LOCAL STRUCTURE AND SHAPING OF FERROELECTRIC DOMAIN WALLS FOR PHOTONIC APPLICATIONS

A Thesis in

Materials

by

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ABSTRACT

Ferroelectric lithium niobate (LiNbO$_3$) and lithium tantalate (LiTaO$_3$) have emerged as key technological materials for use in photonic applications, due to the high quality of crystal growth, optical transparency over a wide frequency range (240nm – 4.5 µm), and their large electro-optic and nonlinear optical coefficients. Emerging fields of optical communications, optical data storage, displays, biomedical devices, sensing, and defense applications will all rely heavily on such ferroelectrics as a versatile solid-state photonic platform.

Diverse functionalities can be created in these materials simply through the patterning of the ferroelectric domains. By creating specific domain features in these materials, it is possible to create new laser wavelengths from existing sources as well as active electro-optic structures that can dynamically focus, shape and steer light. However, the process of domain shaping today is mostly empirical, based on trial-and-error rather than sound, predictive science.

The central focus of this thesis work is to develop a fundamental understanding of how to shape and control domain walls in ferroelectrics, specifically in lithium niobate and lithium tantalate, for photonic applications. An understanding of the domain wall phenomena is being approached at two levels: the macroscale and the nanoscale. On the macroscale, different electric field poling techniques are developed and used to create domain shapes of arbitrary orientation. A theoretical framework based on Ginzburg-Landau-Devonshire theory is developed to determine the preferred domain wall shapes. Differences in the poling characteristics and domain wall shapes between the two
materials as well as differences in material composition relates to nonstoichiometric defects in the crystal. At the nanoscale, these defects influence the local electromechanical properties of the domain wall. Understanding from both of these approaches has been used to design and create photonic devices through micro-patterned ferroelectrics. Increased fundamental understanding of the poling kinetics and domain wall properties developed in this thesis can lead to a more predictive, scientific towards domain wall shaping.
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Chapter 1

Introduction and Motivation of Work

1.1 Ferroelectric materials

The ability of ferroelectric materials to sustain spontaneous polarization in the absence of external electric fields constitutes the basis for their wide technological applicability. First discovered in Rochelle salt in the 1920’s and then in KDP (KH$_2$PO$_4$) in the 1930’s, ferroelectricity was once considered erroneously to occur only in compounds containing hydrogen bonds, which limited the search to hydrogen-containing compounds. The discovery of ferroelectricity in the perovskite BaTiO$_3$ in 1946, led to a surge in new ferroelectric materials and theoretical development. It was quickly realized that the strong electromechanical coupling present in ferroelectrics could be used in applications as sensors, actuators, and transducers. Following the advent of the laser in 1958 by Schawlow$^1$ and the discovery of second harmonic radiation from a quartz crystal by Franken et al in 1961$^2$, further interest in ferroelectrics was generated due to their nonlinear optical properties. In the last decade, ferroelectric materials have been developed as both bulk and thin film “smart” materials which can be used in electromechanical, optical, pyroelectric, capacitor, and nonvolatile memory applications.
Ferroelectric materials must have pyroelectric properties (changes in spontaneous polarization with temperature), and must possess spontaneous polarization along specific directions that can be reversed by the application of an external electric field smaller than the breakdown field of the material. The existence of pyroelectricity is governed by the symmetry of crystals; however, ferroelectricity needs to be experimentally determined for each crystal. This is done through the measurements of the hysteresis loop, where the polarization state is switched between two polarization directions with the application of an external field as shown in Figure 1-1. These two spontaneous polarization directions are equivalent in energy, differing only in the direction of the polarization vector.

Figure 1-1: Hysteresis loops in congruent and stoichiometric LiTaO$_3$. The offset to the congruent material loop is due to the internal field, $E_{\text{int}}$, caused by lithium nonstoichiometry. Diagram adapted from Kitamura.\textsuperscript{3}
1.2 Lithium Niobate (LiNbO$_3$) and Lithium Tantalate (LiTaO$_3$)

Ferroelectricity in lithium niobate (LiNbO$_3$) and lithium tantalate (LiTaO$_3$) was first discovered by Matthias and Remeika in 1949. Large ferroelectric single crystals of LiNbO$_3$ and LiTaO$_3$ became available through the development of Czochralski crystal growth techniques in 1965 simultaneously by S.A. Fedulov in the USSR and by A. A. Ballman in the USA. Ever since, these materials have been the focus of intense research due to their attractive optical and piezoelectric properties. Focused development of the crystal growth has led to very uniform and high quality crystals grown in boules up to 4 inches in diameter. Recently lithium niobate has established itself as a benchmark material for use in optical communications, based on the availability of high quality crystals, optical transparency over a wide frequency range (240nm – 4.5 um), and good nonlinear optical properties. Commercial products in lithium niobate include surface acoustic wave devices, as well as Mach-Zender interferometers for modulation of optical signals.

The trigonal unit cell and the atomic arrangement in the basal plane are shown in Figure 1-2. The lattice constants of the trigonal cell $a = 5.14829$ and 5.154 Å and $c = 13.8631$ and 13.7808 Å for congruent LiNbO$_3$ and LiTaO$_3$, respectively. Both LiTaO$_3$ and LiNbO$_3$ show a second order phase transition from a higher temperature paraelectric phase with space group symmetry $R\bar{3}c$ (point group $\bar{3}m$) to a ferroelectric phase of symmetry $R3c$ (point group $3m$) at Curie temperatures $T_c$ of ~690° C and ~1190° C, respectively. This transition corresponds to a loss of the inversion symmetry at the
transition point which allows the development of the spontaneous polarization along the polar c axis.

The side view of the ferroelectric polar axis is shown in Figure 1.3. The distorted oxygen octahedra are linked together by common faces along the c axis, forming equidistant oxygen layers perpendicular to the c axis with distance c/6. In LiNbO$_3$ along the polar c axis, the Nb atom is displaced by 0.25 Å from the center of its octahedron and the Li atom is displaced by 0.73 Å from the oxygen plane between the Li octahedron and the empty octahedron at 295 K. In LiTaO$_3$, the displacements are 0.20 Å for the Ta 0.60 Å for the Li. In this way, the displacive vector for the Li and Nb (Ta) are defined in the same sense, both pointing in the same crystallographic axis. It is these displacements that give rise to the dipoles producing the spontaneous polarization. Since each near neighbor Li$^+$ - Nb$^{5+}$ (or Ta$^{5+}$) pair is oriented in a specific sense along the trigonal axis; the material has a net spontaneous ferroelectric polarization, $P_s$, oriented along the c-axis. The
stacking sequence along the polar $c$-axis can be described as \( \cdots \text{Li, Nb(Ta)}, \square, \text{Li, Nb(Ta)}, \square, \cdots \) where \( \square \) represents an empty oxygen octahedron, and the spontaneous polarization, \( P_s \), here points from left to right. This is also shown in Figure 1-3. The cation displacements can be in either one of two antiparallel directions along the $c$ axis. The spontaneous polarization then can be aligned either “up” or “down,” giving rise to only two possible polarizations which are 180° to one another, $+P_s$ or $-P_s$. Because of the large offset of the cations from the center positions, these materials have high spontaneous polarization values ($\sim 55 \ \mu$C/cm$^2$ for LiTaO$_3^{12}$ and $\sim 75 \ \mu$C/cm$^2$ for LiNbO$_3^{13}$). During polarization reversal, the Nb (or Ta) ions move from one asymmetric position within its oxygen octahedra to the other asymmetric position, while the lithium atom moves through the close packed oxygen plane to the adjacent empty octahedra. This was initial thought to preclude any domain reversal at room temperature with electric fields because abundant thermal energy was thought to be necessary to promote the movement of the lithium through the oxygen plane.$^{14}$ Further, extrapolation of coercive fields near the Curie temperature to room temperature gave the coercive field to be $\sim 5 \ \text{MV/mm}$ which is far above the breakdown strength of the material, hence the nickname “frozen ferroelectric”.$^{10}$ However, it has since been shown that room temperature polarization reversal can be achieved with coercive fields of $\sim 22 \ \text{kV/mm}$ for both materials.
Although called LiNbO$_3$ and LiTaO$_3$, the phases exist over a wide solid solution range. Commercially available crystals for both systems are actually of congruent composition which is easier to grow from the melt as shown in Figure 1-4. Congruent crystals of LiNbO$_3$ and LiTaO$_3$ are actually lithium deficient, with a composition ratio $C = \frac{\text{Li}}{\text{Li} + \text{(Ta,Nb)}} = 0.485$. Stoichiometric crystals of both systems ($C=0.5$) are also grown, but are difficult to fabricate and not yet widely commercially available.

Figure 1-3: Schematic of the crystal structure of lithium niobate and lithium tantalate. The spontaneous polarization ($P_s$) is pointing up in (a) and down in (b).
Figure 1-4: Representative phase diagram of LiTaO$_3$ near melting point. Diagram adapted from Miyazawa$^{15}$ and Roth.$^{16}$

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There are several different models for how the congruent crystals incorporate the lithium deficiency and the exact defect model is still under considerable debate. One of the first proposed models concluded that lithium vacancies \( (V'_{Li}) \) and oxygen vacancies \( (V''_O) \) dominate at room temperature.\(^9\) However this has since been disproved as the density of the crystals increases with increasing lithium deficiency.\(^17\) This suggests a completely filled oxygen sublattice with charge-balancing Nb antisite defects. There are two competing theories. One model proposes niobium antisites \( (Nb_{Li}^{****}) \) and niobium vacancies \( (V''''_{Nb}) \) as the dominant point defects.\(^18\) However, recent experiments suggest a fully occupied a Nb sublattice,\(^19-21\) and simulations show that the formation of a niobium vacancies are energetically unfavorable compared to a lithium vacancies.\(^22\) This data suggests a defect model with niobium antisites \( (Nb_{Li}^{****}) \) surrounded in the local environment by four lithium vacancies \( (V'_{Li}) \).\(^23\) Several other experimental works support this model, including neutron diffraction studies,\(^24,25\) nuclear magnetic resonance (NMR) spectra,\(^26,27\) and x-ray and neutron diffuse scattering in congruent LiNbO\(_3\).\(^28-30\) All of this data strongly suggests the niobium antite lithium vacancy model of \([Li_{0.95}Nb_{0.01}O_{0.04}]NbO_3\), however no general agreement has yet been achieved. Recently, the organization of these four lithium vacancies around a niobium antisite has been proposed to form a polar defect cluster as shown in Figure 1-5.\(^31\) This dipolar model was proposed to explain the time dependence of the backswitching kinetics in LiTaO\(_3\)\(^31\) as well as the origin and temperature dependence of the internal field in the congruent crystals of both compositions.\(^32\) In this model, the lithium vacancies arrange themselves around the Nb (or Ta) antisite in a low energy configuration with an associated defect
field, $F_d$, that is pointing in the same direction as the spontaneous polarization as shown in Figure 1-5(b). Upon reversal of the spontaneous polarization, the Nb (or Ta) antisite moved through the close packed oxygen plane to the other side, but the associated lithium vacancies are locked in place. The defect field, $F_d$, is now in a frustrated state pointing in the opposite direction of the spontaneous polarization (Figure 1-5(c)). Annealing at temperatures $>150^\circ$C allows these lithium vacancies to move and reconfigure to a lower energy configuration with the defect field pointing in the same sense as the spontaneous polarization as shown in Figure 1-5.

The lithium nonstoichiometry and the associated defect dipoles have a profound influence on many of the properties of the crystal, including the coercive field and the internal field. The nonstoichiometry of the congruent compositions gives rise to a very large coercive field $\sim21-22$ kV/mm for both congruent crystals. These defects also give rise to a large internal field which is manifest in the coercive field loop as a horizontal offset from zero of $\sim2.7-3.5$ kV/mm in LiNbO$_3$ and $\sim4.2-5.0$ kV/mm for LiTaO$_3$.\textsuperscript{33} This is shown in a sample hysteresis loop in Figure 1-1. In the stoichiometric crystals, the internal field disappears and the coercive field drops to $\sim1.7$ kV/mm$^{-1}$ in LiTaO$_3$ and $\sim4.0$ kV/mm$^{-1}$ in LiNbO$_3$.\textsuperscript{13,31} Also it is important to note, that the defects can be in frustrated states, where the field associated with the defect is in an opposite orientation than the spontaneous polarization, as shown in Figure 1-5(c).
1.3 Domain Walls in Ferroelectrics

A uniform volume of material with the same spontaneous polarization direction is called a \textit{domain} and a \textit{domain wall} separates two different domain states. Both LiNbO$_3$ and LiTaO$_3$ have only two polarization states, parallel and antiparallel to the $c$-axis, so a domain wall in these materials separate two oppositely oriented domains. This is perhaps the simplest type of domain wall, and can be thought of as a prototypical system to study.

