METROLOGY OF FERROELECTRIC DOMAIN WALLS WITH
SCANNING TRANSMISSION ELECTRON MICROSCOPY

A Dissertation in
Materials Science and Engineering

by
Debangshu Mukherjee

© 2018 Debangshu Mukherjee

Submitted in Partial Fulfillment
of the Requirements
for the Degree of
Doctor of Philosophy

August 2018
The dissertation of Debangshu Mukherjee was reviewed and approved* by the following:

Nasim Alem  
Assistant Professor of Materials Science & Engineering  
Dissertation Advisor  
Chair of Committee

Venkatraman Gopalan  
Professor of Materials Science & Engineering

Roman Engel-Herbert  
Associate Professor of Materials Science & Engineering

Vincent Crespi  
Distinguished Professor of Physics

James Rondinelli  
Associate Professor of Materials Science & Engineering  
Northwestern University

Suzanne Mohney,  
Professor of Materials Science and Engineering  
Chair of the graduate program

*Signatures are on file in the Graduate School
ABSTRACT

The overarching idea of this thesis research is the metrology of ferroelectric domain walls in the transmission electron microscope. The promise of transmission electron microscopy has always been the visualization of nanostructures with atomic resolution. Since the advent of aberration corrected electron optics, it has been possible over the past decade to realize that vision and image individual atoms in a material. The ability of visualize individual atom positions leads to an obvious follow up question – is it possible to measure the atomic structure?

Several recent path breaking works have shown it is indeed possible to do so – and this thesis work shows how metrology in the transmission electron microscope can be used to elucidate the structural behavior of domain boundaries in ferroelectric crystals.

The first chapter – the introduction gives a brief aerial overview of electron microscopy advancements and the status of modern ferroelectrics research and recent advances in the understanding of ferroelectrics with the aberration corrected electron microscope.

The second chapter explains the development of a custom algorithm, developed as a part of the author’s doctoral research that enables the sub-pixel precision identification of atom positions in non-ideal images, especially in situations where atom columns may be blurred with the intensities tails from one atom column bleeding into the neighboring atom columns. We developed subroutines that deconvolute the observed intensity redistribution from atoms into a combination of multiple Gaussian peaks, allowing the assignment of intensity spikes to the atom in question, and to its neighbors.
The third chapter uses the algorithm developed is then used to understand the crystal structure of the 180° domain boundary in the most commercially important ferroelectric crystal – LiNbO₃. Our work demonstrates the feasibility of measurement of metrology of both the niobium and oxygen columns, allowing the direct visualization of the domain boundaries. We additionally find evidence of bending of the polar niobium-oxygen displacements in the vicinity of the domain boundary. This bending was observed only near the wall, and was absent in the bulk domain. Combined with first principles calculations performed by our collaborators, we demonstrate the origin of the bending as thermodynamic stabilization owing to an increase of the polar configurational entropy. We developed techniques to directly measure the polar entropy from LiNbO₃ electron micrographs, which show high fidelity to predicted values.

The fourth chapter extends the metrology toolkits developed over the course of the author’s doctoral research into a novel class of materials – polar metals, as elucidated in chapter 4. We focus on the compound – titanium doped Ca₃Ru₂O₇, which is structurally equivalent to a ferroelectric, but is a metal at room temperatures while retaining its non-centrosymmetric crystal structure. Our investigations revealed the presence of 90° and 180° domain walls and associated domain junctions.

We extended our metrology toolkit to enable the direct measurement of potential gradients across the observed domain walls. This work focused on rethinking scanning transmission electron microscopy as a collection of summed diffraction patterns from a point electron probe. Utilizing the fact that the probe is charged, since electrons are charged particles, we employed big data techniques to directly measure momentum transferred to the electron probe at every scanning positions – an exercise that entailed
the construction of novel algorithms that could scalably and reliably measure such displacements over millions of diffraction patterns. Our results for the first time demonstrate the feasibility of using the electron microscope to measure mesoscopic potential gradients, with the measured potential gradients demonstrating extremely close adherence to theoretically predicted changes in the Fermi levels.

The fifth chapter, the conclusion section puts the work in this thesis in context – explaining how the structure and the electronic properties of ferroelectric domain walls can be measured reliably and with unprecedented resolution.

The sixth chapter introduces possible future directions in transmission electron microscopy, and how 4D-STEM datasets could be processed with the techniques developed by lensless diffractive imaging to image the projected potential of the crystals with sub-angstrom resolution – the technique also referred to as ptychography.
# TABLE OF CONTENTS

LIST OF FIGURES ........................................................................................................ix

ACKNOWLEDGEMENTS ................................................................................................xvii

1. INTRODUCTION .........................................................................................................1

1.1 Ferroelectricity .........................................................................................................1

   Definition of ferroelectrics .........................................................................................1

   1.1.2 Explanation of ferroelectricity .........................................................................2

   1.1.3 Hybrid Improper Ferroelectrics ......................................................................3

   1.1.4 Ferroelectric Domain Walls .............................................................................6

   1.1.5 Application of ferroelectrics ..........................................................................7

   1.1.6 Research Questions .........................................................................................9

1.2 Transmission Electron Microscopy ........................................................................11

   1.2.1 Description of the TEM .................................................................................11

   1.2.2 Applications to ferroelectrics .......................................................................14

2. DETERMINATION OF ATOM POSITIONS ............................................................17

2.1 Introduction ............................................................................................................17

2.2 Fitting Atom Positions with Gaussians ...............................................................19

2.3 The MPFit Algorithm ...........................................................................................23

2.4 Results and Discussions .......................................................................................25

2.5 Conclusions ...........................................................................................................30

3. DOMAIN WALLS IN LITHIUM NIOBATE .............................................................33

3.1 Introduction ............................................................................................................33
3.2 Materials and Methods

3.2.1 Imaging and Preparation of LiNbO₃ Samples

3.2.2 Quantification of Polar Displacements

3.2.3 First Principles Calculations

3.3 Results and Discussions

3.3.1 Measurement of polar displacements in LiNbO₃

3.3.2 Measurement of Polar Entropy

3.3.3 Measurement of strain

3.4 Conclusions

4. 4D-STEM IMAGING OF DOMAIN WALLS IN POLAR METALS

4.1 Introduction

4.1.1 Polar Metals

4.1.2 Hybrid Improper Ferroelectric Metal - Ca₃Ru₂O₇

4.1.3 Differential Phase Contrast STEM (DPC-STEM)

4.2 Results and Discussions

4.2.1 Optical Microscopy of 5%Ti-Ca₃Ru₂O₇

4.2.2 Focused Ion Beam Sample Preparation

4.2.3 Transmission Electron Microscopy of 5%Ti-Ca₃Ru₂O₇

4.2.4 DPC-STEM of 5%Ti-Ca₃Ru₂O₇

4.2.5 Measurement of CBED disk positions with edge detection

4.2.7 Measurement of CBED disk positions with Hybrid Cross Correlation

4.3 Comparison with theoretical calculations
4.4 Conclusions ................................................................. 111

5. CONCLUSIONS ............................................................... 112

6. FUTURE WORK ................................................................. 115

REFERENCES ................................................................. 118
LIST OF FIGURES

Figure 1.1 | Polar Displacements in Ferroelectrics. Left – Centrosymmetric ABO$_3$ crystal structure with the B site atoms at the center of the blue oxygen octahedral. Right, Non-centrosymmetric structure with the B site atoms displaced, with the displacements marked by the black arrows. .................................................................3

Figure 1.2 | Ruddlesden-Popper Structure. Ferroelectricity originating due to octahedral tilts in two perovskite blocks separated by a rocksalt layer. .........................5

Figure 1.4 | Schematic of ferroelectric RAM. Courtesy Fujitsu .............................7

Figure 1.5 | Rotational domain wall in PbTiO$_3$ ..................................................9

Figure 1.6 | Néel-like rotational domain walls in Pb(Zr,Ti)O$_3$ ..........................10

Figure 1.7 | Cross-section of modern TEM. From the top the electron gun, followed by the monochromator, the condenser lenses, the specimen holder, followed by the objective lense, the aberration correctors and the projector lenses. A CCD or a CMOS detector is below the projector lenses. (courtesy FEI) .................................................................12

Figure 1.8 | Early TEM on domain walls. BF-TEM of domain walls in BaTiO$_3$ ....15

Figure 1.9 | Visualization of polar displacements with aberration corrected STEM. a, Visualization of vortex nanodomains in BiFeO$_3$ thin films grown on TbScO$_3$ substrates by molecular beam epitaxy. The images refer to the polarization vectors overlaid on the ADF-STEM image, and the magnitude and the angle of the polarization vectors. b, Visualization of polar vortices in PbTiO$_3$-SrTiO$_3$ superlattices by aberration corrected STEM.................................................................16

Figure 2.1 | Errors with the single Gaussian approach. a) BF-STEM image of LiNbO$_3$ with the intensity minima marked by red circles. b) BF-STEM image shown in Fig. 1a with intensity minima in red, and fitted single Gaussian peak centers in yellow. c) Summed intensity value from the region marked by the black rectangle in Fig. 1a and Fig. 1b with the blue curve showing the intensity profile, the red arrows corresponding to
the intensity minima and the yellow arrows corresponding to peak positions obtained from fitting a single Gaussian.

Figure 2.2 | Schematic of the Procedure. Red circles correspond to intensity minima or maxima for BF-STEM and ADF-STEM images respectively.

Figure 2.3 | First refinement stage of multi-peak fitting. a) BF-STEM image with the red circles corresponding to intensity minima. b) Evolution of Gaussian peak fit corresponding to the region marked by the black square in Fig. 2.3a. c) Raw data corresponding to region marked by the black square in Fig. 2.3a. d) Contribution of Gaussian peaks from the fitted atom. e) Contribution of neighboring atoms as intensity tails. f) Summation of all peaks with an intensity profile similar to Fig. 2.3c.

Figure 2.4 | Second refinement stage of multi-peak fitting. a) BF-STEM image with the red circles corresponding to intensity minima, and green circles corresponding to the positions from the first fitting stage. b) Evolution of Gaussian peak fit corresponding to the region marked by the black square in Fig. 2.4a. c) Raw data corresponding to region marked by the black square in Fig. 2.4a. d) Contribution of Gaussian peaks from the fitted atom. e) Contribution of neighboring atoms as intensity tails. f) Summation of all peaks with an intensity profile similar to Fig. 2.4c.

Figure 2.5 | 3D representation of peak evolution. a) Raw data, atom contribution as fitted data, intensity tails, and the sum of fitted data and tails for the first stage of multi-peak fitting. b) Raw data, atom contribution as fitted data, intensity tails, and the sum of fitted data and tails for the second stage of multi-peak fitting.

Figure 2.6 | Comparison of peak fits. a) Intensity minima and first stage fitted peaks overlaid on the BF-STEM image as red and green circles respectively. b) Intensity minima, first stage and second stage fitted peaks overlaid on the BF-STEM image as red, green and blue circles respectively. c) Intensity minima, first stage, second stage fitted peaks and positions obtained from a single Gaussian overlaid on the BF-STEM image as red, green, blue and yellow circles respectively.

Figure 2.7 | Comparison of single versus Multi-Peak Fitting. a) Position difference between the fitted peaks obtained from a single Gaussian fit with respect to the intensity minima. b) Position difference between the fitted peaks obtained from the first phase of a multi Gaussian fit with respect to the intensity minima. c) Position difference between the fitted peaks obtained from the second phase of a multi Gaussian fit with respect to the intensity minima.

Figure 3.1 | Schematic of experimental conditions. a, Lithium and niobium Jahn-Teller distortions with respect to oxygen octahedra when viewed from the \{1\bar{1}0\} zone axis, with oxygen atoms in red, niobium atoms in green and lithium atoms in blue respectively. b, Schematic of the unit cell for calculation of niobium-oxygen displacements, represented by gray shaded region in Fig. 1a, with the Ising and Néel
niobium-oxygen displacements directions marked by the blue and red boxes respectively. The displacement magnitudes are exaggerated for clarity.

c, Conventional transmission electron microscopy image of LiNbO$_3$ domain wall from the \{1\overline{1}00\} zone, with the domain wall marked by arrows.
d, Selected area diffraction pattern for LiNbO$_3$ from the TEM image shown in Fig. 1d.
e, BF-STEM image of the area marked by the black box in Fig. 1d, with the inset showing the niobium and oxygen positions. The arrows refer to the domain wall. Scale bar is 2nm.
f, Simultaneous ADF-STEM of the area marked by the box in Fig. 1d, with the inset showing the niobium positions. The arrows refer to the domain wall location. Scale bar is 2nm.

Figure 3.2 | Evolution of BF-STEM image as a function of $\alpha$ tilt. a, Multislice simulations of BF-STEM image of LiNbO$_3$ at the 28.9 mrad convergence angle without aberrations as a function of $\alpha$ tilt from 0mrad (no tilt) to 30mrad of $\alpha$ tilt. b, Zoomed in section from section a with the niobium atoms in green and the oxygen atoms in red overlaid on top. c, Comparison of tilt effects at 0mrad and 30mrad showing how the oxygen atom moves up (red arrow) and the niobium atom no longer maintains a circular shape (green arrow).

Figure 3.3 | Polar displacements at the domain wall. a, Ising Niobium-Oxygen displacement magnitudes along the <0001> zone mapped out over the corresponding BF-STEM image. Scale bar is 2nm. b, c, Plots of Individual niobium displacements in green, oxygen displacements in red and difference in blue per unit cell, with the solid line showing the average along the [0001] axis. d, Néel niobium-oxygen displacement magnitudes along the $\langle1\overline{1}20\rangle$ zone mapped out over the BF-STEM image, identical to the micrograph in Fig. 2a. Scale bar is 2nm. e, f, Plots of Individual niobium displacements in green, oxygen displacements in red and difference in blue per unit cell, with the solid line showing the average along the [0001] axis. g, Rotation color map of $P_{Nb-O}$ polar displacement angle with the overlay with rotation arrows measured per unit cells. h, Plot of rotation angle in degrees for the unit cells with the solid line showing the average along the <0001> direction. i, Curl of polar niobium-oxygen displacement vectors with blue referring to clockwise and red to counter-clockwise rotations. j, Divergence of the polar displacement, with red corresponding to an increase in the displacement magnitude and blue corresponding to a decrease in the displacement magnitude.

Figure 3.4 | ab-initio Simulations of Niobium-Oxygen Displacements | a, Potential energy of displacements with zero niobium-oxygen displacements along the <0001> zone axis demonstrating the classic Goldstone Sombrero potential. b, Radial potential distribution with a minima at 10pm. c, Probabilities of Ising, Néel and Bloch displacements, with zero Ising. d, Displacement probabilities at zero Ising displacements, and e, probabilities with bulk domain displacements (Credit: Sergei Prokhorenko, University of Liege).
Figure 3.5 | Polar displacements in the domain. **a**, Ising Niobium-oxygen displacements mapped over the corresponding BF-STEM image approximately 10nm away from the domain wall along the <0001> zone axis. Scale bar is 1.5nm. **b**, Plot of niobium-oxygen displacement per unit cell, with the solid line showing the average along the [0001] axis. **c**, Néel niobium-oxygen displacements in the (1120) zone plotted over the corresponding BF-STEM image in Fig. 3.5a. Scale bar is 1.5nm. **d**, Plot of Néel niobium-oxygen displacement per unit cell, with the solid line showing the average along the [0001] axis. **e**, Curl of displacement vectors, with blue and red corresponding to clockwise and counter-clockwise directions respectively. **f**, Divergence of the polar vectors, with blue referring to an increase, and red a decrease in the displacement magnitude. **g**, Ising Niobium-oxygen displacements in the bulk domain, approximately 100nm south of the wall mapped over the corresponding BF-STEM image along the <0001> zone axis. Scale bar is 1 nm. **h**, Plot of niobium-oxygen displacement per unit cell, with the solid line showing the average along the [0001] axis. **i**, Néel niobium-oxygen displacements in the (1120) zone plotted over the corresponding BF-STEM image in Fig. 4f. Scale bar is 1 nm. **j**, Plot of Néel niobium-oxygen displacement per unit cell, with the solid line showing the average along the [0001] axis. **k**, Curl of displacement vectors mapped in Fig 3.5f and Fig. 3.5h with blue and red corresponding to clockwise and counter-clockwise directions respectively. **l**, Divergence of the polar vectors, with blue referring to an increase, and red a decrease in the displacement magnitude.

Figure 3.6 | Polar Entropy from niobium-oxygen displacements. **a-c**, Polar entropy contribution as a function of the Ising (0001) and the Néel (11-20) displacements at the domain wall, approximately 10nm away from the domain wall, and inside the bulk domain respectively. **d-e**, Summed entropy contribution as a function of the Ising and the Néel displacements respectively overlaid with the polar entropy calculated at the wall from first principles simulations.

Figure 3.7 | Strain at the domain wall. Mapping of the strain arising at the domain wall, through comparison of the measured unit cell with the known theoretical unit cell size to give the strain values – with $\varepsilon_{xx}$ (Fig. 3.6a), $\varepsilon_{xy}$ (Fig. 3.6b), $\varepsilon_{yy}$ (Fig. 3.6c) and $\theta$ (Fig. 3.6d).

Figure 3.8 | Strain inside the bulk domain. Mapping of the strain arising inside the bulk domain, through comparison of the measured unit cell with the known theoretical unit cell size to give the strain values – with $\varepsilon_{xx}$ (Fig. 3.8a), $\varepsilon_{xy}$ (Fig. 3.8b), $\varepsilon_{yy}$ (Fig. 3.8c) and $\theta$ (Fig. 3.8d).

Figure 4.1 | Structure and electronic properties of titanium doped Ca$_3$Ru$_2$O$_7$. **a**, Resistivity as a function of temperature for different titanium doping concentrations. **b**, The crystal structure of Ca$_3$Ru$_2$O$_7$ viewed from the [011] zone axis.

Figure 4.2 | Electron beam deflection in an electric field. **a**, No deflection, centered on both the opposing detectors in the absence of an electric field. **b**, Rightward beam deflection,
with the Y detector being selectively illuminated under an electric field. c, Leftward beam deflection, with the X detector being more strongly illuminated when the electric field points to the right.

**Fig. 4.3 | Observation of ferroelectric domains with DPC.** a, The BaTiO$_3$ crystal structure. b, Schematic of a 4 segment detector, showing the respective crystal orientations with respect to the detector. c, Subtraction of intensity from detector Y from detector W. d, Subtraction of intensity of detector Z from detector X. 

**Figure 4.4 | 4D-STEM Differential Phase Contrast STEM.** a, Ronchigrams obtained at every scan position with the corresponding simultaneously acquired ADF-STEM in inset on a SrTiO$_3$ sample. b, Ronchigrams from two different regions demonstrating differing momentum redistributions. c, Momentum vector measured from the ronchigram intensity center of mass.

**Fig. 4.5 | Optical Microscopy of Ca$_3$Ru$_2$O$_7$ crystals.** a, Brightfield optical microscope image of 5% Ti doped Ca$_3$Ru$_2$O$_7$. b, Circularly polarized optical microscope image of the same crystal demonstrating birefringence due to domains.

**Fig. 4.6 | Optical Microscopy images showing FIB region of interest.** a, Polarized light optical microscope image demonstrating the location of the domain walls. The domain walls are visible due to optical birefringence. b, Optical microscope image showing multiple FIB cuts.

