-like (Bi_2O_2) and perovskite $(\text{Bi}_2\text{Ti}_3\text{O}_{10})$ layers characteristic of the Aurivillius structure.

It should be noted that the twinned and untwinned films compared in this work were grown on NdGaO_3 substrates of differing orientations: twinned films on (100)-oriented NGO and untwinned films on (001)-oriented NGO. While substrate orientation is known to influence in-plane strain anisotropy and nucleation symmetry, the crystallographic argument would predict that the (001) orientation, where the nearly degenerate in-plane lattice parameters a and b make multiple orientation variants energetically accessible, should be *more* susceptible to twinning, not less. The experimental observation is in fact the opposite: it is the films on the (100)-oriented substrate that exhibit twinning, while films grown under low-supersaturation conditions on the (001) substrate are twin-free. This counterintuitive result is consistent with the conclusion that growth kinetics, specifically the degree of supersaturation, is the dominant determinant of twin formation rather than substrate orientation alone. The substrate difference therefore does not undermine the central hypothesis; if anything, it strengthens the argument that supersaturation control is the decisive factor in suppressing twinning.

To resolve the atomic-scale origin of this macroscopic order, HAADF-STEM was performed (**Figure 5.6 a and 5.6 b**). These images reveal atomically sharp $\text{Bi}_4\text{Ti}_3\text{O}_{12}/\text{NGO}$ interfaces and continuous Aurivillius-layer stacking, confirming coherent epitaxial alignment throughout the film. No mirror-related interfaces or lattice symmetry doubling indicative of twin boundaries are observed, demonstrating that the films grown under low supersaturation conditions are effectively single-orientated and untwinned. The in-plane twinning along $[110]$, characteristic of high-supersaturation growth, is entirely absent. Only occasional OPB defects^[269] features are visible (yellow arrows in **Figure 5.6 b**), which appear as localized disruptions in the stacking periodicity but do not compromise the overall crystallographic registry.

These results affirm that controlled reduction of supersaturation selectively suppresses twin-related orientation variants while preserving long-range structural coherence.

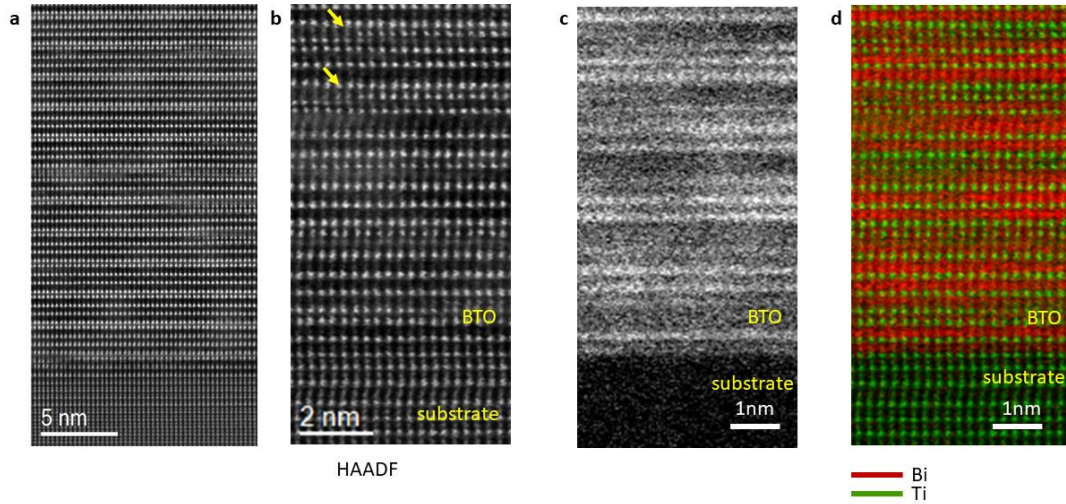


Figure 5.6. HAADF-STEM and EELS analysis of BiT films grown under low supersaturation conditions.. **a-b** HAADF-STEM images along the $[100]$ projection showing a coherent $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ /NGO interface and well-ordered stacking of $(\text{Bi}_2\text{O}_2)^{2+}$ and TiO_6 layers. No mirror-related or rotated lattice variants are observed, confirming the absence of twin boundaries. Isolated OPB defects, marked by yellow arrows, appear as localized disruptions in the periodic stacking but do not affect the overall epitaxial alignment.. **c-d** Corresponding EELS elemental maps of bismuth (green) and titanium (red) reveal alternating cation layers consistent with the layered Aurivillius structure and demonstrate chemical uniformity across the interface.

This structural uniformity is complimented by compositional homogeneity revealed through electron energy loss spectroscopy (EELS) mapping (**Figure 5.6 c** and **5.6 d**). The spatially resolved elemental distributions of bismuth and titanium follow the expected Aurivillius phase stacking sequence, alternating between $(\text{Bi}_2\text{O}_2)^{2+}$ and perovskite-like TiO_6 layers. The overlaid Bi (green) and Ti (red)

elemental maps (**Figure 5.6 d**) clearly delineate the alternating cation layers and demonstrate chemical uniformity across the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ /NGO interface, confirming that both structural and chemical coherence are preserved throughout the film.

To the best of our knowledge, this work provides the first direct experimental demonstration that controlling supersaturation during epitaxial growth can suppress crystallographic twinning in layered Aurivillius phase oxide systems. While previous studies in cubic and perovskite systems have qualitatively linked lower supersaturation to improved epitaxial order, no prior work has established a quantitative thermodynamic-kinetic framework or experimentally validated its ability to eliminate twinning in anisotropic, layered oxide lattices such as $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.

Here we show that reducing saturation fundamentally alters the dominant growth mechanism: the critical nucleation barrier increases, the rate of island formation slows,[339] and adatoms gain sufficient time to migrate toward lattice-matched sites. Consequently, only nuclei that are energetically compatible with the substrate persist, yielding single-oriented, twin-free epitaxial films. This transition from rapid, twin-defect-prone nucleation to diffusion-limited epitaxy demonstrates that supersaturation acts as a decisive kinetic lever for achieving crystallographic coherence in layered oxides, a regime previously thought to be dominated by structural anisotropy rather than kinetic control systems.

Analogous trends have been noted in simpler materials systems such as 3C-SiC and perovskite oxides, where lower supersaturation reduces domain multiplicity and promotes single-orientation epitaxy.[403] It is also important to note that surface diffusion is significantly enhanced under reduced supersaturation.[280] Adatoms can migrate longer distances before being incorporated into a growing nucleus. This

extended diffusion allows adatoms to occupy low-energy lattice sites, thereby maintaining crystallographic coherence and preventing the premature stabilization of misoriented growth fronts. However, in contrast to those isotropic or cubic systems, the present work extends this principle to highly anisotropic Aurivillius phases, where intrinsic lattice modulation along the c-axis and pseudo-orthorhombic symmetry complicate orientation selection. By directly correlating supersaturation with the suppression of twin domains and validating this through AFM, XRD, and atomic-resolution TEM, we establish a unifying kinetic pathway to orientation control in complex oxides.

At the atomic scale, reduced supersaturation not only suppresses the initial formation of rotated variants but also permits lateral overgrowth and reorientation or elimination of misaligned nuclei before they evolve into extended domains. Chen *et al.*[404] demonstrated that enhanced adatom migration can effectively eliminate nascent twin nuclei through surface diffusion, an effect we now confirm in a layered oxide environment. The classical Wagner-Hamilton-Seidensticker (WHS) model[405] likewise predicts that twin interfaces nucleation preferentially under high driving-force conditions. By lowering the supersaturation, these twin-assisted pathways become energetically unfavorable, explaining the near-complete elimination of twin domains observed in our optimized $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films.

The combined structural and chemical analyses thus establish that films grown under reduced supersaturation achieve coherent lattice stacking and compositional uniformity across the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ /NGO interface. This atomic- and chemical-level order provides the foundation for coherent polarisation behaviour, as explored through PFM in the following section.

5.2.5. Ferroelectric Domain Coherence and Switching Enabled by Twin Suppression

Having established the atomic-scale structural and chemical coherence of untwinned $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films, the corresponding ferroelectric functionality can now be examined. In ferroelectric materials, the degree of polarisation coherence, that is, the uniform alignment and phase coupling of polarisation vectors across the film, governs how efficiently domains can switch under an external electric field. Twin boundaries disrupt this coherence by introducing crystallographic discontinuities and electrostatic incompatibilities between adjacent variants, thereby fragmenting the polarisation landscape. In contrast, twin-free, single-oriented films are expected to exhibit spatially continuous polarisation and cooperative domain switching. The effect of suppressing crystal twinning on domain organization and ferroelectric switching were probed using PFM.

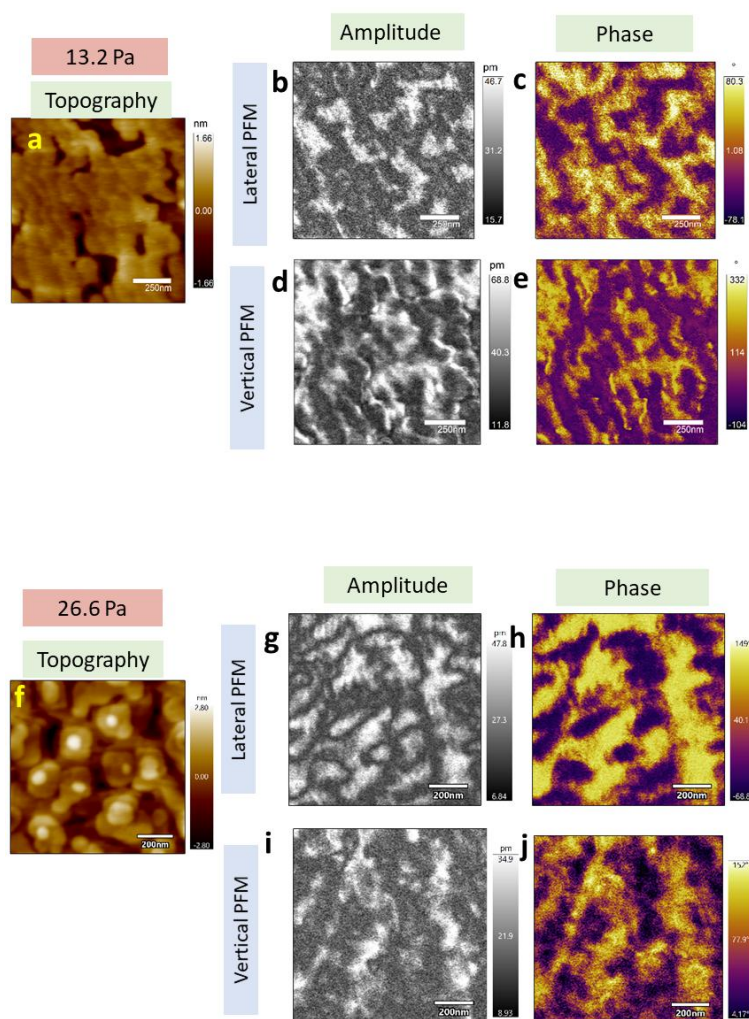


Figure 5.7. LPMF height, amplitude and phase images of BiT films grown under low supersaturation conditions at (a-e) high (26.6 Pa) and (f-j) low (13.2 Pa) oxygen partial pressure. Both films exhibit well-defined ferroelectric domains, with the higher-pressure sample showing enhanced domain continuity and sharper 180° phase contrast, indicative of improved structural order and polarisation coherence.

By contrast to the twinned samples, the untwinned $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films grown under low-supersaturation conditions display a markedly improved ferroelectric response. **Figure 5.7** presents lateral PFM height, amplitude, and phase images acquired for films grown under varying oxygen partial pressures. In the untwinned films (**Figure 5.7 d–f**), the amplitude and phase maps reveal large, well-defined

ferroelectric domains separated by domain walls, indicating coherent polarisation.[125], [129], [144], [406] This behaviour contrasts strongly with the twinned films, where domain contrast is irregular and non-correlated with applied bias (**Figure 5.3 h–i**). This improved polarisation coherence in the untwinned films directly stems from the enhanced structural ordering achieved through supersaturation control, which stabilizes a single crystallographic orientation and eliminates domain pinning at twin boundaries.

The voltage-dependent poling behaviour of the untwinned films is summarized in **Figure 5.8**. Lateral PFM measurements compare films grown at different oxygen partial pressures. The height images (**Figure 5.8 a and 5.8 d**) confirm the continuous, merged grain morphology discussed earlier. Lateral PFM amplitude and phase images (**Figure 5.8 b–c, 5.8 e–f**) show arrays of square poled regions written at different negative and positive voltages. In both cases, clear phase contrast emerges, indicating robust, nonvolatile polarisation reversal. Films grown at higher oxygen partial pressure require a lower threshold switching voltage ($\pm 10\text{V}$) compared to those grown at lower oxygen partial pressure ($\pm 20\text{V}$), consistent with their lower OPB defect density [218] and smoother morphology as established by XRD and AFM trends in **Figure 5.4**. The sharp domain boundaries and stable phase contrast confirm that the suppression of crystal twinning enables not only enhances structural uniformity but also restores long-range polarisation coherence, an essential condition for reliable ferroelectric device performance in future technologies.

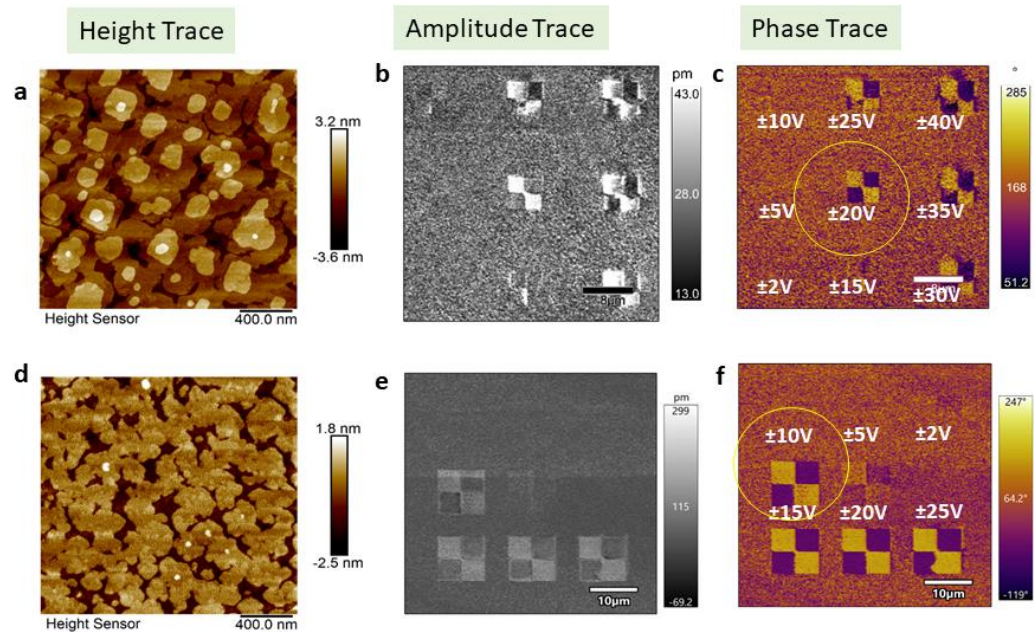


Figure 5.8. a-f. LPMF height, amplitude and phase images of poled untwinned $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films grown under low-supersaturation conditions at (a-c) low (13.2 Pa) and (d-f) high (26.6 Pa) oxygen partial pressure. Arrays of square poled regions demonstrate clear 180° phase contrast, confirming reversible and stable ferroelectric switching. Films grown at higher oxygen pressure exhibit smoother surfaces, improved grain coalescence, and reduced OPB defect density, resulting in a lower threshold switching voltage (± 10 V) compared to the lower-pressure film (± 20 V).

To ensure that the apparent suppression of twinning in low-supersaturation films is not merely a surface effect, AFM nanomachining was employed to probe the structural integrity through the film thickness ([Supplementary Information, Figure S 5.4](#)). Keeney *et al.*[229] previously demonstrated that in some Aurivillius phase thin films, surface 2D islanding can obscure underlying twin domains, producing apparently single-phase XRD diffraction patterns, as well as individual twin variants that retain local ferroelectricity. Upon removal of the upper layers by AFM

nanomachining, subsurface 45° stripe domains indicative of twinning were revealed.[229] In contrast, the present low-supersaturation Bi₄Ti₃O₁₂ films showed no emergence of such stripe contrasts even after sequential material removal of up to ~5 nm ([Supplementary Figure S 5.4](#)), confirming that the suppression of twinning extends throughout the film depth rather than being confined to the surface.