A ferromagnetic domain wall separates two areas of uniform magnetization where the magnetization vector turns over gradually and reverses direction over distances of approximately 300 lattice constants due to the large magnetic exchange energy.\cite{34} This is in contrast to domain walls in ferroelectric crystals which have no analog to the magnetic exchange energy. Because of this, the atomic displacements transition in a domain wall vary over very narrow distances only several lattice constants wide.\cite{34,35} Several authors\cite{36-39} have modeled domain walls in ferroelectric and ferroelastic materials based on continuum Landau-Ginzburg-Devonshire theory. From these models, the domain wall represents a transition region across which the elastic distortion of the material varies smoothly, in a manner quantified by a finite wall width. Numerous experimental works have experimentally measured the wall with to be less than 40 Å in BaTiO$_3$.\cite{40-42} The $a$-$c$ domain wall has been measured using high-resolution transmission electron microscopy (HTREM) in PbTiO$_3$ to be $\sim$1 nm.\cite{43,44} Similar HTREM measurements in LiTaO$_3$ establishes an upper limit of 2.8 Å.\cite{45}

Ferroelectrics possess many cross coupled phenomena which intricately couple elastic, electrical and optical properties through a variety of interconnected phenomena
such as piezoelectricity (strain to electric fields), elasto-optic effect (strain to optical index), and electro-optic effect (electric field to optical index), to name a few. On transitioning from one polarization direction to another, which takes place in a domain wall, these couplings are clearly active. These domain walls are regions of spontaneous polarization gradient and strain which can result in localized electric fields through the piezoelectric effect and can exhibit changes in the optical index. Although the width of the domain wall is quite narrow, the manifestation of many properties associated with transition from one domain state to the other are quite wide. For example, in both LiNbO$_3$ and LiTaO$_3$ very wide regions of strain$^{46}$ and optical birefringence$^{47}$ extending over micrometers have been observed and are shown to correlate strongly with nonstoichiometry of the crystal.$^{48}$

At a more macroscale, these domain walls are allowed only in very specific orientations along planes allowable by crystal symmetry and on which the conditions of mechanical compatibility are satisfied.$^{49}$ The orientations are determined by the free energy minimum and include contributions from the electrostatic energy, the elastic energy, and the interaction of these energies with point defects and dislocations. The crystal non-stoichiometry has a dramatic influence on the allowed domain wall orientation as shown in Figure 1-6.
Ferroelectric domain walls are related to the transition of atomic displacements which are manifest on the nanoscale and microscale at a domain wall, and these domain walls are then organized at the macroscale into specific domain shapes. Therefore, in order to better control and shape ferroelectric domain walls, one needs to understand the phenomenon of domains and domain walls at all of these length scales.

1.4 Applications of Ferroelectric Domain Walls

Recently, considerable attention has been focused on the phenomena of antiparallel (180°) ferroelectric domain walls in lithium niobate and lithium tantalate and their manipulation into diverse shapes on various length scales. For example, optical frequency conversion devices require periodic gratings of antiparallel domains where the period of the domain grating structure determines the frequency of input light that is most efficiently frequency converted. Other devices based on domain patterning include electro-optic gratings, lenses, and scanners, which require manipulation of the domain

![Piezoelectric force microscopy phase contrast images of domain shapes created at room temperature in LiNbO₃ and LiTaO₃. The left image is 35x35 µm and the right image is 70x70 µm.](image)
shapes into more intricate geometries.\textsuperscript{52,53} Therefore, the structure of a domain wall in these materials has become an important subject of study.\textsuperscript{31,54} By precisely controlling the orientation of the domain structures, many devices can be fabricated in lithium niobate and lithium tantalate.

These applications, among others, exploit the fact that antiparallel domains have identical magnitudes but differing signs of the odd-rank coefficients of piezoelectric, \((d_{ijk})\), electro-optic \((r_{ijk})\), and third-rank nonlinear optical \((d_{ijk})\) tensors, where subscripts refer to crystal physics axes in an orthogonal coordinate system. However, the second rank properties such as refractive indices are expected to be identical across a domain wall. This is particularly interesting from a device point of view, because two oppositely orientated domains exposed to the same electric field will show a change in their field dependent properties in a positive sense on one side of the domain and a negative sense on the other. Manipulating domain shapes then can lead directly to field tunable devices.

### 1.5 Research Objectives

The central focus of this thesis work is to develop a fundamental understanding of how to shape and control domain walls in ferroelectrics, specifically in lithium niobate and lithium tantalate. An understanding of the domain wall phenomena is being approached at two levels: the macroscale and the nanoscale. On the macroscale, different electric field poling techniques have been developed and used to create domain shapes of arbitrary orientation. A theoretical framework based on Ginzburg-Landau-Devonshire theory to determine the preferred domain wall shapes has been developed.
Differences in the poling characteristics and domain wall shapes between the two materials as well as differences in composition have been found to relate to nonstoichiometric defects in the crystal. These defects have also been shown to influence the local electromechanical properties of the domain wall. Understanding from both of these approaches has been used to design and create optical devices through micro-patterned ferroelectrics.

1.6 Thesis Organization

Chapter 2 focuses on the creation and manipulation of domain shapes using electric field poling. Different approaches are developed for each material to create arbitrary domain shapes as well as periodic gratings. A new technique involving poling these materials at higher temperatures is explored. Chapter 3 will focus on the electromechanical and electrostatic properties of domain walls measured by scanning force microscopy. Chapter 4 develops the Ginzburg-Landau-Devonshire theory for the preferred domain wall orientations in both LiNbO$_3$ and LiTaO$_3$. These predictions are compared with actual domain shapes, as well as surprising temperature related domain shape changes. Finally in Chapter 5, devices are created using the foundation developed in Chapter 2, and a variety of integrated optical devices based on domain micropatterning are demonstrated. All the experimental and theoretical results will then be compared and linked together in Chapter 6.
References


Jung Hoon Ro, Tae-hoon Kim, Ji-hyun Ro, and Myoungsik Cha, "Defect study by sub-second relaxation of the internal field after polarization reversal in lithium niobate crystals," *Journal of the Korean Physical Society* **40** (3), 488-492 (2002).
Chapter 2

Domain Reversal and Patterning

One of the motivations in this thesis is to understand the dynamics of domains in order to control and shape the ferroelectric domain walls for device applications such as the electro-optic\textsuperscript{1,2} and wavelength conversion devices\textsuperscript{3,4} which will be discussed in Chapter 5. This chapter presents studies on the dynamics of ferroelectric domains in lithium niobate and lithium tantalate and uses the results for controlled domain patterning. Both room temperature and elevated temperature studies are presented.

The outline of the chapter is as follows: Section 2.1 presents a brief overview of the domain kinetics in LiNbO\textsubscript{3} and LiTaO\textsubscript{3} pertinent to domain control. The development of methods to control and shape domain walls in these materials is given in Section 2.2. Temperature dependent poling studies and the creation of periodically poled structures at temperature will presented in Section 2.3 followed by the conclusions in Section 2.4.

2.1 Domain Kinetics in LiNbO\textsubscript{3} and LiTaO\textsubscript{3}

In a ferroelectric, the application of an electric field higher than the coercive field results in a new minimum energy configuration through polarization reversal. Polarization reversal can be accomplished by either the growth of pre-existing domains
parallel to the applied field through their domain-wall motion, or by the nucleation and
growth of new domains. This growth can be either through the thickness of the crystal
along the polar direction or by the sideways motion of the 180° domain walls
perpendicular to the polar direction. Recently, a number of fundamental studies on the
domain switching kinetics exploring the wall velocities, switching times, and stabilization
mechanisms have been performed on lithium tantalate\textsuperscript{5-7} and lithium niobate.\textsuperscript{8-11} The
most important domain properties for domain micropatterning are the (1) wall velocity, (2)
the nucleation density, and (3) the domain backswitching behavior. The major
differences between lithium niobate and lithium tantalate will be briefly highlighted. All
results and discussions in this chapter will be focused only on the \textit{congruent compositions}
of these crystals.

One of the major differences in the kinetics of domain wall motion in congruent
lithium niobate and lithium tantalate is the nature of wall velocity reflected in the
 transient currents observed during domain reversal. In LiTaO\textsubscript{3}, the velocity of the
domain sideways motion is constant for a given electric field for independently growing
domains.\textsuperscript{7} (Merged domain fronts form when independent domains merge, and have a
higher, but constant, velocity at a given field).\textsuperscript{12} Observation of the domain wall motion
under poling fields directly has allowed the determination of wall velocity, \(v_s\), for the
forward poling in lithium tantalate and is given by,

\[
v_s = v_{s, 0} \exp \left( - \frac{\alpha}{E - E_c} \right)
\]

2-1
where $E$ is the applied electric field, $E_c$ is the coercive field, $\alpha$ is the activation field, and $\nu_{s,o}$ is the pre-exponential parameter.\textsuperscript{7} The values of $\nu_{s,o}$ and $\alpha$ are $4.15 \times 10^{-5}$ mm/s and 0.46 kV/cm for values of $(E-E_c) < 2$ kV/mm. The transient current shows a continuous, smooth curve. In contrast, the sideways motion of the domain walls in LiNbO$_3$ is very jerky and irregular, where the velocity at any given time can vary from zero to the maximum value.\textsuperscript{8} The transient current exhibits Barkhausen pulses which are indicative of a strong pinning-depinning mechanism of domain wall motion.\textsuperscript{13}

It is presently believed that the difference between the materials is caused by a higher density of pinning centers in LiTaO$_3$ as compared to LiNbO$_3$.\textsuperscript{14} The jerky wall motion in LiNbO$_3$ is due to discrete depinning events and a fast movement of the domain wall before it encounters the next pinning site. Each depinning event is associated with a discrete spike in the transient current. The higher density of defects in LiTaO$_3$ cause so many pinning events that the current spikes merge together to form one continuous curve. The nature of the abundant pinning centers in LiTaO$_3$ is still unknown. They could be related to oxygen vacancies that are formed under the reducing atmospheres in which the LiTaO$_3$ crystals are grown, compared to the ambient atmospheres used for the LiNbO$_3$ crystals.\textsuperscript{15} Alternatively, the pinning sites may correspond to physical defects such as screw dislocations whose density may vary depending on the quality of the crystal growth\textsuperscript{16,17} or a high density of small Ta$_2$O$_5$ inclusions which have been recently been observed by high resolution electron microscopy.\textsuperscript{18}

For electric field values close the coercive field (low field regime) there is a field independent nucleation rate in both LiNbO$_3$ and LiTaO$_3$.\textsuperscript{12,19-21} The number of independent nucleation sites (to be distinguished from the nucleation at a growing wall)
is related to the presence of intrinsic defects or microdomains on the surface. In-situ studies\textsuperscript{7,22,23} of LiTaO\textsubscript{3} reveal that nucleation of domains originates near line-shaped defects on the surface. These could be local variations in the defect concentration which allow for preferential nucleation. Alternatively, these defects could be related to low angle grain boundaries with an associated strain that gives rise to local electric-field gradients through the piezoelectric effect.\textsuperscript{24} Nucleation originates from similar defects or microdomains in LiNbO\textsubscript{3}, although the number is much less.

Previous literature on lithium niobate and lithium tantalate have established domain switching times, the total time required to switch a given area at a given electric field, and the domain stabilization times, the minimum amount of time the electric field must be applied to stabilize the newly grown domain configuration.\textsuperscript{10,14} For pulse times less than the stabilization time, the domain undergoes backswitching, and returns to the original domain configuration before the application of the electric field. In lithium niobate this backswitching time is \(~\!10\!\) ms while in lithium tantalate it is \(~\!1.4\!\) s and has been directly related to the defect dipoles discussed in Section 1.2.\textsuperscript{25} This backswitching can be used to create high fidelity domain patterns by precisely controlling the amount of backswitching allowed.\textsuperscript{26,27} Applying a stabilizing field immediately after a short backswitching time allows for controlled growth of domains smaller than available through regular pulsed domain growth.
2.2 Domain Micropatterning by Electric Field Poling for Devices

The key fabrication step for domain inverted devices is the fabrication of the patterned domains in the crystal. Lithium niobate and lithium tantalate were originally thought to be “frozen” ferroelectrics meaning their polarization could not be reversed in an external electric field. The coercive field extrapolated from data collected at the Curie temperature to room temperature gives a coercive field value of ~5 MV/mm which is above the breakdown strength of the material. Starting in the early 1980’s, domain engineering was first realized by growing periodic, laminar domain structures using specialized Czochralski techniques. Later, waveguide domain inverted structures were created in bulk crystals through the indiffusion of chemical species like Ti starting in 1989 and electron beam writing starting in 1990. In 1992, it was demonstrated that if the material was thin enough (< 2 mm), poling of the material by applied electric field could be achieved at fields of ~24 kV/mm. This spurned an explosion in papers on electric field poling in LiNbO$_3$ and LiTaO$_3$ particularly creating periodic domain structures. Most notable are the works by Fejer, Shur, and Rosenman. Patterning of domains into other shapes like lenses and prisms began in 1996, with the work by Li et al and Yamada et al.

Electric field poling is the most common and the most controllable technique developed thus far. In this technique, an electric field exceeding the coercive field of the material (~21 kV/mm for congruent LiNbO$_3$ and LiTaO$_3$) is applied to the bulk of the crystal through patterned surface electrodes. A schematic of this process is shown in Figure 2-1.
Critical to device operation is that domain growth only occurs between the top and bottom electrodes. Unwanted growth in non-electroded regions, called domain overshoot, can result in diminished performance, or in the worst case, ruined devices. This is pictured in Figure 2-2 for a domain engineered scanner. This broadening of domains in the plane of the device is a particular problem for periodically poled structures.

Figure 2-1: Controlled growth of domains for domain micropatterning. The poling process is a competition between domain sideways growth and nucleation. Overpoling is the creation of domains beyond the electrode boundary.

Figure 2-2: The apex of a domain reversed scanner element where black is the electrode. The bright fringe at the boundary is the overpoled area and is more pronounced in (b) than (a). (c) shows a case of extreme overpoling which resulted in a ruined device.
Most of the electric field poling work to date is achieved by applying pulsed voltage waveforms to the crystal through lithographically defined metal electrodes, a monitoring of the current through the external circuit, and determination of the domain patterns by etching the structure.\textsuperscript{39,40} Recently, direct monitoring of the domain features in LiNbO\textsubscript{3} and LiTaO\textsubscript{3} during poling has been demonstrated.\textsuperscript{23} This thesis work is the first work to combine in-situ monitoring of domain motion with electric field poling techniques to create engineered domain structures. Excellent control of the domain patterns is achieved by a combination of: (1) surface conduction suppression, (2) using optical techniques to monitor the poling process, and (3) control of the applied voltage and resulting transient current. These are individually described next.