**Fig. 4.7 | Low mag TEM image of FIB sample.** a, Low mag conventional TEM image viewed from the (011) zone axis showing possible domain wall locations visible due to diffraction contrast. b, Schematic showing the possible domain orientations visible from the (011) zone axis.

**Figure 4.8 | Ca$_3$Ru$_2$O$_7$ crystal structure.** a, Schematic of the Ca$_3$Ru$_2$O$_7$ crystal structure, viewed from the (011) zone axis showing the oxygen octahedra with the ruthenium atom sitting at the center of the octahedra. b, Schematic in Fig. 4.5a viewed without the oxygen atoms, demonstrating how the tilt manifests as calcium displacements (blue arrows) and polarization (red arrows).

**Fig. 4.9 | High-resolution ADF STEM of 5%Ti-Ca$_3$Ru$_2$O$_7$.**

**Fig. 4.10 | High-resolution ADF STEM of 5%Ti-Ca$_3$Ru$_2$O$_7$ overlaid with the calcium displacement directions.**

**Fig. 4.11 | Tail to tail domain walls in 5%Ti-Ca$_3$Ru$_2$O$_7$.** a, Meandering 90° tail to tail domain boundary in 5%Ti doped Ca$_3$Ru$_2$O$_7$. b, Zoomed in section corresponding to the region marked by the white box in Fig. 4.4a demonstrating polarization rotation in some layers.
Fig. 4.12 | Head to tail domain walls in 5%Ti-Ca$_3$Ru$_2$O$_7$. a, 90° head to tail domain boundary in 5%Ti doped Ca$_3$Ru$_2$O$_7$. b, Zoomed in section corresponding to the region marked by the white box in Fig. 4.5a.

Figure 4.13 | 4D-STEM imaging of 5%Ti-Ca$_3$Ru$_2$O$_7$. a, ADF-STEM imaging of the sample with 1.1 nm beam. b, BF-STEM image obtained by summing the CBED pattern. c, CBED pattern corresponding to the region marked by the yellow arrow in Fig. 4.11b.

Figure 4.14 | Central beam shift as a function of beam position.

Fig. 4.15 | Shift of center of mass due to potential gradients. a, Schematic of center of mass of an electron beam (green) shifting to the right in the central disk after encountering a potential gradient in the opposite direction. b, Center of mass of the electron beam centered inside the (000) central disk upon encountering a centrosymmetric potential gradient. c, Center of mass of the electron beam shifted to the left inside the (000) central disk upon encountering a potential gradient increasing to the right.

Figure 4.16 | CBED patterns from 4D-STEM. a, CBED patterns with non-overlapping disks demonstrating low signal to noise. The ADF aperture blocking the higher order disks is visible also. b, Zoomed in central disk marked by white square in Fig. 4.13a demonstrating intensity variation and shot noise.

Figure 4.17 | Disk metrology through edge detection. a, Central disk to be measured. b, Calculated edge through Canny edge detection using Otsu lower and upper thresholds. c, Calculated circle in red and white overlaid on the experimental data.

Fig. 4.18 | Measured disk shift using edge detection. a-b, X and Y shift of disk center of mass with respect to the disk center. c-d, X and Y shift of disk center of mass with respect to the detector center.

Fig. 4.19 | Hybrid Cross Correlation Disk Metrology. a, Experimental CBED pattern. b, Theoretically simulated electron beam in the diffraction plane under known experimental conditions. c, Hybrid cross correlation of Fig. 4.16a with Fig. 4.16b.

Figure 4.20 | Ratio of the (002) disk center to the disk radius as a function of the condenser aperture.

Figure 4.21 | Disk radius as a function of the condenser aperture.

Fig. 4.22 | Experimental vs calculated CBED pattern. a, Simulated CBED pattern
using the calculated condenser aperture and momentum pixel spacing. b, Experimental CBED pattern

**Figure 4.23 | Calculated Momentum Transfer.** a, Momentum transfer as a ratio of the beam momentum in the X direction. b, Momentum transfer as a ratio of the beam momentum in the Y direction

**Figure 4.24 | Efficiency of four thickness measurement algorithm**

**Figure 4.25 | Calculated sample thickness after comparison with simulated CBED patterns**

**Fig. 4.26 | Measured sample thickness by EELS.** a, Measured sample thickness in the center region of the sample showing an average thickness of 25nm. b, Measured sample thickness at the edge of the FIB sample

**Figure 4.27 | Time of flight of relativistic electron inside the sample**

**Figure 4.28 | Calculated Electric Field.** a, Electric Field in the X direction. b, Electric Field in the Y direction

**Figure 4.29 | Calculated potential from DPC.** a, Calculated potential using the Findlay formula. b, Calculated potential using the Lazic formula

**Fig: 4.30 | Brightfield STEM Images of a long acquisition.** a, BF-STEM image captured before the experiment. b, BF-STEM image captured during the experiment. c, BF-STEM image captured after the experiment

**Fig. 4.31 | Center of Mass shift in the X direction.** a, BF-STEM images simultaneously captured. b, Measured center of mass shift of the central (000) disk in pixels in the x direction, where the y direction is the long axis and the x direction is the short axis. c, Measured center of mass shift multiplied by the momentum space pixel size to map the $\vec{k}$ vector transferred to the central undiffracted beam along the x direction

**Fig. 4.32 | Center of Mass shift in the Y direction.** a, BF-STEM images simultaneously captured. b, Measured center of mass shift of the central (000) disk in pixels in the y direction, where the y direction is the long axis and the x direction is the short axis. c, Measured center of mass shift multiplied by the momentum space pixel size to map the $\vec{k}$ vector transferred to the central undiffracted beam along the y direction

**Fig. 4.33 | Thickness Measured by comparing with simulated CBED patterns**

**Fig. 4.34 | Measured potential change in the sample**
Figure 4.35 | First principles calculation of 180° walls in Ca₃Ru₂O₇. a, Density of states for the left domain, domain wall and the right domain. b, Theoretically calculated crystal structure of a 180° domain wall in Ca₃Ru₂O₇. (Danilo Puggioni and James Rondinelli, Northwestern University) ..................................................108

Figure 4.36 | Electron accumulation at different possible 90° domain boundary configurations in Ca₃Ru₂O₇ (Danilo Puggioni and James Rondinelli, Northwestern University) ........................................................................................................................................109

Figure 4.37 | Calculated potential at charged and uncharged 90° domain walls in Ca₃Ru₂O₇ (Danilo Puggioni and James Rondinelli, Northwestern University) ....110
ACKNOWLEDGEMENTS

I would first like to acknowledge my advisor, Dr. Nasim Alem for mentoring me both as an electron microscopist and as a scientist. Her timely feedback and prompt corrections was probably the single biggest reason I finished my PhD. Additionally, I have been extraordinarily lucky to have been a part of Penn State MRSEC IRG1, whose leader Dr. Venkatraman Gopalan has been the scientific driving force behind my PhD. Venkat always pushed me to be a better scientist, to analyze my data more thoroughly, and ensured the final product remained impeccable. My committee members Roman, Vin and James were sources of knowledge and I was lucky to have a committee whom I could have a chat with anytime of the day, and who were always ready and eager to help out.

I was also fortunate to have been mentored early on in my graduate career by Dr. Greg Stone, who taught me electron microscopy, coding and how to be a grad student. Numerous friends over the course of my graduate school career, including Jason Lapano, Steve Weitzner, Steve Juhl, Amin Azizi, Jason Munro, Parivash, Shruti, Anushka, Tanushree, Leixin, Kleyser, Matt Brahlek, Matt Gadinski made me the grad student I am today, and immensely enriched my time at graduate school.

And finally, to my wife Ritu, who was there with me every step of the way.

This work was funded by the National Science Foundation MRSEC program at Penn State – the Center for Nanoscale Science through the grant no. 1420620. However, this work does not reflect the positions or the opinions of the federal funding agencies.
1. Introduction

1.1 Ferroelectricity

1.1.1 Definition of ferroelectrics

Ferroelectrics are a class of materials that possess a spontaneous, switchable electrical polarization\(^1\). Thus analogous to ferromagnets, the ferroic order in these systems is related to the electrical rather than the magnetic polarization, and the polarization demonstrates a hysteresis loop as a function of the external, applied electric field\(^2\). This similarity extends further, with the ferroic order disappearing above a certain temperature – the Curie temperature for ferromagnets\(^3\)–\(^5\).

The first ferroelectric that was discovered was Rochelle salt in 1928, and in the following years several more such systems including KDP (Potassium Dihydrogen Phosphate), ADP (Ammonium Dihydrogen Phosphate) which is an antiferroelectric was also
discovered\textsuperscript{1,6,7}. The initial research interest in ferroelectrics was motivated by their piezoelectric properties\textsuperscript{8,9}. Ferroelectrics are also ideal piezoelectrics, and the piezoelectricity made them an attractive material for sonar sensors\textsuperscript{10}. One of the first results of such a concentrated search was the discovery was Barium Titanate – BaTiO\textsubscript{3} – a ferroelectric that is still in use today\textsuperscript{11}.

1.1.2 Explanation of ferroelectricity

The development of X-Ray diffraction techniques led to the first concerted studies into understanding the mechanism of ferroelectricity\textsuperscript{12}. What became fast clear that all known ferroelectrics lacked inversion symmetry in their crystals, and the first idea explained ferroelectricity as the consequence of non-coexistent positive and negative charges in the unit cell\textsuperscript{1}. It was also observed that the vast majority of ferroelectrics discovered belonged to the perovskite class of crystals – where the prototypical crystal is represented by the crystal formula ABO\textsubscript{3} where A atoms refer to the corner atoms, B atoms refer to the body atoms and the O atoms are oxygens, which occupy the face centers. The six oxygen atoms thus form the six corners of an octahedron – thus the perovskite crystal can also be defined as an oxygen octahedron, with the B atom sitting at the center of this oxygen octahedron as shown in Fig. 1.1.
Figure 1.1 | Polar Displacements in Ferroelectrics. Left – Centrosymmetric ABO$_3$ crystal structure with the B site atoms at the center of the blue oxygen octahedral. Right, Non-centrosymmetric structure with the B site atoms displaced, with the displacements marked by the black arrows.

Extending this understanding further – it was also observed that the B atom displacements were often the driving factor behind ferroelectricity – thus the B atoms, which were displaced from the center of the oxygen octahedral were what led to the presence of an electrical polarization – and hence ferroelectricity. These displacements are also referred to as the second order Jahn-Teller displacements$^{13-15}$.

This explanation was extended in the early nineties by Resta and Vanderbilt$^{16-18}$, and is known as the modern theory of ferroelectricity. The modern theory of ferroelectricity defines a Berry phase known as the Born effective charge, which is a tensor$^{19,20}$. The vector multiplication of the effective charge tensor with the displacement vector leads to the electric field. This approach has proved itself an enormously powerful to classify and predict ferroelectrics, with several pioneering first principles calculation making successful ferroelectricity predictions even before experiments could follow.

1.1.3 Hybrid Improper Ferroelectrics
The most successful of the theoretical predictions based on first principle calculations was the phenomenon of hybrid improper ferroelectricity\textsuperscript{21–23}. Ferroelectrics which has the canonical formula of ABO\textsubscript{3}, and have a prototypical centrosymmetric high temperature perovskite phase have their ferroelectricity originate as a consequence of atom displacements. However, atom displacements are not the only factor behind generating a polar crystal structure.

![Diagram of ABO\textsubscript{3} crystal structure with tilt leading to non centrosymmetry](image)

**Figure 1.2 | Tilt leading to non centrosymmetry.** Octahedral tilts resulting in A site displacements in alternating layers.

Octahedral tilts can also make an unit cell lose their inversion center. However, for ABO\textsubscript{3} crystal systems these non-centrosymmetric moments cancel each other out. If on the other hand, an even number of oxygen octahedral can be isolated and separated from other even layers of oxygen octahedral, then the total polar moment residing in each isolated octahedral layer remains uncompensated, and the resulting crystal structure becomes polar. Two popular approaches for isolating even tilted octahedral layers have
been through isolation through rocksalt layers between the octahedral layers, or through the addition of a different crystal structure between the octahedral layers – the so-call superlattice. The first approach results in crystals that belong to the Ruddlesden-Popper family of crystals. Ruddlesden-Popper crystals with an even number of oxygen octahedral layers can be represented by the canonical formula

\[ A_{n+1}B_nO_{3n+1} = (ABO_3)_n + AO \]

Where the ABO₃ refers to the octahedral perovskite layers, n refers to the number of perovskite blocks between the rocksalt layers, and AO refers to rocksalt layers.

\[ A_1B_2O_7 = 2(ABO_3)_2 + AO \]

**Figure 1.3 | Ruddlesden-Popper Structure.** Ferroelectricity originating due to octahedral tilts in two perovskite blocks separated by a rocksalt layer
Two compounds from the Ruddlesden-Popper family of oxides have been demonstrated as ferroelectric – Ca$_3$Ti$_2$O$_7$ and Ca$_3$Mn$_2$O$_7$, thus providing an experimental demonstration of this novel pathway for ferroelectric material formation$^{24-26}$.

1.1.4 Ferroelectric Domain Walls

Ferroelectricity, like ferromagnetism is one of the four possible ferroic orders possible in material systems – with the other two being ferroelasticity and ferrotoroidicity$^{2,27-29}$. By definition, a ferroic order is associated with an order parameter which is a tensor, and this tensor can reverse upon the application of an external driving force. For ferroelectrics, this order parameter is the electrical polarization, with an externally applied electrical field being the external driving force. This results in the presence of hysteresis loops. The two extremities of the hysteresis loop, associated with a maximum in the electrical polarization are thus equally possible energetically in the crystal.

This results in the unique possibility in some crystals of the presence of multiple polarization directions existing simultaneously$^{30}$. However, these multiple possible electrical polarizations directions are not spatially coexistent, but are rather associated with a certain geographical area, with a well-defined boundary between the differing polarization regions.

Borrowing from the terminology of ferromagnets, regions of equidirectional polarization are referred to as domains, and their associated boundaries referred to as domain walls. Contrary to ferromagnets however, ferroelectric domain walls are only a few nanometers in width, and possess crystallographic structure that is absent in the bulk domain$^{30}$. Additionally, if the electrical polarization vectors have uncompensated components
perpendicular to the domain wall, then following Gauss’ law, these domain walls may be associated with local charge accumulation\textsuperscript{31,32}. Charged domain walls were first discovered using conductive Atomic Force Microscopy (c-AFM) in BaTiO\textsubscript{3} and have been demonstrated in systems as diverse as Ca\textsubscript{3}Ti\textsubscript{2}O\textsubscript{7} and EuMnO\textsubscript{3}\textsuperscript{25,33,34}. Recent studies have demonstrated the presence of conducting two-dimensional electron gas (2DEG) at such walls which now results in the novel possibility of engineering local interfaces in bulk oxides with properties distinct from the rest of the crystals\textsuperscript{34}.

1.1.5 Applications of ferroelectrics

The primary application of ferroelectrics have remained what originally drove interest in these unique materials during the Second World War – they are exceptional piezoelectrics. In addition, ferroelectrics have been proposed as promising candidates for non-volatile memory, and analogous to racetrack memory in ferromagnets, ferroelectric domain walls can be used as memory elements too\textsuperscript{35–37}.

Figure 1.4 | Schematic of ferroelectric RAM. \textit{Courtesy Fujitsu}
Many ferroelectric materials, such as LiNbO$_3$, KNbO$_3$ are also strongly non-linear in the optical to near-infrared region due to their lack of inversion centers$^{38-40}$. Domain engineered crystals with alternating polarization directions are routinely used as second harmonic generation sources through quasi phase matching$^{40}$. In fact, the use of LiNbO$_3$ is so widespread in photonics, that it has also been called the “silicon of photonics”$^{41}$. 
1.6 Research questions

Figure 1.5 | Rotational domain wall in PbTiO$_3$.

Several recent advances in this field have however demonstrated that multiple fundamental questions in the field remain unanswered. The original idea of the structure of domain walls was developed by Ising, and eponymously named the Ising wall$^{42-44}$. The underlying idea is that displacements are energetically allowed only along the order parameter axes, so for a 180° domain wall, where the electrical polarization and the atom displacements reverse in direction the polarization decreases linearly in magnitude as it approaches the wall, becomes zero at the wall, and then increase monotonically in the opposite direction after crossing the wall. However, several recent theoretical and experimental studies have made this simplistic picture doubtful. Non-Ising walls, also referred to as Néel and Bloch walls, where the polarization rotates across the wall rather than decreasing in magnitude, have been theoretically predicted in PbTiO$_3$ as shown in Fig. 1.5 and experimentally observed in Pb(Zr,Ti)O$_3$ as demonstrated in Fig. 1.6$^{45,46}$. 
Another recent question that arises from the duality of displacements and electrical polarization – can ferroelectric displacements exist in a metal, which would conventionally screen the electrical polarization? This intriguing possibility, first raised by Anderson and Blount, have been recently observed experimentally both in a proper ferroelectric crystal structure – LiOsO$_3$ and a hybrid improper ferroelectric crystal.
structure – Ca$_3$Ru$_2$O$_7^{47–52}$. Even domain walls have been observed in both systems, which now raises the possibility of a local charge accumulation in a metallic crystal.

1.2 Transmission Electron Microscopy

1.2.1 Description of the TEM

The fundamental idea underpinning microscopy with electrons is based on de-Broglie’s insight – every particle is also associated with a matter wave, and the wavelength of such a matter wave is inversely proportional to their momentum, expressed as the classic equation, where $\lambda$ is the wavelength, $p$ is the momentum and $h$ is the Planck’s constant.

$$\lambda = \frac{h}{p}$$

While electrons are relativistic particles. Their momentum is however still relatively linear with accelerating potentials, and thus at high enough potentials, the resultant electron wavelength can be made really small – for an accelerating potential of 200kV, the electron wavelength is as small as 2.54pm.

In comparison, the optical wavelength is of the order of hundreds of nanometers, and thus the possible resolution in a TEM is orders of magnitude smaller than a light optical microscope. Additionally, while atomic nuclei are of the order of femtometers, ionic radii of most ions are of the order of angstroms, thus allowing imaging of individual atom columns in the electron microscope.

Modern electron microscopy has progressed in two almost parallel tracks – scanning electron microscopy (SEM) and transmission electron microscopy (TEM). In SEM an
electron beam is rastered across a sample surface and the surface is imaged by forming an image from the scattered electrons.

In TEM conversely, the electrons are transmitted through the sample – and these transmitted electrons are subsequently used for imaging. While this places significant

**Figure 1.7 | Cross-section of modern TEM.** From the top the electron gun, followed by the monochromator, the condenser lenses, the specimen holder, followed by the objective lens, the aberration correctors and the projector lenses. A CCD or a CMOS detector is below the projector lenses. *(courtesy FEI)*
constraints on sample preparation (sample thickness < 100nm), the advantages are better resolution, and spectroscopy through both X-Rays (Energy Dispersive X-Ray Spectroscopy) and energy loss (Electron Energy Loss Spectroscopy).

The modern TEM can be operated in two distinct modes – the scanning mode also known as Scanning TEM or STEM, and the conventional TEM (CTEM mode). In the CTEM mode, a wide an approximately parallel beam is used to illuminate the thin sample. The atomic potential interferes with the electron wavefront and the coherent interference leads to formation of images due to interference pattern. Thus atomic columns is CTEM images are also often referred to as lattice fringes.