The ferroelectric switching behaviour observed in untwinned Bi₄Ti₃O₁₂ films emphasizes the intrinsic connection between growth kinetics and functional response. Controlling supersaturation restores the balance between thermodynamic driving force and adatom mobility, suppressing twin formation and enabling coherent polarisation alignment across the film. This kinetic stabilization of structural order directly translates into enhanced ferroelectric performance, manifested as lower switching voltages, sharper domain boundaries, and robust, non-volatile polarisation retention. Together, these results confirm that precise modulation of supersaturation provides a powerful thermodynamic-kinetic lever for engineering twin-free, functionally coherent Aurivillius ferroelectrics.

5.3. Conclusion

This work provides the first direct demonstration that crystallographic twinning in layered Aurivillius thin films can be effectively suppressed through thermodynamic control of supersaturation during MOCVD growth. The degree of supersaturation is shown to dictate the balance between nucleation and surface diffusion, thereby controlling the emergence of orientation variants in Bi₄Ti₃O₁₂ films. Under high supersaturation, rapid isotropic nucleation outpaces adatom diffusion, stabilizing multiple in-plane variants and producing twin domains that disrupt lattice coherence and polarisation continuity. Conversely, reducing supersaturation shifts

growth into a diffusion-limited regime in which adatoms possess sufficient mobility to selectively incorporate at lattice-matched sites, yielding single-oriented, twin-free epitaxy.

By tuning precursor delivery kinetics and oxygen partial pressure, the growth transitions from rapid, nucleation-limited deposition to a diffusion-mediated process, enabling twin suppression without reliance on high substrate temperatures, buffer layers, or complex post-growth treatments. Comprehensive structural and functional analyses (XRD, AFM, HR-TEM, and PFM) confirm this transformation, revealing atomically coherent, untwinned $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films with spatially coherent ferroelectric domain switching.

These findings redefine crystal twinning not as an unavoidable artifact, but as a controllable kinetic consequence of excessive supersaturation. By coupling thermodynamic control of the growth driving force with kinetic regulation of adatom mobility, this work establishes a practical route to deterministic, twin-free epitaxy in layered ferroelectrics. Such control over nucleation dynamics provides a foundation for the scalable integration of high-quality Aurivillius-phase heterostructures in next-generation low-power ferroelectric and multifunctional oxide devices.

Experimental / Methodology: Experimental and measurement methodology is detailed in [Appendix V](#).

V. Conclusion:

This thesis has demonstrated that supersaturation, modulated through precursor delivery kinetics and oxygen partial pressure during DLI-CVD, acts as a unified control variable for three structural challenges that have constrained the integration of Aurivillius phase thin films into vertically addressed ferroelectric devices: the confinement of spontaneous polarisation to the in-plane direction; the absence of predictive frameworks for interpreting the diffraction consequences of three-dimensional OPB defect geometries; and the formation of crystal twins that disrupt domain coherence and impede reliable switching. The three experimental chapters address these in sequence, each examining a distinct consequence of growth-mode selection, and providing the structural vocabulary that the next requires.

The first part of the thesis, **Chapter III**, established that growth spirals in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films generate inclined out-of-phase boundary (OPB) defects that promote an out-of-plane polarisation component typically absent in these layered oxides. The observation that OPB inclination correlates with measurable polarisation canting indicates that the spontaneous polarisation vector, often regarded as inherently in-plane, can acquire a vertical component through growth-induced structural distortions. This result does not imply that Aurivillius materials become intrinsically out-of-plane ferroelectrics, but rather that their polar behaviour is sensitive to defect geometries associated with spiral-driven growth. The ability to achieve such reorientation without chemical modification or extrinsic strain offers a practical means of aligning material properties with the requirements of vertically stacked device architectures.

The second component of this thesis, **Chapter IV**, addressed the absence of predictive tools capable of interpreting the diffraction consequences of non-parallel OPB geometries. Conventional X-ray diffraction treatments assume planar fault configurations and therefore cannot account for the peak splitting, angular broadening, or reflection selectivity observed in films with spiral-derived OPBs. The analytical framework developed here extends the structure-factor formalism to incorporate pyramidal boundary geometries, enabling the prediction of which 00ℓ reflections exhibit splitting and how this relates to OPB inclination, density, and spacing.

While the model does not replace atomistic simulations, it provides a computationally efficient approach for extracting physically meaningful defect parameters from routine diffraction data. This capability is valuable because OPBs influence both the magnitude and directionality of ferroelectric polarisation, making their quantification relevant for interpreting functional behaviour.

The final strand of the thesis, **Chapter V**, examined crystal twinning, a recurring phenomenon in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ growth that disrupts domain uniformity and complicates polarisation switching. Through controlled variation of supersaturation during deposition, it was shown that twinning is avoidable. At low supersaturation, enhanced adatom mobility reduces the nucleation of competing orientation variants, resulting in films that exhibit reduced twin densities and improved structural coherence. This finding does not eliminate all variant formation mechanisms, but it demonstrates that twinning can be mitigated without altering substrate orientation or resorting to post-growth treatments, an observation with implications for scalable processing.

Taken together, these results illustrate that the ferroelectric response of Aurivillius films is governed not solely by crystallographic symmetry, but by the interplay

between defect structures, growth kinetics, and local lattice distortions. By identifying clear mechanistic links between growth spirals and polarisation orientation, between OPB geometry and diffraction response, and between supersaturation and twinning suppression, the thesis contributes a set of experimentally grounded principles that support more deliberate control of ferroelectric behaviour in these layered materials. These contributions offer a coherent basis for future investigations into how defect engineering, morphology selection, and growth thermodynamics may be combined to optimise functional response.

Future Directions

(1) Growth Spirals and Out-of-Plane Polarisation

The results presented here establish that spiral-mediated growth can be used to generate and stabilise out-of-plane polarisation in layered Aurivillius thin films, but the technological viability of this approach remains untested. An essential next step is to transition from microscopic characterisation to device-level assessment. This will require deposition of top and bottom electrodes, lithographic patterning, and fabrication of capacitor structures or ferroelectric tunnel junctions (FTJs) that incorporate spiral-rich regions. Such devices would enable direct measurement of tunnelling electroresistance, switching endurance, retention, and imprint behaviour, allowing us to determine whether spiral-induced symmetry breaking translates into practical gains, such as lower switching voltages, more stable polar states, or enhanced tunnelling contrast. Demonstrating a functioning FTJ based on spiral-engineered films would move this work beyond structural observation and establish spirals as an active design element for vertically integrated architectures rather than a passive microstructural curiosity. In parallel, mapping whether this phenomenon extends to

other layered oxide systems (such as Ruddlesden–Popper ferroelectrics or Aurivillius phases with different Bi-layer counts) would clarify whether spiral-assisted polar anisotropy is a general symmetry-coupling mechanism or a unique trait of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.

(2) OPB-Sensitive XRD Modelling

The analytical XRD model developed in this thesis provides the first quantitative framework for identifying OPB defects arising from spiral growth, offering a route from reciprocal-space signatures to real-space defect architecture. While the underlying formalism requires no immediate conceptual extension, its broader value lies in dissemination and scalability. Many layered materials, including higher-order Aurivillius phases, Dion–Jacobson structures, and van der Waals-stacked oxides, exhibit non-parallel stacking faults and terraced growth modes that yield asymmetric diffraction profiles currently interpreted only qualitatively. Applying the present model to these systems would test the universality of OPB-driven diffraction asymmetry and may uncover defect–structure relationships not accessible by electron microscopy alone. While the current XRD model captures the essential features of OPB-induced peak asymmetry and splitting, it assumes a single-valued steric offset associated with each boundary. In real films, especially those containing multiple spiral centres or interacting dislocation arrays, OPB step heights, boundary inclinations, and local strain fields are expected to vary spatially. Extending the model to incorporate a statistical distribution of offsets and defect geometries would enable reconstruction of OPB networks with greater fidelity and may provide a direct, non-destructive route to quantifying defect densities and Burgers-vector multiplicity in growth-spiral-dominated films.

To enable adoption beyond specialist groups, an important avenue for future work is the development of a software implementation with automated peak-fitting routines and graphical visualisation of defect parameters. Such a tool would transform the model from a theoretical construct into a practical diagnostic platform for non-destructive evaluation of layered ferroelectric thin films, establishing OPB analysis as a standard complement to microscopy-based characterisation.

(3) Supersaturation-Controlled Suppression of Crystal Twinning

The suppression of crystal twinning through supersaturation control demonstrates that growth chemistry can be used to select crystallographic orientation without altering substrate choice, a capability that has broader implications beyond $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. The next logical step is to test whether this kinetic mechanism generalises to other layered oxide families where twinning disrupts ferroelectric response, carrier mobility, or interfacial coupling. Candidate systems include BiFeO_3 , Pb-based Aurivillius derivatives, and layered hybrid perovskites, which also exhibit nucleation-driven orientation variants that degrade device performance. By varying precursor supersaturation, oxygen partial pressure, and substrate–film lattice mismatch, it may be possible to determine whether twinning is suppressed through a universal competition between nucleation rate and surface diffusion or whether the effect is material-specific. Such studies would not only validate the generalisability of the method introduced here but could also establish supersaturation as a materials-agnostic control knob for selecting ferroelastic variants, enabling orientation-engineered ferroelectric heterostructures for memory and neuromorphic devices.

In summary, this thesis has demonstrated that structural motifs arising during film growth exert a measurable influence on the ferroelectric properties of Aurivillius

phase oxides. By clarifying how these motifs originate, how they manifest in diffraction space, and how they may be moderated through growth conditions, the work provides a practical framework for interpreting and refining the ferroic behaviour of layered ferroelectrics intended for vertical electronic applications. While additional development is required to translate these findings into commercial device contexts, the principles established here indicate that the structural complexity of Aurivillius materials, once viewed primarily as a limitation, can be approached as a design variable within ferroelectric thin-film engineering. The three experimental chapters together trace a single progression in which supersaturation, varied through precursor delivery kinetics and oxygen partial pressure during DLI-CVD, selects the growth regime and thereby determines the structural and functional character of the resulting film. Table 6 summarises this progression.

Table 6. Supersaturation progression across Chapters III–V.

Supersaturation (σ)	Growth Mode	Key Result / Challenge Solved		Chapter
High σ (simultaneous injection)	Nucleation-limited; 2D step-meandered	Planar OPB defects; predominantly in-plane polarisation	± 20 V switching baseline	Ch. III, Ch. V (twinning problem)
Low α (sequential injection + reduced pO_2)	Dislocation-mediated spiral growth	Pyramidal OPB arrays; symmetry-lowering distortions; inclined OPB-encoded asymmetric 00 ℓ XRD splitting	Enhanced out-of-plane polarisation; ± 5 V switching	Ch. III ; Ch. IV
Low α (sequential injection + increased pO_2)	Diffusion-limited, single-variant epitaxy	Complete twin suppression; coherent PFM switching; sharp Laue fringes	Spatially coherent ferroelectric domain switching	Ch. V

Appendix I. – Supplementary Information for Chapter 3

I. Comparison of device-relevant materials with spiral-mediated BiT (Table S 3.1)

<i>Material</i>	<i>Growth Method</i>	<i>Thickness (nm)</i>	<i>OOP response</i>	<i>Switching Voltage</i>	<i>Thickness-normalized switching (V/nm)</i>	<i>Notes</i>
Bi₄Ti₃O₁₂ (spiral-mediated)	DLI-CVD (low- α , spiral growth)	~25	8.7 pm/V	±5 V	±0.2	This work. Lead-free; spiral-mediated vertical response; low local bias; scalable route; needs device validation.
Bi₄Ti₃O₁₂ (2D step-meandered)	DLI-CVD (high- α , 2D step-meandered growth)	~25	3.7 pm/V	±20 V	±0.8	This work. Weak OOP; higher bias under same thickness.
Pb(Zr,Ti)O₃ (PZT)	PLD on SRO/STO or Si	~30-40 [407]	~200-330 pm/V[407], [408], [409]	±1.5-3V[410]	±0.05-0.075	Pb toxicity (RoHS)[411], electrode/oxygen issues[412], [413]; benchmark OOP response.[135]
PbTiO₃ (including relaxor variants)	PLD / MBE	~2.6[414]	20 pm/V[414]	±2.5kV–9kV[415], [416]	±961.5-3461.5	High coercive field (±2.5-9kV[415], [416]), relaxors have low T _c (~115 °C)[417], [418] Pb toxicity[411]; integration challenges on common substrates[419].
Hf_{0.5}Zr_{0.5}O₂ / HfO₂-based	ALD / sputtering	~10–20[420]	~2–6 pm/V[420]	±1MV–4 MV[421], [422]	±100,000-200,000	Very high coercive field[421], [422]; metastable orthorhombic phase window[420]; wake-up/fatigue[423]; lower piezoresponse than perovskites[424]; CMOS-friendly[424].

SrBi₂Ta₂O₉ (SBT)	PLD / MOCVD	~100–150 (116 orientation) [425], [426]	~5–8 $\mu\text{C cm}^{-2}$ [425]*	±20 V (in 116 films only)[426]	±0.2–0.133*	Excellent fatigue resistance[427], but low Pr (5–8 $\mu\text{C cm}^{-2}$)[425] and typically thicker films needed for switching[162]. Low voltage for FeRAM stacks[162], but not suitable for FTJs as ultrathin films aren't switchable.
Bi_{3.25}La_{0.75}Ti₃O₁₂ (BLT)	PLD on Pt/Si [428]	~150–200 (118/104-oriented) [428]	~0–1.1 $\mu\text{C cm}^{-2}$ * [428] (Is dominantly in-plane in a c-axis oriented thin film)	~50–116 kV [429], [430]	±33.33–580*	Lead-free; dominantly in-plane polarisation[428]; high-T growth (~700 °C) common; OOP component limited; thicker films needed for switchability.
Nd-Bi₄Ti₃O₁₂ (NBT)	PLD/MOCVD on STO	100–200 (104-oriented) [327]	~6–12 $\mu\text{C cm}^{-2}$ [322], [327] *	±15–24V(In 104 oriented films only) [322]	± 0.15–8.33*	Intrinsic polarisation of NBT lies in-plane ; not a true out-of-plane ferroelectric; any apparent vertical switching arises only in misoriented films where the in-plane polarisation vector projects partially along the film normal[322]; not suitable for ultrathin FTJ applications where symmetry-breaking requires native OOP polarisation. High coercive field[322]; thick films needed for switchability

* The polarisation measurements units are not consistent due to the lack of availability of d_{33} values of thin films of comparable thickness. Below is the estimation of the values in pm/V:

Estimating the piezoresponse from the given polarisation values using the standard electrostrictive relation:

$$d_{33,eff} \approx 2 \cdot Q_{11} P \cdot \epsilon_0 \epsilon_r$$

where Q_{11} is the longitudinal electrostrictive coefficient (m^4/C^2), P is in C m^{-2} , $\epsilon_0 = 8.854 \times 10^{-12} \text{ F m}^{-1}$, ϵ_r is the out-of-plane relative permittivity.

1. SBT ($\text{SrBi}_2\text{Ta}_2\text{O}_9$)

Polarisation (Pr): Pt/SBT/Pt capacitor studies consistently report thin-film OOP $P_r \approx 5\text{--}8 \mu\text{C cm}^{-2}$ in the 100–200 nm range[162].

Permittivity (ϵ): thin-film SBT values depend on stack and anneal; reported $\epsilon \approx 120\text{--}200$ [431];

Electrostriction Q_{11} : **0.03–0.05 m^4/C^2** (perovskite-family range from Damjanovic/Haun[431]; conservative for layered oxides).

Estimation:

$$2 \times 0.03 \times 0.05 \times (8.854 \times 10^{-12}) \times 120 = 3.2 \times 10^{-12} \text{ m/V} \approx 3.2 \text{ pm/V}$$

→ Final Estimation:~ **3 pm/V**.