2.2.1 Sample Preparation and Experimental Setup

Single domain crystal wafers of 2.5-3 inch diameters and thicknesses 300-500 µm were purchased from Castech (LiTaO\textsubscript{3}) and Crystal Technologies (LiNbO\textsubscript{3}). The crystals were diced to appropriate dimensions by first mounting the crystals +z face down on glass plates using Crystalbond 509 with a melting point ~120ºC. The sample was heated and cooled at a rate of ~1-2ºC/minute to avoid damage to the crystals. The wafers were then cut on a Dicing Technology Basic Dice II saw to the appropriate dimensions and then marked by a diamond scribe to indicate sample number and crystal orientation. These crystals were then detached from the substrate by soaking in acetone.
Lithography was performed by first cleaning the surface well with acetone. If the sample was large (> 10 mm x 10 mm) the sample was first attached to a slightly larger piece of silicon wafer by a few drops of photoresist followed by a soft bake of 30 minutes at 100°C. Next, Shipley 1813 photoresist was applied to the substrate and then spun down to a thickness of ~1.3 µm on a spinner operating at 4000 rpm for 40 seconds. This was followed by a soft bake at 100°C for 5 minutes. If the sample was 10 mm x 10 mm or smaller, it was placed on a piece of silicon prior to the soft bake step. This caused the ferroelectric to stick to the silicon (via the pyroelectric effect) to protect it through the following lithographic steps. After the soft bake, the lithography is performed on a Kurt Suss MJB3 and pattern was exposed using for a time 0.7-2 minutes (longer for larger samples). The pattern was then developed for 20 seconds in Microposit 351 developing solution mixed in a ration of 1:5 with water followed by a 40 second agitation in deionized water.

The sample was then reactive ion etched for 6 minutes using a Plasma Therm PT720 reactive ion etcher with a gas flow of 50 sccm of O₂ and 5 sccm Ar and power of 75 W. This step was found to increase the adhesion of metal films to the sample surface. Metal electrodes are then sputtered on the surface using a Lesker CMS-18 sputtering tool. Various metal films have been sputtered and found to be sufficient electrode materials. These include tantalum, titanium, and chrome overcoated with gold, all of thicknesses ~200-300 nm. The underlying photoresist pattern was then removed by exposure to acetone and gentle agitation using a soft cotton swab. Care must be taken so that the free floating metal particles do not stick to the bare surfaces of the crystal.
A layer of Shipley 1813 was then spun uniformly onto the top surface to cover the electrode pattern. The sample was placed on a silicon substrate and was hard baked to remove the solvents from the photoresist. This was done either in a box oven at 110°C for 3 hours or on a hotplate at 120°C for 30 minutes. The sample was heated and cooled to peak temperature at a rate of ~1-2°C/minute.

The sample was then placed into a sample holder pictured in Figure 2-3. The holder was made from Plexiglas with the high voltage sealant silicone rubber sheets. The positive electrode was the Ta-film pattern on +z face to which electrical contact was made by piercing through the surface photoresist, while a uniform water electrode was used on the -z face as the ground. If two water electrodes are to be used the bottom electrode of the fixture was replaced by a water cell identical to the top cell. The holder was then placed in a Ziess Axioplan2 optical microscope. The maximum objective that could be used with the holder was 10x, limited by the water cell between the sample and the microscope objective. If the sample was going to be poled by ramping the voltage, the

![Figure 2-3: Schematic of in-situ domain micropatterning apparatus with simultaneous optical imaging system in reflection mode to track domain nucleation and growth during device fabrication. The bottom patterned electrode can also be replaced with a water cell.](image-url)
leads of the sample holder are attached to an IRCO C12-20 power supply capable of supplying 15 kV and 60 W. The power supply was controlled and the current was monitored by a PC running Labview 6. If the sample was to be poled by pulsing the voltage, the holder was connected to a Trek 20/20C high voltage amplifier capable of 20 kV and 20 mW which amplifies a waveform programmed and supplied by an HP 33120A function generator. The voltage and current monitor outputs of the power supply were connected to a TDS 340A oscilloscope. A PC running Labview 6 was used to trigger the function generator and collect the data from the oscilloscope.

2.2.2 Surface Conduction Suppression

The surface conduction is suppressed by applying a dielectric coating to the crystal surface not covered by the metallic electrodes. This suppresses domain reversal beyond electrode edges by reducing the charge delivery from that region to the nearest electrode edge. The transient current delivers a charge, $Q$, to the sample that is required for compensation of the reversed spontaneous polarization which is given by $Q = \int i \, dt = 2P_s A$, where $i$ is the transient current, $P_s$ is the spontaneous polarization, and $A$ is the area of the domain-reversed region. This transient current is directly related to the area of device that is poling, and is related to the efficiency of domain reversal in the patterned areas. At the electrode edges, there are high fringing fields present that extend beyond the electrode boundaries. The dielectric layer then prevents the flow of charge into non-electroded area adjacent to the electrodes. In the absence of compensating
charge flowing from the electrodes, domain reversal cannot occur in the areas adjacent to the metal electrode and overshoot is prevented.

2.2.3 In-Situ Domain Poling by Electric Field Poling

The domain structure of ferroelectrics can be imaged by a variety of methods, including etching, surface decoration, electron microscopy, and scanning force microscopy.\(^{41}\) The last technique will be discussed extensively in Chapter 3. None of these techniques (with the exception of electron microscopy for specific conditions)\(^{42,43}\), however, provide real time information on the domain poling process while it is occurring. The \textit{in-situ} observation of domain motion using cross-polarizers was first used in the observation on BaTiO\(_3\).\(^{44}\) This technique allows the observation of nucleation and growth of domains to be continually monitored as electric fields are applied to the sample, and has been dubbed electro-optic imaging microscopy (EOIM).\(^{23}\) A schematic of the setup is shown in Figure 2-3.

Through the electro-optic effect, under a uniform electric field along the polar axis, \(E_3\), there is an index difference of \(2\Delta n_o\) at the boundary of two oppositely oriented domains given by \(2\Delta n_o = n_o^3 r_{13} E_3\), where \(n_o\) is the ordinary refractive index and \(r_{13}\) is the electro-optic coefficient. This index difference at the wall will cause scattering of transmitted or reflected light in the crystal, making the domain walls appear dark. This can be used to image domains walls through the crystal thickness in a \(z\)-cut crystal in an optical microscope, with or without any polarizers. In this way, the movement of the
180° domains can be directly observed during the domain patterning process and correlated to the transient current. This is of great benefit to micropatterning domains because the location of nucleation and the method of domain wall growth and motion can be directly observed.

### 2.2.4 Domain Micropatterning LiTaO$_3$

Patterning domains in LiTaO$_3$ was first demonstrated in the literature in 1994 by Chen et al. who demonstrated a waveguide scanner with ~20 µm deep surface domains poled via proton exchange. Later, Baron et al. demonstrated poling in LiTaO$_3$ through a combination of chemically patterning the surface by proton exchange or Ti indiffusion followed by a electric field poling step. This work demonstrates poling in LiTaO$_3$ without the use of chemical patterning. This is achieved through transient current monitoring in combination with in-situ observation.

As discussed in Section 2.1, the domain wall motion in LiTaO$_3$ is constant for a given electric field. In LiTaO$_3$, a higher electric field exponentially increases both the number of nucleation sites and lateral domain wall velocity. The ideal conditions for domain patterning during device fabrication in LiTaO$_3$ are a combination of homogeneous nucleation and moderate wall velocities. Inhomogeneous nucleation results in the completion of domain reversal in areas under the electrode where nucleation occurs first, while other areas under the electrode may not undergo domain reversal until a much later time. Eventually, this leads to domain overshooting beyond the electrode
edges in the former areas while the domain reversal is being completed in the rest of the areas. It was observed that domains always start nucleating at the edges of the metal pattern due to the enhancement of the field, so longer switching times will result in more overshooting of domains beyond the pattern. However, a very fast wall velocity results in a very short switching time, and therefore does not allow a real-time control of the process. The appropriate electric field or transient current that allows for a uniform nucleation and moderate domain wall motion was experimentally determined through poling a series of crystals with identical triangular metal electrodes. The device was poled while keeping the transient current at an average value between 1 and 3 µA. The best results were obtained when the transient current was kept around 1.2 µA. At this value, the domain nucleation was uniform and the domain walls moved at a controllable rate of 3-19 µm/s. Below this value the switching took too long and allowed domains to grow into the areas without electrodes. At higher transient current levels the domain growth occurred too quickly to be monitored properly and resulted in overgrown domain features.

To control the transient poling current, a computer program continually monitored the current and controlled the voltage during poling. A starting field less than the coercive field was applied to the sample and increased at a rate of 5 V/s. As the applied field crosses the coercive field, poling begins and the transient current begins to flow. While the current is below the experimentally determined optimal current, referred to here as the clamping current, the voltage was increased at a rate of 5 V/s. When the current exceeds the clamping current, the voltage is held constant until the current drops below the clamping current. In this way, the transient current was kept at around the
optimal value of $1.2 \pm 0.223 \mu A$. A graph of the voltage and current data from a poling event is shown in Figure 2-4. The inset plot shows a magnification of the current and voltage data over a 2 second interval with the horizontal line showing the clamping current. The total switching time was $\sim 140s$ and the average domain reversal rate was $\sim 2.4 \text{ mm}^2/s$.

![Graph showing voltage and current data](image)

Figure 2-4: The voltage-transient current response during domain micropatterning in LiTaO$_3$. The transient current is maintained at a mean value of 1.2 $\mu$A by holding the voltage when the current reaches or exceeds the set point, and incrementally ramps the voltage up when the current dropped below this set point. The inset plot shows a magnification over a 2 second interval, showing how the voltage is modified to hold the transient current relatively constant around the clamping current setpoint (shown by the horizontal dotted line). Crystal thickness is $\sim 300 \mu m$.

In addition to monitoring the transient current, the domain wall motion was observed directly. Figure 2-5 shows selected frames from the in-situ observation the poling process during the device fabrication on LiTaO$_3$. The spacing between successive frames is 3 seconds. The white triangular shaped area at the right of each frame is the vertex of one of the prism triangles and does not have a Ta-film top electrode, while the
rest of each frame is a Ta electrode. Nucleation occurs at the electrode edges and advances to the left under the Ta electrode. Through a combination of controlling the transient current and direct domain observation, a well-controlled domain reversal process is achieved and domain reversal in areas not covered by the electrode is thus minimized.

Figure 2-5: Selected video frames from in-situ observation of domain growth in a patterned LiTaO$_3$ using optical imaging in reflection. Selected video frames from in-situ observation of domain growth in a patterned LiTaO$_3$ using optical imaging in reflection. Three regions, labeled in frame (f) are, the original crystal beneath a Ta-film electrode [region (3)], the domain inverted region underneath the Ta-film electrode [region (2)], and the original crystal with no Ta-film electrode forming the prism pattern [region(1)]. The black region is contrast visible at the boundary between domains. Domain growth starts at electrode edge and advances into the electrode. Each successive frame shown here is separated by 3 seconds.
2.2.5 Domain Micropatterning LiNbO₃

For lithium niobate, because the nucleation sites are much sparser than in lithium tantalate (see Section 2.1), simply ramping the voltage through the coercive field will not work, as the domain walls move too fast to control and result in significant over poling. The approach most taken in the literature is a pulsed approach, where the coercive field is exceeded in short bursts, but specifics of the time or field applications are often not specified. 37,48-50 In this work, a pulsed approach was developed where the poling voltage is applied in short intervals (but greater than the stabilization time of 10 ms) that exceeds the coercive field and creates domains, followed by a stabilization phase where the voltage is held at 20% of the peak value to stabilize the newly formed domains. Many such pulses may need to be applied to the crystal as each pulse switches only a portion of the crystal. Combinations of pulse widths (10-500 ms) with different peak voltages (100-2000 V above the coercive field) could produce a range of domain growth. Longer periods or higher voltages favor rapid, less-selective domain growth, while shorter lower voltage pulses including some backswitching allowed for fine, very selective, domain growth. This small backswitching allows the domains to retreat from areas most difficult to pole i.e. areas not covered directly by the metal electrodes. A sample waveform used to fabricate devices is shown in Figure 2-6(a).
The poling pulse in Figure 2-6(a) corresponds to a field of 25 kV/mm, approximately 4 kV/mm above the coercive field in a region of higher nucleation rate. The integrated charge pulse delivered to the sample in the pulse pictured in Figure 2-6(a) is \(~3.2\) \(\mu\)C. Shown in Figure 2-6(b) is the amount of charge, \(Q\), per 20 ms pulse as a function of electric field strength in LiNbO\(_3\).

The poling pulse in Figure 2-6(a) corresponds to a field of 25 kV/mm, approximately 4 kV/mm above the coercive field in a region of higher nucleation rate. The integrated charge pulse delivered to the sample in the pulse pictured in Figure 2-6(a) is \(~3.2\) \(\mu\)C. Shown in Figure 2-6(b) is the amount of charge, \(Q\), per 20 ms pulse as a function of electric field strength in LiNbO\(_3\). Exactly tailoring the pulse height is important in device fabrication. Although more area per pulse can be switched at higher voltages, the selectivity is much lower and domain growth is less controllable.

This data in Figure 2-6(a) was taken from the controlled poling of 42.6 mm\(^2\) pattern requiring 63.9 \(\mu\)C for complete domain inversion. A total of 17 pulses were required to completely pole the pattern which was verified by in-situ observation of the domains as shown in Figure 2-7. Each pulse delivered approximately the same amount of charge which gives a total of \(~54.6\) \(\mu\)C – only \(~85\)% of the predicted amount. This
highlights some of the difficulty in poling LiNbO$_3$. It is believed that some of the pinning and movement of the domain wall occurs so quickly that the current spike cannot be measured correctly using the poling setup. This would lead to an underestimation of the poling area if looking at the current data alone; however, when coupled with the in-situ monitoring of the poling, proper poling can be achieved.