In the STEM mode, a converged beam is rastered across the sample, and the beam undergoes a combination of both coherent and incoherent scattering effects. The scattered electron beams are collected with ring shaped annular detectors. While coherent scattering mostly occurs at lower scattering angles, incoherent scattering occurs mostly at higher scattering angles. Images formed from incoherently scattered electrons with the scattering angles being greater than 80-90 mrad are also referred to high angle annular dark field scattering (HAADF) STEM images. Since electron scattering does not occur in vacuum, vacuum is dark while atom columns are brighter. Since incoherent scattering is predominantly due to Rutherford scattering, the scattering angle and hence the intensity is almost linearly proportional to the charge of the nucleus – leading to what is also known as Z contrast imaging.

One of the primary drivers behind aberration correctors has been the development of spherical aberration correctors for the STEM probe. While the probe size determines the final resolution of the STEM image, the probe size itself is dominated by spherical
aberrations. At an accelerating voltage of 200kV, a non-aberration corrected probe has a probe diameter of approximately 150pm, while the best aberration corrected probes routinely reach probe sizes of 50pm. To note, the Bohr radius of the hydrogen atom is 52pm, and thus modern aberration corrected HAADF STEM allows the direct visualization of atom columns and their relative displacements.

1.2.2 Applications to ferroelectrics

One of the major achievements of the modern theory of polarization has been to provide a theoretical description of how the ferroic order parameter in ferroelectrics is expressed as atomic displacements. This has been confirmed through X-Ray diffraction measurements with a very high degree of accuracy. However, a noted shortcoming of using such an approach is that it cannot provide an understanding of the local crystal structure in the vicinity of interfaces and domain walls.
Initial transmission electron microscopy experiments before the discovery of aberration correction focused on using transmission electron microscopy to deduce the polarity through electron diffraction and using diffraction contrast to calculate the width of domain walls, as shown in the CTEM imaging of BaTiO$_3$ domains$^{53}$. However, the advent of spherical aberration correctors have revolutionized the imaging of ferroelectrics in the electron microscope.
Figure 1.9 | Visualization of polar displacements with aberration corrected STEM. 

a, Visualization of vortex nanodomains in BiFeO$_3$ thin films grown on TbScO$_3$ substrates by molecular beam epitaxy. The images refer to the polarization vectors overlaid on the ADF-STEM image, and the magnitude and the angle of the polarization vectors. 

b, Visualization of polar vortices in PbTiO$_3$-SrTiO$_3$ superlattices by aberration corrected STEM.

Pioneering TEM experiments in recent years have demonstrated the possibility of using TEM to measure the ferroic order parameters in BiFeO$_3$ thin films, YMnO$_3$ bulk crystals, polar vortices in oxide superlattices and ferroelectricity in lutetium ferrite superlattices to name a few as shown in Fig. 1.9$^{54-59}$. Most of these experiments were performed with HAADF-STEM imaging with the observed atom position was supersampled above the Nyquist-Shannon sampling limit, which was then subsequently refined to perform sub-pixel precision displacement measurements.
2. Determination of atom positions

2.1 Introduction

The development of spherical aberration correction for Scanning Transmission Electron Microscopy (STEM) imaging has enabled us to achieve sub-angstrom resolution. Several pioneering STEM experiments in recent years have demonstrated the feasibility of aberration-corrected STEM as a great technique not only for direct visualization of atom positions but also for quantitative sub-angstrom structural measurements. While the typical aberration corrected STEM probe has a diameter of approximately fifty picometers, super-sampling probe positions below the Nyquist-Shannon sampling limit and the subsequent fitting of the probe image with a two-dimensional Gaussian peak for the sub-pixel assignment of atom column positions allows picometer precision metrology of crystal structures from STEM images. This technique has been used for atomic
displacement measurements across thin films and 2D crystals, and domain boundaries and has enabled the experimental observation of novel structural phenomena such as polar vortices\textsuperscript{54,57,58,73,74}.

While Gaussian peak fitting of atom columns is an extraordinarily powerful technique for quantitative measurements, one noted shortcoming of this approach is that it assumes well separated atoms with no overlap or negligible aberrations in the beam – conditions that are only available under a certain limited set of imaging conditions\textsuperscript{54,57}. Typically, such an imaging setup uses an annular detector with the outer and inner circles centered at the microscope optic axis. Such a configuration will have an inner collection angle of approximately 85-90 mrad to capture only incoherently scattered electrons, and is conventionally referred to as High Angle Annular dark Field STEM (HAADF-STEM) imaging\textsuperscript{63,75}. The dark field refers to atoms being bright from scattering electrons with the vacuum being dark. Incoherent electron scattering at high angles is a consequence of the Rutherford scattering where the electron is scattered due to nuclear Coulombic forces\textsuperscript{76,77}. Since the Coulombic force is directly proportional to the number of protons in the nucleus, HAADF-STEM images generate highly Gaussian peaks with an almost linear relationship of intensity with the atomic number (the so-called \textit{Z} contrast imaging)\textsuperscript{78–80}.

\textit{Z}-contrast imaging conversely renders this technique unsuitable for imaging lighter elements such as oxygen, boron or carbon\textsuperscript{58,74,75}. However, structural metrology for many scientifically important material systems like ferroelectrics needs the imaging and quantification of lighter atoms as well as heavier elements\textsuperscript{1,20}. This problem can be significantly mitigated in Brightfield Field STEM (BF-STEM) imaging, where compared
to annular detectors a circular detector is used with the detector center coinciding with the optic axis of the microscope. The conventional collection angle in BF-STEM imaging can extend up to 15mrad, which is significantly lower than the inner collection angle for HAADF-STEM\textsuperscript{81,82}. Because unscattered electron beams are captured by this technique, vacuum is bright while atom positions have comparatively lower intensity. The ideal BF-STEM image would thus have an intensity profile complementary to the images obtained from HAADF-STEM imaging. However, in reality owing to coherent scattering effects due to low collection angles, atom positions are blurrier from aberrations that are more prominent in BF-STEM images\textsuperscript{83}. Additionally, since BF-STEM images capture both light and heavy atom positions the inter-atomic distances are substantially smaller. These effects result in atom positions that are non-Gaussian in shape, and often have intensity overlaps from neighboring atom intensity tails making position metrology challenging in BF-STEM images.

2.2 Fitting Atom Positions with Gaussians

A typical scanning transmission image approximately has 2048 X 2048 or 4096 X 4096 scan positions, with each scan position corresponding to an image pixel. The best modern aberration corrected microscopes can generate beam sizes that are of the order of 0.5 Å, or 50pm. Super-sampling the beam by a factor of five results in scan positions about 10pm apart from each other. In HAADF-STEM images with no visible oxygen atom columns, inter-atomic distances are of the order of 1.5 Å with the atomic potential extending out to almost an angstrom. This creates well-separated atom columns that can be approximated with a two-dimensional Gaussian intensity profile with a FWHM of
about 50-75pm. Given this condition, one can quantitatively determine the atom positions as the peak of the Gaussian intensity profiles with accuracies approaching 0.5pm\textsuperscript{57,72}. It is this combination of aberration-corrected imaging and Gaussian peak fitting that has enabled modern electron microscopy to quantitatively measure the structural distortions at the domain walls, grain boundaries, and defects with single picometer precision, making STEM imaging so powerful.

**Figure 2.1 | Errors with the single Gaussian approach.** a) BF-STEM image of LiNbO\textsubscript{3} with the intensity minima marked by red circles. b) BF-STEM image shown in Fig. 1a with intensity minima in red, and fitted single Gaussian peak centers in yellow. c) Summed intensity value from the region marked by the black rectangle in Fig. 1a and Fig. 1b with the blue curve showing the intensity profile, the red arrows corresponding to the intensity minima and the yellow arrows corresponding to peak positions obtained from fitting a single Gaussian.

The described approach, however, runs into problems when applied to BF-STEM imaging. In Fig. 2.1a, we show a typical BF-STEM image of LiNbO\textsubscript{3} with 4.9 pm
scanning pixel size. The bright regions correspond to vacuum while the darker regions are the niobium and oxygen atom columns, with the red dots corresponding to the intensity minima of the atomic columns. While the intensity minima can be used as an initial estimate of atom positions, the error in such a measurement is at least of the order of the pixel size (~5 pm in our case), and thus an order of magnitude worse than the best HAADF-STEM results. Fig. 2.1b demonstrates the intensity minima with red points, and the refined atom positions (yellow points) obtained from fitting the intensity distribution with a Gaussian peak. The yellow points are the intensity minima of the fitted Gaussian peaks into the raw atomic intensity columns. A visual estimation shows that the fitted Gaussians do not reliably converge on the atom positions, and are often tens of picometers away when the intensity minima is weak, or the neighboring atom is close.

This can be understood by profiling the summed intensity distribution (Fig. 2.1c) from the region shown by the black rectangle in Fig. 2.1b. The red arrows correspond to the intensity minima, while the yellow arrows correspond to the refined atom positions after Gaussian fitting. The presence of an atomic intensity tail from a neighboring atomic column can give rise to a multiple dips in the intensity away from the original minima as artifacts. Due to such an intensity artifact, the atomic Gaussian peak fittings may converge to a local minima arising from the intensity artifacts rather than the actual atomic columns. This scenario can be seen in the intensity line profile in Figure 1c at the pixel distance “16” in the x-axis, where the yellow arrow shows the spacing between two atom columns as the refined atom position.

Previous BF-STEM imaging has attempted in circumventing such issues by using a multi-parameter single-Gaussian peak, or performing image metrology through
multivariate statistics rather than fitting each individual atomic column\textsuperscript{58,74}. Both approaches require an initial knowledge of the crystal structure being imaged. Multi-parameter single-Gaussian fits also need an estimation of the approximate number and position of the nearest neighbors. Thus this may not be a robust technique as it necessitates different fitting equations for different images. Here, we propose a novel multi-Gaussian refinement routine – MPFit - that does not require knowledge of the crystal structure and can accurately refine a wide variety of images by deconvoluting a subsection of the image (atomic column) into multiple overlapping two-dimensional Gaussians. The benefit of this technique mostly shows itself in BF-STEM images where the image can suffer from aberrations and overlapping atomic columns. Since HAADF-STEM imaging refinement requires less stringent conditions, our algorithm extends equally well to such images too.

\textbf{Figure 2.2} | Schematic of the Procedure. Red circles correspond to intensity minima or maxima for BF-STEM and ADF-STEM images respectively.
The smaller squares surrounding the red dot refer to the nearest neighbor cutoff region while the yellow crosses refer to the refined atom positions.

2.3 The MPFit algorithm

A Gaussian curve is a centrosymmetric curve with wide uses in single processing for approximating symmetric impulse functions. Thus, single-Gaussian processing of well-separated atoms works well if we have minimal image aberrations and symmetric atom column projected potentials. Moreover, it has been demonstrated that given a sufficiently large number of Gaussians, any non-infinite signal can be approximated as a sum of overlapping Gaussians\textsuperscript{84,85}. In our algorithm, this insight is extended into two dimensions by first modelling our observed atom intensity as a sum of overlapping Gaussians. The second key idea is to recognize that not all Gaussians that are approximating the region of interest are in fact originating the atom column whose position we are trying to refine. Thus the Gaussians are subsequently sorted and only a subset of the Gaussians that approximate the atom position are used to refine the atom. The flow chart of our algorithm is illustrated in Figure 2.2. The steps of the MPFit algorithm can be described as:

1) \textit{Get intensity minima/maxima}: The initial starting point of this algorithm are the intensity minima for BF-STEM images and intensity maxima for ADF-STEM images. The robustness of the algorithm allows the use of both.

2) \textit{Calculate median inter-neighbor distance}: Following the identification of intensity minima the median inter-peak distance is calculated.

3) \textit{Get region of interest}: The region of interest is cutoff as a square with the intensity minima as the central pixel, and the sides of the square given by:
\[ s = \eta + 1 \]

Where \( s \) is the side of the square and \( \eta \) is the nearest even number to the median inter-peak distance. Thus the \((\eta/2 + 1, \eta/2 + 1)\) pixel in the square is the intensity minima that were the original starting point.

4) *Fit iteratively with Gaussians:* The region of interest is then fitted by a single parameter Gaussian with a user determined tolerance factor. The fitted Gaussian is subtracted from the original region of interest, and the residual is subsequently fitted again. This process continues for a pre-determined number of iterations, with the sum of all the Gaussians then subsequently representing the atomic intensity in the original square. The number of iterative Gaussians is the more important factor and leads to reasonable accuracy of the processed images. In this work, the processed images were obtained using a tolerance of \(10^{-8}\) and 12 iterative Gaussians.

5) *Sort peaks and get refined position:* The Gaussian peaks for each atomic column are then subsequently sorted based on their distance from the original minima with only peak positions whose distances less than half the nearest neighbor distance used for refinement. The refined atom position is then amplitude normalized peak position of all the selected Gaussians.

6) *Repeat steps 1-5 with refined positions:* Steps 1-5 are repeated one more with the new starting point being the refined peak position rather than the initial minima used for the first set of calculations. Repeating the process significantly reduces the error of the fit and spread of atom positions.
2.4 Results and Discussions

Figure 2.3 | First refinement stage of multi-peak fitting. a) BF-STEM image with the red circles corresponding to intensity minima. b) Evolution of Gaussian peak fit corresponding to the region marked by the black square in Fig. 2.3a. c) Raw data corresponding to region marked by the black square in Fig. 2.3a. d) Contribution of Gaussian peaks from the fitted atom. e) Contribution of neighboring atoms as intensity tails. f) Summation of all peaks with an intensity profile similar to Fig. 2.3c.

Figure 2.4 | Second refinement stage of multi-peak fitting. a) BF-STEM image with the red circles corresponding to intensity minima, and green circles corresponding to the positions from the first fitting stage. b) Evolution of Gaussian peak fit corresponding to the region marked by the black square in Fig. 2.4a. c) Raw data corresponding to region marked by the black square in Fig. 2.4a. d) Contribution of Gaussian peaks from the fitted atom. e) Contribution of neighboring atoms as intensity tails. f) Summation of all peaks with an intensity profile similar to Fig. 2.4c.
Using the MPFit algorithm, we have successfully obtained the refined atom positions in BF-STEM LiNbO$_3$ image (Fig. 2.3a). Starting from the identification of the intensity minima for each atom column, the median inter-peak distances were calculated. This measurement gives the obtained value for each square size to be 41.6173 pixels, resulting in “$\eta$” of 42 and “s” value of 43 pixels. This measurement gives a square of 43 X 43 pixels for one atom column as indicated by a black square in Fig. 3a. To fit the atom position in this region, the intensity of the atomic column was fitted through a succession of 12 Gaussians, with Fig. 3b showing the evolution of the Gaussian sum as the iteration count increases. For the region denoted with a black square, Fig. 3c demonstrates the raw experimental data in color, Fig. 3d shows the Gaussian peak contributing to the atom column, and Fig. 3e shows the tail values of the neighboring atoms. Visual examination of the sum of the raw data with the sum of the Gaussians (tail and main fitted atom) shown in Fig. 3f confirms the similarity between the two fits. Additionally, we observe the distance between the refined atom position (green dot) and the intensity minima (red dot) in Figure 3f to be of the order 4 pixels. Considering that the pixel size is of the order of 5pm, we observe 20 pm of peak shift as a result of peak refinement. This significant modification of the atomic peak position demonstrates the need of peak refinement since metrology with intensity minima can subsequently result in significant displacement errors on the order of tens of picometers. The refined peak position in Fig. 2.3f is used as the initial calculation point for a second peak refinement process as described above.
**Figure 2.5 | 3D representation of peak evolution.** a) Raw data, atom contribution as fitted data, intensity tails, and the sum of fitted data and tails for the first stage of multi-peak fitting. b) Raw data, atom contribution as fitted data, intensity tails, and the sum of fitted data and tails for the second stage of multi-peak fitting.

The red circle shows the initial minima that we started with, while the green circles in Fig.2.3c-f refers to the fitted positions that are independent of tail contributions. These refer to the first fitting stage. Going further, these first fitted positions are now used for the subsequent fitting stage, with the first fits now used as the initial calculation starting point rather than intensity minima.

This two-stage fit allows for a more precise determination of the median nearest neighbor distance and a more precise starting point compared to intensity minima which are more sensitive to noise and intensity fluctuations.

The same region of the LiNbO$_3$ image is now shown in Fig. 2.4a with the red points referring to the intensity minima and the green points referring to refined peak positions.
obtained after the first stage of fitting. Using the green data points, the new median nearest neighbor distances are recalculated to be 40.8426 pixels, modifying the new calculation box to be 41X41 pixels across. Unlike the first stage of the fit, with the region of interest centered on the intensity minima, the region of interest is now centered on the refined atom positions (green dots) resulting from the first refinement. From here, we proceed in a similar fashion, with a succession of 12 Gaussian peak iterations used to deconvolute the region of interest (Fig. 2.4b). Then the Gaussian peaks are subsequently sorted to get the final refined position shown by the blue dot in Fig. 4c-f. Compared to the first refinement stage, the second stage generates a refined atom position that is often less than a pixel away from the initial starting position, demonstrating how an additional iteration step is superior to using intensity minima and can significantly reduce the error of peak positioning.

Figure 2.6 | Comparison of peak fits. a) Intensity minima and first stage fitted peaks overlaid on the BF-STEM image as red and green circles respectively. b) Intensity minima, first stage and second stage fitted peaks overlaid on the BF-STEM image as red, green and blue circles respectively. c) Intensity minima, first stage, second stage fitted peaks and positions obtained from a single Gaussian overlaid on the BF-STEM image as red, green, blue and yellow circles respectively.
Figure 2.5 demonstrates the 3D evolution of the region of interest refined in Fig.3 and Fig.4, with the intensities inverted to aid visualization. The intensities are scaled from 0 to 1, and as the refined peak demonstrates the intensity of that peak is only 0.2, while the tail intensities are often significantly higher, demonstrating why a single Gaussian peak fitting approach often fails to converge to the atom position.

Fig. 2.6 shows how the atom peak positioning evolves with the initial intensity minima (red), the first fit of peak refinement (green), the second fit (blue), and the single Gaussian approach (yellow). As this figure shows, when the atom positions are well-separated with no intensity tail leaking into the neighboring atom columns, the single Gaussian and the multi-Gaussian approach converges to the same solution. However, in the case of neighboring intensity distributions merging into each other, the single Gaussian peak often converges to an intensity position between the atom columns, while the MPFit algorithm can separate and precisely position the neighboring atom columns.

**Figure 2.7 | Comparison of single versus Multi-Peak Fitting.**

a) Position difference between the fitted peaks obtained from a single Gaussian fit with respect to the intensity minima.

b) Position difference between the fitted peaks obtained from the first phase of a multi Gaussian fit with respect to the intensity minima.

c) Position difference between the fitted peaks obtained from the second phase of a multi Gaussian fit with respect to the intensity minima.
To statistically visualize the comparison with the single Gaussian fit versus the MPFit algorithm, the distances between the intensity minima and the fitted positions are plotted in Fig. 7. As Fig. 7a demonstrates while the majority of atoms converge to positions close to the original intensity minima, a specific subset don’t converge, leading to the rectangular shaped clustering of peak distances. Even the first phase of the MPFit algorithm almost completely eliminates this issue as can be observed in Fig. 7b, while using the second phase of refinement, where our initial starting position was the refined atom positions after the first phase, the refined atom positions are tightly clustered around the initial intensity minima, demonstrating how this approach is impervious to the effects of intensity tails from neighboring atoms.