Similarly, upon performing this calculation with closest-to-reported P_r and Q_{11} values for $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ (BLT) and $\text{Nd-Bi}_4\text{Ti}_3\text{O}_{12}$ (NBT), we get the following estimations for OOP piezoresponse:

BLT: ~2.3 pm/V; NBT : ~16 pm/V

II. Supersaturation Variation

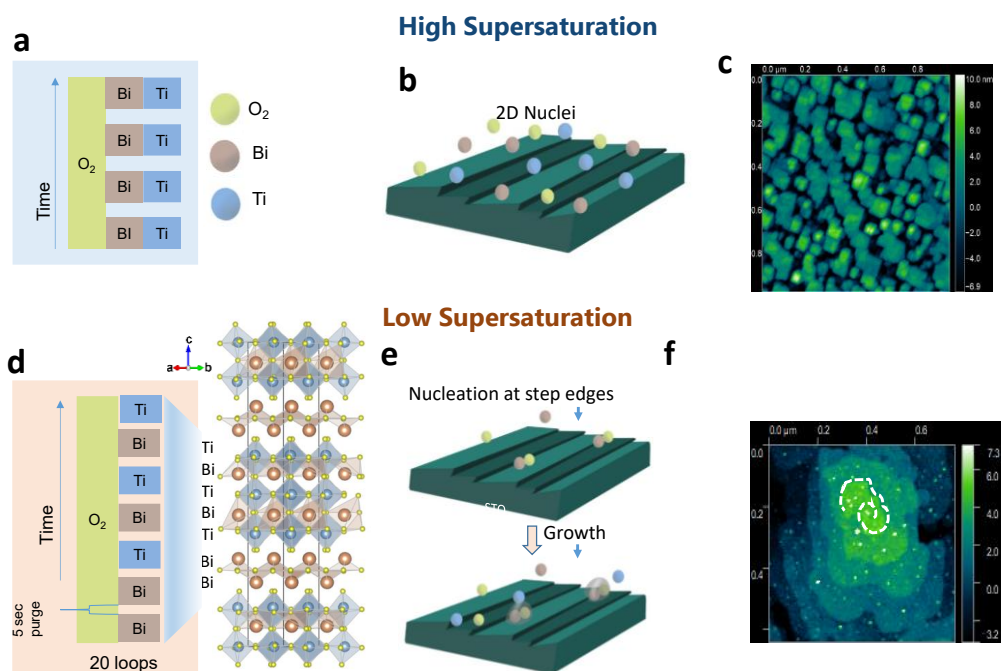


Figure S 3.1: *a* Simultaneous injection of Bi and Ti precursors during direct liquid injection chemical vapour deposition (DLI-CVD) of $Bi_4Ti_3O_{12}$ (BiT) in an oxygen environment, leading to *b* the formation of dense 2D nuclei on the substrate due to high supersaturation conditions. *c* Atomic force microscopy (AFM) height image showing rectangular 2D islands and pits. *d* Sequential injection of Bi and Ti precursors during DLI-CVD enabling low supersaturation conditions, mimicking the $n = 3$ structure of BiT, resulting in *e* step-flow growth and the formation of growth spirals as shown in *g* the AFM height image of a growth spiral.

III. High Supersaturation Growth

a. Morphology

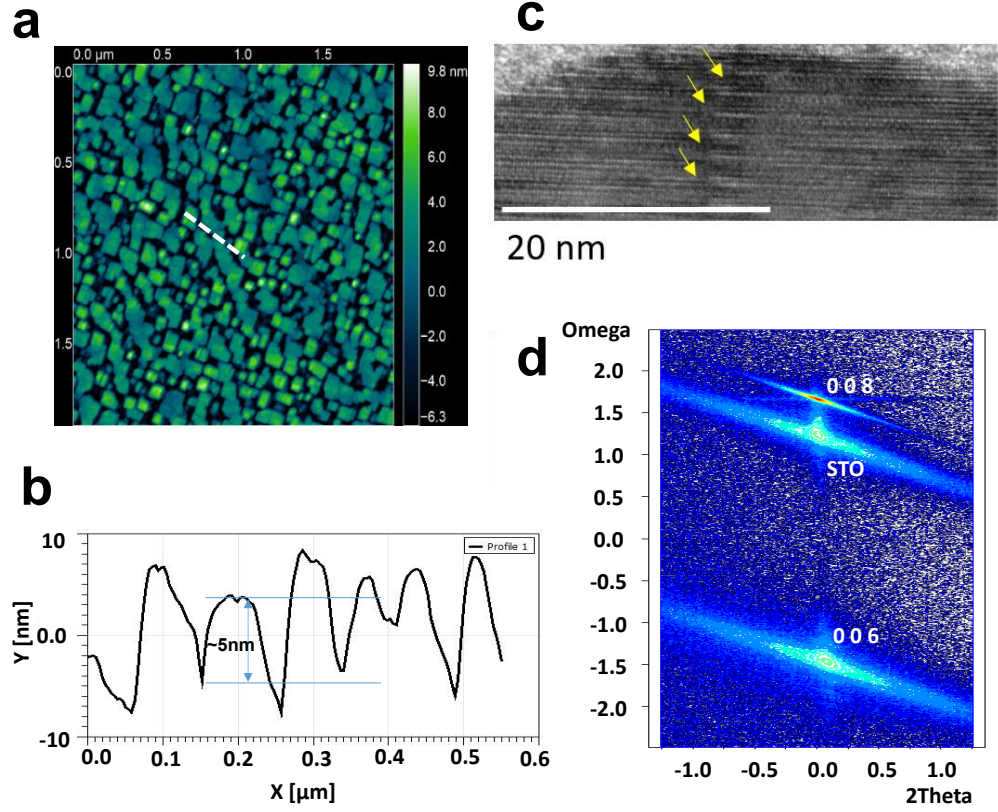


Figure S 3.2: High supersaturation growth during DLI-CVD. **a** AFM topography images of a $2\ \mu\text{m} \times 2\ \mu\text{m}$ BiT film surface where the brightest points correspond to a height of 10 nm and the darkest points to a relative height of -6.9 nm. **b** Height profile (x-axis: distance; y-axis: height) taken from the line section in **a**, showing 2D islands and pits with heights corresponding to multiples of half unit cells ($\sim 5\text{-}8\text{ nm}$). **c** TEM image revealing out-of-phase boundary (OPB) defects interrupting the layered structure of Aurivillius-phase bismuth titanate, with defect locations highlighted by yellow arrows. **d** X-ray diffraction reciprocal space map (RSM) showing the 008 and 006 diffraction peaks of BiT, along with the 100 peak of the SrTiO_3 (STO) substrate. The horizontal alignment of the film peaks with the substrate

peak indicates that the in-plane lattice parameter of the film is closely matched to that of the substrate ($a = 3.905 \text{ \AA}$; lattice mismatch = +0.39% compared to the pseudolattice parameter of the perovskite-type layer (a_p') in BiT of $3.837 \text{ \AA}$)[144], suggesting pseudomorphic growth or partially relaxed strain. A vertical offset of 0.15° in the Omega/2Theta direction between the 006 BiT film peak and the substrate peak reflects a difference in out-of-plane lattice parameters, indicative of tensile or compressive strain along the growth direction and consistent with epitaxial growth.

IV. Low Supersaturation Growth

a. Growth Spiral Formation

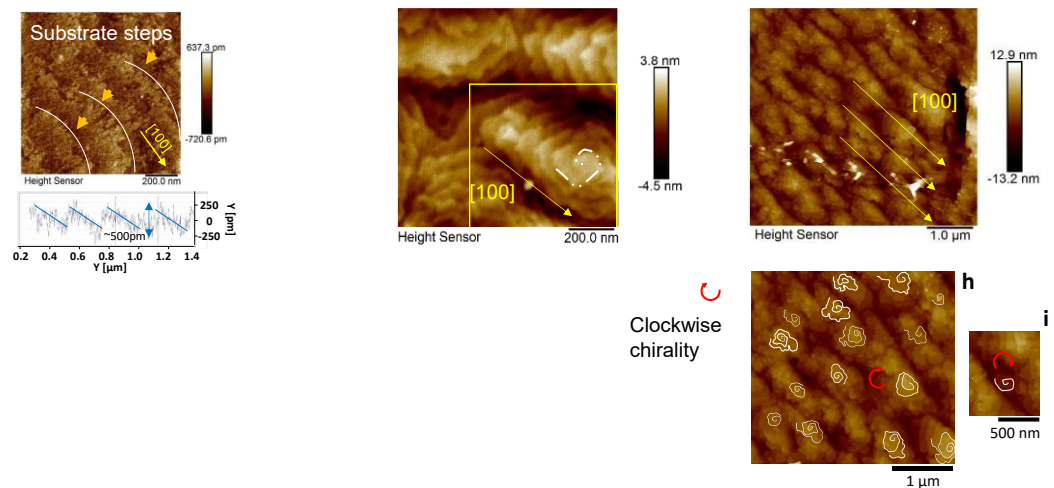


Figure S 3.3: Spiral Growth Mechanism: **(left)** SrTiO₃ substrates exhibit atomic steps along the [100] direction, with a step height of ~500 pm. **(middle)** AFM topography images showing the oriented growth spirals. **(right)** White traces along the AFM topography highlighting clockwise chirality in the film. A zoom-in showing existence of smaller spirals in the ‘valley’ between two spirals.

Spiral growth at low supersaturation arises from the interplay between growth rate and supersaturation, both key factors in determining crystal morphology (**Supplementary Figures S 3.1 (d to f) and S 3.3**).^[331] Screw dislocations act as continuous sources of atomic steps,^{[232], [233], [328]} with their substantial Burgers vector component largely accommodated by the periodic step structure of the STO substrate (**Supplementary Figure S 3.3 b**). The STO [100] surface exhibits ~0.5 nm high steps with terrace widths of ~100 nm, providing energetically favorable sites for adatom attachment, thereby facilitating step-flow growth.^{[240] [241]} As nucleation occurs at step edges, a self-propagating growth front^[230] expands in a spiral path, consistent with anisotropic growth along the [100] substrate orientation (**Supplementary Figure S 3.1 f, S 3.3 g**).

When a screw dislocation intersects the film surface, it forms a step that serves as a preferential adatom attachment site, enabling continuous step expansion. This mechanism resembles a carpet spiraling up a staircase,^[233] with material preferentially added at step edges. In layered films at low supersaturation, growth occurs predominantly perpendicular to the *c*-axis. The epitaxial BiT thin films maintain stoichiometry and electrical neutrality by growing in integral multiples of half-unit cells (**Figure 3.1 e**). Similar behaviour has been observed in layered superconductors such as YBa₂Cu₃O₇ under comparable conditions.^[230] At low supersaturation, adatom attachment and surface diffusion dominate, with steps and kinks acting as preferred nucleation sites, promoting step-flow growth. This mode is favored by reduced supersaturation and slow growth rates, as demonstrated by Lovette

et al.[339] and Zurbuchen *et al.*[212] Lower nucleation rates suppress the formation of new crystals, allowing uninterrupted spiral expansion.

In other bismuth-containing systems, such as $\text{SrBi}_2\text{Ta}_2\text{O}_9$, spiral growth commonly occurs under oxygen-deficient pulsed laser deposition conditions, where enhanced bismuth migration facilitates screw dislocation-driven growth.[332] Increasing the oxygen partial pressure suppresses this migration by promoting the formation of a Bi–O wetting layer on the substrate interface.[432] [433] [434] This layer increases the Bi–O sticking coefficient, stabilizing bismuth at the surface and reducing the driving force for dislocation-mediated nucleation and spiral formation. Consequently, the growth mode transitions from spiral growth to a smoother, two-dimensional meandered step-flow regime. The differentiation between the 2D growth under high and low supersaturation is described in **Supplementary Section V**.

b. X-Ray Diffraction

XRD Reference

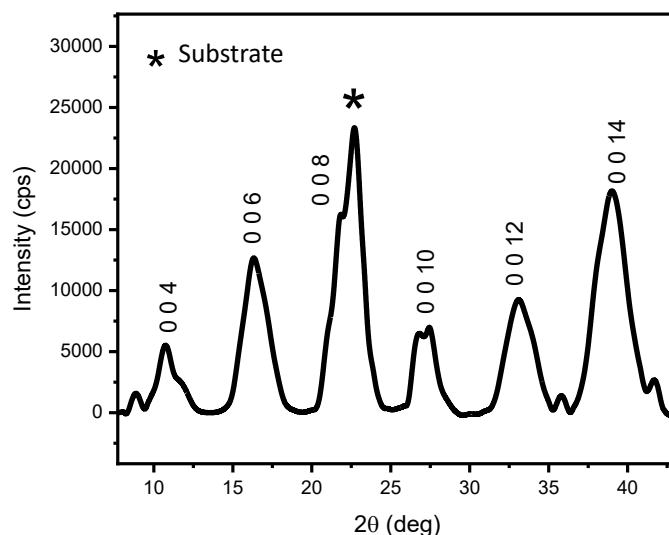


Figure S4: XRD pattern of a BiT thin film synthesized at 13.2 Pa, exhibiting growth spirals. Peak reflections were assigned using the reference pattern for $n = 3$ $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (black) reported by Hervoches et al.[213] A key characteristic of OPBs and stacking faults in Aurivillius and other layered structures is their effect on the XRD pattern, often leading to peak splitting.[269] The XRD data presented here exhibit clear splitting of the 004 and 00 10 reflections, indicating a high density of OPB defects.

c. **Effect of Varying Oxygen Partial Pressure**

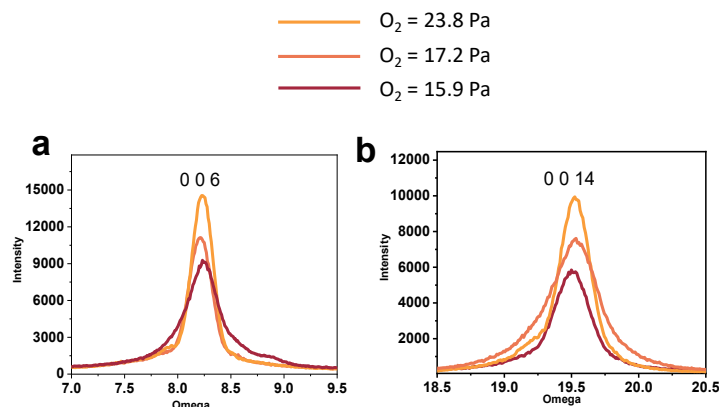


Figure S5: XRD rocking curve analysis of the **a** 006 and **b** 00 14 peaks of BiT films grown under low supersaturation conditions, showing increased broadening with decreased oxygen partial pressure.

Higher densities of OPB defects and the emergence of spiral growth under reduced oxygen conditions indicate a decrease in lattice plane alignment, as evidenced by rocking curve analysis shown in **Figure S 3.5**. This technique evaluates crystal quality by measuring the angular spread of diffraction peaks, where a narrower full width at half maximum (FWHM) reflects better alignment of crystal planes. The FWHM of the rocking curve peaks of the 006 reflection (**Figure S 3.5 a**) increases from 0.379° to 0.409° , and that of the 00 14 reflection rises from 0.425° to 0.533° as the O_2 partial pressure decreases from $N_2:O_2 = 2:3$ (23.8 Pa) to $N_2:O_2 = 3:2$ (15.9 Pa) (**Figure S 3.5 b**). This broadening indicates increased lattice misorientation and the presence of periodic defects under lower oxygen conditions.