![Figure 2-7: Selected video frames from in-situ observation of domain growth in a patterned LiNbO$_3$ using optical imaging in reflection. Between each successive frame a pulse similar to Figure 2-6 has been applied. Domain walls are highlighted by arrows.](image)

2.2.6 Domain Patterning for Periodic Poling

The majority of effort in poling structures in both LiNbO$_3$ and LiTaO$_3$ has been focused on the creation of periodic grating structures for second harmonic generation. Since first demonstrated by Yamada in 1992, various techniques have developed for the
fabrication of periodically poled lithium niobate (PPLN) and periodically poled lithium tantalate (PPLT) which consist of periodic arrangement of up and down domains.\textsuperscript{34,36}

Many of these techniques have been detailed in Section 2.2 and are reviewed in a paper by Houe and Townsend.\textsuperscript{51} These periodic structures can act as laser frequency conversion devices, where an incident wavelength of light is frequency up-converted or down-converted to a different frequency, and the output laser frequency is dependent upon the domain period (for details see Appendix A). A brief survey of the various period sizes and conversion efficiencies obtained by various groups are given in Table 2-1. In the table, a higher the conversion efficiency indicates better periodicity of the domain patterns.

Table 2-1: Selected electrically poled PPLN and PPLT structures for second harmonic generation

<table>
<thead>
<tr>
<th>Material</th>
<th>Method</th>
<th>Method</th>
<th>$\lambda$ (nm)</th>
<th>Period, $\Lambda$</th>
<th>Aspect Ratio</th>
<th>Efficiency</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNbO\textsubscript{3}</td>
<td>Congruent</td>
<td>pulsing</td>
<td>1064?532</td>
<td>6.5 (\mu\text{m})</td>
<td>77</td>
<td>42%</td>
<td>\textsuperscript{36}</td>
</tr>
<tr>
<td>LiNbO\textsubscript{3}</td>
<td>Congruent</td>
<td>Back-switching</td>
<td>920?460</td>
<td>4 (\mu\text{m})</td>
<td>125</td>
<td>43%</td>
<td>\textsuperscript{52}</td>
</tr>
<tr>
<td>LiNbO\textsubscript{3}</td>
<td>MgO doped congruent</td>
<td>pulsing</td>
<td>725?362.5</td>
<td>1.8 (\mu\text{m})</td>
<td>200</td>
<td>11%</td>
<td>\textsuperscript{53}</td>
</tr>
<tr>
<td>LiNbO\textsubscript{3}</td>
<td>MgO doped Stoichiometric</td>
<td>pulsing</td>
<td>800?400</td>
<td>7.8 (\mu\text{m})</td>
<td>130</td>
<td>20.5%</td>
<td>\textsuperscript{54}</td>
</tr>
<tr>
<td>LiTaO\textsubscript{3}</td>
<td>Congruent</td>
<td>pulsing</td>
<td>1064?532</td>
<td>7.5 (\mu\text{m})</td>
<td>67</td>
<td>38%</td>
<td>\textsuperscript{40}</td>
</tr>
<tr>
<td>LiTaO\textsubscript{3}</td>
<td>Congruent</td>
<td>pulsing</td>
<td>786?384</td>
<td>2.4 (\mu\text{m})</td>
<td>125</td>
<td>35%</td>
<td>\textsuperscript{55}</td>
</tr>
<tr>
<td>LiTaO\textsubscript{3}</td>
<td>Stoichiometric</td>
<td>pulsing</td>
<td>1064?532</td>
<td>8 (\mu\text{m})</td>
<td>100</td>
<td>41%</td>
<td>\textsuperscript{56}</td>
</tr>
</tbody>
</table>

As laser sources push toward the UV, the domain grating period gets smaller. For example for wavelength conversion from 710nm to 355 nm in LiTaO\textsubscript{3}, gratings with periods of 2.1 \(\mu\text{m}\) must be created uniformly along 1-2 cm of crystal as well as through the crystal thickness. The aspect ratio of the domains, the ratio of crystal thickness of a
Z-cut crystal to inverted domain size in the lateral direction (in the x-y plane), currently determines the limits of devices. Current state of the art devices have aspect ratios approaching 250.\textsuperscript{53,57} In commonly available 500 µm thickness crystals, this translates to gratings with a period of ~4 µm (individual domains 2 µm wide). Most of these high aspect ratio gratings have been fabricated in Mg doped or stoichiometric LiNbO\textsubscript{3} where the coercive field and the photorefractive effects are much less than in congruent LiNbO\textsubscript{3}. However, these materials are much more expensive and more difficult to obtain than commercially available congruent compositions, so the development of gratings in congruent composition has economic advantages.

Two different techniques were explored for the fabrication of periodic poling in congruent LiNbO\textsubscript{3}. Both of these techniques were demonstrated by other groups in the literature (see Table 2-1), although specifics such as exact fields and durations are often not specified. These techniques were duplicated here with the specific purpose to understand the limitations of the electric field poling for creating domain gratings.

The first technique utilizes the backswitching phenomena. This technique was used by Batchko et al. to create quasi-phase matched structures in congruent lithium niobate with a grating period of 4 µm.\textsuperscript{26} High fidelity structures could be obtained, although uniformity of the gratings in the plane of the device was an identified problem.
To investigate the feasibility of backswitching to creating large area periodically poled samples, a series of pulses of shape given in Figure 2-8 are applied to the top metal electrode and a grounding bottom water electrode. In this scenario, a forward switching pulse much higher than the coercive voltage was immediately followed by a backswitching pulse where the voltage was reduced to zero, followed by a stabilization phase where the voltage was increased to 20% of the peak value. The slow ramp-and-hold before the forward switching was designed to minimize breakdown seen if the peak pulse was applied directly to the crystal. The peak voltage and the length of the backswitching pulse were varied. Again, as pictured in Figure 2-6(b), a higher electric field on the forward pulse leads to more switched area. Allowing more backswitching reverses a greater amount during the reverse pole. The best poling conditions were achieved for 8500 peak voltage corresponding to a field of 28 kV/mm (where coercive

Figure 2-8: Backswitching pulse of 10 ms forward switching followed by 8 ms backswitching for periodic poling of LiNbO₃. The dotted curve is the desired voltage curve, while the solid black line is the actual voltage. Crystal thickness was ~300 µm.
field is about 21 kV/mm or ~6300 V) for a duration of 10 ms with 8 ms backswitching. A single pulse pictured in Figure 2-8 can be thought of as a net domain growth step of 1 ms. Several pulses (~10) were required for proper poling. The current limit supplied by the power supply was 2 mA, so the number of pulses events could be reduced with higher current limits. It was found, similar to the work of Batchko et al.,\textsuperscript{26} that this approach was able to create very fine features as shown in Figure 2-9, but could not easily create patterns uniformly throughout the grating area.

Figure 2-9: Etched sample of PPLN created by pulsed poling. The domain gratings are supposed to be uniform, but instead are not completely poled in the middle. This doubling of the period was unintentional, and a result of nucleation at the edges of the electrode and possible some subsequent backswitching in the middle of the electrode.

The second technique that was developed was the application of a single long duration (~100 ms) pulses as shown in Figure 2-10. The pulse was very close to the coercive field to take advantage of the extreme sensitivity of the switching rates near the coercive field\textsuperscript{25} as pictured in Figure 2-6(b). In this technique, the coercive field for each sample was determined exactly by slowly incrementing the voltage until domain nucleation could be observed at the edges of the patterns. This was done because the coercive field value was found to vary from crystal to crystal with a value of 20.6 ± 0.6
kV/mm (~± 200 V of the coercive voltage). Knowing the exact coercive field, a pulse was applied ~200 V above this value which slowly decreased below the coercive voltage over the 100 ms pulse. This corresponds to a field just above the coercive field ~21.2 ± 0.6 kV/mm. For the poling event pictured in Figure 2-10, the poling area was approximately 35.6 mm² which corresponded to a charge of ~53.4 µC needed for proper reversal. The integrated charge of Figure 2-10 is only ~51.9 µC. The uniformity was still a problem in these devices, but further tailoring the exact form of the voltage can lead to better fidelity domains. A picture of the best grating created by long duration pulse is shown in Figure 2-11.

Figure 2-10: Long duration pulses for periodic poling congruent LiNbO₃. The horizontal dashed line is the coercive voltage. Crystal thickness was ~300 µm.
The best domain features achieved with either of the poling techniques was domain periods of 6.7 µm which penetrated through the full 300 µm crystal thickness. This is not as good as many works in the literature (see Table 2-1). However, the purpose of this work was not to improve existing poling techniques, but to understand the difficulties of periodic poling in bulk crystals. The limitation of electric field poling as gleaned from these experiments is the ability to create periodic gratings uniformly in large areas. Part of this difficulty, especially in LiNbO$_3$ is the nucleation density. For large areas, nucleation starts at several discrete locations on the sample and domain wall movement dominates the process. This is illustrated in Figure 2-12, where individual nucleation sites are located at the middle of each roughly hexagonal shape. A side view of the inhomogeneous gratings is given in Figure 2-13. Improvements in the creation of periodically poled gratings LiNbO$_3$ and LiTaO$_3$ could be improved if the nucleation density could be increased.
2.2.7 Wall Orientation of Micropatterned Domains

To conclude the micropatterning section, the domains created using the previous techniques are examined to see the alignment of domain features along arbitrary in-plane orientations (i.e. along a curved surface in the x-y plane). It is known that domain walls can only arise along planes allowable by crystal symmetry and on which the conditions of

Figure 2-12: Incomplete poling of gratings in lithium niobate showing nucleation density. Coalescence of distinct nucleation sites by wall motion. The dashed hexagon is the extent of domain growth from an individual site in the middle. Notice the merged domains at the center of every hexagon. Dotted lines indicate direction of electrode gratings which uniformly cover the area. Ideal poling should have uniform grating over entire area.

Figure 2-13: Side view of gratings in LiNbO₃ illustrating non-uniformity through the length of the device. Inhomogeneous nucleation results in erratic growth.
mechanical compatibility with additional stresses are satisfied. The orientations are determined by the free energy minimum and include contributions from the electrostatic energy, the elastic energy, and the interaction of these energies with point defects and dislocations. Further theoretical development of this is given in Chapter 4. The preferred wall orientations for each material are pictured in Chapter 1 in Figure 1-6.

Shown in Figure 2-14(a) are domain features in LiTaO$_3$ observed by piezoelectric force microscopy (PFM – for details see Chapter 3). The domain walls are able follow the electrode boundaries very well. If one examines Figure 2-14(b) closely, a serration of the domain wall can be noticed. It is surmised that the greater number of defect sites, responsible for the constant wall velocity during poling in LiTaO$_3$, allows the serrations to be over very small length scales. This behavior is very different from that in LiNbO$_3$. The domain wall features in LiNbO$_3$ are pictures in Figure 2-15 observed by (a) PFM and (b) optical microscopy. In Figure 2-15(a) the domain walls do not closely follow the electrode edge and are pinned by widely separated pinning sites. Figure 2-15(b) highlights the importance of crystal orientation for domain patterning. Very nice domain gratings can be created when the gratings are aligned parallel to the y-axes; however, domain patterning in misaligned crystals is not desirable for regular gratings.
Figure 2-14: Piezoelectric force microscopy images of domain walls in patterned LiTaO₃ where the dark areas are opposite domain orientation than the light areas. (a) a portion of an individual lens and (b) a wall from a scanner. All dimensions are in microns. The two domain states are separated by 180° degrees.

Figure 2-15: (a) Piezoelectric force microscopy image of domain walls in a patterned LiNbO₃ scanner where the dark areas are opposite domain orientation than the light areas. Dimensions are in microns. (b) optical microscope image of etched periodically poled sample with misalignment of the grating electrodes with the y-axis. Contrast is provided by preferential etching of the –z face in dilute HF. Dotted lines in both figures indicate the approximate boundaries of the electrodes.
2.3 Temperature Dependent Poling Studies

The poling of LiTaO$_3$ at 400°C by Ballman in 1974 was the first creation of domains at temperatures not close to the Curie temperature.$^{28}$ Extrapolating from his data to room temperature predicted a room temperature poling field of 5000 kV/mm, well above the breakdown strength of the material. Since the discovery of room temperature poling in thin crystals at much lower fields (~21 kV/mm), poling at elevated temperatures has been largely abandoned except during crystal growth. The poling of LiTaO$_3$ in the temperature range from 25-250°C were recently performed by Battle et al., who showed a decrease of the coercive field by ~70%, an unspecified increase in domain nucleation density from the room temperature values.$^{59}$ High temperature poling, then, could be used to create better domain structures in both materials, particularly LiNbO$_3$ by increasing the nucleation density, and utilizing the much slower switching times and lower coercive fields to better manipulate the domain structure. These effects could be used to potentially create domains with aspect ratios higher than 250, the current limit of this technology. In this section, poling properties in the range of 25-200°C will be investigated in LiNbO$_3$ and LiTaO$_3$.