Through the first step of peak fitting, the error associate with converging the data and generation of rectangular-shaped clustering of peak distances is eliminated. However, we see a larger spread between the refined points and the initial minima arising from the contribution of atomic tails introducing errors. Going through the second step multi-peak fitting, the refined atom positions are tightly clustered back around the initial intensity minima, demonstrating how the MPFit algorithm can precisely identify and position the atomic columns and is impervious to the effect of intensity tails from the neighboring atoms.

2.5 Conclusions

Single Gaussian peak fitting approach can adequately determine atomic column positions for the majority of S/TEM experiments when image aberrations are minimal and the neighboring atom columns are well separated with no overlap. This method, however,
fails to converge to atom solutions leading to erroneous results for certain non-ideal imaging conditions, such as the neighboring atom columns whose intensities merge into each other. Here we present a few Multi-Peak Fitting approach, MPFit that can precisely separate the neighboring atomic columns and eliminate the contribution of the neighboring atomic column intensities from the atomic column of interest. While the result from MPFit and single Gaussian refinement are identical for well-separated atoms, the MPFit algorithm can successfully resolve the atom positions that fail to converge through single Gaussian peak fitting approaches. While single Gaussian peak fitting, can determine the atom column positions for HAADF-STEM images with round and well-separated atomic columns, MPFit can successfully separate and determine the atom column positions in for BF-STEM images with aberrations and atomic intensities merging into each other.

Additionally, it has to be kept in mind, that even with parallelization implemented, the MPFit algorithm solves for 24 Gaussians compared to one for the single Gaussian approach thus making it run an order of magnitude slower.

Future planned improvements include solving for neighboring peaks simultaneously using the tail functions to deconvolve the full obtained image as an independent set of impulse functions originating from individual atoms. Additionally, atom columns whose separation distances are below the resolution limit of the microscope may be particularly suited for the approach, to enable the super-resolution imaging of atom positions with the electron microscope.

In the next chapter we utilize the atom position fitting techniques described here to directly measure with sub-pixel precision the picometer scale displacements of individual
niobium and oxygen columns in the ferroelectric crystal – LiNbO$_3$. Our techniques enable the visualization of domain boundaries in LiNbO$_3$, which closely match first principles theoretical predictions.
3. Domain Walls in Lithium Niobate

3.1 Introduction

Ferroelectric materials have a spontaneous and switchable electrical polarization, which is a consequence of the lattice distortions in the crystal structure that break inversion symmetry\textsuperscript{1,19,20}. This elegant link between crystal symmetry and ferroelectric polarization does an admirable job of predicting the possible ferroelectric polarization directions, or domains, and the associated domain walls\textsuperscript{28,30,86}. Here we demonstrate through aberration corrected scanning transmission electron microscopy experiments and first principles based molecular dynamic simulations how this symmetry derived polarization behavior is only an approximate even in hard uniaxial ferroelectrics like LiNbO\textsubscript{3} this symmetry derived polarization behavior is only approximate\textsuperscript{39,42}. STEM imaging shows the domain wall to be associated with polar distortions with increased local entropy up to tens of nanometers away from the wall. First principles calculations also demonstrate
increased local entropy from the non-Ising displacements at the domain wall as a consequence of the classic Goldstone sombrero potential associated with spontaneous symmetry breaking\textsuperscript{87}. Our results demonstrate presence of polar entropy in classical, proper ferroelectrics and further paves the way for an understanding of non-ideal polar behavior in other systems like relaxor ferroelectrics\textsuperscript{88}.

Symmetry provides a concise and mathematical description in crystals\textsuperscript{89}. Crystals could be classified into point groups and space groups, allowing a rapid prediction of the crystal properties just from the group of the crystal itself\textsuperscript{2}. The mathematics of symmetry has been the basis for the phenomenological theories of ferroelectricity developed originally by Landau and Ginzberg, and further by Devonshire\textsuperscript{11,90}. The explanation of the observable materials through symmetry-based arguments paralleled approaches in other fields like high energy physics and particle physics\textsuperscript{91}. However, even in the earliest days – discrepancies appeared in such theories. The predicted electric fields required to switch the ferroelectric polarization from a phenomenological approach are often orders of magnitude higher than experimental values due to local crystal imperfections and domain boundaries\textsuperscript{1,92,93}. Thus, the global symmetry is often only an approximate at a local scale – a lesson that is pretty consistent across multiple branches of physics.

The simplest symmetry-breaking event in a ferroelectric is a domain boundary – where the order parameter, the ferroelectric polarization or the cation-anion displacement, changes over a certain length scale\textsuperscript{86}. Phenomenological theories predict this change to monotonically occur over a few nanometers – or what is
classically known as the Ising wall\textsuperscript{42}. For LiNbO\textsubscript{3} which is a displacive ferroelectric, this occurs when both niobium and lithium cations displace from the centers of their neighboring oxygen octahedra (Fig. 3.1a) when the crystal is viewed from the \{1\overline{1}00\} zone axis\textsuperscript{12}. The face sharing oxygen octahedra are represented by the wire frames with both niobium and lithium atoms inside the octahedral. When viewed from the \{1\overline{1}00\} zone it is suitable to choose a two-dimensional unit cell that is one third of the size of the full LiNbO\textsubscript{3} cell along the \langle0001\rangle axis. This unit cell, represented by the gray box in Fig. 3.1a is further expanded in Fig. 3.1b with the oxygen displacements exaggerated for clarity. To further quantify the symmetry breaking across the domain wall, this unit cell is overlaid on the image to measure the relative displacement of oxygen and niobium centers of mass (indicated by cross) with respect to each other.

![Figure 3.1 | Schematic of experimental conditions. a, Lithium and niobium Jahn-Teller distortions with respect to oxygen octahedra when viewed from the \{1\overline{1}00\}](image)

...
zone axis, with oxygen atoms in red, niobium atoms in green and lithium atoms in blue respectively. b, Schematic of the unit cell for calculation of niobium-oxygen displacements, represented by gray shaded region in Fig. 1a, with the Ising and Néel niobium-oxygen displacements directions marked by the blue and red boxes respectively. The displacement magnitudes are exaggerated for clarity. c, Conventional transmission electron microscopy image of LiNbO$_3$ domain wall from the {$\{1\bar{1}00\}$} zone, with the domain wall marked by arrows. d, Selected area diffraction pattern for LiNbO$_3$ from the TEM image shown in Fig. 1d. e, BF-STEM image of the area marked by the black box in Fig. 1d, with the inset showing the niobium and oxygen positions. The arrows refer to the domain wall. Scale bar is 2nm. f, Simultaneous ADF-STEM of the area marked by the box in Fig. 1d, with the inset showing the niobium positions. The arrows refer to the domain wall location. Scale bar is 2nm.

3.2 Materials and Methods

3.2.1 Imaging and preparation of LiNbO$_3$ samples

Periodically poled single crystal congruent LiNbO$_3$ crystals with 6.7µm domain repetition were sourced from Deltronic Industries. Focused ion beam was used for sample preparation using a FEI Helios G2 system with a 30keV gallium ion beam used for sample lift–out with the domain walls lying edge on. The initial lift out sample was approximately 2 µm thick and 20µm X 20µm across. This were subsequently carbon welded onto copper V grids from Ted Pella, with the V notch deepened to a depth of around 100µm to prevent copper redeposition during ion beam milling. The welded sample was progressively thinned using a succession of lower voltage ion beams with the final polishing was performed with 0.5kV ion beams till the sample became electron transparent at an accelerating of 2kV to ensure that the sample was thin enough for imaging oxygen atoms$^{94}$. Following the preparation of electron transparent samples, LiNbO$_3$ foil is first imaged by conventional TEM (CTEM) mode, with the diffraction pattern in Fig 3.1e
demonstrating that the sample is being observed from the zone of interest - the \(1\bar{1}00\). The samples were imaged in the CTEM mode with a slight defocus (~5nm) for help in locating the domain walls through diffraction contrast. S/TEM imaging was performed with FEI Titan\(^3\) aberration corrected transmission electron microscope corrected for third order spherical aberrations. ADF–STEM imaging was performed using Fischione detectors at a camera length of 145mm with an inner collection semi–angle of 32mrad, and an outer collection semi–angle of 188 mrad. BF–STEM imaging was performed with Gatan detectors with an outer collection semi–angle of 15mrad. Simultaneous BF–STEM and ADF–STEM imaging was performed with fast scan directions oriented at \(-5^\circ\) and \(85^\circ\) with respect to the domain wall. The two image sets were combined and subsequently corrected for scan drift using a pre-developed procedure\(^{95}\).

To ensure that tilt does not play a role in the displacements measured through BF-STEM, we performed tilt simulations using the MacTempasX software, with the simulations demonstrated in Fig. 3.2a, as a function of increasing tilt angle. At zero tilt angle, as shown in Fig. 3.2b, the individual oxygen and niobium atoms can be easily distinguished from each other. However, as the tilt angle increases to approximately 30mrad in Fig. 3.2c, the oxygen and niobium atom intensities start merging with each other.

Considering, that our experimental BF-STEM images, in Fig. 3.1e demonstrate well separated oxygen and niobium atom centers, we can conclude that tilt plays a minimal role in the atom positions imaged in the current experimental setup.
3.2.2 Quantification of polar displacements:

Custom developed MATLAB scripts were used for finding the highest intensity spots as a first pass to estimate atom positions in ADF-STEM and inverted contrast BF-STEM images. Peak positions were subsequently refined by fitting a seven parameter Gaussian peak around the observed atom peak to get the refined atom positions. The refined peak positions were sorted into the representative unit cell (Fig. 3.1c), with displacements being calculated individually for each unit cell. The center of all the niobium atoms per unit cell was used to measure the niobium atoms, and a similar process was used to measure the oxygen center. The polar displacements...
were calculated as the vector leading from the oxygen center to the niobium center.

3.2.3 First Principles Calculations

First principles calculations were done using the density functional theory approximation as implemented in the Abinit software package, by our collaborator – **Dr. Sergei Prokhorenko**. We chose the libxc implementation of PBEsol GGA functionals to describe the exchange-correlation energy contribution, and the all-electron potentials were approximated using the optimized norm-conserving Vanderbilt pseudopotentials. The planewave kinetic cut-off energy was taken to be equal to 50 Ha and the Brillouin zone was sampled using a $6 \times 6 \times 6$ Monkhorst-Pack mesh of special k points. To determine the structure of the paraelectric $R\overline{3}c$ phase structure of LiNbO$_3$, we have considered a primitive 10 atom unit cell and performed a relaxation of atomic positions followed by an energy optimization with respect to changes both in lattice vectors and the reduced atomic coordinates under an imposed constraint of the fixed $R\overline{3}c$ space-group symmetry. The high-accuracy structural relaxation was performed until the calculated force magnitudes were less than $10^{-8}$ eV/Å and the absolute values of stress tensor components do not exceed $10^{-7}$ GPa. To determine the most important low-energy atomic displacements patterns we further performed the density functional perturbation theory calculations so as to identify low frequency phonon modes for the obtained ground-state.

3.3 Results and Discussions

3.3.1 Measurement of polar displacements in LiNbO$_3$

We use aberration-corrected S/TEM to image and probe the metrology of the domain walls in LiNbO$_3$. Following identification of the region of interest from conventional
TEM images (see Fig. 3.1c), the microscope was switched to the scanning mode, and simultaneous atomic resolution STEM images were obtained in both the BF and the annular dark field (ADF) modes (Fig. 3.1e-f). Since BF-STEM images can image both niobium and oxygen as opposed to ADF-STEM images, the displacement wall metrology was performed using BF-STEM images exclusively\(^{58}\). Oxygen-Niobium centers of mass were determined from the BF-STEM image within the chosen cell already presented in Figure 3.1b. The chosen unit cells throughout the BF-STEM image were selected through template matching and were put together to generate a mean image unit cell from the whole image as a reference point. This mean unit cell has the dimensions of 263\(\text{pm}\) X 456\(\text{pm}\) which is similar to the theoretically reported value of the LiNbO\(_3\). To determine the metrology of the domain wall, we measured the niobium and oxygen centers of mass individually for each unit cell and calculated a displacement vector per unit cell from the mean unit cell center to the niobium and oxygen center positions, the displacement vectors of the individual oxygen centers of mass for each cell was subtracted from the displacement vectors of the niobium centers of mass. The resulting vector from this subtraction represents the polarization effects the crystal experiences across the domain wall.
Figure 3.3 | Polar displacements at the domain wall. a, Ising Niobium-Oxygen displacement magnitudes along the $<0001>$ zone mapped out over the corresponding BF-STEM image. Scale bar is 2nm. b, c, Plots of Individual niobium displacements in green, oxygen displacements in red and difference in blue per unit cell, with the solid line showing the average along the [0001] axis. d, Néel niobium-oxygen displacement magnitudes along the $\langle 1120 \rangle$ zone mapped out over the BF-STEM image, identical to the micrograph in Fig. 2a. Scale bar is 2nm. e, f, Plots of Individual niobium displacements in green, oxygen displacements in red and difference in blue per unit cell, with the solid line showing the average along the [0001] axis. g, Rotation color map of $P_{\text{Nb-O}}$ polar displacement angle with the overlaid with rotation arrows measured per unit cells. h, Plot of rotation angle in degrees for the unit cells with the solid line showing the average along the $<0001>$ direction. i, Curl of polar niobium-oxygen displacement vectors with blue referring to clockwise and red to counter-clockwise rotations. j, Divergence of the polar displacement, with red corresponding to an increase in the displacement magnitude and blue corresponding to a decrease in the displacement magnitude.

Fig. 3.3a demonstrates a representative image of a $180^\circ$ domain wall, from the region
in the sample marked by the black box in Fig. 3.1c. Blue regions refer to displacements along \([000\bar{1}]\) while displacements along the \([0001]\) direction are overlaid in red, with the color saturation scaled to the absolute displacement intensities. The 180° nature of the wall and the domain reversal across only one to two unit cells can be immediately ascertained. Figure 2b indicates the position of the Nb and O centers of mass for every cell in the image. Both niobium and oxygen atoms show sudden displacements in the \(<0001>\) direction across the domain wall. This indicates that the final polarization order parameter is driven by both the niobium and oxygen atoms. Figure 3.3c shows the polar displacement values across the domain wall with further subtraction of Nb-O center of mass previously show in the Fig. 3.3b. This displacement shows 60pm across the domain walls which is extremely close to the theoretically predicted value of 55pm\(^{96}\). This combined plot, which is averaged over approximately 40 unit cells, is similar in nature to the monotonically changing Ising wall. But as Fig. 3.3a demonstrates, this globally averaged symmetry picture is misleading, and the local microscopic symmetry picture of the polarization is not uniform in the vicinity of the wall with kinks and bends, something that has also been noted from ADF-STEM imaging of LiNbO\(_3\) domain walls\(^{56}\).

In addition, we observe completely unexpected polar Néel type displacements along the \((11\bar{2}0)\) direction in Fig. 3.3c with a slight increase observed at the domain wall. Similar to the Ising displacement measurements, the combined niobium-oxygen displacements (Fig. 3.3f) show approximately 10pm of displacements all throughout the image. The combination of non-zero \((11\bar{2}0)\) displacements and zero \(<0001>\)
displacements at the wall imparts a rotational component to the polarization as shown in Fig. 3.3g, with its average value shown in Fig. 3.3h. The vector plot clearly shows both Ising and Néel displacements across the domain wall and the symmetry breakdown. However, the average displacement plot in Fig. 2h hides the symmetry breakdown that is occurring at the domain boundary.

To further determine the variations in the polar displacement vector, the curl and divergence of each vector in Fig. 3.3g is calculated and shown in Figures 3.3(i-j) respectively. A perfect Ising wall should have no curl components throughout the whole region. In contrary, the curl of the polar displacements in Fig. 3.3i shows a high entropy polar state consistent with spontaneous symmetry breakdown with the polar displacement vector rotating in a random fashion in clockwise (blue) and anti-clockwise (red) directions. This symmetry breakdown is predominantly associated with clockwise (blue) rotations right at the domain walls, an observation that is borne out in the divergence map (see Fig. 3.3j) too.
Figure 3.4 | *ab-initio Simulations of Niobium-Oxygen Displacements* | a, Potential energy of displacements with zero niobium-oxygen displacements along the <0001> zone axis demonstrating the classic Goldstone Sombrero potential. b, Radial potential distribution with a minima at 10pm. c, Probabilities of Ising, Néel and Bloch displacements, with zero Ising. d, Displacement probabilities at zero Ising displacements, and e, probabilities with bulk domain displacements (Credit: Sergei Prokhorenko, University of Liege)

First principle calculations that were performed as described in Section 3.2.2 were further employed to understand the instability associated with the atomic displacements and observation of polar entropy at the domain wall. The energy landscape related to the displacements of atoms strictly perpendicular to the <0001> axis complies with SU(1) rotation symmetry resulting in the famous Goldstone sombrero potential shape with zero Ising component (Fig. 3.4a). According to this plot, the suppression of the Ising displacements ($\tau_z$) in the <0001> direction lead to spontaneous symmetry breakdown giving rise to the Néel ($\tau_x$) and Bloch ($\tau_y$)
displacements. The radial magnitude of the symmetry displacements (Fig. 3.4b) indicates an energy minima with Néel/Bloch displacements of about 10pm, which closely matches with the experimental observations. While the experimental and theoretical displacement measurements closely match for the Néel displacements, STEM imaging cannot confirm the metrology of the individual $\tau_y$ (Bloch) displacements from this zone axis. Thus it is not possible to determine whether the resultant polar bosons are Goldstone modes (massless) or massive (Higgs). Based on the energetics of the symmetry breakdown, we can thus predict the probability of the polar displacements both at the wall and within the domain. While, within the domain, the displacements are mostly Ising-like (see Fig. 3.4c), at the domain wall the polar displacements are a mixture of Ising, Néel, and Bloch modes. Taking a slice of the probability at the domain wall, we plot the probability distribution of Ising ($\tau_z$) and Néel ($\tau_x$) displacements (Figs. 3.4d-e) and observe a spread in displacement probabilities centered at the two possible Ising displacement values of $\pm 25\text{pm}$ but with associated with $\pm 10\text{pm}$ of Néel displacements at each domain, with the probability maxima being only 0.004. Based on the probabilities, we thus observe an increase in the entropy which reaches a minima at the two ideal values of $\pm 26\text{pm}$ of Ising displacements and no Néel displacements. It is this entropy that is driving the symmetry breakdown in the vicinity of the wall, and thus we cannot expect a perfect polarization landscape at the domain wall, even if our bulk averaged measurements conform to those predictions.
Figure 3.5 | Polar displacements in the domain. 

a, Ising Niobium-oxygen displacements mapped over the corresponding BF-STEM image approximately 10nm away from the domain wall along the <0001> zone axis. Scale bar is 1.5nm. 
b, Plot of niobium-oxygen displacement per unit cell, with the solid line showing the average along the [0001] axis. 
c, Néel niobium-oxygen displacements in the (1120) zone plotted over the corresponding BF-STEM image in Fig. 3.5a. Scale bar is 1.5nm. 
d, Plot of Néel niobium-oxygen displacement per unit cell, with the solid line showing the average along the [0001] axis. 
e, Curl of displacement vectors, with blue and red corresponding to clockwise and counter-clockwise directions respectively. 
f, Divergence of the polar vectors, with blue referring to an increase, and red a decrease in the displacement magnitude. 
g, Ising Niobium-oxygen displacements in the bulk domain, approximately 100nm south of the wall mapped over the corresponding BF-STEM image along the <0001> zone axis. Scale bar is 1 nm. 
h, Plot of niobium-oxygen displacement per unit cell, with the solid line showing the average along the [0001] axis. 
i, Néel niobium-oxygen displacements in the (1120) zone plotted over the corresponding BF-STEM image in Fig. 4f. Scale bar is 1 nm. 
j, Plot of Néel niobium-oxygen displacement per unit cell, with the solid line showing the average along the [0001] axis. 
k, Curl of displacement vectors mapped in Fig 3.5f and Fig. 3.5h with blue and red corresponding to clockwise and counter-clockwise directions respectively. 
l, Divergence of the polar vectors, with blue referring to an increase, and red a decrease in the displacement magnitude. 