Bismuth is a highly volatile element, that tends to diffuse out of thin films during growth at high temperatures. Due to the physical constraints of the underlying substrate and insufficient activation energy for structural rearrangement, these losses cannot be fully compensated. This can potentially lead to crystallographic shear, sub-unit cell crystallographic defects, and secondary phase impurities.[172], [212], [361] Chemical vapour deposition (CVD), operating at relatively high gas pressures (typically 0.6 to 70 mbar) and oxygen-rich environments (100 to 2000 sccm; 5 to 70% O₂), offers a means to suppress Bi₂O₃ migration over a broader range of growth conditions compared to high-vacuum techniques.[332] Increasing the oxygen partial pressure further mitigates defect and impurity formation, as adsorbed oxygen is believed to hinder surface species diffusion at higher pressures.[435], [436] Micard *et al.*[437] demonstrated that optimizing oxygen flow during metal-organic chemical vapour deposition (MOCVD) significantly improves the structural and compositional quality of BiFeO₃ films on IrO₂/Si substrates. Their study showed that an initial high-oxygen flow step (900 sccm for 10 minutes) promoted the nucleation of multiple BiFeO₃ sites, while a subsequent lower-flow step (150 sccm for 50 minutes) facilitated denser film growth, resulting in improved film morphology and quality. This can be correlated to the observations made in this BiT system, supporting the critical role of oxygen partial pressure in tailoring film quality.

hkl	N ₂ :O ₂ =1:2 =26.6 Pa	N ₂ :O ₂ =2:3 =23.8 Pa	N ₂ :O ₂ =4:3 =17.2 Pa	N ₂ :O ₂ =3:2 =15.9 Pa	N ₂ :O ₂ =2:1 =13.2 Pa
0 0 4	1.33	2.10	2.10	2.15	2.15
0 0 6	1.52	2.17	2.23	2.25	3.01
0 0 10	0.93	1.25	1.43	1.92	1.93
0 0 12	1.72	2.47	2.54	2.59	2.63
0 0 14	1.94	2.02	2.28	2.41	2.43

Table S 3.2: Full width at half maximum (FWHM) values (degrees) obtained from XRD peaks (Figure 2 a) of BiT thin films grown under low supersaturation conditions, arranged from left to right in order of decreasing oxygen partial pressure (orange to red to black). The data show that reducing the oxygen partial pressure leads to broader peaks, indicating increased structural disorder. FWHM values were extracted using Gaussian fitting after baseline correction, with an average standard error of ± 0.048 .

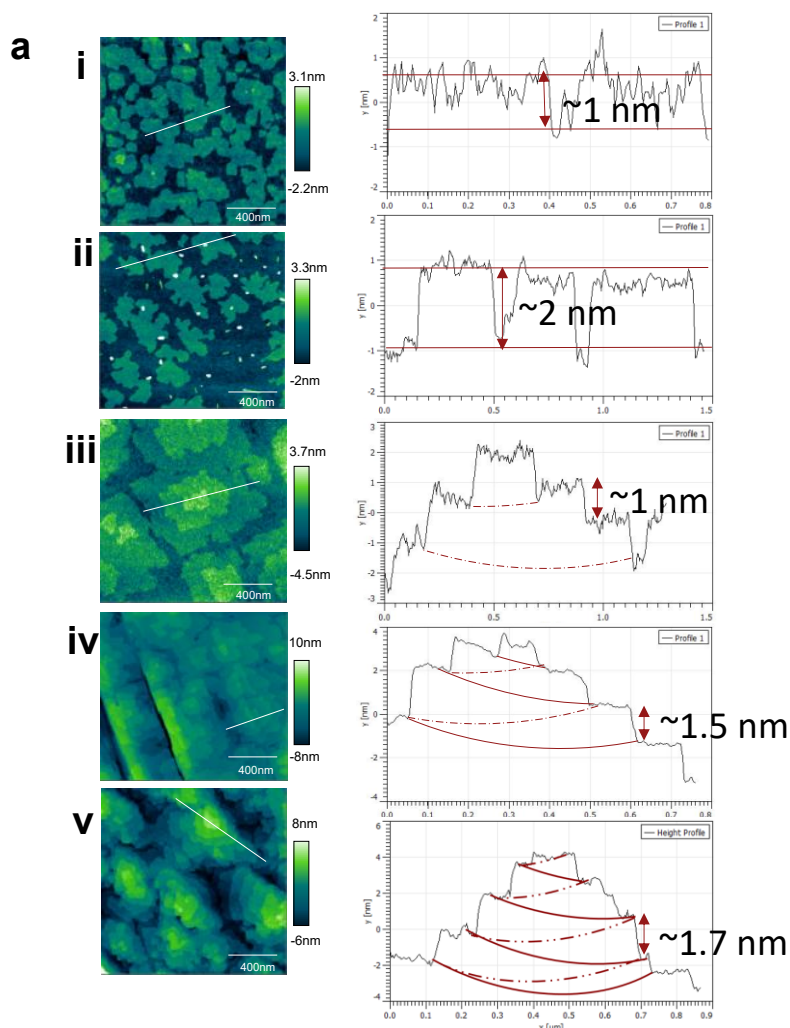


Figure S 3.6: *e* AFM topography trend of thin films and their respective step heights extracted from their height profiles under decreasing oxygen partial pressures (**i-v**) (26.6 Pa to 13.2 Pa) taken from Figure 2 b(i-v).

As the XRD in the main text (**Figure 3.2 a**) shows splitting with decreasing oxygen partial pressure and decreased degree of coalescence from the AFM, the AFM height profiles show that the step heights (**Figure S 3.6**) agree with this trend. As the oxygen pressure is increased, the step height decreases from ~ 1.7 nm to ~ 1 nm (**Figure S 3.6 e**), before transitioning to 2D meandered growth.

V. 2D Growth Terminology

The term *two-dimensional (2D) growth* warrants clarification in this context to prevent misinterpretation. Under high supersaturation, growth proceeds via rapid nucleation and layer-by-layer completion, characteristic of Fran-van der Merwe mode. This results in flat terraces with straight, well-defined, step edges, as abundant adatoms quickly saturate nucleation sites (**Supplementary Figure S 3.2**). The high adatom concentration and mobility also help suppress step-edge instabilities.[438] In contrast, under low supersaturation and high oxygen partial pressure, the growth regime shifts to step-flow, where adatoms preferentially attach at existing step edges rather than forming new nuclei. However, the lower adatom concentration and slower kinetics increase the likelihood of lateral instabilities, such as Bales–Zangwill step meandering.[223] This instability arises from an uphill adatom current, where adatoms preferentially attach to ascending step edges. Over time, slight step-edge curvatures are amplified, disrupting linear step propagation. The Schwoebel–Ehrlich (SE) barrier,[226], [227] an energy barrier inhibiting adatom descent to lower terraces, reinforces this uphill flux, promoting step meandering. Therefore, throughout this work, to the term *two-dimensional growth* specifically refers to two-dimensional meandered step-flow growth occurring under low-supersaturation, high-oxygen partial pressure conditions, and is distinct from classical layer-by-layer growth under high supersaturation.

VI. Effect of Oxygenated Cooling

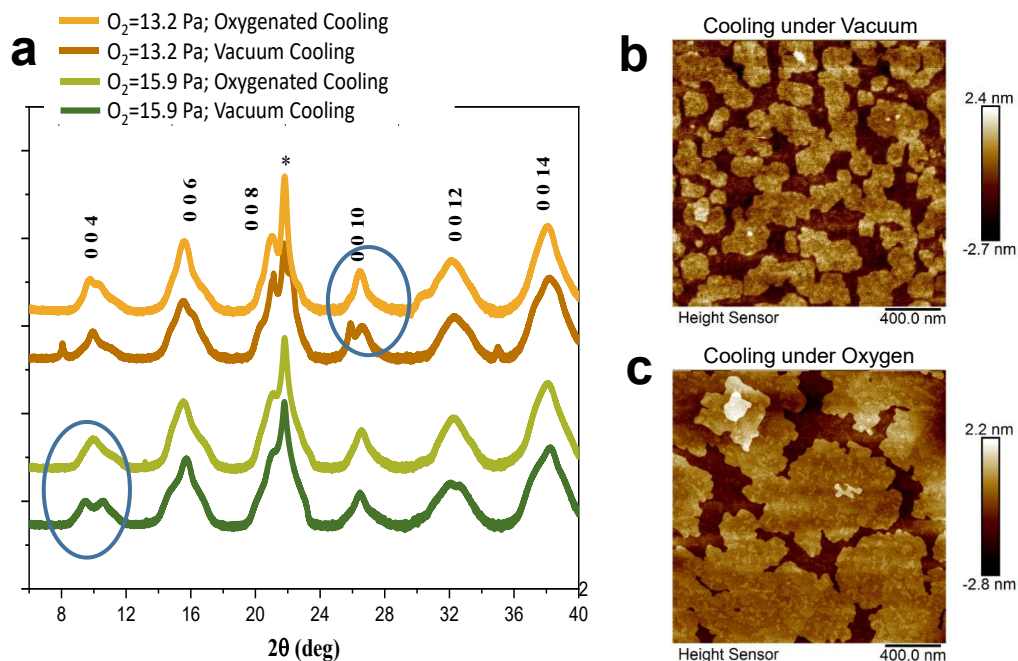


Figure S 3.7: Tunability of OPBs through cooling conditions: *a* XRD patterns of films synthesized under $N_2:O_2 = 2:1$ (13.2 Pa O_2) and $N_2:O_2 = 3:2$ (15.9 Pa O_2), cooled either under vacuum (without oxygen flow) or under oxygen flow. Reduced peak splitting of the 004 and 00 10 reflections is observed for samples cooled under oxygen flow, indicating a lower density of OPB defects. Representative AFM topography images of BiT films grown under identical oxygen partial pressure conditions ($N_2:O_2 = 1:2$; 26.6 Pa) but cooled under different atmospheres: *b* vacuum and *c* oxygen flow.

Films synthesized under $N_2:O_2$ ratios of 2:1 (13.2 Pa O_2) and 3:2 (15.9 Pa O_2) exhibit reduced splitting of the 004 and 00 10 peaks, respectively, when cooled under continuous oxygen flow (**Figure S 3.7 a**). For films grown at $N_2:O_2 = 2:1$ (13.2 Pa O_2), the full width at half maximum (FWHM) of the 004 peak decreases from 2.15°

under vacuum cooling (without oxygen) to 1.92° under oxygenated cooling. Similarly, the FWHM of the 00 10 peak decreases from 1.93° to 1.25° . AFM topography images corroborate the XRD findings, showing enhanced grain coalescence under oxygenated cooling. The degree of coalescence (D_c) increases from approximately 0.75 under vacuum cooling (**Figure S 3.7 b**), to 0.95 under oxygenated cooling (**Figure S 3.7 c**), corresponding to a 26.7% increase.

VII. Ferroelectric Domains

a. Domain Structure in 2D-Meandered Step-Flow Grown BiT Films

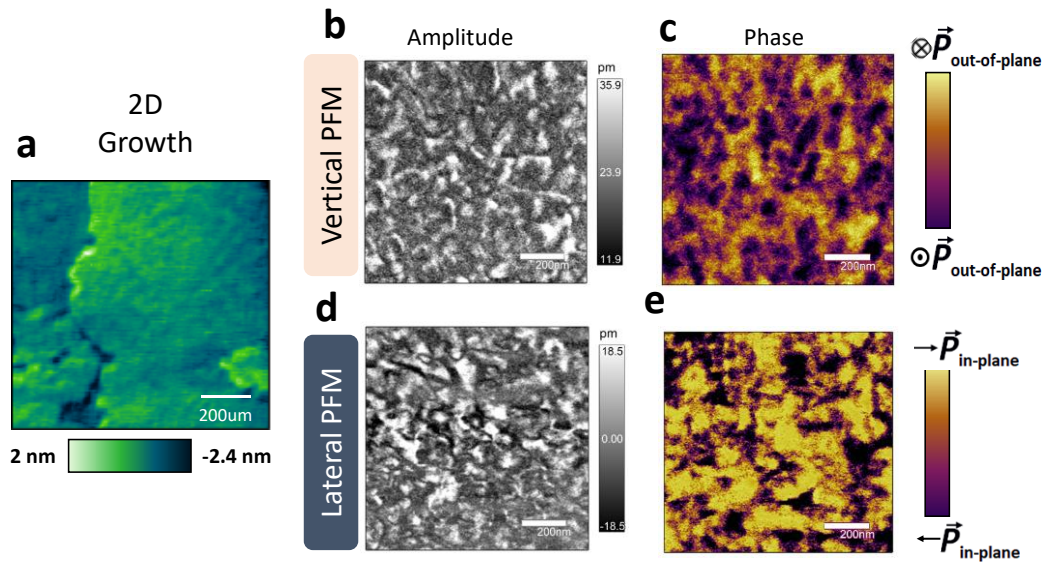


Figure S 3.8: *a* AFM topography image of a 2D-meandered step-flow grown sample. *(b, c)* VPFM amplitude ($\Delta=24$ pm) and phase images of the 2D-meandered step-flow grown sample and *(d, e)* LPFM amplitude ($\Delta = 37$ pm) and phase images showing ferroelectric domain structure in the 2D-meandered step-flow grown sample.

VIII. AFM-Based Nano-Machining Studies

a. Studying Vertical Ferroelectric Domains at Decreased Film Thickness

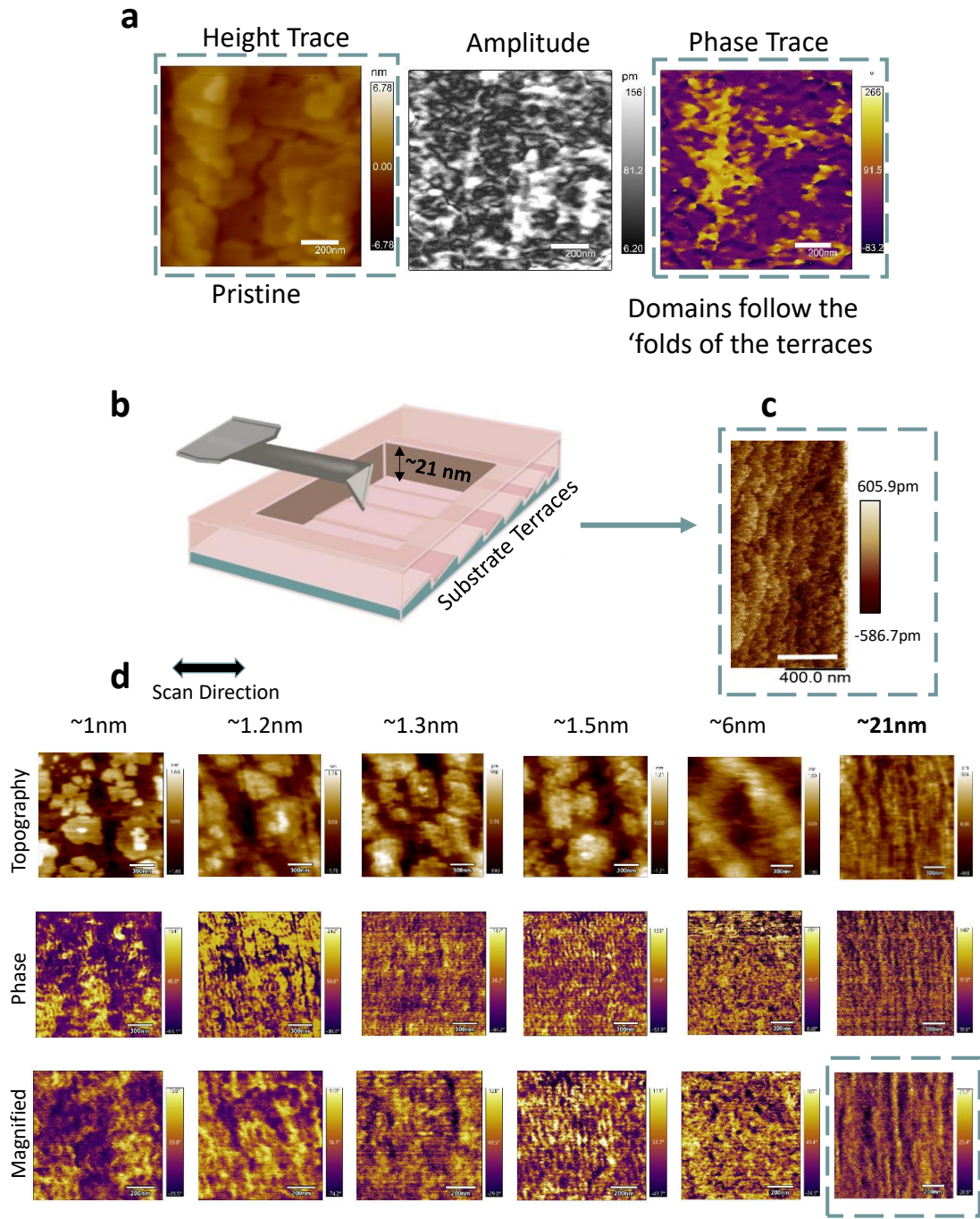


Figure S 3.9: AFM-based nanomachining followed by VPFM imaging: *a* AFM topography, VPFM amplitude, and VPFM phase images acquired over a $700\text{ nm} \times 700\text{ nm}$ area of the BiT thin film reveal ferroelectric domain alignment coinciding with the folding of the film along substrate step terraces. This folding is guided by the underlying (100)-oriented substrate topology composed of atomically flat terraces

*separated by steps, as shown in the AFM image of the bare SrTiO₃ (STO) substrate (below). The correlation between surface topography and vertical domain orientation indicates substrate-induced ferroelectric domain alignment. **b** Schematic illustration of the AFM-based nanomachining technique, where a diamond AFM cantilever is employed to incrementally remove nanometers of the film, thereby exposing and enabling imaging of sub-surface ferroelectric domain configurations. **c** AFM image of the bare substrate. **d** AFM topography and VPFM phase images taken after sequential nano-machining depths, ranging from ~1 nm to ~21 nm. After approximately 21 nm of material removal, a pronounced domain alignment along the [100] crystallographic direction becomes clearly discernible.*

To investigate the internal ferroelectric domain structure and its evolution with depth, the spiral-grown BiT film was subjected to localized nanomachining using a diamond AFM probe. The goal was to reveal buried domain configurations while preserving lateral resolution. The STO substrates used in this work had a slight miscut angle of 0.2° relative to the (001) plane. This intentional miscut produces a stepped surface with atomically flat terraces, which can facilitate epitaxial growth and can potentially induce anisotropic properties in the resulting film. Before nanomachining, the pristine surface exhibited vertically aligned ferroelectric domains that followed the surface folding pattern, which itself mirrored the step-terrace direction of the (100)-oriented substrate (**Figure S9 a**). To assess whether this alignment was a surface-localized effect or extended through the film, domains were imaged at incremental depths exposed by controlled nanomachining (**Figure S9 d**). The findings confirm that the substrate-induced domain alignment persists consistently throughout the film thickness, demonstrating structural continuity and the strong influence of interfacial templating effects on domain organization.