2.3.1 Temperature Effects in Ferroelectric

The coercive field in a ferroelectric is known to depend strongly upon temperature.$^{60-63}$ A ferroelectric like LiNbO$_3$ and LiTaO$_3$ with a second order phase
transition\textsuperscript{64} can be modeled as the energy difference between the paraelectric and ferroelectric phases given as the Gibbs free energy, \( G \), as

\[
G = -\frac{\alpha_o (T_c - T)}{2} P^2 + \frac{\beta}{4} P^4
\]

where \( \alpha_o \) and \( \beta \) are material specific constants, \( T_c \) is the Curie temperature, and \( P \) is the spontaneous polarization.\textsuperscript{41} The equation of state, \( E = dG/dP \) defines the theoretical \( P \) versus \( E \) hysteresis loop. The coercive field, \( E_c \), is defined as the turning point of the hysteresis loop, \( (dE/dP)_{E=E_c} = 0 \), which determines the polarization, \( P_c \), at the coercive field as

\[
P_c = \pm \sqrt{\alpha_o (T - T_c) / \beta}.
\]

The theoretical coercive field as a function of temperature can then be found as

\[
E_c = \frac{2\alpha_o}{3} \sqrt{\alpha_o (T - T_c)^{3/2}}.
\]

This is plotted for both LiNbO\textsubscript{3} and LiTaO\textsubscript{3} in Figure 2-16 using the calculated values for \( \alpha_o \) and \( \beta \) as \( \alpha_o = 1/(2\varepsilon_{33}) \) and \( \beta = \alpha_1 / P_s^2 \) with \( \varepsilon_{33} = 28.1 \varepsilon_o \) and \( P_s = 0.75 \text{ C/m}^2 \) for LiNbO\textsubscript{3} and \( \varepsilon_{33} = 44 \varepsilon_o \) and \( P_s = 0.55 \text{ C/m}^2 \) for LiTaO\textsubscript{3}.\textsuperscript{65,66}

While the theoretical coercive field value calculated using this approach is orders of magnitude higher than experimental values (~543 kV/mm for LiNbO\textsubscript{3} and ~250 kV/mm for LiTaO\textsubscript{3} compared to experimental value of ~21 kV/mm for both the congruent materials at room temperature), it still gives a theoretical form for the change in the coercive field. The degree of coercive field change predicted by this theory gives a change of coercive field in the region from 25-200°C is a decrease of 36.5% for LiTaO\textsubscript{3} and 17.5% in LiNbO\textsubscript{3}. However, this theory does not take into account the temperature
dependence of the nucleation and growth which has a dramatic effect on the poling properties.

It has been shown by Miller and Weinreich that the sideways motion of 180° domain walls occurs by preferential nucleation of new 180° domains at the existing 180° walls, thus giving an exponential behavior of velocity with the field, $v \propto \exp(-\alpha / E)$.

Following the analysis of Fatuzzo we can write the switching time, $t$, as

$$ t = t_o \exp \left( \frac{\delta}{E - E_c} \right) = t_o \exp \left( \frac{x\alpha + (1-x)\beta}{E - E_c} \right) \quad 2-4 $$

where $\delta$ is a constant at fixed temperature, $\alpha$ is the contribution of sideways growth, $\beta$ is the contribution of the nucleation of new domains (not at preexisting walls), and $0 < x < 1$ describes the relative contribution of each term. In BaTiO$_3$ it has been observed that switching time drops with increasing temperature for the same applied field strength, and that the nucleation rate of new domains is accelerated at elevated temperatures.$^{13,67}$

Figure 2-16: Theoretical dependence of coercive field on temperature for LiTaO$_3$ and LiNbO$_3$ based on Ginzburg-Landau theory, but does not account for nucleation and growth.
Miller and Weinreich determined the wall velocity, $v$, in BaTiO$_3$ to be $\propto \exp(-\gamma / E)$ where $E$ is the applied field and $\gamma$ is a constant at a fixed temperature whose value increases with temperature.$^{24}$ In TGS, the temperature dependence is different, with $\gamma$ decreasing with increasing temperature.$^{61}$

2.3.2 Free Charge Effects in Ferroelectrics

The effects of optical illumination on the properties of ferroelectrics like BaTiO$_3$, PLZT, and LiNbO$_3$ have been studied by a number of investigators. These studies have shown that incident light can effect the domain formation and stability,$^{68-70}$ hysteresis,$^{71,72}$ Curie point,$^{68,73}$ coercive field,$^{74}$ and birefringence.$^{75}$ Additionally, light induced effects are particularly prevalent in the photorefractive properties and holographic creation and storage in LiNbO$_3$.$^{76-78}$ The commonality of all this behavior involves the creation and distribution of free charges in the material, usually promoted from shallow traps into the conduction band.$^{79}$ Similar free charge creation can be achieved with heating, as the conductivity for both lithium niobate and lithium tantalate increases by several orders of magnitude with temperature in the 20-200°C range.

A description of the required activation energy of a nucleus formation was given by Landauer$^{80}$ as

$$\Delta U = -2EpsV + \sigma_wA + \frac{1}{2}NP_s^2V$$  \hspace{1cm} (2-5)
where the first term is the interaction energy created between $P_s$ and the applied electric field $E$ where $V$ is the volume of the nucleus. The second term is the nucleus surface energy where $\sigma_w$ is the wall energy and $A$ is the area. The final term is the depolarization energy, $E_d$, caused by the divergence of polarization along the domain boundary, where $N$ is the depolarization factor and is related the shape and dielectric properties of the nuclei.

This theory stresses the importance of the screening of the depolarization field by the charges provided during the switching process. These charges, $Q_{tot}$, are the sum of the charges provided by the external circuit through the electrodes, $Q_{ext}$, and free charges in the material, $Q_{free}$. This is expressed as

$$Q_{tot} = Q_{ext} + Q_{free} = \int_0^{\tau_{sw}} i dt + Q_o \left(1 - e^{-\tau_{sw}/\tau}\right)$$  \hspace{1cm} 2-6$$

Where $i$ is the current through the external circuit, $Q_o$ is the total free space charge, $\tau_{sw}$ is the polarization switching time, and $\tau$ is the dielectric relaxation time given by

$$\tau = \frac{\varepsilon_o \varepsilon}{\sigma}$$  \hspace{1cm} 2-7$$

where $\varepsilon$ is the dielectric permittivity and $\sigma$ is the dc conductivity. For low conductivity ferroelectrics like LiNbO$_3$ and LiTaO$_3$ with room temperature conductivity $\sim 10^{-18} \ \Omega^{-1} \text{m}^{-1}$, the dielectric relaxation, $\tau$, is $\sim 10^8 \ \text{s}$, implying the screening is exclusively provided by the charges flowing from the electrodes. However, at 200ºC the conductivity in these materials is $\sim 10^{-9} \ \Omega^{-1} \text{m}^{-1}$, giving the relaxation time, $\tau$, of $\sim 1 \ \text{s}$ meaning that free charges can profoundly influence the switching process. This model will be revisited later in Section 2.3.4.
Additionally, these free charges can enable energetically unfavorable configurations to exist in the crystal by screening the depolarization charges at domain boundaries with polarization discontinuities (i.e. head to head or tail to tail configurations).\(^{71}\) The increased free charges may also increase the nucleation rate \(R\) due to the trapping of free charges.

### 2.3.3 Conduction Mechanisms in LiNbO\(_3\) and LiTaO\(_3\)

The conduction mechanism in LiTaO\(_3\) and LiNbO\(_3\) can be broken down into three separate temperature regimes. A low temperature (< ~150ºC) regime which shows hopping due to small polarons, a medium temperature (150-725ºC) where ionic conduction dominates, and a high temperature regime (>750ºC) dominated by intrinsic conduction (ionic conduction in regular atmospheres, and electronic conduction via electrons in reducing atmospheres).\(^{82-86}\)

In the temperature range of interest (25-200ºC), both electronic and ionic conduction mechanisms are active. The current model of conduction between 25ºC and ~120ºC hinges on the existence of excess Nb\(^{5+}\) ions which form Nb\(_{Li}\) antisite defects. These Nb\(_{Li}\) defects are deep electron traps which form polarons.\(^{82,87-89}\) Conduction occurs when the polarons have enough energy to overcome the energy barrier and move to a neighboring site. This hopping behavior is described by

\[
\sigma = \sigma_0 \exp \left( \frac{-E_a}{kT} \right)
\]  

2-8
where $\sigma$ is the conductivity, $k$ is Boltzmann’s constant, $T$ is the temperature, and $E_a$ is the activation energy. The reported activation energies in this temperature range for LiNbO$_3$ vary widely between 0.49-0.9 eV$^{82-84,90,91}$ and for LiTaO$_3$ are between 0.5-0.90 eV.$^{92,93}$

The thermal fixing of holograms in both materials is achieved by heating the crystals above 100ºC which allows compensation of the electric space charge field created during light exposure by redistribution of ionic species. This ionic conductivity becomes prominent at higher temperatures (~125ºC) with an energy of activation of ~1.1-1.23 eV.$^{76,77}$ The exact ionic species is under considerable debate, and has been attributed to hydrogen diffusion$^{76,94,95}$ or lithium vacancy diffusion.$^{77,96-98}$

Extrinsic conduction mechanisms in this material are mainly from iron impurities incorporated into the crystal from the starting raw materials.$^{64,84,99}$ Iron plays such a large role in the photosensitivity and hologram recording that holographic LiNbO$_3$ crystals are grown with an optimal excess content of 0.06 wt% Fe$_2$O$_3$.$^{100}$ These Fe ions occur as Fe$^{2+}$ and Fe$^{3+}$ and can be converted into each other by reduction and oxidation treatments, respectively. During sensitization light exposure, electrons are excited from deep center Fe$^{2+}$ ions and are trapped at intrinsic niobium antisites. Subsequent holographic exposure excites electrons from these polarons to the conduction band.$^{88}$ Lithium niobate crystals used in this work were provided by Crystal Technology with Fe contamination at the 1-2 ppm levels. Similar Fe contamination is found in LiTaO$_3$ crystals.
Two point electrical conductivity measurements as a function of temperature in the range from 25-200ºC were performed using a HP 3478A multimeter and shown in Figure 2-17. The samples were 300 µm thick crystals coated uniformly on both sides with a Ta film ~ 200 nm thick. Below ~125ºC the data is increasingly inaccurate as the maximum resistance the instrument can measure is 30.3 MΩ. An estimation of the conductivity of LiNbO$_3$ at room temperature is $10^{-18}$ Ω$^{-1}$ m$^{-1}$. From the experimental measurements, the activation energy in the range from 125-200ºC for LiNbO$_3$ is $0.77 \pm 0.06$ eV and for LiTaO$_3$ is $0.68 \pm 0.11$ eV. These values are within the range of values in the literature for LiNbO$_3$ ($0.49-0.9$ eV$^{82-91}$) and for LiTaO$_3$ ($0.5-0.90$ eV$^{92,93}$).

2.3.4 Coercive Field, Switching Time, and Transient Current at Temperature

Samples for poling at elevated temperatures were prepared on 300 µm thick congruent crystals of both LiNbO$_3$ and LiTaO$_3$. Electrodes of Cr/Au or indium tin oxide...
(In$_2$O$_3$:SnO2 (90/10 wt%), ITO) are sputtered by DC magnetron sputtering uniformly on the –z crystal face and through a shadow mask on the +z face to give circular electrode pads of 0.66 cm$^2$. The ITO was sputtered in a 50 sccm argon gas flow with 5 sccm of oxygen. The Cr/Au electrode thickness was 10 nm of Cr covered by 140 nm of Au and the ITO thickness was 300 nm. Copper electrode leads were connected to the crystal surface using conductive silver epoxy. The samples were then suspended by the electrode leads in Dow Corning 710 silicone dielectric fluid. This geometry was adopted to eliminate the influence of mechanical stress during poling. The fluid bath was then placed on a hot plate and could be controllably heated up to 200ºC with stable temperatures. The electrode leads were then connected to a power supply and the transient poling current could be measured.

The ITO electrodes were chosen because of its transparent properties and reduction of ferroelectric fatigue.\textsuperscript{101} In$_2$O$_3$ has the cubic bixbyite structure where three-fourths of the tetrahedral interstices of the In$^{3+}$ ion array are filled in an ordered way by O$^{2-}$ ions.\textsuperscript{102} The relatively high carrier concentration (\textasciitilde$10^{18}$ cm$^{-3}$) of the “pure” material has been explained by oxygen deficiencies.\textsuperscript{103} Each oxygen vacancy generates two electron carriers. The ionic conductivity is negligible when compared to the electrical conduction properties. The tin is added as a cationic dopant which results in $n$ doping of the lattice. ITO has a lower carrier density than metals, $\sim10^{20}$ cm$^{-3}$ compared to $\sim10^{28}$ cm$^{-3}$.\textsuperscript{103} The material shows a linear increase in resistivity with temperature (metallic behavior) in the range from 25-225ºC.\textsuperscript{104,105}
It was found that the choice of electrodes was critical. The results of all the electrode combinations discussed below are summarized in Table 2-1. Reliable poling could not be obtained when using metal electrodes on both surfaces of the crystal. The crystals could be held at a constant voltage just below the onset of poling (~100 V less than the coercive voltage) for times up to 10 minutes. However, as soon as the voltage was increased above the coercive voltage to initiate poling and the transient current began to flow, catastrophic breakdown of the samples occurred either near the middle or edge of the electrode. This was a particular problem for LiNbO$_3$ where no poling with two metal electrodes was successful. However, when the –z face electrode was replaced by ITO on both materials, poling could more reliably be achieved, and when both electrodes were ITO, very few breakdown events occurred in either materials. Poling could be performed for LiTaO$_3$ when replacing the +z face with ITO and the –z face kept CrAu, however breakdown resulted in the LiNbO$_3$ for the same geometry. The exact reason for this higher breakdown rate in LiNbO$_3$ is unclear. However, it was noted that during the creation of domain-inverted devices in LiNbO$_3$ using a patterned metal electrode on the +z face and a water ground electrode, the crystals were particularly prone to breakdown (~10% of devices broke during poling). Filament breakdown in LiNbO$_3$ has been

<table>
<thead>
<tr>
<th>Sputtered face</th>
<th>Frequency of Breakdown</th>
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<tr>
<td>+z CrAu</td>
<td>Always</td>
</tr>
<tr>
<td>-z CrAu</td>
<td>Frequent</td>
</tr>
<tr>
<td>LiNbO$_3$</td>
<td></td>
</tr>
<tr>
<td>LiTaO$_3$</td>
<td></td>
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</tbody>
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Frequent ~30%, Infrequent ~10%
attributed to regions of higher impurities or structural defects where ionization of Nb$^{5+}$ sites results in avalanche breakdown.\textsuperscript{106}

2.3.4.1 Results

A series of poling experiments were carried out for each material with a set of samples with Cr/Au electrodes on the +z face and ITO on the –z face and another set of samples with ITO electrodes on both surfaces. Despite the difficulty involved with poling a metal coated +z face, there is still interest in the CrAu electrode because of the quality grating patterns that can be created through lithography and etching. For the poling experiments, the voltage was applied at a value below the coercive field and ramped at a rate of 5 V/s. The voltage was held constant as soon as the current exceeded 1 \( \mu \)A. This was found to minimize the dielectric breakdown of the samples related to runaway currents. A sample poling measurement in LiTaO$_3$ with ITO top and bottom electrodes at 175ºC is shown in Figure 2-18(a). Because the sample becomes conductive at higher temperatures, a baseline correction was determined by measuring the current for a range of voltages values much below the coercive field. A baseline was fit to the current data, and this baseline was subtracted from the transient current data. If the voltage was held constant, the conductive current baseline was held constant. The total integrated charge, $Q = \int i \, dt = 2P_sA$ where $A$ is the electrode area, was determined from the transient data. This is plotted as $P_s = Q/2A$ and shown in Figure 2-18(b). Values of the electric field and poling time were determined at 3, 50, and 97% of the total charge
Poling in lithium tantalate behaved as expected, with the $P_s$ value found from integrating the charge very close to the literature value of 50-55 µC/cm$^2$. Lithium niobate, on the other hand, showed very anomalous poling behavior at elevated temperatures. A sample poling event for LiNbO$_3$ with double ITO electrodes at 150°C is shown in Figure 2-19(a). The calculated $P_s$ value is shown in Figure 2-19(a).