Our theoretical predictions are further confirmed in Fig. 3.5 where the polar displacement vectors are calculated within each domain as we move further away
from the wall. Figures 3.5a-f demonstrate a section of the bulk domain approximately ten nanometers away from the 180° wall, and the bottom panel (Fig. 3.5g-l) demonstrates a section of the bulk domain approximately hundred nanometers away from the wall. According to Figure 4a-d, Néel displacements, along the <0001> direction, can be observed, while Ising displacements continue to hold with some local instabilities, contrary to classical predictions. This behavior is also reflected in the curl and divergence maps in Fig. 3.5e-f which demonstrate the directional instability of the niobium-oxygen dipole moment, and the instability in the polarization magnitudes respectively.

Moving further away from the domain wall (Fig. 3.5g-l), Ising displacements continue to hold with their local instabilities in the <0001> significantly reducing. The Néel displacements, in contrast, further reduce and reach an average value of zero along the (1120) direction as indicated by Fig. 3.5j. The curl and divergence maps in Fig. 3.5k-l both indicate that while the rotational components reduce, they do not completely disappear. The polar displacement vectors at the domain wall and the within the domain, both indicate $E_u$ mode instability as the basis for symmetry breaking. While, this symmetry breaking is suppressed the further we move away from the domain wall. The shallow thermodynamic landscape, predicted by first principles calculations, still enables local symmetry fluctuations within the crystal.

3.3.2 Measurement of Polar Entropy

Using the calculated probability distribution measurements from STEM datasets, Gibbs-Boltzmann entropy is further calculated, based on the entropy formula given in Section 3.2.2. Entropy measurements are performed using three sets of STEM
data:

1. BF-STEM images taken at the domain wall
2. BF-STEM images taken at the vicinity of the domain wall – at approximately 20-30nm away from the wall.
3. BF-STEM images taken inside the bulk domain – more than 100nm away from the domain wall.

Since the average pixel size for the experimental setup is approximately 10pm, and the approximate image size is approximately 2000X2000 pixels, thus a representative image can visualize a 400nm² area.

**Figure 3.6 | Polar Entropy from niobium-oxygen displacements.** a-c, Polar entropy contribution as a function of the Ising (0001) and the Néel (11-20) displacements at the domain wall, approximately 10nm away from the domain wall,
and inside the bulk domain respectively. d-e, Summed entropy contribution as a function of the Ising and the Néel displacements respectively overlaid with the polar entropy calculated at the wall from first principles simulations.

Thus images that were captured at the domain wall, and have the domain wall centered in the image field of view, still have approximately 10nm of the domain itself imaged. Entropy calculations are performed on one full image itself, and thus domain wall entropy measurements also necessarily include contributions of 10nm of the domain approximately.

As mentioned previously, the individual Néel and Ising polar niobium-oxygen displacements are calculated individually for each unit cell. On an average, a BF-STEM image for our experimental conditions correspond to approximately 800 unit cells. A total of five images were captured and quantified at the domain wall, four in the vicinity of the domain wall, and four at the bulk domain. The polar displacements at each of the individual location were subsequently sorted into 0.1pm bins, from -50pm (minimum) to 50pm (maximum) of displacement – both for Ising and Néel displacements. Thus a total of 1001X1001 displacement configurations are possible. Thus, if a certain unit cell corresponds to an Ising displacement of 25.386pm, and a Néel displacement of -12.456pm, it will be assigned to the bin corresponding to the displacements of 25.3 to 25.4 Ising displacements, and -12.5 to -12.4pm of Néel displacements. Thus each unit cell corresponds to one displacement observation. Following assignment of all the observed displacements at a location into their respective bins, the total number of observations for each bin is divided by the total number of observations for the whole image itself. This is thus the probability of
observing a displacement corresponding to that bin position. The entropy of

displacements were subsequently calculated from the probability distributions as per
the following formula:

\[ S = \sum_{N} k_B \rho \ln(\rho) \]

where \( S \) is the Gibbs-Boltzmann entropy, \( k_B \) is the Boltzmann’s constant and \( \rho \) is the
probability distribution\(^97\). The term \( \sum_{N} \rho \ln(\rho) \) individually is also referred to
as the Shannon information entropy\(^98\).

This process thus allows to quantify the probability distribution as a function of the
Ising and the Néel displacement magnitudes, allowing the measurement of the
Shannon entropy from the probability distribution, and the Gibbs-Boltzmann entropy
by multiplying the Shannon entropy with the Boltzmann constant.

Fig. 3.6a-c shows the contribution of the experimentally measured Gibbs-Boltzmann
entropy as a function of the polar displacement magnitude. As expected, at the bulk
domain wall, the entropy contribution is bimodal with respect to the Ising
displacement magnitude, since the Ising displacement direction switches by 180°
across the domain boundary. However, the entropy contribution is significantly
diffuse at the domain wall, and becomes sharper as we move away from the wall in
Fig.3.6b-c. This is a consequence of the wider probabilities of Ising displacements in
the vicinity of the wall, and the narrowing of the possible Ising displacements in the
bulk domain. Additionally, while the displacement entropies are scattered with
respect to the Néel displacement magnitudes at the wall, they are centered at zero
Néel displacements at the bulk domain thus confirming our theoretical predictions
which state that Néel and Bloch displacements arise as a consequence of the reduction in the canonical Ising displacement magnitude.

Since the total measured entropy is the sum of the entropy contribution from all the measured observations, to visualize the entropy contributions as a function of the displacement directions they are summed up the along the Néel displacements for the Ising displacement contribution (Fig. 3.6d). The process is similar for the Néel displacement contribution, as shown in Fig. 3.6e where the entropy contributions are summed up for all possible Ising displacement magnitudes.

We observe, at the domain wall, a bimodal Ising displacement contribution with contributions centered at the theoretical niobium-oxygen displacement magnitudes of 25pm, but contributions also occur from even zero Ising displacements. The theoretically calculated entropy contributions, overlaid in red match closely with the experimental measurements. A similar story is observed also for the Néel contributions, with the peak centered at zero displacements – but there is a broadening associated with the range of displacement magnitudes, with the measured experimental contributions agreeing closely with the first principle calculations.

3.3.3 Measurement of strain
**Figure 3.7 | Strain at the domain wall.** Mapping of the strain arising at the domain wall, through comparison of the measured unit cell with the known theoretical unit cell size to give the strain values – with $\varepsilon_{xx}$ (Fig. 3.6a), $\varepsilon_{xy}$ (Fig. 3.6b), $\varepsilon_{yy}$ (Fig. 3.6c) and $\theta$ (Fig. 3.6d).

Since the niobium-oxygen atoms that were visualized in the BF-STEM datasets are organized into corresponding unit cells, we can thus measure the size of each individual unit cell and compare our measurements to the known theoretical values for the unit cell of LiNbO$_3$ at room temperature.

The strain is measured by calculating the length of the niobium axes calculated from the corner atom positions of the niobium atoms. The two vectors can be represented as

$$\frac{\text{LiNbO}_3^{\text{long}}}{2} = \frac{Nb_{\text{top-left}} - Nb_{\text{bottom-left}} + Nb_{\text{top-right}} - Nb_{\text{bottom-right}}}{2}$$
And

\[
\frac{\text{LiNbO}_3^{\text{short}}}{\text{LiNbO}_3^{\text{long}}} = \frac{\text{N}_\text{top-left} - \text{N}_\text{top-right} + \text{N}_\text{bottom-left} - \text{N}_\text{bottom-right}}{2}
\]

Thus the two unit cell vectors can be represented in the following matrix:

\[
\begin{pmatrix}
\text{LiNbO}_3^{\text{long}} & 0 \\
0 & \text{LiNbO}_3^{\text{short}}
\end{pmatrix}
\]

This matrix when divided by the reference unit cell matrix, gives us a T matrix, which is the strain matrix plus the identity matrix. Thus subtracting the identity matrix from the T matrix gives us strain as per the following equation:

\[
T - \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix}
\varepsilon_{xx} & \frac{\theta - \varepsilon_{xy}}{2} \\
\frac{\theta + \varepsilon_{xy}}{2} & \varepsilon_{yy}
\end{pmatrix}
\]

This procedure was performed to measure strain at the domain wall and the bulk domain as shown respectively in Fig. 3.7 and Fig. 3.8.

The measured strain in the bulk domain is compressive and close to zero, however this picture is radically different at the domain wall, as the domain wall is associated with a tensile strain approximating 2%. This demonstrates that while the bulk domain remains mostly unstrained, the domain wall is associated with strain fields that extend at least 110nm away from the wall with negligible decrease in strain magnitude.

This is similar to previous optical microscopy reports on tensile strain fields in LiNbO$_3$ originating at the domain wall measured through calculating the refractive index variations arising from strain distorting the LiNbO$_3$ crystal structure and thus
modifying the birefringent properties\textsuperscript{99}. However, the optical microscopy results reported strain fields that are two orders of magnitude smaller than our experimental data, while also being present several microns away from the wall.

In contrast, as our bulk BF-STEM images taken approximately 100nm away from the domain wall demonstrate the strain fields die away at far shorter lengths – and in fact the strain fields measured through BF-STEM are also localized to distances that are at least two orders of magnitude smaller.

\textbf{Figure 3.8 | Strain inside the bulk domain.} Mapping of the strain arising inside the bulk domain, through comparison of the measured unit cell with the known theoretical unit cell size to give the strain values – with $\varepsilon_{xx}$ (Fig. 3.8a), $\varepsilon_{xy}$ (Fig. 3.8b), $\varepsilon_{yy}$ (Fig. 3.8c) and $\theta$ (Fig. 3.8d).

This can be understood in the context of the different resolutions achievable in the
electron and the optical microscope, with the optical microscope resolutions limited to approximately one micron compared to sub-angstrom resolution in the aberration corrected transmission electron microscope.

3.4 Conclusions

We were successful in preparing electron microscopy foils of LiNbO$_3$ that could be imaged in the STEM mode, and allow the precise identification and quantification of oxygen atom positions. The ability to simultaneously image and quantify oxygen and niobium atom positions thus allows the measurement and mapping the niobium-oxygen polar displacement vectors which give rise to ferroelectricity in LiNbO$_3$ throughout the sample. This allowed us to image and visualize the domain wall, and also the polarity in the bulk ferroelectric domain. This picometer precision mapping allowed also the quantification of the disorder in the polar picture – i.e the polar entropy.

The final picture that arises from our observations is thus very intriguing, and challenges the rigid classification of ferroelectrics into proper and relaxor ferroelectrics. Entropy from variation in the polarization order parameter is a feature that is present at both the domain and the domain wall, with its maxima at the domain wall due to spontaneous symmetry breakdown. While the entropy decreases as we move away from the wall it never disappears completely. This is even more surprising in light of the fact that LiNbO$_3$ is a hard uniaxial ferroelectric where the polarization can only assume two crystallographic orientations. The advent of aberration corrected STEM now enables similar measurements in other ferroelectric systems and we propose that the local structure in ferroelectrics is significantly
more random and complex at room temperatures because of the energetic stability provided by the increase in polarization entropy.

Additionally, we were also experimentally able to observe the strain fields originating at the domain wall, and compare them with strain fields in the bulk domain. Our experimental results demonstrate that while the strain is not only significantly larger than previously reported, they are also localized to a few tens of nanometers around the domain boundary.
4. 4D-STEM imaging of Domain Walls in Polar Metals

4.1 Introduction

4.1.1 Polar Metals

One of the most significant advances in the field of ferroelectrics has been understanding of the role of crystal structure in determining ferroelectric properties\textsuperscript{19,20}. This understanding is now backed from first principle quantum mechanical arguments, and is commonly referred to as the modern theory of ferroelectricity\textsuperscript{17,18}. Thus, it would appear to someone new to the field that crystal structure and ferroelectricity are two sides of the same coin, and one cannot exist without the other. Additionally, all known ferroelectrics are also dielectrics, since an electrical polarization cannot exist inside a metal due to shielding\textsuperscript{1,100}. However, in the 1960s, it was first proposed by Anderson and Blount that this might not in fact be
the case\textsuperscript{47}. Certain materials, like V\textsubscript{3}Si may undergo a second order martensitic like structural phase transitions into a non-centrosymmetric crystal structure while retaining their metallic behavior\textsuperscript{101}. In the 1970s, neutron scattering studies, however, demonstrated that the non-centrosymmetry in V\textsubscript{3}Si was not accurately measured, and the idea of a polar metal remained as an intellectual curiosity with little to no experimental backing\textsuperscript{102}.

The field, however, completely changed upon the discovery of LiOsO\textsubscript{3} in 2014\textsuperscript{48,103}. LiOsO\textsubscript{3} at room temperature is a metal, and remains metallic all the way down to 0\textdegree{}K. Additionally, at room temperature its crystal structure is centrosymmetric, belonging to the $R\bar{3}c$ space group, which is also the high temperature space group of paraelectric LiNbO\textsubscript{3} above the Curie temperature\textsuperscript{5,12,103}. However, below 140K, LiOsO\textsubscript{3} undergoes a structural transition to the $R3c$ space group, adopting a structure that is identical to ferroelectric LiNbO\textsubscript{3} while remaining a metal. This is thus identical to the Curie temperature structural transition in LiNbO\textsubscript{3}, but it is observed in a metal, thus experimentally proving the Anderson-Blount hypothesis.

Similar behavior has also been observed in NdNiO\textsubscript{3} thin films, which adopt a non-centrosymmetric crystal structure driven by the induced octahedral rotations from the substrate, while remaining a metal\textsuperscript{49}.

4.1.2 Hybrid Improper Ferroelectric Metal - Ca\textsubscript{3}Ru\textsubscript{2}O\textsubscript{7}

Another material that is a polar metal however was discovered in the early 1990s, while remaining hidden in plain sight\textsuperscript{104}. As originally mentioned in section 1.1.3, while proper ferroelectrics such as BaTiO\textsubscript{3}, LiNbO\textsubscript{3} have the B-site atom positions displaced from the center of the oxygen octahedra leading to non-centrosymmetry, in
hybrid improper ferroelectrics the destruction of the inversion center arises from uncompensated octahedral tilts$^{1,21}$. Thus the B site atoms are at the center of the oxygen octahedra, but the octahedra themselves are tilted$^{24}$. If the chemical composition of the structure corresponds to the canonical perovskite formula, then the non-centrosymmetry arising from the octahedral tilts cancel each other out. An example of such a structure would be CaTiO$_3$, which have alternating oxygen octahedral rotations. While such a system is not ferroelectric, they do however demonstrate the presence of 180° domain boundaries across which the octahedral tilts reverse in direction$^{105}$. However, if layering can be implemented in such a system – through either superlattice ordering or rocksalt layers, and if the octahedral layers contain an even number of oxygen octahedra, then the non-centrosymmetry from the tilts remain uncompensated making the whole structure polar$^{23,26}$.

**Figure 4.1 | Structure and electronic properties of titanium doped Ca$_3$Ru$_2$O$_7$. a, Resistivity as a function of temperature for different titanium doping concentrations. b, The crystal structure of Ca$_3$Ru$_2$O$_7$ viewed from the [011] zone axis$^{106}$.**
The first experimentally proven hybrid improper ferroelectric is the Ruddlesden-Popper Ca$_3$Ti$_2$O$_7$, where CaO rocksalt layers separate the uncompensated octahedral tilts in the CaTiO$_3$ perovskite blocks$^{25}$. Ca$_3$Ti$_2$O$_7$ has demonstrated the presence of domain walls analogous to ones existing in CaTiO$_3$ and has been experimentally switched with piezo-responsive force microscopy (PFM)$^{107,108}$. Another material, Ca$_3$Ru$_2$O$_7$, however has the exact same non-centrosymmetric polar space group (Cmc2$_1$) as of Ca$_3$Ti$_2$O$_7$ and is a metal at all temperatures$^{106}$. Ca$_3$Ru$_2$O$_7$ was first synthesized in early 1990s, even before the discovery of hybrid improper ferroelectricity$^{109}$. The metallic behavior in Ca$_3$Ru$_2$O$_7$ arises as a consequence of the strongly correlated electrons originating from the unpaired $d$ electrons in the Ru$^{4+}$ ion$^{110,104}$. This strong electron correlation makes Ca$_3$Ru$_2$O$_7$ an extraordinarily rich system, which displays both ferromagnetism and anti-ferromagnetism at different temperatures$^{111–113}$. Recent studies have shown that under uniaxial pressure, the magnetic structure of Ca$_3$Ru$_2$O$_7$ could be tuned and the antiferromagnetic to ferromagnetic transition temperatures could be changed$^{113}$.

Since Ca$_3$Ti$_2$O$_7$ and Ca$_3$Ru$_2$O$_7$ have the same crystal structures, they are miscible in solid solutions at all concentrations without phase separation, while maintaining the same polar Cmc2$_1$ space group$^{106}$. However, the addition of titanium, which displaces the ruthenium atoms, induces metal-insulator transitions above 0.03% of titanium concentration – making the material a Mott metal, as shown in Fig. 4.1a. The Mott transition temperature can be tuned by the titanium concentration increasing from $67^\circ$K at 5% Ti doping to $109^\circ$K at 10% Ti doping$^{106}$. The Ca$_3$Ru$_2$O$_7$ crystal structure
shown in Fig. 4.1b demonstrates the non-centrosymmetry with the ruthenium centered oxygen octahedra tilting in opposite direction in alternate perovskite layers. However, as can also be noted, the octahedra are displaced by half a unit cell (perovskite) after crossing the rocksalt layer, thus making the tilts uncompensated leading to polarity.

Since charged head-to-head and tail-to-tail domain walls have already been proven to exist in Ca₃Ti₂O₇, the tantalizing possibility of similar domain configurations existing in Ca₃Ru₂O₇ now arises. To study the crystal structure of possible domain configurations in a hybrid improper ferroelectric metallic structure, we thus chose titanium doped Ca₃Ru₂O₇, as a model system, which is metallic at room temperatures, but undergoes a metal-to-insulating Mott transition at 67K. While the structure of domain configurations can be reliably probed with aberration corrected STEM imaging, as demonstrated in chapter 3, proving the existence of charge accumulation in these systems is challenging with conductive Atomic Force Microscopy (cAFM) – the preferred approach to probing charge accumulation in ferroelectric domain walls³¹,³²,³⁴. This is because a standard ferroelectric is also a dielectric, and thus charge accumulation in a domain wall is reflected in an increased carrier concentration at the wall itself when compared to the bulk domain, and thus a decrease in electrical resistivity³¹. However, since in a polar metal, the domain itself is also metallic, this technique is not as suitable.