IX. Ferroelectric Switching Studies

a. Determining the Minimum Vertical Switching Voltage in Spiral-Grown BiT Films

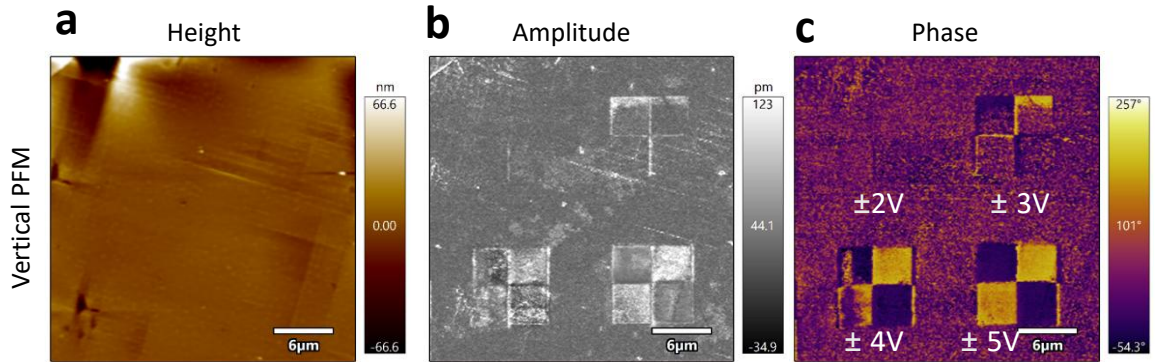


Figure S 3.10: Determination of the minimum vertical switching voltage in spiral-grown BiT films. A series of out-of-plane poling voltages ($\pm 2V$, $\pm 3V$, $\pm 4V$, and $\pm 5V$) was applied to identify the threshold voltage required for full ferroelectric switching. Partial switching is evident at $\pm 3V$, while complete polarisation reversal is achieved at $\pm 5V$. The presence of edge effects during poling is attributed to the probe-surface contact occurring between two adjacent spiral growth fronts. Due to the finite radius of the AFM tip, the generated electric field is not perfectly localized, leading to fringing fields that extend beyond the targeted poling region.

b. Ferroelectric Switching Studies

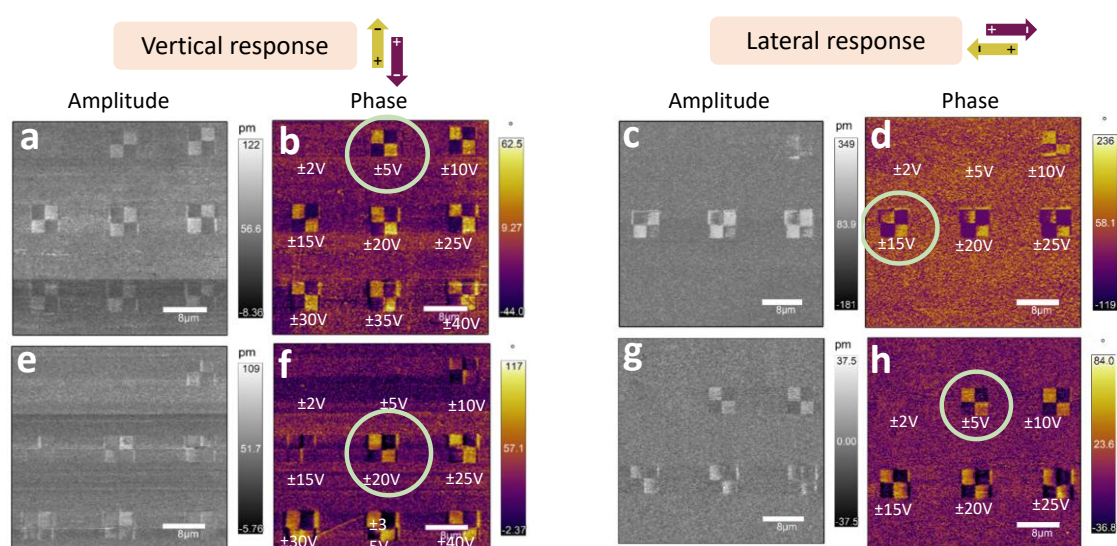


Figure S 3.11: PFM poling studies: Amplitude and phase traces of BiT films after PFM (piezoresponse force microscopy) lithography. **(a-b)** VPFM (vertical PFM) images of BiT films exhibiting growth spirals, showing a minimum out-of-plane switching voltage of ± 5 V. **(c-d)** LPFM images of BiT films exhibiting growth spirals, showing a minimum switching in-plane voltage of ± 15 V. **(e-f)** VPFM images of 2D-meandered step-flow grown BiT films, showing a minimum out-of-plane switching voltage of ± 20 V. **(g-h)** LPFM images of 2D-meandered step-flow grown BiT films showing a minimum in-plane switching voltage of ± 5 V. These studies reveal that spiral growth facilitates lower switching voltages for vertical domains, whereas 2D-meanderd step-flow growth reduces switching voltages for lateral domains.

c. Surface Potential Studies

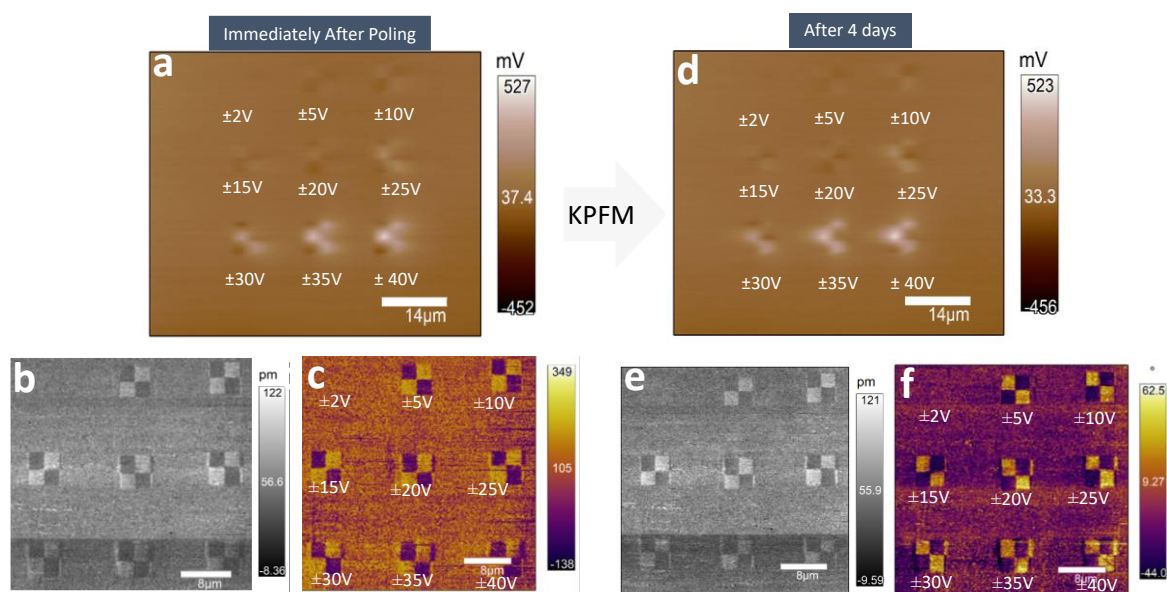


Figure S 3.12: Surface potential measurements and domain structure evolution in spiral-grown BiT thin films following local poling: *a* Surface Kelvin Probe Force Microscopy (SKPFM) surface potential image of the poled regions acquired immediately after poling. *b* VPFM amplitude image and *c* VPFM phase image of the same region. *d* SKPFM surface potential image, *e* VPFM amplitude image, and *f* VPFM phase image of the same poled area acquired four days after poling.

The SKPFM and PFM measurements presented in **Figure S12** reveal the surface potential distribution and ferroelectric domain structure in a BiT thin film exhibiting spiral growth features, following localized bias poling with voltages ranging from ± 2 V to ± 40 V. Characterisation was carried out immediately after poling (Figures S10 (a–c)) and again four days later (Figures S12 (d–f)). VPFM probes the electromechanical response of ferroelectric domains, providing information on domain orientation and stability. In contrast, SKPFM measures local surface potential,

offering complementary insight into the distribution of surface-bound charges and local work function variations resulting from polarisation-induced charge compensation. These surface electrostatic signatures are crucial for understanding domain imprint, charge trapping, and long-term retention. These are key parameters for non-volatile ferroelectric memory applications.

Figures S 3.12 a and **S 3.12 d** display surface potential maps obtained by SKPFM. The contrast in these images originates from localized surface charges induced during poling. This contrast becomes more pronounced with increasing poling voltage and is largely retained after four days, suggesting moderate temporal stability of the poling-induced surface charge states. **Figures S 3.12 c** and **S 3.12 f** show the corresponding VPFM phase images, which reveal the spatial distribution and orientation of switched ferroelectric domains. The square-shaped poled regions remain well-defined after four days, confirming retention of stable polarisation states across all applied voltages.

The persistence of the SKPFM signal over several days suggests that surface screening charges, necessary to compensate for the internal polarisation, remain effectively stabilized. This implies that the polarisation has not relaxed or backswitched. If the observed contrast were solely due to electrostatic charging or charge injection, the SKPFM signal would typically decay within hours as the injected charges dissipate. Moreover, the continued presence of clear PFM contrast indicates that the ferroelectric polarisation states are stable and not subject to rapid relaxation due to leakage or depolarisation—hallmarks of genuine ferroelectric switching.

d. Investigating Ferroelectric Switchability as a Function of Film Thickness

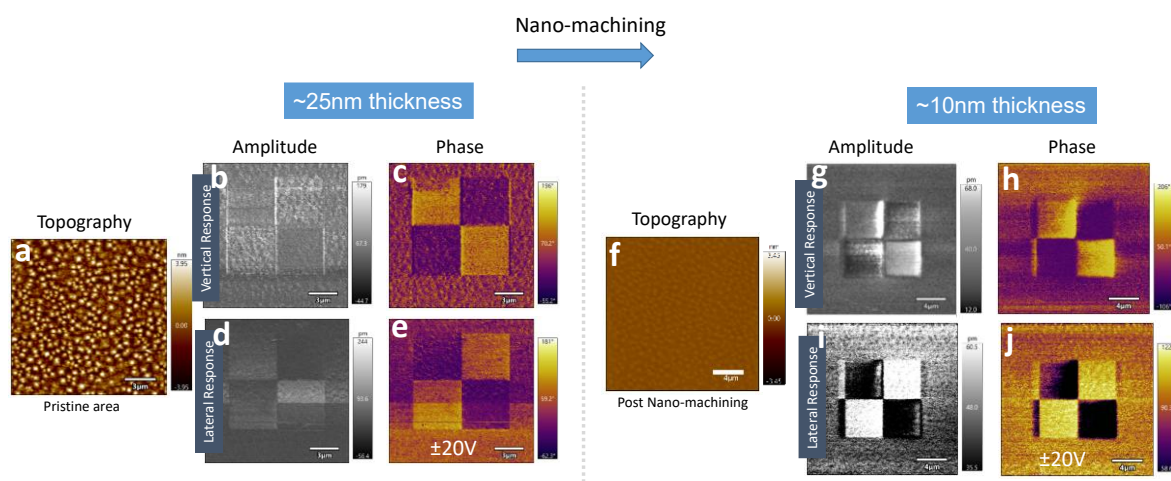


Figure S 3.13: Ferroelectric Switching Behaviour in Spiral-Grown BiT Films at Different Depths: (Left) Vertical PFM images of a pristine film (~ 26 nm thickness) following PFM lithography with a ± 20 V bias, showing clear ferroelectric switching contrast. **(Right)** Vertical PFM images acquired after PFM lithography on a nanomachined region (~ 10 nm remaining thickness), also poled with a ± 20 V bias, revealing preserved switchability in the thinner region.

The pristine BiT film was initially poled using a ± 20 V bias, as shown in **Figure S 3.13 (a–e)**. After AFM-based nanomachining reduced the film thickness from approximately 26 nm to ~ 10 nm (**Figure S 3.13 f**), ferroelectric switching remained clearly observable at the same applied voltage (**Figure S 3.13 (g–j)**). This confirms that vertical ferroelectric switching behaviour is preserved even after substantial thinning, highlighting the intrinsic robustness of switchable polarisation in the spiral-grown BiT films at reduced dimensions.

X. DFT Calculations

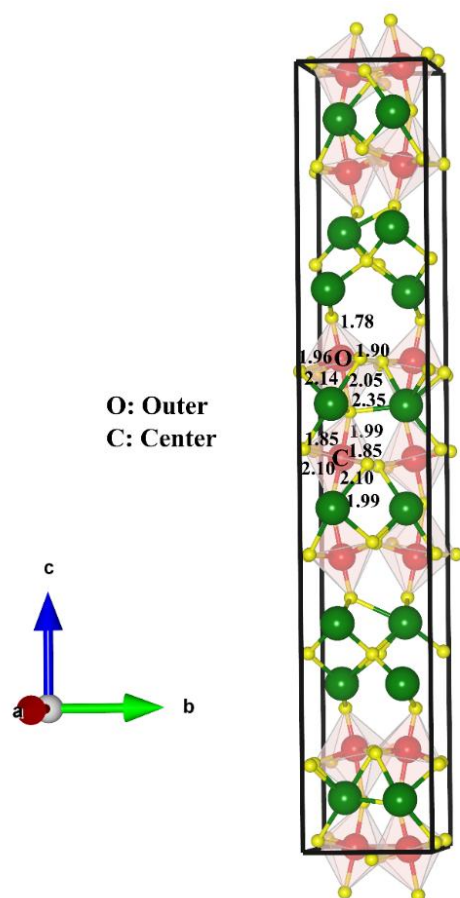


Figure S 3.14: Density Functional Theory (DFT)-Optimized Atomic Structure of Defect-Free BiT: DFT optimized atomic structure of BiT in the absence of out-of-phase boundary (OPB) defects. Ti-O bond lengths in both the outer and centre perovskite-like layers are highlighted to illustrate local structural variations. The structure was visualized using VESTA, with atomic coordinates adapted from Hervoches et al.[213] **Figure 5 a** in the main text shows zoomed-in views of the outer and central perovskite octahedra, along with the corresponding Ti–O bond lengths and octahedral tilt angles.