Figure 2-18: LiTaO$_3$ with ITO top and bottom electrodes at 175°C. (a) The conductivity of the samples is corrected by fitting a baseline to the current and subtracting this value. (b) The integrated charge curve indicating 3, 50, and 97% poling completion.

Figure 2-19: LiNbO$_3$ with ITO top and bottom electrodes at 150°C. (a) The conductivity of the samples is corrected by fitting a baseline to the current and subtracting this value. (b) The integrated charge curve indicating 3, 50, and 97% poling completion.

The summary of the poling experiments in LiTaO$_3$ and LiNbO$_3$ is shown in Figures 2-20 and 2-21 with ITO/ITO electrodes and +z-CrAu/-z-ITO electrodes. The coercive field decreases by ~48% in LiTaO$_3$ and ~51% in LiNbO$_3$, which is greater than
the 36.5% and 17.5% predicted by looking at the temperature dependence of the coercive field discussed in Section 2.3.1. This indicates that the change in the coercive field is not strictly dependent upon the decrease in the polarization and probably related to change in the nucleation and growth rates. Another possible reason for this additional decrease with increasing temperature is a breakup of the proposed organized point defect complexes as proposed in literature.\textsuperscript{59} These proposed complexes are composed of a tantalum or niobium antisite (\( \text{Nb}_{\text{Li}}^{\text{***}} \) or \( \text{Ta}_{\text{Li}}^{\text{***}} \)) surrounded by four lithium vacancies (shown graphically in Chapter 1, Figure 1-5). The increase in number of these defect complexes is directly correlated with the increase in material’s coercive field.\textsuperscript{6,7,10,107} The increased ionic conduction processes at \( \sim 125^\circ \text{C} \) arises from a movement of the lithium vacancies,\textsuperscript{77,96-98} which, therefore, results in a disorder in the defect complexes, and a could result in lower coercive fields. However, the exact nature of the temperature dependence of nucleation and growth needs to be determined.

The switching time also increases overall with temperature, as shown in Figures 2-20(b) and 2-21(b), (with some anomalies in the 100-180°C). The curves indicate that at higher temperature the switching process is much different than at room temperature. Refering to Miller and Weinreich theory discussed in Section 2.3.1 and given in Equation 2-4, it can be seen that the values of \( \alpha \), the contribution of sideways growth, and \( \beta \), the contribution of the nucleation of new domains, are clearly changing with temperature. Since at all temperatures, the value of \( (E-E_c) \) during poling is kept \( \sim 0.33 \) kV/mm, \( \delta \) must clearly be increasing with temperature. This could mean that there is a change in the relative contribution of nucleation and domain growth (variable \( x \)), or the
values of $\alpha$ and $\beta$ are changing with temperature. As will be seen in the next section, the nucleation density increases drastically, indicating a shift to nucleation dominated process ($x$ approaching 1) or that the value of $\beta$ is increasing. Further, in-situ experiments need to be performed to characterize the contributions of wall velocity and nucleation density.

Figure 2-20: (a) Forward coercive fields and (b) switching time dependence for congruent LiTaO$_3$.

Figure 2-21(a) Forward coercive fields and (b) Switching time dependence for congruent LiNbO$_3$. 
The integrated charge curves given as $P_s = Q / 2A$ for all the poling experiments in LiTaO$_3$ are shown in Figure 2-22 starting from approximately 1% of the total integrated charge, $Q$, at time 0. The discrepancies in the poling charge cannot be fully accounted for by increase in the poling area, as measured domain areas are within 5% of the electrode areas which would give a maximum $P_s$ value of $\sim$57.5 µC/cm$^2$. The double ITO electrodes were reasonably well behaved with calculated $P_s$ values between 50-60 µC/cm$^2$. The CrAu/ITO electrode case showed higher discrepancies, the maximum integrated $P_s$ values were $\sim$ 75 µC/cm$^2$, an increase of 30%.

![Fig 2-22](image1.png)

Figure 2-22: (a) The integrated transient poling curves for LiTaO$_3$ with ITO/ITO electrodes for a variety of temperatures. (b) The peak $P_s$ value for each temperature.

![Fig 2-23](image2.png)

Figure 2-23: (a) the integrated transient poling curves for LiNbO$_3$ with ITO/ITO electrodes for variety of temperatures. (b) the peak $P_s$ value for each temperature.
The charge discrepancy is particularly pronounced in LiNbO$_3$ as shown in Figure 2-23. Polarization values calculated from the integrated charge are as large as 1200 $\mu$C/cm$^2$, an increase of 16 times the room temperature value of 75 $\mu$C/cm$^2$. Again, this increase in charge cannot be accounted for by an increased poling area, as the area of the poled sample was measured to be within 5% of the electrode area. It is clear that at higher temperatures, in addition to the transient current due to domain inversion and to the baseline conductivity, an additional charge creation process is occurring concurrent with domain reversal. Charge discrepancies of 50-500% were also measured by Battle et al. for poling of LiTaO$_3$ using two tantalum electrodes. The nature of this increased charge is unknown but possible mechanisms will be discussed in the next section.

The differences between the charges measured between the Cr/Au electrodes and the ITO electrodes could be due to the differences in the work functions of the electrodes. The range of literature values for the bandgap in both materials (3.6-3.930 eV$^{108-110}$) and the electron affinity (0.25-0.4 eV$^{108,110}$) creates a Schottky barrier on both ITO (4.28-5.245$^{111-114}$) and Cr (4.25 eV$^{115}$). Depending upon the oxygen content during sputtering or the sample surface treatment prior to sputtering, the work function of ITO can be modified greatly and accounts for the wide variety of values in the literature. The bandgaps of the materials and the work functions of the electrodes also show temperature dependence which complicates the analysis. Additional studies are necessary to elucidate the differences.
Once the domain had been forward poled, it was observed that reverse poling could not be achieved for the majority of samples. The exceptions are the breakdowns that occurred in LiNbO$_3$ at particular temperatures and the high temperature (>175ºC) reverse poling. The reverse poling results are summarized in Table 2-3. In the majority of cases, some process occurred during the forward poling such that domain reversal to the original domain orientation could not occur. The polarization could not reversed even after removing the electrodes and poling with water electrodes at room temperature. Possible reasons for this domain pinning will be discussed in the next section.

### 2.3.4.2 Discussion

Poling at higher temperature offers much different domain kinetics that could be exploited to create finer domain shapes than are possible at room temperature. The increased nucleation density at higher temperatures is particularly exciting. However, as mentioned in the last chapter, there are some interesting issues that that could impede the development of this technique. The first is associated with the large anomalous charge

<table>
<thead>
<tr>
<th>Temperature (ºC)</th>
<th>LiNbO$_3$</th>
<th>LiTaO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CrAu/ITO</td>
<td>ITO/ITO</td>
</tr>
<tr>
<td>25</td>
<td>Reversal</td>
<td>No reversal</td>
</tr>
<tr>
<td>100</td>
<td>Breakdown</td>
<td>Breakdown</td>
</tr>
<tr>
<td>125</td>
<td>Breakdown</td>
<td>No reversal</td>
</tr>
<tr>
<td>150</td>
<td>Breakdown</td>
<td>No reversal</td>
</tr>
<tr>
<td>175</td>
<td>No reversal</td>
<td>No reversal</td>
</tr>
<tr>
<td>200</td>
<td>No reversal</td>
<td>Reversal</td>
</tr>
</tbody>
</table>
measured during domain poling and the second is the locking of the polarization in the forward poled direction.

Figure 2-24: The (a) optical image and (b) schematic of a charged domain wall shown in cross section in LiNbO$_3$ created with double ITO electrodes at 125ºC and 20% $Q$. The horizontal line is a polishing error.

It is believed that both of these processes are related to the formation of charged domain walls as shown in Figure 2-24. These walls occur between the nuclei growing from the $+z$ face toward the $-z$ face, and are charged positively due to the head-to-head alignment of the polarization tips. Cross sections taken of the completely poled samples indicate charged domain walls are located adjacent to the $-z$ face, however they do not completely terminate and form a jagged boundary ~50 µm from the bottom surface. Only at higher temperatures (>175ºC) do the domains penetrate to the other side of the sample. The formation of charged domain walls at room temperature in LiNbO$_3$ created with double ITO electrodes has been previously observed.$^{116}$ The domains could not be
reversed up to fields of 22.5 kV/mm. The authors attributed the formation to an intrinsic dielectric gap formed near the surface that makes the screening and redistribution of these charges impossible.

Keeping in mind the charged domain walls, we will first discuss the origin of the anomalous charge. Let us suppose that a charged domain wall moving from one electrode to the other requires compensation of the charged wall at every wall position while traveling through the crystal. This required charge can be calculated by

\[ Q = P_s \cdot A_{dw} \cdot N \]

where \( P_s \) is the spontaneous polarization, \( A_{dw} \) is the area of the charged domain wall, and the thickness of the crystal is expressed as \( N \) number of unit cells (crystal thickness divided by unit cell parameter, \( c \sim 1.3 \) nm). For a 500 \( \mu \)m thick LiNbO\(_3\) crystal with \( P_s = 75 \) \( \mu \)C/cm\(^2\) and a 1 cm\(^2\) charged wall area, this charge is extremely large \( \sim 2.8 \times 10^7 \) \( \mu \)C. Compare this to the value of charge required by the compensation of the surface area, \( Q = 2P_sA \), which only 150 \( \mu \)C for a 1 cm\(^2\) electrode area. While clearly the increased charge is nowhere near the magnitude of wall compensation at every position, there is an additional charge that is present during the switching process. To account for this, let us expand the total charge, \( Q_{tot} \), as

\[ Q_{tot} = Q_s + Q_{dc} + Q_{dw} \]

where, \( Q_{dc} \) is the baseline charge related to the finite dc conductivity of the sample unrelated to domain reversal (i.e. in the non-poling regime) and \( Q_{dw} \) is the charge required by the moving charged domain wall. The charge required to compensate the surface is given by \( Q_s = 2P_sA \) where \( P_s \) is the spontaneous polarization and \( A \) is the areas
of the top and bottom electrodes. Returning to the model presented in Equation 2-6, the externally measured charge, $Q_{ext}$, is given as

$$Q_{ext} = Q_s + Q_{dc} + Q_{dw} - Q_{free}$$

where the free charges in the sample are given by $Q_{free}$. The baseline conduction charge can be easily subtracted from the total charge by examining the current through the sample at voltages below the coercive field. We will therefore focus on the last two terms of Equation 2-10 which can be expressed at any given time interval, $d\tau$, as

$$Q(d\tau) = Q_{dw} - Q_{free} = A_{dw}\sigma_{avg}[E_{bulk} - E_{local}]d\tau$$

where $Q_{dw}$ is the charge flowing from the electrodes through the crystal to the charged domain wall and $Q_{free}$ is the free charge available in the vicinity of the charged domain wall. In this expression $A_{dw}$ is the area of the charged domain wall, $\sigma_{avg}$ is the average conductivity, $E_{bulk}$ and $E_{local}$ are the electric fields in the bulk and the local wall region, respectively. As an approximation, $E_{bulk} \approx E_{ext}$ and $E_{local}$ is due to the divergence in the polarization at the charged wall. A schematic is shown in Figure 2-25.

---

Figure 2-25: Simple model of compensation of the charged domain wall motion through sample conductivity
At room temperature during the poling process, the extremely low crystal conductivity makes $\sigma_{\text{avg}}$ effectively zero and the externally measured charge, $Q_{\text{ext}}$, is just the compensation of the sample surface, $Q_s$. As the temperature goes up and the conductivity in the crystal increases, the moving domain wall can receive charge drawn either from bulk conductivity ($Q_{\text{dw}}$) through the external circuit or by thermally generated free carriers in the near vicinity of the wall ($Q_{\text{free}}$). At intermediate temperatures, the bulk crystal still has relatively low amounts of free charge, so a large amount of charge is pulled from the electrode to partially compensate the charged domain wall. At higher temperatures, more internal charges compensate the wall and the reliance on charge from the external circuit is lessened. This is reflected in the peak in total charge seen at intermediate temperatures in Figure 2-22 and Figure 2-23.