To thus probe the charge accumulation and potential changes associated with charge accumulation in domain walls in 5%Ti- Ca₃Ru₂O₇ we chose Differential Phase Contrast (DPC) STEM as the candidate technique.
4.1.3 Differential Phase Contrast STEM (DPC-STEM)

The defining idea behind electron microscopy has been better resolution enabled through sub-Ångström wavelength de-Broglie waves. Indeed, the hunt for resolution has defined most of electron microscopy developments over the past few decades – progressing in two distinct phases\(^ {60}\).

The first phase focused on increasing the electron accelerating voltages to enable smaller electron wavelengths\(^ {114}\). A flip side of this approach is that such electrons also have significantly higher momentum making imaging of beam sensitive samples extraordinarily challenging. Since the early nineties, the second phase of the resolution hunt tried developing detours around the Scherzer equation, and developing hexapole and octapole aberration correctors which have pushed the resolution of modern transmission electron microscopes to 47pm at 200kV\(^ {61,82}\).

However, in 1979, Harald Rose, one of the pioneers of aberration corrected electron optics also pointed out that electron imaging is a consequence of the Aharonov-Bohm effect\(^ {115}\). As per the Aharonov-Bohm effect, when a charged quantum particle experiences an electromagnetic field, the complex wavefunction of the charged particle undergoes a change that is proportional to the magnitude of the electromagnetic field experienced by the quantum particle\(^ {116}\). Thus, electron microscopy imaging is inherently a phase imaging technique. Rose pointed it out that because of the Aharonov-Bohm effect the phase of the electron wavefunction must also be sensitive to mesoscopic electric fields.

Because electron diffraction is an example of far field Fraunhofer diffraction, the diffraction plane in the electron microscope can be reasonable approximated as the
Fourier plane of the real sample. Since phase change in real space is equivalent to displacement in the Fourier space and vice versa, thus it should be possible to image electric and magnetic fields in a TEM sample if the momentum transfer of an electron beam in the diffraction plane could be imaged. To accomplish this, Rose proposed segmented detectors replacing annular detectors in the diffraction plane for STEM probes, with the intensity ratio of the segments allowing the metrology of the momentum transferred to the electron beam. Rose referred to the technique as Differential Phase Contrast (DPC) STEM imaging.

Figure 4.2 demonstrates a schematic of such a proposed setup, where a four segment detector can measure the changes in momentum transfer to an electron beam by measuring the intensity variations across the individual detector segments.

**Figure 4.2 | Electron beam deflection in an electric field.**

- **a**, No deflection, centered on both the opposing detectors in the absence of an electric field.
- **b**, Rightward beam deflection, with the Y detector being selectively illuminated under an electric field.
- **c**, Leftward beam deflection, with the X detector being more strongly illuminated when the electric field points to the right.
Thus in the absence of an electric field, the electron beam will illuminate two opposing beam detectors equally as shown in Fig. 4.2a. However, as observed in Fig. 4.2b-c in the presence of an electric field, the electron beam will be steered in the direction opposite to the electric field vector since electrons are negatively charged.

Segmented detectors for measuring electric fields were first implemented by Shibata to measure charge accumulation at BaTiO$_3$ domain walls$^{19}$. As shown in Fig. 4.3a, BaTiO$_3$ is a non-centrosymmetric oxide where the central titanium atom is displaced relative to the center of the oxygen octahedra. However, as Fig. 4.3b-d demonstrates, rather than picking up electron accumulation at domain walls, the contrast reversal in segmented detectors is dominated by the domain contrast.

This occurs because while the central undiffracted disk, or the (000) disk is not dependent on the crystal structure below the elastic scattering length, the higher diffraction disks correspond to atomic planes$^{75,120–124}$. 
Fig. 4.3 | Observation of ferroelectric domains with DPC. a, The BaTiO$_3$ crystal structure. b, Schematic of a 4 segment detector, showing the respective crystal orientations with respect to the detector. c, Subtraction of intensity from detector Y from detector W. d, Subtraction of intensity of detector Z from detector X$^{119}$.

In non-centrosymmetric ferroelectric crystals thus the diffraction intensity in higher order disks is non-centrosymmetric too, and as Fig. 4.3 demonstrates the measured intensity variation across the detector segments is dominated by the intensity variation arising from non-centrosymmetry$^{103,122}$.

In fact, the point group of the crystal being imaged is reflected in the point group of the convergent beam electron diffraction (CBED) pattern, and several electron microscopy techniques like Position Averaged CBED (PACBED) routinely analyze the symmetry of the CBED patterns to elucidate the symmetry of the crystal being imaged$^{122,125}$. 
Figure 4.4 | 4D-STEM Differential Phase Contrast STEM. a, Ronchigrams obtained at every scan position with the corresponding simultaneously acquired ADF-STEM in inset on a SrTiO$_3$ sample. b, Ronchigrams from two different regions demonstrating differing momentum redistributions. c, Momentum vector measured from the ronchigram intensity center of mass$^{126}$.

To better distinguish between the contribution of crystal symmetry and mesoscopic electric fields, Muller et. al. proposed using a pixelated detector in the diffraction plane for STEM probes, and visualizing the entire CBED pattern generated$^{126}$. This allowed the imaging of electron beam ronchigram at every probe position, as visualized in Fig. 4.4a, with inset showing the simultaneously collected ADF-STEM image for the SrTiO$_3$ sample.

Looking at two different ronchigrams from two different beam positions in Fig. 4.4b, it can be observed that the intensity distribution varies depending on where the beam is. The authors determined a technique to measure the intensity distribution inside a single ronchigram as per the following equation$^{126}$:

$$\langle p_\perp \rangle = \int p_\perp I(p_\perp) \delta p_x \delta p_y$$

where $p_\perp$ refers to the momentum perpendicular to the electron beam, and the $\langle p_\perp \rangle$ is
the expectation value of the perpendicular momentum observed by the electron beam. Thus the center of the mass of the ronchigram generates the expectation value of the momentum. Fig. 4.4c plots the momentum transferred to the electron beam perpendicular to the beam propagation direction. As could be observed, atomic columns are associated with momentum transfers. However, closer observation of Fig. 4.4c shows that the momentum is always transferred away from the atomic column. This is a highly counter-intuitive result since oxygen columns should be negatively charged and strontium columns should be positively charged, and thus the momentum transfer direction should reverse.

However, it has to be kept in mind, that these experiments were performed with aberration corrected electron probes at an accelerating voltage of 300kV with an approximate probe diameter of 50pm. As a point of comparison, the ionic radius of O$^{2-}$ is 152pm, as per the Pauling formula$^{127}$. Thus the probe is significantly smaller than even the ionic radius, and it is nuclear charge that dominates the momentum transfer and not mesoscopic electric fields. In fact, as the authors reported, this technique fails even in quantifying nuclear potentials above a sample thickness of 3.2nm.

The following sections present how the chemical and atomic structure of 5% Ti doped Ca$_3$Ru$_2$O$_7$ was determined initially across domain boundaries with polarized light microscopy to first visually identify the location of domain walls. Following such visual identification, the structural metrology of the domain boundaries were performed with aberration corrected HAADF-STEM. In order to realize the original vision of Harald Rose – the imaging of mesoscopic electric fields in the transmission
electron microscope we also describe how a 4D-STEM experimental setup was realized with non-converging electron diffraction patterns in the Fourier space, and how such patterns were used to image the momentum change across domain boundaries in 5% Ti doped Ca$_3$Ru$_2$O$_7$.

4.2 Results and Discussions

4.2.1 Optical Microscopy of 5%Ti-Ca$_3$Ru$_2$O$_7$

![Brightfield Optical Microscopy](image1.png) ![Polarized Optical Microscopy](image2.png)

Fig. 4.5 | Optical Microscopy of Ca$_3$Ru$_2$O$_7$ crystals. a, Brightfield optical microscope image of 5% Ti doped Ca$_3$Ru$_2$O$_7$. b, Circularly polarized optical microscope image of the same crystal demonstrating birefringence due to domains.

Initial estimation of the polar 5% Ti doped Ca$_3$Ru$_2$O$_7$ samples were first performed by a combination of brightfield and polarized optical microscopy. Fig. 4.5a shows the optical microscopy image of a 5%Ti doped Ca$_3$Ru$_2$O$_7$ crystal under incoherent illumination. Since it is a room temperature metal, it is reflective and opaque under illumination. Switching to circularly polarized illumination, however demonstrates the presence of birefringence as demonstrated in Fig. 4.5b. Birefringence is a consequence of the reversal of the crystal structure in a non-centrosymmetric structure, and thus is the sign of a domain boundary. This demonstrates that 5%Ti-
Ca$_3$Ru$_2$O$_7$ is not only a polar metal, but may be associated with domain walls too.

Fig. 4.6 | Optical Microscopy images showing FIB region of interest. a, Polarized light optical microscope image demonstrating the location of the domain walls. The domain walls are visible due to optical birefringence. b, Optical microscope image showing multiple FIB cuts.

4.2.2 Focused Ion Beam Sample Preparation:

To further observe the structure of the hypothesized domain walls in 5%Ti-Ca$_3$Ru$_2$O$_7$, electron transparent samples were prepared by focused ion beam (FIB) across the birefringence change. As demonstrated in Fig. 4.6a-b the FIB samples were taken from across the regions showing intensity variations owing to birefringence. Focused Ion Beam (FIB) was chosen as the method for sample preparation since it allows the preparation of site specific samples from a small area while allowing for the domain wall to be placed edge on inside the sample.

Samples were prepared on copper V-post grids sourced from Ted Pella, with a 100µm dug at the V trench to prevent copper sputtering during the ion milling. To enable multiple domain junctions to be imaged in one electron microscopy experimental setup, the GIB chips were made 50µm deep, and were approximately
25µm wide. This necessitated creating 75µm X 30µm trenches around the domain boundary, with two trenches being dig separated by approximately 5µm. Following this procedure, the region between the trenches was lifted off, and polished using the gallium ion beam at increasingly lower accelerating voltages, starting from 30kV, with final polishing occurring at 0.5kV accelerating voltages till the samples became electron transparent at 2kV electron accelerating voltages.

**Fig. 4.7** | **Low mag TEM image of FIB sample.** a, Low mag conventional TEM image viewed from the (011) zone axis showing possible domain wall locations visible due to diffraction contrast. b, Schematic showing the possible domain orientations visible from the (011) zone axis.

### 4.2.3 Transmission Electron Microscopy of 5%Ti-Ca₃Ru₂O₇

Following the preparation of electron transparent samples by FIB, the samples were imaged at low magnifications using conventional TEM, as demonstrated in Fig. 4.7a. The presence of diffraction contrast in Fig. 4.7a indicated the presence of domain boundaries. Considering that the optical birefringence occurred due to the presence
of a hypothesized 90° domain boundary, which is visible through the sample, the presence of multiple domain junctions indicated that the TEM sample was associated with not only 90° domain boundaries, but also additional 180° domain boundaries too.

The orientation of the multiple domain boundaries and junctions when viewed from the (001) zone, which is the zone from which the FIB samples were prepared, are illustrated in the schematic illustrated in Fig. 4.7b. The polar axis of Ca₃Ru₂O₇ is oriented at 45° to the (011) axis, with an in plane and an out of plane component. Across a 90° domain boundary, only one of these components switch in direction, while both the in plane and out of plane polar components switch across a 45° domain boundary. Thus a 90° domain boundary can assume three possible configurations:

1. **Head-to-Tail/Tail-to-Head:** When the out of plane component reverses in direction
2. **Tail-to-Tail:** When the in-plane component switches directions, with the polar axes pointing away from the domain boundary.
3. **Head-to-Head:** When the in-plane component switches directions, with the polar axes pointing towards from the domain boundary.
**Figure 4.8 | Ca$_3$Ru$_2$O$_7$ crystal structure.** a, Schematic of the Ca$_3$Ru$_2$O$_7$ crystal structure, viewed from the (011) zone axis showing the oxygen octahedra with the ruthenium atom sitting at the center of the octahedra. b, Schematic in Fig. 4.5a viewed without the oxygen atoms, demonstrating how the tilt manifests as calcium displacements (blue arrows) and polarization (red arrows). Thus the 90° domain boundary, under certain configurations assumes a configuration, which gives, rise to a charged domain boundary in conventional insulating ferroelectrics. Fig. 4.7 illustrates the in-plane polar axis of the Ca$_3$Ru$_2$O$_7$ crystal structure. Fig. 4.7a demonstrates a representative crystal, when viewed from the (011) zone axis, with the oxygen octahedra associated with the ruthenium atoms shown in yellow, the oxygen atoms in red, and the calcium atoms in blue. As could be observed the octahedra are present in layers of two, with a layer being separated from its adjacent layer with a CaO rocksalt layer. The octahedra in one layer are tilted in opposite directions, and half a perovskite block shifts the octahedra in the
adjacent layer. The combination of these two structural features gives rise to the non-centrosymmetry in the crystal structure.

In fact, the polar axis direction can be ascertained from just comparing the positions of the calcium atoms. Fig. 4.7b shows the calcium and ruthenium atoms, and it can be easily seen that the octahedral tilt is manifested by the central calcium atom in a perovskite block being displaced horizontally with the top and the bottom calcium positions, with the displacement direction marked by blue arrows in Fig. 4.7b. The direction of the polar axes is opposite to the direction of displacement of the central calcium atom. This can be understood based on the fact that while the central calcium atoms is being displaced relative to the top and bottom calcium atoms, in reality all three calcium atoms are being displaced relative to the oxygen octahedral centers. The top two calcium atoms are displaced in the opposite direction to the central one, thus the cumulative polar displacement is in opposite direction to the displacement of the central calcium atom.
Switching the microscope to the scanning mode, high-resolution aberration corrected STEM imaging in the sample demonstrates the presence of the rocksalt layers with the alternating octahedral positions indicating the presence of the Ruddlesden-Popper structure. Since the atomic number of ruthenium is significantly higher than that of calcium (44 versus 20), ruthenium atoms are brighter. Additionally, since this a HAADF-STEM image, unlike BF-STEM images used for analyzing atom positions in LiNbO$_3$ in Chapter 3, the oxygen atom positions are not visible. Visual analysis of the displacement of the central calcium atom relative to the top and bottom atoms confirms that the structure is indeed polar. In fact, as we also observe, in a different section of the image the calcium atom displacement direction changes – indicating the presence of domain boundaries.
Mapping the calcium displacement directions, as shown in Fig. 4.10, when overlaid over the HAADF-STEM image demonstrates in fact the presence of a domain junction between a 90° domain boundary and a 180° domain boundary. The 90° domain boundary switches from a tail-to-head wall in the top half of the image to a tail-to-tail domain boundary below the 180° domain wall.

In fact, further analysis of the 90° domain boundary reveals that the wall is not in fact straight throughout the sample. As can be observed from Fig. 4.11a, the region image corresponds to a meandering tail-to-tail domain wall. Zooming in on the section marked by the white box in Fig. 4.11a, we even observe slight rotation across the domain boundary too in some of the polar calcium layers (Fig. 4.11b).
**Fig. 4.11 | Tail to tail domain walls in 5%Ti-Ca₃Ru₂O₇.** a, Meandering 90° tail to tail domain boundary in 5%Ti doped Ca₃Ru₂O₇. b, Zoomed in section corresponding to the region marked by the white box in Fig. 4.4a demonstrating polarization rotation in some layers.

Other regions of the domain structures in 5%Ti-Ca₃Ru₂O₇ sample demonstrates the presence of head-to-tail 90° domain walls as shown in Fig. 4.12a. Head-to-tail domain walls are characterized by the unchanging direction of the in-plane polarization with a corresponding reversal of the out of plane polar component (not detectible here). However, as we observe in Fig. 4.12a-b, the domain wall itself shows a noticeable decrease in polarization magnitude across two to three unit cells, and similar to the head-to-head and the tail-to-tail 90° domain walls is not straight and meanders through the structure.
Fig. 4.12 | Head to tail domain walls in 5%Ti-Ca$_3$Ru$_2$O$_7$. a, 90° head to tail domain boundary in 5%Ti doped Ca$_3$Ru$_2$O$_7$. b, Zoomed in section corresponding to the region marked by the white box in Fig. 4.5a.

Thus the HAADF-STEM images of the domain boundaries in 5%Ti-Ca$_3$Ru$_2$O$_7$ demonstrate a striking amount of richness in complexity of the domain configurations that are present in the sample. Not only are a varied amount of domain configurations present, but they are also associated with domain junctions across which the polarization behavior of the wall switches.

In fact, several of the walls imaged demonstrate tail-to-tail and head-to-head behaviors, thus demonstrating configurations that are structurally analogous to charged domain boundaries. The next section investigates the changes in the electronic structure precipitated by these domain configurations through differential phase contrast microscopy.

4.2.4 DPC-STEM of 5%Ti-Ca$_3$Ru$_2$O$_7$

In order to experimentally determine the possibility of charge accumulation and
changes in the Fermi level arising from charging in the domain walls observed in the 5\%Ti-Ca$_3$Ru$_2$O$_7$ we chose DPC-STEM microscopy. However, as elucidated in section 4.1.3, current DPC imaging approaches have been unable to visualize mesoscale electronic potential gradients at interfaces. To enable such imaging, our experimental setup implemented two modifications:

1. **Collection of the entire CBED pattern:** While the idea behind segmented detectors is extremely elegant, and simple to implement with an only small increase in the amount of data collected, they also suffer from the inability to accurately measure the momentum transferred to the probe. Muller’s approach with pixelated detectors, where the entire diffraction pattern is captured demonstrated that if the sample thickness was below 3nm, DPC worked accurately. Thus we chose to capture the entire diffraction pattern at every scanning pixel, resulting in a four dimensional data set, where two dimensions correspond to the scanning positions in the real space, and two dimensions correspond to the diffraction directions in momentum or Fourier space.

2. **Large, nanometer sized probes:** Additionally, we hypothesize that the two previous approaches suffered from two different flaws – both arising from electron beams that were too small. For a typical aberration corrected STEM setup, the electron probe diameter is inversely proportional to the convergence angle generated by the condenser aperture. For a typical 30mrad convergence angle, this corresponds to a probe size of typically 50pm. While the size of nuclei is of the order of femtometers, the ionic radii of most
elements are of the order of angstroms, with the Pauling radius of the $\text{O}^{2-}$ ion being approximately $1.52\text{Å}$. Thus, the probe size in aberration corrected microscope is smaller than the ionic radii of most of the elements being imaged. In fact, aberration corrected probes now routinely reach sizes below $50\text{pm}$ at $300\text{KV}$ accelerating voltages, which is even smaller than the Bohr radius of the hydrogen atom, which is $52.9\text{pm}$ approximately. And while the total charge in the nucleus and the electronic cloud is of a similar magnitude, given the several orders of magnitude difference between nuclear and ionic radii (a few femtometers versus hundreds of picometers), the volumetric charge density of the nucleus is thus fourteen orders of magnitude higher than the charge density of the nucleus. Thus it is completely understandable why DPC picks up nuclear potentials rather than potential gradients from interfaces. Thus our probes need to be at least an order of magnitude bigger, which results in convergence angles no bigger than $3\text{mrad}$. In fact, that is still not big enough. As the experimental results with segmented detectors demonstrate, the possibility of picking up contrast from the lack of inversion symmetry owing to the ferroelectric crystal structure can easily happen. Thus we need our probes to be big enough, that the CBED disk from individual diffraction planes do not overlap. This will allow us to pick up the effect of potential gradients across just the central undiffracted (000) disk, without the confounding effects of noncentrosymmetric crystal structures that are present in the higher order diffracted disk. To enable this, thus the probe must be at least the size of the unit cell. Thus the probes need to be of the order of a nanometer, which was implemented by choosing a convergence angle that was around $1\text{mrad}$.
in size. It is instructive to note that such a convergence angle is thirty times smaller than the typical convergence angle used in STEM imaging, and since the probe is bigger than even the individual unit cell, no atomic contrast is visible in the BF-STEM or the HAADF-STEM images.