XI. High Angle Annual Dark Field Scanning Transmission Electron Microscopy (HAADF- STEM)

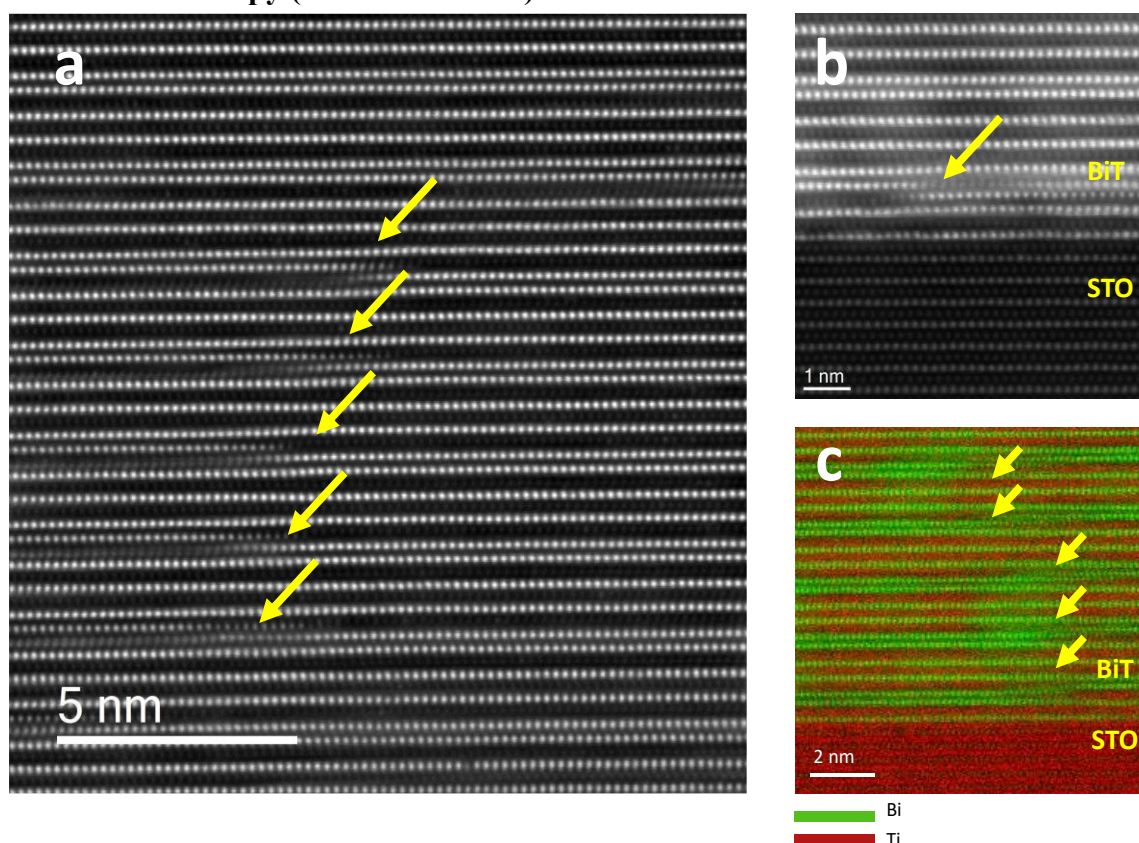


Figure S 3.15: Structural Characterisation of OPB Defects in Spiral-Grown BiT

Thin

Films:

a Cross-sectional HAADF-STEM (High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy) image of a spiral-grown BiT film showing the presence of out-of-phase boundary (OPB) defects. **b** Magnified view of an OPB defect originating near the BiT film-STO substrate interface. **c** HAADF-STEM image overlaid with EELS (Electron Energy Loss Spectroscopy) elemental mapping, highlighting variations in Bi and Ti atomic positions at the OPB. Approximate locations of OPB defects are marked with yellow arrows.

Appendix II. — Supplementary Information for Chapter 4

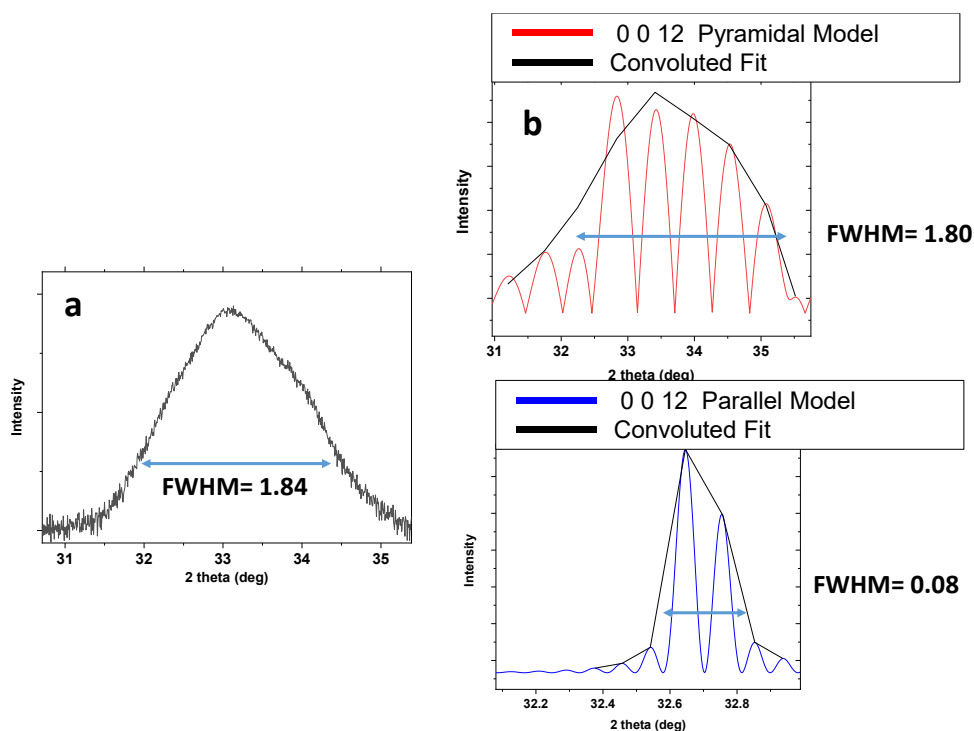


Figure S 4.1: **a-** Experimental XRD pattern of the 00 12 reflection of spiral-grown $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ showing an FWHM of 1.84° (all FWHM values shown are in degrees ($^\circ$)). **b-** Simulated 00 12 peak from the pyramidal OPB model (red) when $\delta = 4 \text{ \AA}$, shown with its convoluted fit (black), yielding a FWHM of 1.80° . **c-** Simulated of 00 12 peak from the parallel OPB model (blue) for $\delta = 4 \text{ \AA}$, with the corresponding convoluted fit (black), giving an FWHM value of 0.08° .

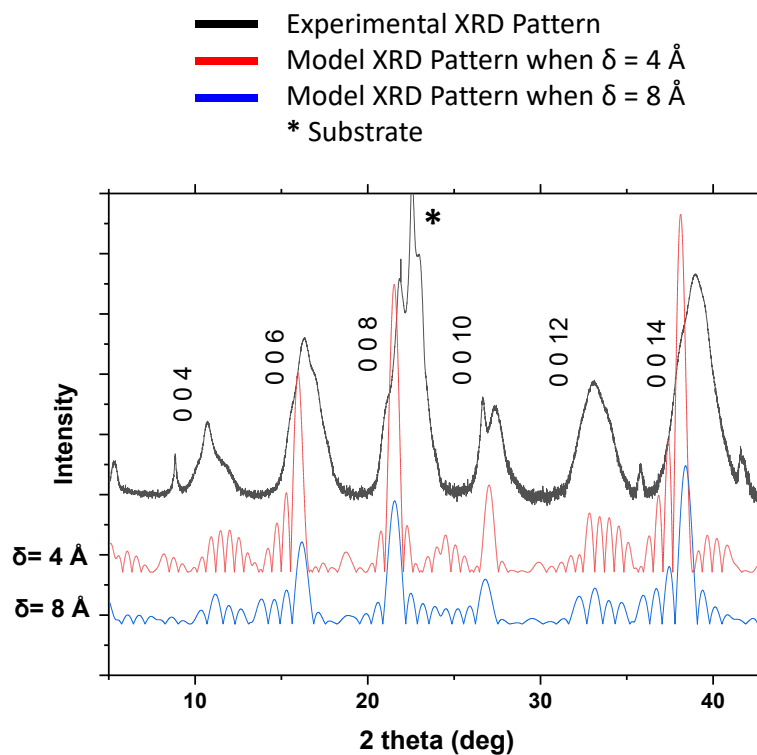


Figure S 4.2: Comparison of the experimental XRD pattern (black) , in which the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ reflections were indexed using the reference pattern for its known orthorhombic structure (space group $B2cb$) reported by Hervoches *et al.*, [213] with simulated patterns from the pyramidal OPB model for $\delta = 4 \text{ \AA}$ (red) and $\delta = 8 \text{ \AA}$ (blue).

Appendix III- Supplementary Information for Chapter 5

VI. Twin Domain Terminology

In this work, the term “twin domain” refers to crystallographic orientation variants of BiT that are rotated by $\sim 45^\circ$ about the [001] axis relative to the NGO substrate lattice. The corresponding “twinned grains” observed by atomic force microscopy represent the surface expression of these orientation variants. In contrast, “ferroelectric domains” describe regions within a single crystallographic variant that possess uniform polarisation orientation, as resolved by PFM. Distinguishing between these structural and ferroelectric domains is essential for understanding how epitaxial twinning influences polarisation continuity and switching behaviour in layered ferroelectric oxides.

VII. High vs. Low Supersaturation

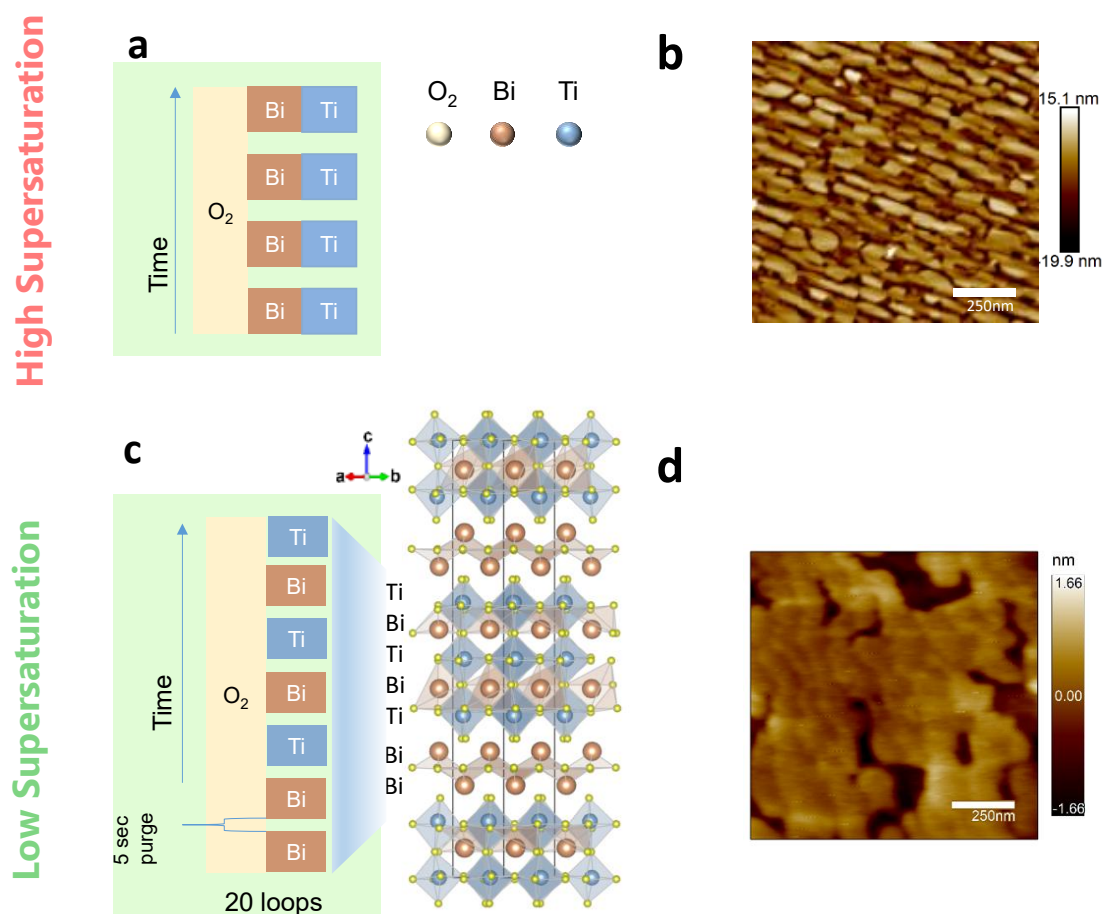


Figure S 5.1: Effect of Precursor Delivery Mode on Supersaturation and Twin Formation in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ Thin Films. **a)** Schematic representing the simultaneous injection of Bi and Ti precursors to produce a high supersaturation environment, promoting rapid nucleation and crystal twinning. **b)** Atomic Force Microscopy (AFM) image showing crystal twinned $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ grains aligned along the $[110]$ plane. **c)** Schematic illustrating sequential precursor injection scheme, where alternating Bi and Ti delivery over 20 cycles reduces instantaneous supersaturation and promotes ordered layer formation. **d)** AFM image of the resulting twin-free $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin film grown under low-supersaturation conditions.

VIII. Lateral Piezoresponse Force Microscopy (LPFM) after 90 degree rotation

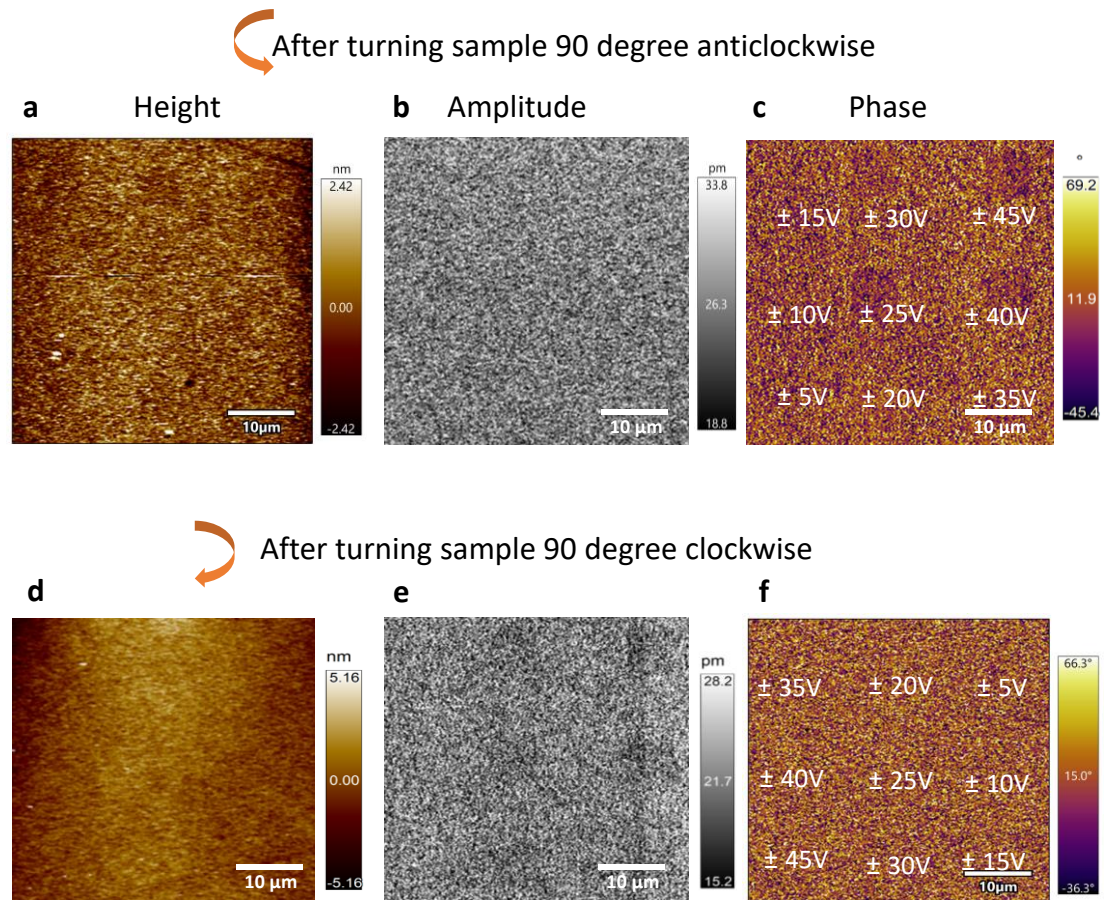


Figure S 5.2: Lateral piezoresponse force microscopy (LPFM) analysis of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films demonstrating the absence of ferroelectric switching in twinned samples. Height, amplitude and phase traces recorded under applied biases from ± 5 V to ± 45 V show no measurable polarisation reversal after rotating the sample 90° in either direction: (a-c) anticlockwise and (d-f) clockwise.