This model gives a nice, intuitive explanation of the process. However, the exact details regarding the drift velocity, current densities, local and external fields, and screening charges all need to be worked out. It is a complex process due to the transient nature of the charge, screening fields, and position of the wall. Similar analysis of electron drift and compensation under the influence of external fields are calculated for the photorefractive effect during holographic exposure. Similar detailed calculations and theory remains to be performed in future work, starting from the simple model proposed here.
It is clear that the presented model should express a dependence upon the thickness of the crystal – thicker crystals should require more transient charge because the charged domain wall has to travel a further distance. To test this, the transient current in two different thickness crystals is shown in Figure 2-26. A total charge of 2509 µC was measured for the poling of the 500 µm crystal compared to 1663 µC in the thinner 300 µm thick crystal. This gives a charge ratio of ~1.5 to a thickness ratio of ~1.67. The higher total charge measured in the thicker crystal supports the validity of the model proposed here, although further work needs to be done to validate the model and to explain the differences between LiNbO₃ and LiTaO₃.

The locking of the polarization in the forward direction is thought to originate from the formation of stable charged domain walls. The locking of the polarization near the electrodes is one of the primary causes of ferroelectric fatigue.¹¹⁸,¹¹⁹ This is thought to be related to either the accumulation of defects at the electrodes (like oxygen vacancies) which pin the domain walls¹²⁰ or the electrostatic effects of charges trapped at

Figure 2-26: Intermediate charges measured in LiNbO₃ at 150°C for two different crystal thicknesses.
the ferroelectric/electrode interface or injected into the ferroelectric near the electrode.\textsuperscript{119,121} There has been no systematic work on the ferroelectric fatigue properties of congruent LiNbO\textsubscript{3} and LiTaO\textsubscript{3} so the exact nature of this fatigue is unclear. Every systematic study of switching kinetics in LiNbO\textsubscript{3} and LiTaO\textsubscript{3} in the literature uses two water electrodes. However, recent work in vapor transport exchanged LiTaO\textsubscript{3}, which has almost perfect stoichiometry and coercive fields as low as 200 V, has shown that ferroelectric fatigue is a major issue when using metal electrodes.\textsuperscript{107}

2.3.5 Nucleation Density

Previous reports on high temperature poling suggested that there is a higher nucleation density at higher temperatures, though specific quantification had not been performed.\textsuperscript{59} In order to quantify the nucleation density, three sets of temperatures were chosen for each material and a series of poling experiments were performed by stopping the poling process at 5, 20, 40, 60, and 80\% of the total integrated charge, \( Q \). The electrodes were removed by a short etch in 5\% HF in 95\% water. The domain structure could be observed with the optical microscope as shown in Figure 2-27, however, individual nucleation sites could not be discerned in the high temperature cases with optical microscopy.
Higher resolution images were taken with piezoelectric force microscopy (PFM). For details on this technique see Section 3.2.1. The nucleation density was determined by scanning a 100 x 100 µm area in 10 random locations on the poled sample surface. The individual nucleation sites that were free standing from other domains were counted as one site. The smallest domain that could be resolved was ~1 µm. As a check, the area of total domain reversed area was calculated for each PFM image area to determine the degree of poling. These results are summarized in Table 2-4.

The measurement of nucleation density is difficult, especially at room temperatures in LiNbO₃, because the nucleation density is so low and is not distributed randomly. They tend to be grouped in clusters in arcing or linear paths, or near larger domains already growing. The large standard deviation for the LiNbO₃ values reflects this. For the room temperature densities, the values given in the literature are 200-1000 nuclei/mm² for LiNbO₃ and 200-1000 nuclei/mm² for LiTaO₃. However, these values are not really comparable to this study, as the nucleation density depends greatly upon the poling field, showing an exponential increase in the number of nuclei with higher fields. In this study, the poling field is always just above the coercive field value

Figure 2-27: Optical microscopy images of nucleated domains in LiTaO₃ under a 1000 V bias to enhance contrast. Poling was stopped at 20% total Q at temperatures of (a) 25°C and (b) 150°C. Domains in (b) are to small to individually resolve.
for all samples and temperature, making comparisons between samples appropriate. The results are summarized in Table 2-4 and plotted in Figure 2-28. As shown in Figure 2-28 the nucleation density peaks in LiTaO$_3$ at 125°C then decreases with increasing temperature, while in LiNbO$_3$ the density shows a sharp increase at 175°C. It has been shown that in the low field regime, nucleation density is related to pre-existing defects. At increased temperature, the increased thermal energy and free charge density allows more pre-existing defects, which normally do not have enough energy to nucleate domains at room temperature, to be expressed.

<table>
<thead>
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<th>Temperature (°C)</th>
<th>Avenue</th>
<th>Standard Deviation</th>
<th>Reversed</th>
<th>Avenue</th>
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<td>1960</td>
<td>650</td>
<td>5.7%</td>
<td>175</td>
<td>11850</td>
<td>7100</td>
</tr>
</tbody>
</table>

Figure 2-28: Nucleation density for (a) LiTaO$_3$ and (b) LiNbO$_3$.

Representative PFM images are presented in Figure 2-29 measured on the +z face of LiTaO$_3$. In general, the nucleation density was higher and domains smaller at 125°C than at the higher temperatures of 165°C or 200°C, although the total reversed areas in
each case were very similar (see Table 2-4). A series of images taken in LiTaO$_3$ at 125°C are shown in Figure 2-30.

Examination of the $-z$ faces by PFM found marked differences from the $+z$ face. Except for the high temperature (>175°C) samples, not many domains could be located on the $-z$ face. This is directly related to the formation of stabilized charged domain walls which prevent the polarization from completely reaching the $-z$ face.

![PFM images](image)

Figure 2-29: PFM images of partially domain reversed LiTaO$_3$ samples (a) 125°C (b) 165°C and (c) 200°C.

The most striking feature of the poling at elevated temperatures is the differences in the domain shapes as a function of temperature. When formed at room temperature the domains walls in each material are formed along specific crystal orientations. In LiTaO$_3$, the domain shapes are *triangular* with domain walls parallel to the $x$-axes forming $x$-walls in Figure 2-31(a). In LiNbO$_3$, the domain shapes are *hexagonal* with domain walls parallel to the $y$-axes forming $y$-walls as shown in Figure 2-32(a).
Figure 2-30: PFM images of a series of growth steps in LiTaO$_3$ at 125°C for total $Q$ of (a) 5%, (b), 20%, (c), 60%, and (d) 80%. Each image is 100 µm x 100 µm. All pictures have the same axes as in (a) and (d).

Figure 2-31: PFM images of evolution of LiTaO$_3$ structures with temperature. (a) trigonal $y$-walled domains at room temperature, (b) hexagonal $y$-walled domains at 125°C, (c),(d) trigonal $y$-walled domains at 165°C and 200°C. All images +z face. Samples (b)-(d) poled to 20% total $Q$. 
At elevated temperatures, these shapes are significantly modified. In LiTaO$_3$, at 125°C as shown in Figure 2-31(b) the domain shapes are hexagons formed by $y$-walls. At higher temperatures, the wall shape maintains the $y$-wall orientation but becomes triangular, although with very rounded corners as seen in 2-31(c),(d). At each temperature, these shapes were observed for all stages of growth, 5% - 80% of total $Q$. This shows two very significant results. (1) It indicates that the domain wall orientation in congruent LiTaO$_3$ is a strong function of temperature. At room temperature the
material shows triangular \(x\)-walls, however at 125°C the walls become hexagons with \(y\)-wall orientations - the same as LiNbO\(_3\) and the same as stoichiometric LiTaO\(_3\). At higher temperatures, the domain walls are still \(y\)-walls, only composed only of 3 walls to form trigonal domains. The domain shapes will be discussed further in Chapter 4. (2) If samples are periodically poled at 125°C the allowed domain wall orientations have parallel faces which are needed for fabricating gratings, avoiding many of the difficulties seen in generating gratings in LiTaO\(_3\).\(^{40}\)

Lithium niobate also shows some temperature mediated domain shape changes, although the effects are not as striking as in LiTaO\(_3\). There is no change in the domain wall shape from room temperature to 125°C as shown in Figure 2-32(a) and (b). At 150°C the hexagonal shapes coexists with triangular shapes each of \(y\)-wall orientation. At 175°C the triangular and hexagonal shapes are still present in much larger numbers. Additionally, the appearance of areas of platelet-like domain features is shown in Figure 2-32(d). These patterns appear to be randomly distributed in specific areas. It is not clear exactly what the shapes of the small features are. The larger features (> 5 \(\mu\)m) have some angular edges, but the smaller spots (< 2 \(\mu\)m) become more rounded and curved and are not easily distinguishable by the PFM technique. Perhaps these features are areas of damage to the sample surface. The preferred domain wall orientations will be discussed in detail in Chapter 4 including a discussion of the observed temperature mediated changes.
2.3.6 Periodically Poled Gratings Using Temperature

Some of the difficulties in periodically poling were discussed in Section 2.2.7. The major identified issue for creating uniform patterns both in the plane and through the thickness is nucleation density. If homogenous distribution of nuclei under the electrodes could be created, much finer features would be possible. As shown in the previous section, higher temperature increases nucleation density. Additionally, as shown in Section 2.3.4, the domain kinetics such as switching times are drastically different. Very few studies of using temperature have been reported in the literature. Domains were created in Mg doped LiNbO$_3$ with periods of 30 $\mu$m domains in 3 mm thick crystals (aspect ratios of 200) at 80$^\circ$C and 170$^\circ$C using aluminum electrodes.$^{122,123}$ As a proof of concept, periodically poled gratings will be created at higher temperatures in congruent LiNbO$_3$.

Sample gratings were defined on the top surface of LiNbO$_3$ by uniformly coating the +z surface with CrAu, lithographically defining the grating features, then etching to create the patterns. Domain gratings were created with periods of 6.5, 6.7, 6.9, and 10 $\mu$m. The bottoms surface was coated with 300 $\mu$m of ITO. As before, the electrode leads were attached to the surface with silver epoxy and copper leads and the device suspended in dielectric fluid on a hot plate.

Poling was performed by ramping the voltage slowly through the coercive field and clamping the voltage when the current exceeded 1 $\mu$A. This was performed in LiNbO$_3$ at temperatures of 125, 150, and 175$^\circ$C. While the nucleation density is much higher at 175$^\circ$C, the created domains became merged at both surface forming gratings.
only in the interior of the sample. The most successful features were created in LiNbO$_3$ at 150ºC as shown in Figure 2-33. The domain growth was stopped at 20% of the total integrated charge to show the nucleation density in Figure 2-33(a). The interior of these growing nuclei showed very sharp domain features as shown in Figure 2-33(b). The cross sections of these features are shown in Figure 2-34.

![Figure 2-33: Elevated temperature poling of LiNbO$_3$ gratings at 150ºC stopped at 20% of total calculated $Q$. (a) wide view and (b) zoom in on individual sites. Contrast enhanced by etching the sample surface in dilute HF.](image)

The creation of domain gratings at high temperatures shows very promising results due to the much higher nucleation densities. However, further techniques need to be developed to pole uniform gratings throughout the sample. As shown in Figure 2-34 the gratings do not penetrate through to the other side of the sample. The walls stop part way through the device and are stable at an intermediate position. This might be the drawback to implementing this technique. If the domains are kept from terminating on the –z face, then uniformity through the thickness of the device will be compromised.
Further experimental work should be done to optimize the poling temperatures. Perhaps an ideal temperature can be found that has the desired high nucleation but does not form stable charged domain walls. Alternatively, the nucleation step could be performed at high temperatures, followed by a room temperature poling using the techniques in Section 2.2.7. It is clear that too much conductivity in the crystal also leads to very poor fidelity domains as evidenced in the periodical poling of KTiOPO₄ (KTP). In this case, the crystal are actually cooled to low temperatures (-100°C) to lower the conductivity. The periodic poling at temperature in both LiNbO₃ and LiTaO₃ probably should be optimized in the range from 80-125°C where conductivity is still very low.
2.4 Conclusions

Methods were developed to create and shape domain walls in LiNbO$_3$ and LiTaO$_3$ through a combination of in-situ monitoring of the domain wall motion combined with the monitoring of the transient poling fields. Using these techniques domain shapes down to ~5 µm are able to be reproducibly created and will be used to create optical devices in Chapter 5.1. The main difference between the poling kinetics between the two materials is due to the numerous pinning sites in LiTaO$_3$ which give the domain wall velocity a constant value. These pinning sites also allow LiTaO$_3$ to adopt arbitrary shapes better than LiNbO$_3$.

Poling in both materials was performed at elevated temperatures up to 200ºC. The coercive fields decrease by ~48% in LiTaO$_3$ and ~51% in LiNbO$_3$ relative to their room temperature (25ºC) values, switching times increase greatly, and the nucleation density increases at higher temperatures. The formation of stable charged domain walls was observed. The creation of gratings at elevated temperatures shows great promise due to the high nucleation density, but additional work should be done to optimize the temperatures and poling conditions.

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Jonas Webjorn, Frederik Laurell, and Gunnar Arvidsson, "Fabrication of periodically domain-inverted channel waveguides in lithium niobate for second


L. Kovacs and K. Polgar, in *Properties of lithium niobate* (INSPEC, IEE, 2002), pp. 91-96.


Chapter 3

Local Structure of Ferroelectric Domain Walls

Since the phenomenon of domains and domain walls originate on the nanoscale and are manifest in the macroscale, it forms a key link between the atomic structure and defects in a ferroelectric and its macroscale properties. Therefore, in order to control and shape ferroelectric domain walls, one needs to understand the phenomena of domains and domain walls on both of these length scales. In this chapter, the local structure of the domain wall will be examined using scanning force microscopy techniques.