Since both 4D-STEM detectors and such small convergence angles were not available at Penn State, these experiments were performed using the Gatan K2 detector attached to the TEAM1 microscope at the National Center for Electron Microscopy at the Lawrence Berkeley National Laboratory. The Gatan K2 is a direct electron detector, enabled with electron counting, and measures 1920X1792 pixels. Since the storage data format is single bit unsigned integer, each single CBED pattern is approximately 4MB in size. The acquisition size in scanning pixels is thus limited by the on board memory of the acquisition computer, which was 512GB for our experimental setup. This corresponds to a maximum of 125,000 CBED patterns in a 4D-STEM dataset and thus the typical 4D-STEM image has 300X400 scanning pixels. As can be noted this is significantly smaller in number than the typical ADF-STEM image, which has 2048X2048 or 4096X4096, scan positions. However, a supersampling factor of 5 results in a scanning pixel size of 0.2nm or 200pm. The typical ADF-STEM is acquired at 10pm scanning pixel sizes to ensure a supersampling of approximately 5, which is almost 20 times smaller than the 4D-STEM pixel size. Thus while the total number of scan points are almost two orders of magnitude lower in our 4D-STEM experiments, the field of view is in fact larger than the typical aberration corrected atomic resolution ADF-STEM image.

Fig. 4.13a demonstrates simultaneously collected HAADF-STEM image. Since the
The experimental beam is now of the order of nanometers – no atomic structure is visible in this image. The central dark line passing through the image is a $90^\circ$ domain wall, with the white rectangle referring to the region where the DPC-STEM imaging was performed.

**Figure 4.13 | 4D-STEM imaging of 5\%Ti-Ca$_3$Ru$_2$O$_7$.** a, ADF-STEM imaging of the sample with 1.1 nm beam. b, BF-STEM image obtained by summing the CBED pattern. c, CBED pattern corresponding to the region marked by the yellow arrow in Fig. 4.11b.

Fig. 4.13b shows the brightfield image of the DPC pattern, obtained by summing up the intensity observed at a probe position. As can be observed, the domain wall is still visible. However, each individual scanning pixel of this dataset has now one corresponding CBED pattern, with Fig. 4.13c demonstrating the CBED pattern from one pixel (pointed by the yellow arrow) in Fig. 4.13b. The central bright disk is Fig. 4.13c is the zeroth order diffraction disk, and a visual examination confirms that the diffraction disks do not overlap, thus allowing the measurement of the individual
momentum transfer in each diffraction disk.

**Figure 4.14 | Central beam shift as a function of beam position.**

Comparing the central disk across three positions in a 4D-STEM dataset as shown in Fig. 4.14, we observe that the disk positions change based on their location with respect to the 90° domain wall. Region 1, marked in red is away from the wall, while region 2 marked in blue is near the domain wall. However, while this is interesting visually, such a comparison for 120,000 patterns is impossible manually and is imprecise quantitatively.

To quantitatively measure the potential gradients across the entire dataset, we thus need to implement a procedure that measures the center of momentum displacement across each of the zeroth order disks. As per the Ehrenfest’s theorem, the total momentum transfer experienced by the beam can be given by:\(^ {126} \)

\[
\langle p_\perp \rangle = \int p_\perp I(p_\perp) \delta p_x \delta p_y
\]
where $p_\perp$ refers to the momentum perpendicular to the electron beam, and the $\langle p_\perp \rangle$ is the expectation value of the perpendicular momentum observed by the electron beam. This could be visually understood by the schematic in Fig. 4.15. In Fig. 4.15a, the electron beam experiences a momentum gradient going from right to left, where blue indicates a lower absolute potential, and red indicates a higher absolute potential, which is reversed in Fig. 4.15c. In Fig. 4.15b, since the beam experiences no net phase change, the center of momentum of the beam remains unchanged. As per the Aharonov-Bohm effect, thus the complex phase of the electron beam experiences a change that is a convolution of the beam intensity in real space and the potential gradient. This phase change in real space thus leads to a deviation of the beam in the Fourier or diffraction space, which manifests itself as a change in the center of momentum of the zeroth order disk. In reality, this phase change is present in every single diffracted disk, but in higher order disks it is convoluted with the phase change imparted from the crystal structure itself, making it challenging to untangle the two effects. Thus only the center of momentum of the central beam is measured, as this beam will demonstrate only the effects from mesoscopic potential gradients, and not the crystal structure itself. The center of mass of the central disk in pixels thus multiplied by the momentum pixel spacing will give us the wavevector change inside the central disk or the $\vec{k}$ redistribution across the central disk. Since momentum ($\vec{p}$) and $\vec{k}$ can be related as per the de Broglie equation:

$$\vec{p} = \frac{\hbar}{2\pi} \vec{k}$$

where $\hbar$ is the Planck’s constant, the momentum redistribution can be calculated, by
measuring the center of mass displacement of the central disk.

Fig. 4.15 | Shift of center of mass due to potential gradients. a, Schematic of center of mass of an electron beam (green) shifting to the right in the central disk after encountering a potential gradient in the opposite direction. b, Center of mass of the electron beam centered inside the (000) central disk upon encountering a centrosymmetric potential gradient. c, Center of mass of the electron beam shifted to the left inside the (000) central disk upon encountering a potential gradient increasing to the right.

Thus the accurate measurement of potential gradients requires the measurement of the center of momentum change in every central disk of the entire CBED pattern dataset. To measure the center of momentum change inside the disk, we at first need to know the location of the disks itself.

4.2.5 Measurement of CBED disk positions with edge detection
Figure 4.16 | CBED patterns from 4D-STEM. a, CBED patterns with non-overlapping disks demonstrating low signal to noise. The ADF aperture blocking the higher order disks is visible also. b, Zoomed in central disk marked by white square in Fig. 4.13a demonstrating intensity variation and shot noise.

Fig. 4.16 shows why this is extremely challenging analytically. Fig. 4.16a demonstrates an experimental CBED pattern from a 4D-STEM dataset, with the white rectangle bordering the central zeroth order disk, which is shown separately zoomed out in Fig. 4.16b. While the human brain is exceptionally good at pattern recognition, honed by millennia of selective evolution to escape predators on the African savannah - this, is however not the case yet with computers. It is only in the recent one or two years, with the development of convolutional neural nets and machine learning implemented on exceptionally large GPU clusters that computers have started approaching the human brain’s pattern recognition capabilities\textsuperscript{128}. While the human eye and brain combination can visually point out the presence of disks in Fig. 4.16a-b almost immediately, the computer is unable to do so, especially in the presence of shot noise, which can be clearly observed in Fig. 4.16b as intensity
spikes in the disk’s neighboring regions. Additionally the intensity distribution in the disk itself is far from uniform and there are pixels, which correspond to zero intensity even inside the central diffraction disk. Thus a simple edge filtering algorithm, i.e. a Sobel filter, that records the second order diffraction spikes of the image as edges will fail here.

Figure 4.17 | Disk metrology through edge detection. **a,** Central disk to be measured. **b,** Calculated edge through Canny edge detection using Otsu lower and upper thresholds. **c,** Calculated circle in red and white overlaid on the experimental data.

Our initial approach was to implement a combination of the Otsu thresholding and the Canny edge detection algorithm. For a given gray scale image, Otsu thresholding divides the image intensity into two different classes. The goal is to maximize the inter-class variance and minimize the intra-class variance. The intra-class variance is given by

\[
\sigma_{\omega}^2(t) = \omega_1(t)\sigma_1^2 + \omega_2(t)\sigma_2^2
\]

where \(\omega_1\) and \(\omega_2\) are the probability of the two classes, with the \(\sigma_1\) and \(\sigma_2\) referring to the variance of the two classes. Thus thresholding with the Otsu algorithm allows us to define an upper and lower threshold of intensity in the image. This is then subsequently fed into the Canny edge detection procedure, originally developed by
John Canny. The steps of the Canny edge detection algorithm follows as:

1. A Gaussian blur is first applied to smooth out the image and remove shot noise and salt and pepper noise.
2. A two-dimensional intensity gradient is estimated. This uses a differentiation matrix, and the Sobel matrix is commonly used in this step.
3. Thin the edge. Since multiple diffraction spikes are observed using the Sobel filter. Only if the edge strength of a pixel is greater than the edge strength of the neighboring pixels, the pixel is assigned to an edge – otherwise it is discarded.
4. Use thresholding to determine the edges generated from the Sobel filter. Even after edge thinning multiple edges still remain which are spurious. Edges that are at the threshold edges are kept. Normally, in a Canny edge detection the thresholding parameters are user determined, and requires tweaking. To automate the edge detection procedure, we used the upper and lower thresholds calculated from the Otsu thresholding as the Canny edges.
5. Finally edges that are below a certain number of linked pixels (10 pixels in our implementation) are discarded, and thus a single continuous edge is obtained.

Fig. 4.17a demonstrates the central disk obtained from one of the CBED patterns, while Fig. 4.17b demonstrates the calculated edge obtained. Only edge values are 1, while all the rest of the values are zero. Thus as we observe through Otsu thresholding and Canny edge detection it is possible to reliably locate the edge of the central disk. Following the edge detection, the edge points can then be solved for a
circle using the algorithm given by Pratt\textsuperscript{131}. As demonstrated in Fig. 4.17c, the calculated circle fits the central disk perfectly. Thus this technique allows us to not only locate the central disk, but also to measure the disk radius with sub-pixel accuracy. This allows us thus to measure both the disk shift and change in the center of momentum ($\langle p_L \rangle$).

\textbf{Fig. 4.18 | Measured disk shift using edge detection.} \textit{a-b,} X and Y shift of disk center of mass with respect to the disk center. \textit{c-d,} X and Y shift of disk center of mass with respect to the detector center.

Fig. 4.18a-b demonstrates the shift in the center of mass, or the momentum transfer of the central disk with respect to the center of the disk in the x and y directions, while Fig. 4.18c-d demonstrates the shift with respect to the center of the diffraction pattern. Visual observation of the disk shifts and the momentum transfers illustrates three important points:

1. The momentum transfer across the domain wall is immediately visible, and it is more pronounced along the X direction as expected.
2. The contribution of disk shift is negligible, and it is the momentum redistribution across the central disk that is the major change across a domain
wall.

3. The disk shifts are inherently noisy, and while global trends are visible, local fluctuations are obscured by noise. However, this analysis, while scalable enough to work on our large datasets is not robust. The presence of pixel jump errors are present throughout the image itself demonstrating that the disk center assignment has an unacceptably high error range. So while edge assignment is fast, and works well with an accuracy of approximately a pixel, we need a technique that is precise to approximately 0.01 pixels. To implement this, we chose to use hybrid cross-correlation\textsuperscript{132}.

4.2.7 Measurement of CBED disk positions with Hybrid Cross Correlation

Cross correlation is a mathematical procedure that enables image registration, that is how shifted is a moved image with respect to a reference image. Since the brightest feature of our CBED pattern is the central undiffracted disk, thus if we choose a disk with exactly the same pixel size as compared to the size of the diffraction disk in our experimental dataset, and which is centered in the image by comparing our reference disk with the experimental CBED pattern we should be able to measure the center of our original disk with subpixel precision.
Fig. 4.19 | Hybrid Cross Correlation Disk Metrology. a, Experimental CBED pattern. b, Theoretically simulated electron beam in the diffraction plane under known experimental conditions. c, Hybrid cross correlation of Fig. 4.16a with Fig. 4.16b.

Fig. 4.19a demonstrates a representative CBED pattern with the brightest disk corresponding to the zeroth order central disk, while Fig. 4.19b demonstrates the theoretically simulated diffraction disk under equivalent experimental conditions. These two images are hybrid correlated with each other, as per the following equation\textsuperscript{132}:

\[
\mathcal{F}(g_1 \otimes g_2) = \frac{G_1 \odot G_2^*}{|G_1 \odot G_2^*|^n}
\]

where \(g_1 \otimes g_2\) refers to hybrid correlation, \(\mathcal{F}\) refers to Fourier transform, \(G_1\) refers to Fourier transform of \(g_1\), \(\odot\) refers to element wise multiplication and \(G_2^*\) refers to the complex conjugate of \(G_2\). \(n\) is the hybridization parameter. For \(n = 0\), this operation thus refers to the classical cross-correlation, while \(n = 1\) refers to phase correlation. Hybrid cross-correlation, as referred to by Pekin and Ophus recommends \(0.2 < n < 0.4\)\textsuperscript{132}. Fig. 4.16c shows the result of the hybrid correlation of the two images, 4.16.a and 4.16.b, with \(n = 0.25\). Using this hybrid correlation, the central disk can now be observed as a two-dimensional Gaussian distribution. The advantage of such an approach is that the resulting central disk, as marked by the white circle in Fig. 4.16c can be fitted with a two-dimensional Gaussian distribution, and the Gaussian peak gives a sub-pixel estimation of the central disk location.

However, the accuracy of this technique obviously depends on the similarity of our original reference disk to the experimental disk. Since the size of the diffraction disk
is proportional to the size of the condenser apertures used experimentally, thus the to ensure sub-pixel estimation, we also need precise knowledge of the experimental parameters – both the size of the pixels in the CBED pattern, and also exact convergence angle from the condenser aperture. While the initial estimates – 0.0045Å⁻¹ for the momentum pixel size, and 1mrad for the convergence angles are known, we chose to simulate CBED patterns under varying experimental conditions to quantify the exact pixel size and the aperture size.

4.2.8 Estimating experimental conditions from simulations

![Graph showing the ratio of the (002) disk center to the disk radius as a function of the condenser aperture.](image)

**Figure 4.20 | Ratio of the (002) disk center to the disk radius as a function of the condenser aperture.**

The exact momentum pixel spacing can be estimated by measuring the position of the (002) disk center relative to the center of the (000) disk and comparing it with the known values from Ca₃Ru₂O₇ diffraction patterns. Comparing with the known values, we estimated the momentum pixel spacing to be 0.0044Å⁻¹, which is close to
our original estimate, but this new more precise value allows us to improve the precision of our metrology.

We estimated the condenser aperture through two different sets of simulations. In the first approach, we compared the ratio of the radius of the central disk to the known (002) disk center as a function of the condenser aperture size. Since the (002) disk center is a crystal structure constant it remains unchanged, while the disk radius increases with increasing condenser aperture size, as plotted in Fig. 4.20. In the second approach, we plotted the disk radius in nm\(^{-1}\) as a function of the condenser aperture size, as demonstrated in Fig. 4.21.

![Figure 4.21 | Disk radius as a function of the condenser aperture.](image)

Since this approach does not need \textit{a priori} knowledge of the crystal structure, this technique is more robust and allows the estimation of the condenser aperture with just the knowledge of the momentum pixel spacing itself. Our simulations showed that the condenser apertures for our two different data sets were 0.8935 and 0.9241
mrad respectively – which is again close to the original guess of 1 mrad – but is significantly more precise.

**Fig. 4.22 | Experimental vs calculated CBED pattern.** a, Simulated CBED pattern using the calculated condenser aperture and momentum pixel spacing. b, Experimental CBED pattern.

The knowledge of condenser aperture size and the momentum pixel spacing allows us to simulate CBED pattern and compare them with our experimentally obtained datasets – as shown in Fig. 4.22. Comparison between the two patterns demonstrated equivalent disk spacings, thus indicating the accuracy of our measurements.
Figure 4.23 | Calculated Momentum Transfer. a, Momentum transfer as a ratio of the beam momentum in the X direction. b, Momentum transfer as a ratio of the beam momentum in the Y direction.

We applied this procedure to estimate the momentum redistribution across the 4D dataset, originally measured in Fig. 4.18, and compared to the edge fitting approach demonstrated before, this technique is much less noisy and allows the direct sub-pixel precision estimation of momentum transfer, with Fig. 4.23a demonstrating a clear momentum reversal across the 90° domain wall in the image along the x direction.

However, to estimate the projected potential from momentum transfer measurements, we need to know how thick the sample is. This is because the momentum accumulated is a function of both the force and the time duration of the force. While the force is itself directly related to the potential gradient, the time the electron experiences that force is inversely proportional to the thickness of the sample, assuming that the electron velocity remains unchanged inside the sample. Thus we need to measure the thickness of the sampled imaged by the electron beam.
The hypothesis behind our thickness measurement approach is that the intensity distribution of the disks inside the CBED pattern is dependent of the thickness on the sample. Thus, our approach was to compare simulated CBED patterns with the experimental CBED patterns to measure the thickness. To test this, we simulated 300 CBED patterns for \( \text{Ca}_3\text{Ru}_2\text{O}_7 \) in steps of 0.5nm, starting from 0.5nm of thickness, and going all the way up to 150nm. Since an a representative 4D-STEM experimental dataset contains on average 20,000 unique CBED patterns, thus visual estimation of thickness by the manual comparison of six million CBED patterns is thus frankly impossible. While more advanced GPU based pattern recognition algorithms that generate neural nets from the CBED patterns is certainly possible in the future, for our current approach we tried four different comparison approaches:

1. **Multiplying the variance normalized absolute CBED matrices:** The
experimental and the simulated CBED pattern were both normalized to have a zero mean and unit variance. The two matrices were multiplied using element wise multiplication, and the sum of the matrix is taken as the comparison score.

2. **Calculation of a 2D cross-correlation score:** A cross correlation score is calculated for the two matrices.

3. **Absolute sum of the multiplication of the Fourier transforms of the two CBED patterns being compared**

4. **Absolute sum of the cross-correlation of the CBED patterns.**

To test the validity of our approaches, we compared our simulated CBED data with each other. We take one pattern from the library of the 300 simulated CBED patterns and compare the pattern with the library, and repeat this for all the 300 patterns. Thus, we obtain a 300X300 matrix, as shown in Fig. 4.24. If a technique is successful in identifying the pattern, then either the maxima or the minima should occur when the patterns match.

We observed that in the first three cases the maxima occurred when the thickness of the two compared CBED patterns were equivalent, and thus the first three approaches are valid approaches towards calculating sample thickness. Of these three approaches the fastest computation speeds were observed in the first approach and thus it was used for thickness estimation.
The obtained sample thickness based on our approach was approximately 21nm in the sample, as shown in Fig. 4.25. To test the validity of this approach we also compared our performed thickness measurements using plasmon imaging in EELS, where the intensity of the zero loss EELS peak is compared to the intensity of the plasmon peak, and the ratio generates the sample thickness\textsuperscript{75}. The calculated sample thickness was approximately 25nm for our sample, as shown in Fig. 4.26 – demonstrating the validity of the approach.

**Fig. 4.25 | Calculated sample thickness after comparison with simulated CBED patterns.**

**Fig. 4.26 | Measured sample thickness by EELS. a,** Measured sample thickness in the center region of the sample showing an average thickness of 25nm. **b,** Measured sample thickness at the edge of the FIB sample
The estimation of the thickness thus allows the estimation of the time spent by the electron beam in the sample, since the relativistic electron velocity at an accelerating voltage can be calculate as per the following equation:

\[
\vartheta = c \sqrt{1 - \frac{1}{\left(1 + \frac{Ve}{m_e c^2}\right)^2}}
\]

Where \( \vartheta \) refers to the relativistic velocity, \( V \) refers to the accelerating voltage, \( e \) refers to the charge of an electron, \( m_e \) refers to electron rest mass and \( c \) refers to the speed of light.