IX. X-Ray Diffraction Pattern of Twinned Films

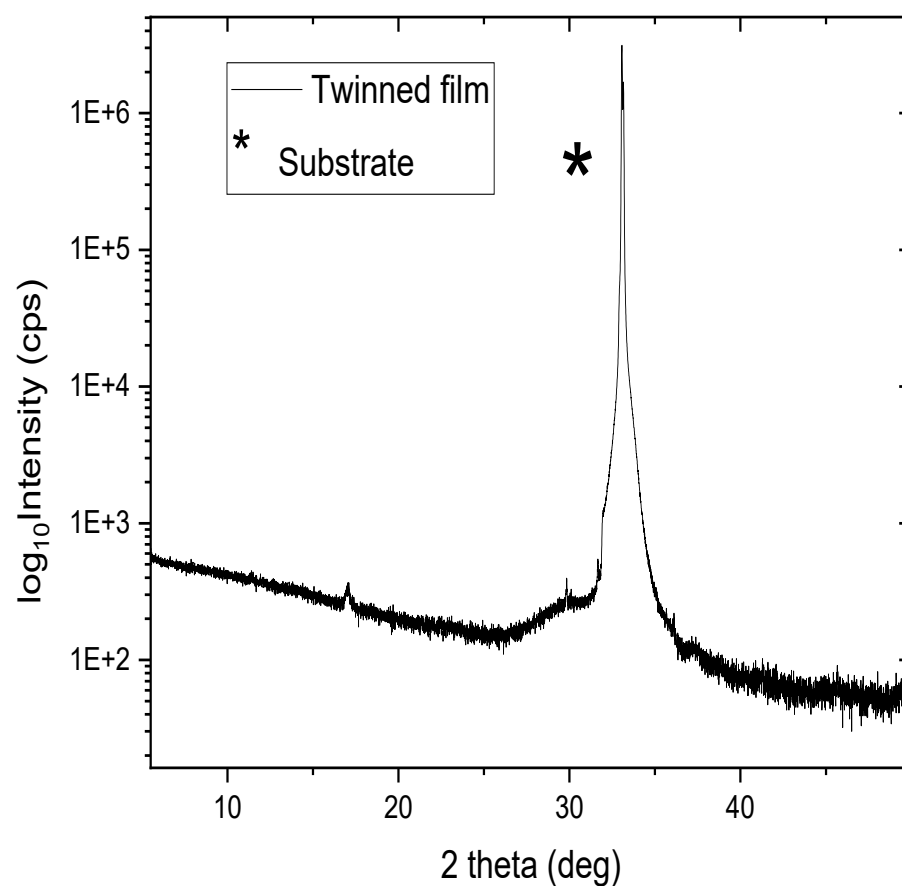


Figure S 5.3: X-Ray diffraction pattern of a twinned $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ film showing the absence of well-defined Bragg peaks. The diffuse background and lack of distinct reflections arise from incoherent scattering and destructive interference caused by multiple in-plane twin variants.

X. Nano-machining

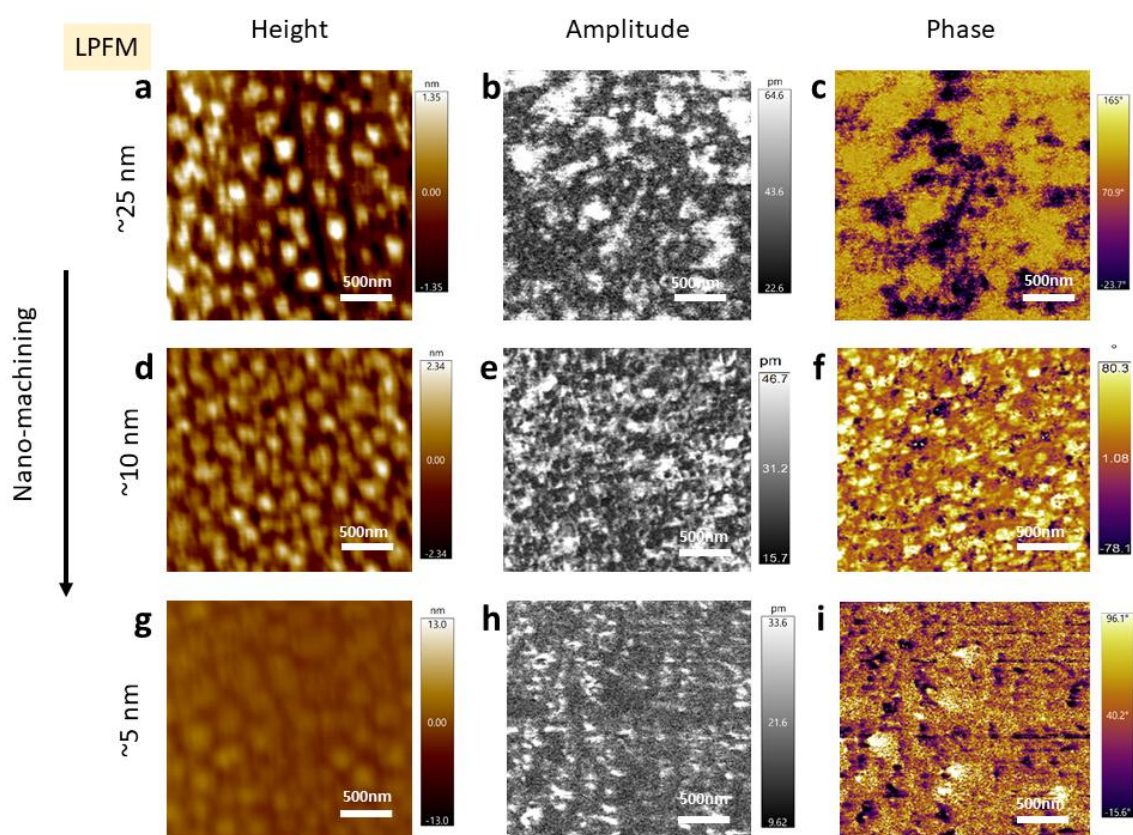


Figure S 5.4. AFM nanomachining combined with LPFM performed on low supersaturation-grown $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ film through the film thickness (as indicated on the left hand side) to verify the absence of subsurface twinning. The uniform piezoresponse signal confirms that the films remain single-oriented throughout, unlike previously reported Aurivillius thin films where buried twin domains manifested as subsurface stripe contrasts.[229]

To assess the depth dependence of ferroelectric behaviour in untwinned $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films, a progressive AFM-based nano-machining approach was employed, followed by lateral piezoresponse force microscopy (LPFM) imaging. A sufficiently stiff diamond-coated tip (Adama NMRC (Spring constant ~ 350 N/m)) operated in contact

mode was used to mechanically delayer the film surface in successive scans, removing material gradually, typically a few nanometers per cycle, while maintaining precise control over the machined depth.. After each nano-machining step, the same surface region was re-imaged to record the surface topography (height), electromechanical response (amplitude), and polarisation orientation (phase).

As shown in **Figure S 5.4**, the initial as-grown surface (~ 25 nm film thickness; **a–c**) exhibits topographical undulations and strong phase contrast with well-defined ferroelectric domains, indicative of un-twinned domains. After progressive thinning to ~ 5 nm remaining thickness (**Figure S 5.4 g–i**), the phase contrast remains robust but more diffuse, confirming that the underlying layer retains stable polarisation and show no evidence of buried stripe domains indicative of twinning.[229] This AFM-based de-layering and imaging sequence demonstrates that the interior of the film maintains coherent, intrinsic ferroelectric domains free from subsurface twin defects.

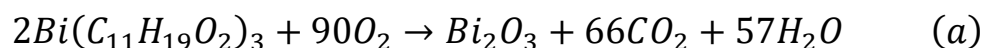
Appendix IV: Supersaturation Estimation and Partial Pressure Calculation

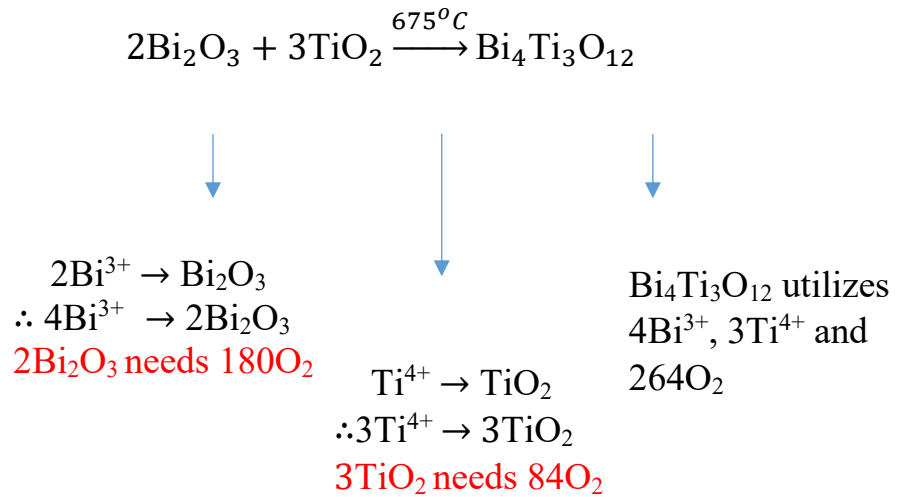
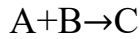
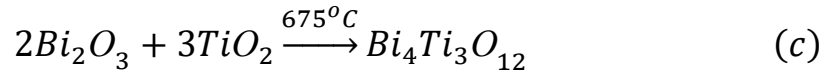
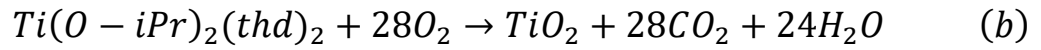
I. Supersaturation Estimation

When the two organometallic precursors: $\text{Ti}(\text{O-iPr})_2(\text{thd})_2$ and $\text{Bi}(\text{thd})_3$ (where thd = 2,2,6,6-tetramethyl-3,5-heptanedionate; O-iPr = iso-propoxide) are heated to 675 °C, they undergo pyrolysis, during which the organic ligands decompose, leaving behind an oxide network of bismuth and titanium. This thermal decomposition and oxidation process results in the formation of bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$).

Mechanism:

At elevated temperatures (675 °C), the organic ligands attached to the metal centres decompose. For the Ti precursor, the isopropoxide ligands undergo C–O bond cleavage, releasing small volatile organic molecules such as alkenes and alcohols, which are oxidised further to CO_2 and H_2O . Similarly, the β -diketonate ligands in both the Ti and Bi precursors decompose thermally, generating gaseous organic products that oxidize in the presence of oxygen to form CO_2 and H_2O . As the organic components are eliminated, the metal centres (Bi and Ti) oxidize, forming Bi–O and Ti–O bonds. These condense to form Bi_2O_3 and TiO_2 , which undergo a solid-state reaction, to produce the Aurivillius phase $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. No significant secondary phases were observed in the XRD profiles; hence, the formation of secondary phases is not considered here.





(This also explains the results in Main Text Figure 2 as with increasing oxygen, we increase the chances of abundant Bi_2O_3 formation, which forms the wetting layer.)

a. Simultaneous Injections/High Supersaturation Conditions

O_2 gas phase flow rate = 1000sscm = $1 \times 10^{-3} \text{ m}^3/\text{min}$

N_2 gas phase flow rate = 2000sscm = $2 \times 10^{-3} \text{ m}^3/\text{min}$

Reactor temperature = $675^\circ C = 948.15 \text{ K}$; Pressure = 8.5 mbar = 850 Pa

O₂ and N₂ are gases, so we can use the ideal gas law:

Gas Law: $= \frac{PV}{RT}$; n= number of moles, R= 8.31441 J K⁻¹mol⁻¹

$$O_2 \text{ (moles)} = \frac{850 \times 1 \times 10^{-3}}{8.31441 \times 948.15} = \mathbf{1.078 \times 10^{-4} \text{ mol}}$$

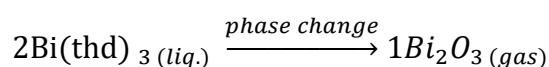
$$N_2 \text{ (moles)} = \frac{850 \times 2 \times 10^{-3}}{8.31441 \times 948.15} = \mathbf{2.156 \times 10^{-4} \text{ mol}}$$

Bi(thd)₃ liquid flow rate = 965 sscm = $9.65 \times 10^{-4} \text{ m}^3/\text{min}$;

Concentration of Bi(thd)₃ = 0.1 mol/dm³

$$\text{No. of moles (n)} = \text{Concentration} \left(\frac{\text{mol}}{\text{dm}^3} \right) \times \text{Volume}(\text{dm}^3)$$

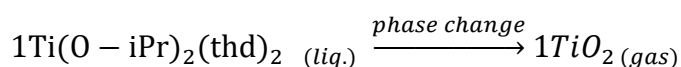
$$n = 0.1 \text{ mol/dm}^3 \times 0.965 \text{ dm}^3 = 0.0965 \text{ mol}$$



∴ no. moles **Bi₂O₃** gas= **0.04825 mol**

Ti(O-iPr)₂(thd)₂ liquid flow rate 391 sscm = $3.91 \times 10^{-4} \text{ m}^3/\text{min}$;

Concentration of Ti(O-iPr)₂(thd)₂ = 0.1 mol/dm³



∴ no. moles **TiO₂** gas= **0.0391 mol**

X_n= total no. of moles = O₂ + N₂ + Bi₂O₃ + TiO₂ = 0.0876743 moles

Mole fraction Bi₂O₃ =0.5503

Partial pressure Bi₂O₃ =

467.8 Pa

Mole fraction $\text{TiO}_2 = 0.446$

Partial pressure $\text{TiO}_2 = 379.1 \text{ Pa}$

b. Sequential Injections / Low Supersaturation Conditions

Low Oxygen Partial Pressure (13.2 Pa)

Deposition rate = 0.74 nm/min

O_2 gas phase flow rate = 1000 sscm = $1 \times 10^{-3} \text{ m}^3/\text{min}$

N_2 gas phase flow rate = 2000 sscm = $2 \times 10^{-3} \text{ m}^3/\text{min}$

Reactor temperature = $675^\circ\text{C} = 948.15 \text{ K}$; Pressure = $8.5 \text{ mbar} = 850 \text{ Pa}$

$$\text{O}_2 (\text{moles}) = 1.078 \times 10^{-4} \text{ mol}$$

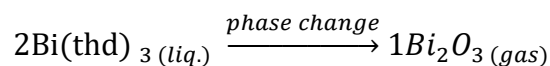
$$\text{N}_2 (\text{moles}) = 2.156 \times 10^{-4} \text{ mol}$$

$\text{Bi}(\text{thd})_3$ liquid flow rate = 206 sscm = $2.06 \times 10^{-4} \text{ m}^3/\text{min}$;