![Figure 4.27 | Time of flight of relativistic electron inside the sample.](image)

Dividing the thickness by the relativistic velocity, we obtain the time spent by the electron in the sample, as shown in Fig. 4.23 with a slightly higher time spent at the domain wall owing to its increased thickness.

The time of flight thus allows the estimation of the electric field as per the following formula:

\[
\vec{E} = \frac{\langle \vec{p} \rangle}{et}
\]

Where \( \vec{E} \) refers to the electric field, \( \langle \vec{p} \rangle \) refers to measured momentum change at the
scanning position, \( e \) refers to the charge of the electron, and \( t \) refers to the time of flight at that scanning position.

**Figure 4.28 | Calculated Electric Field.** a, Electric Field in the X direction. b, Electric Field in the Y direction.

Since the thickness is already accounted for in the time of flight calculations, thus the electric fields calculated are independent of the sample thickness, and should be better reported as the Z averaged electric field, where Z refers to the beam propagation direction along the optic axis. As Fig. 4.24 demonstrates, the calculated electric fields are of the order of \( 10^7 \text{ Vm}^{-1} \), indicating significantly high electric fields in the vicinity of the domain wall.

The obtained electric fields can now be integrated to obtain the Z averaged momentum change for the sample. There have been two slightly different formulae for calculating momentum changes. The first, from Findlay\textsuperscript{133,134}: 
\[ \varphi(x, y) = \mathcal{F}^{-1} \left[ \frac{\mathcal{F}[I_x(x, y)](k_x, k_y) + i\mathcal{F}[I_y(x, y)](k_x, k_y)}{2\pi i(k_x + ik_y)} \right] \]

While the second formula is given by Lazic\textsuperscript{135}:

\[ \varphi(x, y) = \mathcal{F}^{-1} \left[ \frac{k_x\mathcal{F}[I_x(x, y)](k_x, k_y) + k_y\mathcal{F}[I_y(x, y)](k_x, k_y)}{2\pi i(k_x^2 + k_y^2)} \right] \]

Where \( \varphi(x, y) \) refers to the potential, and \( k_x \) and \( k_y \) refer to the Fourier coordinates.

**Figure 4.29 | Calculated potential from DPC.** 

a, Calculated potential using the Findlay formula. b, Calculated potential using the Lazic formula.

As Fig. 4.25 demonstrates both the approaches give really similar results, and show 0.2V of potential change in the vicinity of the domain wall. The magnitude of the potential change is right in line with predicted decrease in the work function, demonstrating the viability of this technique for measuring mesoscopic electric fields.
A second set of 4D-STEM experiments were also performed, with a significantly long scanning axis along the 90° domain wall to capture the evolution of differential phase contrast and potential change along the wall. The experimental setup was also modified to allow the capture of the BF-STEM image before the 4D-STEM scan, during the 4D-STEM scan and after the 4D-STEM scan, as demonstrated in Fig. 4.30a-c. As observed, in Fig.1 the electron microscope sample undergoes minimal changes over the course of the experiment. Additionally, it can also be observed that while there is a central 90° domain wall, and multiple 180° domain walls, only a certain few of these are visible in the BF-STEM images. The intensity measured in the BF-STEM image is a function of the total nuclear potential observed by the electron beam. Thus this depends on both the mean inner potential of the crystal, and the thickness of the sample. The ideal mean inner potential is given by the following formula\textsuperscript{136,137}:
where $V_0$ is the mean inner potential, $\Omega$ is the unit cell volume and $\nu_p$ is the potential associated with an atom at position $(x, y)$. Thus the mean inner potential is a function of the chemical composition, and the unit cell volume, and can vary due to the presence of strain, which can change $\Omega$ or the chemical composition, which modifies $\nu_p(x, y)$. The BF-STEM intensity is a function of the mean inner potential, multiplied by the sample thickness.

Thus the absence of contrast at the domain walls indicates negligible change in the strain, chemical composition and sample thickness across the domain walls, which remain invisible. In fact, to classify, only the bottom portion of the 90° domain wall is visible in the BF-STEM images, while none of the 180° domain walls are visible.

However, when measuring the center of mass of the central (000) disks from the obtained 4D-STEM datasets, we observe something completely different. Observing the x shift of the center of mass of the central disk in Fig. 4.31b, where the x direction is along the short axis of the image, the 90° domain wall at the center of the image demonstrates x shift throughout the length of the image, while two of the of the 180° domain walls also demonstrate x disk shifts. Since the pixel size in the CBED pattern has been previously calibrated, we can directly measure the $\vec{k}$ vector arising from the disk displacement along the x direction.
**Fig. 4.31 | Center of Mass shift in the X direction.**

**a,** BF-STEM images simultaneously captured. 

**b,** Measured center of mass shift of the central (000) disk in pixels in the x direction, where the y direction is the long axis and the x direction is the short axis. 

**c,** Measured center of mass shift multiplied by the momentum space pixel size to map the $\vec{k}$ vector transferred to the central undiffracted beam along the x direction.

The $\vec{k}$ vector is given by the following formula:

$$\vec{k} = c \cdot \overline{COM}$$

where $c$ is the pixel size in inverse length units, which is 0.0013 Å$^{-1}$ for the current experimental setup and $\overline{COM}$ is the measured center of mass shift of the central (000) disk in pixels. Following an identical procedure, the y displacement of the center of mass of the central disk was also calculated, as demonstrated in Fig. 4.32b-c. Similar to the observations of the x displacement of the central disk, the y displacement also demonstrates disk shift along the 90° central domain wall, along with disk shifts along 180° domain walls that remain almost invisible in the BF-STEM images.
Fig. 4.32 | Center of Mass shift in the Y direction. a, BF-STEM images simultaneously captured. b, Measured center of mass shift of the central (000) disk in pixels in the y direction, where the y direction is the long axis and the x direction is the short axis. c, Measured center of mass shift multiplied by the momentum space pixel size to map the $\mathbf{k}$ vector transferred to the central undiffracted beam along the y direction.

Even more interestingly, we observe that in the top left of the image, a different 180° domain wall demonstrates disk shifts. Thus, we can conclude there are potential variations observed by the central disks, which are however independent of total projected nuclear potential, as they do not show up in the BF-STEM images.
Following the similar procedure implemented in the previous section, we also calculated the sample thickness by comparing the experimentally measured CBED patterns, with the theoretically simulated CBED patterns, as demonstrated in Fig. 4.33. We observe uniform thickness in the bulk domain and a decrease in the measured thickness right at the domain boundary. We propose that while the thickness measurement using CBED works at the domain boundary itself, it fails to accurately measure the thickness at a charged domain boundary. The electron beam because the intensity pattern of the central disk does not remain the same as the theoretical uncharged simulation at the domain boundary due to momentum redistribution occurring in the diffraction disks from
potential gradients. Since our thickness measurement algorithms work by comparing
diffraction disk intensities of the experimental and the simulated CBED patterns for
which the beam does not experience any potential gradient, our technique currently fails
to accurately take into account contributions from intensity variations owing to effects
independent of thickness and thus gives erroneous results.

**Fig. 4.34 | Measured potential change in the sample.**

Thus, in light of these we do not take the thickness measured for our momentum
transfer calculations, and perform our calculations with the calculated median
thickness of 21nm observed in the image, which is shown in Fig.4.34. We observe a
0.2V dip in potential across the 90° domain boundary, and a 0.14V dip in the
potential at the 180° boundary. Interestingly, this 180° domain boundary does not
show up in the BF-STEM images indicating that the potential drop measured is not arising from projected potential variations, but arising entirely due to changes in the Fermi level. The change in the Fermi level itself could be either due to the crystal structure itself or may be an effect of charge accumulation, however our technique currently cannot distinguish between the two. Additionally, the width of the potential measured along the 90° domain boundary itself is not consistent, and is varies. This can be understood in light of the fact that the 90° domain wall itself changes in nature as it crosses a domain junction with a 180° domain boundary. Additionally, we also observe the width of the domain wall is around five scanning pixels approximately, which corresponds to around 2.5nm. The resolution of this DPC technique is ultimately also determined by the size of the probe – which was around 1.3nm for our experimental setup. Thus while the DPC potential measurements are convoluted with the probe size, the potential decrease approximately happens around a 1-1.5nm region of the domain boundary. Observing the 180° domain boundary, we also notice that the potential drop is not uniform across the boundary, with deeper and wider gradients near the junction, which decrease as we move away from the domain junction.

This indicates that not only is there a potential drop associated with the Fermi level, the interaction with the 90° domain boundary may result in charge transferred to the 180° domain wall, with the magnitude of the charge transfer decreasing as a function of the distance from the domain junction.

4.3 Comparison with theoretical calculations

To further understand our results we compared our experimental results with first
principles calculations performed by the Rondinelli group at Northwestern University. Since the 5% titanium doping concentrations would result in enormously large calculation unit cells, the simulations were performed for undoped Ca$_3$Ru$_2$O$_7$. Fig. 4.35a demonstrates the density of states for the calcium atoms, the ruthenium atoms and the oxygen atoms for the left domain, 180° domain wall and the right domain marked by the blue, black and orange boxes respectively.

![Figure 4.35](image)

**Figure 4.35** | **First principles calculation of 180° walls in Ca$_3$Ru$_2$O$_7**. a, Density of states for the left domain, domain wall and the right domain. b, Theoretically calculated crystal structure of a 180° domain wall in Ca$_3$Ru$_2$O$_7$. (Danilo Puggioni and James Rondinelli, Northwestern University)**

Fig. 4.35b demonstrates the theoretically calculated crystal structure of the 180° domain wall with the polar axis switching from left to right across the wall. Theoretical simulations demonstrate the varying density of states arising from the calcium s orbitals, the ruthenium d orbitals and the oxygen p orbitals. While the
oxygen $p$ orbitals remain unchanged at the $180^\circ$ domain boundaries when compared to the bulk domain, the ruthenium $d$ orbitals change at the domain wall itself, indicating a change in the Fermi surface that is driven by the ruthenium atoms.

Fig. 4.36 calculates the electron concentration of the three different possible $90^\circ$ domain boundaries – head-to-tail, head-to-head and tail-to-tail domain boundaries.

Figure 4.36 | Electron accumulation at different possible $90^\circ$ domain boundary configurations in Ca$_3$Ru$_2$O$_7$ (Danilo Puggioni and James Rondinelli, Northwestern University)

We observe that the bulk electron concentration of the domain itself is 35.7 electrons per unit cell. However all three possible $90^\circ$ domain boundaries show increased carrier concentrations compared to the bulk domain, with the tail to tail domain wall at 36.3 electrons per unit cell, the tail-to-head domain wall at 36.1 electrons per unit cell, and the head-to-head domain wall at 35.9 electrons per unit cell.

This indicates the carrier concentration of the $90^\circ$ domain boundary is always higher when compared to the bulk domain. This result is illustrated again in the potential measurements performed using first principles calculations at the three types of $90^\circ$ domain walls, as shown in Fig. 4.37. Since all three walls have a higher charge
accumulation compared to the bulk domain, it is reflected by the decrease in the average potential at the wall compared to the bulk domain.

Even the uncharged 90° domain walls, shown in blue demonstrate 0.09V decrease in the potential compared to the bulk. For negatively charged head to head walls, the potential decrease is approximately -0.15V, while for positively charged tail-to-tail domain walls the potential decrease is approximately -0.03V.

**Figure 4.37 | Calculated potential at charged and uncharged 90° domain walls in Ca₃Ru₂O₇ (Danilo Puggioni and James Rondinelli, Northwestern University)**

Comparing with our experimentally measured potential variations across the domain boundaries in 5%Ti- Ca₃Ru₂O₇ we see a similar pattern, where the domain boundaries show a similar magnitude of potential change across the domain wall. This illustrates that the potential measured by the DPC technique can reliably measure nanometer resolution changes in the structural potential, with values that are similar in magnitude to values predicted theoretically.
4.4 Conclusions

Thus we have demonstrated for the first time, the existence of charged domain walls in a polar hybrid improper ferroelectric crystal. Our investigations demonstrate an unprecedented richness of the structural and electronic landscape of Ca$_3$Ru$_2$O$_7$ with the possibility of further tenability of electronic properties with dopant concentrations. The polar landscape also demonstrates the possibility of not only multiple types of domain walls, but also domain junctions, and the intriguing prospect of multiple domain walls interacting with each other to create novel electronic states in domain boundaries.

Additionally, we have described and implemented a complete methodology to measure potential changes with the electron microscope. The promise of the electron microscope has always been ultra-high resolution structural metrology, but our results here demonstrate that with modifications to the experimental conditions, DPC can be reliably used to measure electric potentials originating from interfaces and domain boundaries.

Thus the electron microscope can not only be used to image and quantify the structure, but also simultaneously measure the resultant electronic features that occur from the structure – enabling the full spectrum of structure-property measurements in one single experiment.
5. Conclusions

In this thesis we have demonstrated the possibility and methodology of metrology of ferroelectric domain walls using transmission electron microscopy. We initially developed a novel approach – the MPFit algorithm – to reliably measure atom positions from STEM images. We demonstrate how this technique works even when the atom positions are not easily picked up by standard Gaussian peak fitting approaches. Our technique is robust and works on a significantly wider range of datasets.

We then subsequently used this technique to measure the niobium-oxygen displacements across 180° domain walls in LiNbO₃. While the canonical Ising type of displacements matched closely with theoretical predictions, we also observed discontinuous regions of Néel displacements, a completely unexpected results. Using
first principles calculations we demonstrated that the origin of these rotational components was the decrease in thermodynamic energy arising from an increase in the polar configurational entropy. We measured the polar entropy from STEM images, with our results demonstrating close fidelity to theoretical predictions. This demonstrates that even in hard uniaxial ferroelectrics like LiNbO$_3$, the polar landscape is significantly more disordered at room temperature than previously understood, and provides a pathway towards understanding more disordered polar crystals like relaxor ferroelectrics.

We also used our custom developed displacement metrology analysis toolkit to study the crystal structure of the metallic hybrid improper ferroelectric – 5% titanium doped Ca$_3$Ru$_2$O$_7$. We observed three different configurations of 90° domain boundaries – head-to-head, head-to-tail and tail-to-tail walls. We also observed domain junctions with 180° domain walls across which the 90° domain boundary changed its’ configuration. To measure the electronic structure of the observed domain boundaries, in association with the National Center for Electron Microscopy at the Lawrence Berkeley National Laboratory we developed DPC-STEM imaging using four dimensional electron microscopy datasets obtained using pixelated detectors in the Fourier plane. We developed novel analysis techniques for these datasets, enabling the measurement of mesoscopic potential change for the first time in the electron microscope. The potential changes we measured, of the order of -0.2V demonstrated close fidelity to the predicted average potential changes by first principles calculations of domain boundaries in Ca$_3$Ru$_2$O$_7$. Our work demonstrates the astonishing complexity of domain features in such a novel material, whose
applications range from thermoelectrics to memory devices. Additionally, the DPC techniques developed by us is not restricted to just the samples imaged. They are applicable to studying the potential landscape of any interfaces, and our method for the first time, demonstrates how to implement DPC as an imaging technique. Thus, in conclusion, this thesis demonstrates that scanning transmission electron microscopy is a viable tool for analyzing the structural and electronic features in ferroelectric domain walls.
6. Future Work

A noted shortcoming of the current DPC technique proposed in this work is that while interface potentials can be reliably measured, to do such measurements the beam has to be necessarily bigger than the unit cell to prevent disk overlap in the diffraction plane. This results in beam sizes that are larger than a nanometer, making it impossible to image the atomic resolution crystal structure. While fast switching between condenser apertures can allow the imaging of the region of interest for the DPC experiments to be subsequently imaged at atomic resolutions with STEM, a one-on-one registry between the atomic resolution image and the DPC data would be challenging. This will be compounded by the fact that owing to different sampling rates for DPC and aberration corrected atomic resolution imaging; the mechanical and thermal drift would be different in the two experimental datasets. Additionally,
for beam sensitive samples, multiple imaging sessions over the same region introduce defects induced by the electron beam, and thus the material itself may change between the two experiments.

However, this issue may be resolved by rethinking the STEM image itself. In a STEM experiment, an electron probe is rastered across a sample, with the intensity captured by a series of concentric detectors. 4D-STEM does away with the circular detectors and uses a pixelated detector in the diffraction plane to capture the entire diffraction pattern at every scanning point. Thus every STEM image is necessarily four-dimensional, with the two momentum dimensions summed up along a certain radial value to obtain a STEM image. When the summation is from 0 to 15mrad, the resultant image is a BF-STEM image, and when it occurs from 85mrad onwards it is a HAADF-STEM image.

With this insight, we can capture the projected atomic potential observed by the electron beam at every point, if there is redundancy in our dataset as per the Nyquist-Shannon sampling theorem. Thus, if our beam sizes are of the order of a nanometer, scanning pixel separation distances of approximately 0.2nm ensure a redundancy of at least 5 in the data. This approach is also referred to as ptychography, where the atomic potential is reconstructed from the observed electron beam.

Future research directions for 4D-STEM image can incorporate ptychography to simultaneously image the atomic structure with sub-angstrom resolution, and use the obtained DPC measurements to measure the mesoscopic electronic potential. The additional advantage of ptychography is the ability to distinguish between the
structural component and the electronic component.

Thus areas where metrology is still uncertain, owing to BF-STEM intensity variations, which may arise from strain, thickness or ionicity variations can be reliably measured, and just the Fermi level potential gradients can be measured. In fact, while this work focused on domain walls owing to structural homogeneity on both sides of the interface, ptychography combined with DPC would enable metrology even across varying interfaces like two-dimensional electron gas formations across the LaAlO$_3$-SrTiO$_3$ interfaces$^{137}$.

Another future area of algorithm development should be focused on leveraging the power of graphical processing units. Compared to the sputter in Moore’s law, Amdahl’s law has seen a steady march in the recent decades$^{141}$. Many of the analytical problems in electron microscopy are embarrassingly parallel – making them ideal for GPU computation.

The advances in neural networks and machine learning also now raise the possibility of creating large training datasets. The thickness metrology issue mentioned in chapter 4 can be circumvented using a training dataset of CBED patterns, to train convolutional neural networks, and use machine learning to guess the thickness.

The single biggest change in science in the past few years has probably been the rise of data analytics. With aberration corrected microscopy, the operational aspects have become easier than previous decades – and thus an electron microscope image should now not be thought of as an image – but as part of a bigger dataset. Utilizing advances in big data analytics will allow even more detailed metrology that is currently possible.
References


VITA

Debangshu Mukherjee was born in Calcutta (now Kolkata), India. He finished a dual degree from the Indian Institute of Technology Kharagpur, India with a B.Tech. (Hons.) in Metallurgical and Materials Engineering, and a M.Tech. in Metallurgical Engineering from 2006 to 2011. He then finished a MS degree in Materials Science and Engineering from Boston University in 2013. From 2013 to 2018, he completed his PhD in Materials Science and Engineering at Penn State in Materials Science and Engineering, where he worked on developing new STEM techniques as a part of his PhD dissertation research. Debangshu aims to continue that work as a postdoctoral researcher at Oak Ridge National Laboratory.