Concentration of $\text{Bi}(\text{thd})_3 = 0.1 \text{ mol/dm}^3$

$$\text{No. of moles } (n) = \text{Concentration} \left(\frac{\text{mol}}{\text{dm}^3} \right) \times \text{Volume}(\text{dm}^3)$$

$$n = 0.1 \text{ mol/dm}^3 \times 0.206 \text{ dm}^3 = 0.0206 \text{ mol}$$



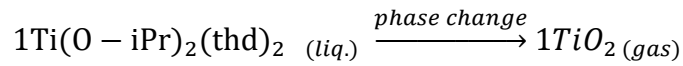
$\therefore$ no. moles Bi_2O_3 gas = **0.0103 mol**

Ti(O-iPr)₂(thd)₂ liquid flow rate = 27 sscm = $0.27 \times 10^{-4} \text{ m}^3/\text{min}$;

Concentration of Ti(O-iPr)₂(thd)₂ = 0.1 mol/dm³

$$\text{No. of moles } (n) = \text{Concentration} \left(\frac{\text{mol}}{\text{dm}^3} \right) \times \text{Volume}(\text{dm}^3)$$

$$n = 0.1 \text{ mol/dm}^3 \times 0.027 \text{ dm}^3 = 0.0027 \text{ mol}$$



∴ no. moles **TiO₂** gas= **0.0027 mol**

X_n= total no. of moles = O₂ + N₂ + Bi₂O₃ + TiO₂ = 0.0133234 moles

Mole fraction Bi₂O₃ =0.77307

Partial pressure Bi₂O₃ = 657.1 Pa

Mole fraction TiO₂ =0.20265

Partial pressure TiO₂ = 172.3 Pa

$$\propto = \frac{P_{\text{Bi}_4\text{Ti}_3\text{O}_{12}}}{P_{\text{Bi}_4\text{Ti}_3\text{O}_{12eq}}} = \frac{(P_{\text{Bi}_2\text{O}_3})^2 (P_{\text{TiO}_2})^3}{(P_{\text{Bi}_2\text{O}_{3eq}})^2 (P_{\text{TiO}_{2eq}})^3}$$

Equilibrium partial pressures are the same under both high and low supersaturation conditions since the temperature remains constant at 675°C. Therefore, a supersaturation ratio can be calculated[232], [439] to compare the high supersaturation and low supersaturation conditions as follows:

High Supersaturation : Low Supersaturation

$$(P_{Bi_2O_3})^2(P_{TiO_2})^3_{High} : (P_{Bi_2O_3})^2(P_{TiO_2})^3_{Low}$$

$$(467.8)^2 \times (4379.1)^3 : (657.1)^2 \times (172.3)^3$$

$$1.192 \times 10^{13} : 2.207 \times 10^{12}$$

1:0.2 or 5.4:1

II. Partial Pressure Calculations

N₂:O₂	$n = \frac{PV}{RT} = 2.073 \times 10^{-4}$		Mole Fraction (x) $= \frac{\text{moles}}{\text{Total moles } n} = \frac{\quad}{0.0133234}$	Partial pressure = x × 8.5 (mbar)	Partial pressure (Pa)
2:1	N ₂	$2 \times 2.073 \times 10^{-4} = 4.146 \times 10^{-4}$	0.03130	0.26565	26.6
	O ₂	$1 \times 2.073 \times 10^{-4} = 2.073 \times 10^{-4}$	0.01556	0.13225	13.2
3:2	N ₂	$1.8 \times 2.073 \times 10^{-4} = 3.7314 \times 10^{-4}$	0.02800	0.23800	23.8
	O ₂	$1.2 \times 2.073 \times 10^{-4} = 2.4876 \times 10^{-4}$	0.01867	0.158703	15.9
4:3	N ₂	$1.7 \times 2.073 \times 10^{-4} = 3.542 \times 10^{-4}$	0.02658	0.22597	22.6
	O ₂	$1.3 \times 2.073 \times 10^{-4} = 2.6949 \times 10^{-4}$	0.02023	0.171928	17.2
2:3	N ₂	$1.2 \times 2.073 \times 10^{-4} = 2.4876 \times 10^{-4}$	0.01867	0.158703	15.9
	O ₂	$1.8 \times 2.073 \times 10^{-4} = 3.7314 \times 10^{-4}$	0.02800	0.23800	23.8
1:2	N ₂	$1 \times 2.073 \times 10^{-4} = 2.073 \times 10^{-4}$	0.01556	0.13225	13.2
	O ₂	$2 \times 2.073 \times 10^{-4} = 4.146 \times 10^{-4}$	0.03130	0.26565	26.6

Calculated Oxygen Partial Pressures under Low Supersaturation Conditions

Appendix V: Experiments and Methods

a. Thin Film Synthesis

Bismuth Titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) thin films were synthesized using a horizontal flow AIXTRON AIX 200/4FE Oxide atomic vapour deposition system via the direct liquid injection chemical vapour deposition (DLI-CVD) technique, following established protocols by Keeney *et al.*[144] and Deepak *et al.*[168] In this process, bismuth and titanium precursors were injected into a Tri-JetTM vapourizer via a nitrogen (N_2) carrier gas, then transported into a CVD reactor maintained at a pressure of 850 Pa, where gas phase reactions occurred and films deposited on the surface of an epitaxial substrate. Substrate preparation involved ultrasonication in isopropyl alcohol, followed by sequential cleaning with acetone, isopropyl alcohol, and de-ionized water, and drying under nitrogen flow. Single-side polished (100)-orientated SrTiO_3 substrates with a miscut angle of $<0.2^\circ$ (Crystal GmbH) were used. The DLI-CVD process utilized a Tri-JetTM vapourizer to enable the transport of low-volatility precursors. The precursors were vapourized at 220°C and injected into the chamber using injectors pulsed at a frequency of 1 Hz. The precursor solutions, specifically 0.1 M $\text{Bi}(\text{thd})_3$ and $\text{Ti}(\text{O-iPr})_2(\text{thd})_2$ (where thd = 2,2,6,6-tetramethyl 3,5-heptanedionate and O-iPr = isopropoxide), were obtained from Epivalence Ltd. and maintained under a nitrogen atmosphere in stainless steel bubblers. For high supersaturation synthesis, $\text{Bi}(\text{thd})_3$ and $\text{Ti}(\text{O-iPr})_2(\text{thd})_2$ were injected simultaneously into the reactor. In contrast, for low supersaturation synthesis, the precursors were alternately injected to mimic the structure of the $n = 3$ Aurivillius BiT phase (**Figure 3.1**). In both cases, the process temperature was maintained at 675°C , and a rotating, infrared-heated susceptor was used to ensure uniform deposition. Key growth

parameters, including reaction temperature and bismuth precursor concentration, were optimized and subsequently held constant across all experimental runs. A significant bismuth excess was used to compensate for its volatility during and after nucleation. Specifically, a 400% bismuth excess was used in the low supersaturation regime where alternating injections and subsequent purge steps can further reduce bismuth availability. This excess was critical to minimize inhomogeneities and prevent the formation of non-stoichiometric secondary phases that could compromise film purity and functionality.[93], [273] This is particularly necessary due to the purge step after each set of injections in the sequential injection processes, where the removal of residual precursor species could further deplete bismuth availability, exacerbating volatility-induced inhomogeneities in the film. For high supersaturation growth, a 200% bismuth excess was sufficient. In this regime, the simultaneous injection of precursors and absence of purge steps allowed a greater fraction of the bismuth to incorporate into the growing film, reducing the need for higher precursor concentrations. The total gas flow ($N_2 + O_2$) within the reactor chamber was maintained at 3,000 sccm. The oxygen component was modulated between 2,000 and 1,000 sccm to investigate its effect on thin film morphology. $N_2:O_2$ flow ratios of 1:2, 2:3, 4:3, 3:2, and 2:1 were used.

b. Simulated Structure

The simulated crystal structures of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BiT) and NdGaO_3 (NGO) shown in **Figures 5.1** and **5.2** were generated using crystallographic information files (.CIFs) constructed from experimentally reported reference structures. The BiT structure was based on the standard Aurivillius-phase crystallographic data reported by Hervoches *et al.*,[213] while the orthorhombic NGO structure was generated from the crystallographic data provided by Savyitskii *et al.*[440] The unit-cell parameters and Wyckoff positions from these references were used directly to construct the .CIF files without modification.

The structural models were visualised and rendered using VESTA, a three-dimensional crystal structure visualisation program. Atom positions, layer stacking, and projection directions were extracted directly within VESTA to generate the figures. VESTA was used in accordance with its terms of use and is referenced as: Momma, K. & Izumi, F. “VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data.” *J. Appl. Crystallogr.* 44, 1272–1276 (2011).[441] These simulations were used solely for structural illustration and not for fitting, refinement, or quantitative analysis.

c. Measurements

i. X-Ray Diffraction

The crystalline properties of the films were characterized using a PANalytical MRD X-ray diffraction (XRD) system with the filtered Cu K α radiation source (45 kV and 40 mA) over the range $5 \leq 2\theta \leq 50^\circ$. The XRD spectra were baseline-corrected using a 'BSpline' function and by doing a weighted average of the global minimas. The FWHM was recorded after a standard Gaussian fit over every compared spectra in **Table S 3.2 (Supplementary Information)** as well as in **Figure 4.5**. The Reciprocal Space Map (**Figure S 3.2 d**) was measured with a 2-axes measurement between ω (range of 3 and step size of 0.0098) and $2\theta\omega$ (range of 2 and step size of 0.01). Rocking Curve measurements were also performed on the PANalytical MRD X-Ray diffractor, where the range of ω was set to 3. In this study, the XRD peaks for BiT were assigned using a reference pattern based on its known orthorhombic structure (space group *B2cb*) by Hervoches *et al.*[213] The peak indexing and assignment were performed using CrystalDiffract 7 software, which allowed for comparison of the experimental diffraction pattern with the calculated reference pattern. The refinement and analysis confirmed the structural model and peak assignments.

ii Topographical characterisation

The surface morphology of the thin films was measured using an atomic force microscope (AFM), Bruker Dimension Icon in PeakForce Tapping mode using Bruker SCANASYST-AIR probes (Al reflex coated, 2 nm tip radius, 70 kHz resonant frequency).

iii High resolution electron microscopy

Lamella preparation was achieved by using a Tescan Solaris FIB-SEM. First protection layer was done by a dot of Sharpie, followed by ion-beam deposited layer of carbon 2 μm thick. Coarse milling with Ga^+ -beam at 5 nA at 30 kV, final polishing with 30 pA at 5 kV. Final FIB lamella thinning was performed using a Fischione NanoMill. STEM characterisation was performed on an aberration-corrected Nion UltraSTEM 200 equipped with a Gatan Enfinium EELS spectrometer, operating at 200 kV with a 27 mrad semi-convergence angle. HAADF-STEM imaging was performed with a probe current of approximately 35 pA and a dwell time of 8 μs dwell time, by collecting frames of 2048 x 2048 pixels. Sample charging and drift effects were minimised by subsequent non-rigid registration post-processing of image stacks using the SmartAlign software plug-in for Gatan DigitalMicrograph.[442] STEM-EELS was performed using a probe current of approximately 150 pA, 5 ms dwell time, and 256 x 256 pixels for each image. All STEM images were taken along the [110] crystallographic zone axis. Polarisation vector maps were performed using the TopoTEM module of the TEMUL Toolkit Python package,[302] which itself is based on the Atomap TEM image analysis Python package.[301]

iv Nanoscale ferroelectric measurements

Piezoresponse Force Microscopy Piezoelectric measurements were conducted using an Asylum Research MFP-3D Atomic Force Micro-scope set in contact mode, augmented by an HVA220 Amplifier for enhanced piezoelectric force microscopy (PFM) measurements. The Dual AC Resonance Tracking (DART) PFM mode was employed to enhance the piezoresponse signals, with the advantage of tracking and measuring at the contact resonance frequency between the tip and the sample, which

is known to improve the signal-to-noise ratio. A drive frequency of 200-300 kHz in vertical mode and 700-800 kHz in lateral mode were used to enable the detection of lateral and vertical piezoelectric responses. The ferroelectric domains were imaged using Super Sharp conductive diamond probes AD-2.8-SS (boron doped, Au re-flex coated, ~ 5 nm tip radius, 75 kHz resonant frequency) from Adama Innovations. The phase hysteresis loops as well as the butterfly displacement amplitude (strain) loops of the bismuth titanate thin films were obtained with an Olympus AC240TM-R3 probe using triangle stepped waveforms with DC biases applied in stepped increments at a frequency of 0.2 Hz, alternating between 'on' and 'off' states, while an AC bias (500 mV) reads the remnant polarisation. Ferroelectric lithography for poling and switching studies was performed using the same probe (Olympus AC240TM-R3), with a high contrast black-and-white PNG file selected to guide the bias lithography pattern. The black parts of the image were assigned negative bias, and the white parts of the image were assigned positive bias ranging from ± 5 V to ± 45 V to measure the lowest required voltage for switching the ferroelectric thin films. The coordinates of the poling area were selected to enable a systematic increase in switching voltage. The lowest voltage that achieved visibly complete poling was identified as the minimum threshold required to reliably switch the film. Drive amplitudes of 0.5 to 1 V were used to image the switched areas in vertical and lateral 'read' modes. To demonstrate the reversibility of ferroelectric switching and polling, initially, $4\text{ }\mu\text{m} \times 4\text{ }\mu\text{m}$ micron regions of the films were poled using a negative DC bias of -5 V. Subsequently, $3\text{ }\mu\text{m} \times 3\text{ }\mu\text{m}$ regions within the positively poled regions were reverse-poled by applying an opposite, positive DC bias of +5V. Atomic force microscopy (AFM) nano-machining of the ultrathin films was carried out using an Asylum Research MFP-3D™ system in ambient conditions. A commercially available single-crystal diamond cantilever

(model Adama Innovations NM-RC, Au-reflex coated, <10 nm tip radius, boron-doped), purchased from Adama Innovations was used. The resonant frequency of the cantilever in free-air was ~469 kHz and the nominal spring constant k was calibrated using the Sader method based on a thermal tune (1000 samples) in ambient air. The calibrated spring constant was 1.9×10^2 N/m ($\pm 7.49\%$) as determined by the method of Sader *et al.*[443]

Normal loading forces F during the nano-machining scans were calculated using Hooke's law ($F = k \cdot z$), where z is the vertical deflection (m) derived by multiplying the calibrated deflection sensitivity (m/V) by the set-point photodiode voltage (V). Loading forces ranged from ≈ 1.76 μ N to ≈ 4.59 μ N. Successive scans ($8 \mu\text{m} \times 8 \mu\text{m}$) were performed at a scan frequency of 0.75 Hz, and the cantilever scan angle was set to 90° unless otherwise stated. Depth of material removal per scan was approximately ~ 0.3 nm/scan, allowing progressive exposure of sub-surface layers. This procedure follows the methodology described by Keeney *et al.*[229]

v. First Principles Calculations

First-principles calculations based on density functional theory (DFT) are performed using the Vienna Ab-initio Simulation Package (VASP),[444] employing the projector-augmented wave (PAW) method.[445] The exchange-correlation interactions are treated within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional.[446] To model the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BiT) structure containing out-of-phase boundaries (OPBs), a $4 \times 1 \times 1$ supercell is constructed based on the orthorhombic $B2cb$ phase of BiT Hervoches *et al.*[213] (Shown in **Figure 1 a**). Structural optimization is performed under constrained conditions, where atomic positions are fully relaxed while maintaining a fixed cell volume. A plane-wave energy cut-off of 500 eV is employed to ensure convergence

of the total energy. For Brillouin zone integration, a $1\times 5\times 1$ Monkhorst-Pack k-point mesh[447] is used for the large supercell containing 304 atoms. Self-consistent field (SCF) calculations are considered converged when the total energy change between iterations is less than 10^{-4} eV. The structural relaxation is continued until the residual forces on each atom are reduced below 0.02 eV/Å.

vi. Statistical Analysis

All image-derived quantities (e.g., ferroelectric domain area, piezoresponse amplitude) were extracted using Igor Pro and validated using ImageJ. Data were baseline-corrected and checked for outliers prior to analysis; no normalization or transformation was applied because distributions remained physically representative. Data are presented as mean $\pm$ standard deviation (SD) unless otherwise stated. For ferroelectric domain size comparison between spiral-mediated and step-flow BiT films, sample areas of 2 sq. micron were used. XRD FWHM values were extracted by Gaussian fitting with baseline correction, with an average standard fitting error of $\pm 0.048^\circ$.

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