This chapter will be organized as follows: the scanning force microscope techniques will be introduced in Section 3.2 followed by the electromechanical imaging data presented in 3.3 and the electrostatic imaging data in Section 3.4. The electromechanical response of the surface will be modeled by FEM in Section 3.5, followed by a discussion in Section 3.6.

3.1 Introduction

Ferroelectrics possess a host of interesting elastic, electrical and optical properties that intricately couple through a variety of interconnected phenomena such as piezoelectricity (strain to electric fields), elasto-optic effect (strain to optical index), and
electro-optic effect (electric field to optical index), to name a few. On transitioning from one polarization direction to another, which takes place in a domain wall, these couplings are clearly active. These domain walls are areas of spontaneous polarization gradient, which also imply gradients in the spontaneous strain, optical index, and electric fields going across a wall.

The current explosion of literature in nanoscience and nanotechnology is undoubtedly being fueled by the prevalence and utility of the atomic force microscope (AFM), which allows property measurements at the nanoscale. In this technique, a sharp tip, a few microns long and often less than 100 Å in diameter is located at the free end of a micrometer sized cantilever. Forces between the tip and the sample surface cause the cantilever to distort, and these small distortions are translated into maps of the sample surface. Aside from topography, the real utility of AFM derives from the ability of the tip to interaction with a wide number of forces such as magnetic and electrostatic forces or chemical interactions.¹

The nanoscale local nature of antiparallel domain walls is a fundamental property of interest. However, recent studies on LiNbO₃ and LiTaO₃ suggest that antiparallel domain walls can exist with differing refractive indices and lattice parameters across a 180° wall.² Such asymmetry in optical and elastic properties across a wall is unexpected and has been shown to arise from the presence of non-stoichiometric defects in these crystals.³ Here we show that local electromechanical properties across these walls in lithium niobate show an asymmetric response as well. We present a detailed experimental and theoretical modeling investigation of the piezoelectric response at a single antiparallel ferroelectric domain wall. This is probed using the following scanning
probe microscopy techniques: piezoelectric force microscopy (PFM) and electrostatic force microscopy (EFM). Together, these results suggest that while the structure of an ideal ferroelectric domain wall is well understood to be atomically sharp (1 to 2 unit cells wide)\(^4\) small amounts of defects can change the local structure of a domain wall dramatically through defect-domain wall interactions.

### 3.2 Spatially Resolved Imaging of Ferroelectric Domain Walls

There are a number of methods to observe the orientation of domain walls in ferroelectrics including, but not limited to, optical birefringence (as in Chapter 2.2.2), etching, surface decoration, and UV photoemission.\(^5\) Most of these techniques suffer from poor resolution (~ 1 \(\mu\)m resolution limited by optical diffraction) and may damage the surface of the sample. Higher resolution can be obtained using electron-beam techniques but significant problems such as sample charging, local heating, and beam damage complicate the process.\(^4,6,7\) Significant progress has been made in imaging ferroelectric domains through the use of the scanning force microscopy. Various scanning force microscopy techniques used to image ferroelectric surfaces and the resolution of each technique is summarized in Table 3-1. Many studies have been done characterizing the domain-related topographic data using vertical and lateral force microscopy.\(^8,9\) Recently, alternative scanning force techniques which image non-topographic manifestations of the domain structure have become important. Two of the most prominent techniques are piezoelectric force microscopy (PFM)\(^10-13\) which utilizes
the local electromechanical response of the surface, and electrostatic scanning probe
techniques like electrostatic force microscopy (EFM) and scanning surface potential
microscopy (SSPM) which image using the long range electrostatic forces above the
ferroelectric surface. These two techniques, PFM and electrostatic force microscopy,
will be used in this work.

Table 3-1: Selected SPM Imaging of Ferroelectric Domain Walls

<table>
<thead>
<tr>
<th>Technique</th>
<th>Measured Property</th>
<th>Material</th>
<th>Resolution</th>
<th>Source</th>
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<td>Friction forces</td>
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<td>18,19</td>
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<td>Electrostatic force gradient (EFM)</td>
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<tr>
<td></td>
<td></td>
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</tr>
<tr>
<td>Scanning surface potential</td>
<td>Effective surface potential (SSPM)</td>
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<tr>
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<td></td>
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<td>PZT Thin Film</td>
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<td></td>
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3.2.1 Piezoelectric Force Microscopy

Piezoelectric force microscopy (PFM) has been used to study the antiparallel
domain states of bulk crystals like triglycine sulfate (TGS), BaTiO₃, and thin film
piezoelectric samples of random domain orientations. As shown in Figure 3-1, the
technique involves bringing a conductive tip in contact with the sample surface, a
distance of 0.1 to 1 nm. A modulated AC voltage is applied to the sample through the
tip, and the first harmonic oscillations of the cantilever are detected by a lock-in
technique. If the sample surface is piezoelectric, the oscillating electric field causes
deflection of the sample surface through the converse piezoelectric effect. This offers a
technique to examine domain and domain structures of piezoelectric materials at the
micrometer and nanometer scale, as the electromechanical response of the sample surface
gives information about the orientation of the polarization direction below the tip as well
as the relative orientations between adjacent domains.

If an oscillating voltage of the form

$$V_{tip} = V_{dc} + V_{ac} \cos(\omega t)$$

is applied to a piezoelectric surface, where $V_{dc}$ is the a dc bias voltage, $V_{ac}$ the magnitude
of the oscillating voltage, $\omega$ is the frequency of oscillation, and $t$ is time, then the
amplitude of displacement of the surface is given by

$$d = d_0 + A \cos(\omega t + \varphi)$$

where $d$ is deformation of the sample surface, $d_0$ is the static deflection due to any bias
voltage, $A$ is the amplitude of the oscillation, $\omega$ is the frequency of oscillation, and $\varphi$ is
the phase of the electromechanical response of the sample surface. In the vertical imaging
mode, surface displacements perpendicular to the sample surface, both the
amplitude (the magnitude of surface displacement) and the phase (a measurement of the
phase delay between the applied electric field and the response of the sample surface), are
measured. In-plane oscillations can also be investigated by observing the torsioning of
the cantilever in the lateral imaging mode.
3.2.2 Electrostatic Force and Scanning Surface Potential Microscopy

In a ferroelectric, the surface charge density is \( \sigma = P_s \cdot n \) where \( P_s \) is the polarization vector and \( n \) is the unit normal to the surface. On traversing a 180° domain wall, where \( P_s \) is perpendicular to the surface as in LiTaO\(_3\) and LiNbO\(_3\), the polarization direction changes sign, so the sign of surface charge density should be opposite on either side of the domain wall. This surface charge is always screened in a ferroelectric, due to adsorbates and/or surface states of free charges with associated depletion or accumulation layers. The degree of compensation can be complete, or more likely, some remnant unscreened surface charge can be present on the surface.\(^{33}\)

Figure 3-1: Schematic of piezoelectric force microscopy (PFM) setup. The forces acting in the vertical plane (\( F_z \)) give the vertical signal, the forces in the horizontal plane (\( F_x \)) gives the lateral signal. \( V_{tip} \) is an oscillating voltage applied to the sample. Up and down are the signals from the top and bottom 2 quadrants of the photodiode, while left and right are the signals from the left and right 2 quadrants.
Two methods capable of distinguishing the electrostatic state of the surface are electro-static force microscopy (EFM) and scanning surface potential microscopy (SSPM). Both of these techniques are non-contact, where the tip is kept above the sample surface – typically 30 to 100 nm separation – and vibrated near a natural frequency of the cantilever. In this regime, the tip is also very susceptible to electrostatic forces. The electrostatic force between the tip and sample above a dielectric material is a sum of two contributions: the first owing to the charge-induced charge interaction, and the other owing to the capacitance. The total expression for the electrostatic force can be written as the charge-charge interaction and the capacitive energy given by

\[ F(z) = \frac{Q_s Q_t}{4\pi \epsilon_o z^2} + \frac{1}{2} \frac{dC(z)}{dz} \left(V_{ac} + V_{dc}\right)^2 \]

where \( Q_s \) is the effective surface charge on the sample, \( Q_t \) is the charge on the tip, \( V_{ac} \) and \( V_{dc} \) are biases applied between the cantilever and surface (if present), and \( C(z) \) is the effective capacitance of the tip-sample system which is dependent upon tip geometry, surface topography, and tip-surface separation, \( z \).

In electrostatic force microscopy (EFM), a conductive cantilever is vibrated above the sample surface as in standard non-contact mode operation. If the tip is grounded \((V_{ac}=0 \text{ and } V_{dc}=0 \text{ in Equation 3-3})\), the surface charges \( Q_s \) induce image charges of the opposite sign on the probe \( Q_t \) and result in the attractive force that will deflect the cantilever toward the sample. This force results in a change of the cantilever resonant frequency that is proportional to the force gradient\(^1\)

\[ \Delta \omega = \frac{\omega_0}{2k} \frac{dF(z)}{dz} \]

\(^1\)
where $k$ is the spring constant and $\omega_o$ is the resonant frequency of the cantilever. Resonance is maintained by adjusting the driving frequency $\omega_p$ and the frequency shift $\Delta\omega = \omega_p - \omega_o$ is collected as the EFM image.\textsuperscript{34} Regions with equal but opposite surface charge densities (e.g. $c^+$ and $c^-$ domains) cannot be distinguished because there will always be an attractive force between the surface charges and the induced image charges in the tip of opposite sign. However, any deviations from uniform values will change the force gradient, which can be used to map the sample surface. When the tip is dc biased, ($V_{dc} \neq 0$ in Equation 3-3) then $Q_t = -Q_s + Q_{dc} = -Q_s + V_{dc}C$ and Equation 3-3 becomes\textsuperscript{1}

$$F(z) = \frac{Q_s^2}{4\pi\varepsilon_o z^2} + \frac{Q_s V_{dc} C}{4\pi\varepsilon_o z^2} + \frac{1}{2} \frac{dC(z)}{dz} V_{dc}^2.$$  \hspace{1cm} 3-5

These additional two terms provide more information about the charge state of the sample surface, but interpretations of the images are not straightforward and require multiple scans of the surface at different biases. This technique has been used successfully to determine the sign and density of surface charges in bulk TGS,\textsuperscript{15,35} GASH,\textsuperscript{20,36} PZT\textsuperscript{37}, and BaTiO$_3$.\textsuperscript{17}

In scanning surface potential microscopy (SSPM), an oscillating voltage is instead applied to the cantilever ($V_{ac} \neq 0$ in Equation 3-3). If the sample surface is characterized by slowly varying surface potential, $V_{surf}$, then the potential between the oscillating tip voltage (as in Equation 3-1) and the surface is $V = (V_{dc} + V_{ac} \sin \omega t - V_{surf})$. Equation 3-3 can then be expanded into dc, first, and second harmonic components, of which the first harmonic component is\textsuperscript{17}
This component is kept equal to zero by varying the dc component of the signal, which is the SSPM map of the sample surface. This technique allows high (~mV) potential resolution and has been successfully used to image domain walls in BaTiO$_3^{38,39}$ and KTP.$^{40}$ However, because this is a non-contact technique, the resolution is less than the resolution of PFM.$^{9,15,16}$ Measurements of potential screening on BaTiO$_3$ and charged grain boundaries in SrTiO$_3$ by EFM and SSPM indicate that the lateral resolution is limited to ~300 nm.$^{22,23}$

3.3 Electromechanical Imaging

3.3.1 Samples and Measurement Details

$Z$-cut lithium niobate crystals (polarization, $P_z$, along the thickness direction) with thickness ~300 µm were used in this study. Randomly nucleated antiparallel domains were created in the crystals by electric field poling starting from a single domain state. Briefly, two water cells located on the opposite sides of the crystal were used as electrodes. Electric fields greater than the coercive field of the crystal, (~22 kV/mm in these crystals), were applied by slowly ramping the voltage on the water cells at room temperature. The field was removed when the domain poling process was partially completed, leaving many small domains of opposite orientation which penetrated through
the thickness of the crystal in a matrix of original orientation. The domain sizes created varied from 4 to 500 \( \mu m \) with average size of \( \sim 100 \mu m \).

Measurements were made using an Explorer AFM head manufactured by Thermomicroscopes. Cantilevers (fabricated by Ktek) of varying stiffness from 2 and 20 N/m were used in the imaging. The tips were coated with Ti-Pt and are electrically connected to an external voltage supply with the ground plane on the back of the sample mount. Since coated tips degrade due to the peel-off of the conductive coating, the tips were replaced frequently and images presented in this paper where taken with minimally used tips (only enough to characterize the tips and locate the feature of interest). The tips have a nominal radius of curvature of 50 nm as provided by the vendor, but the exact radius of curvature will be slightly different dependent upon the degree of use. A Stanford system SR830 lock-in amplifier was used to lock onto the raw CCD signals and to generate the imaging oscillation voltage waveform. A HP32120 function generator was sometimes used to generate higher voltage signals (up to 10 V peak). Most images were taken at 5 V peak (3.5 RMS) imaging voltage with the frequency of oscillation around 35 kHz.

Our system was calibrated using a similar technique to Christman\textsuperscript{41}, where the amplitude of a uniformly electroded sample of \( x \)-cut quartz was measured as a function of applied voltage for various low frequency oscillations and contact forces. The slope of the maximum amplitude versus applied voltage of the sample surface was assumed to be equal to the \( d_{11} \) coefficient of the quartz at low frequencies of 1 kHz or less. This allowed us to calibrate the amplitude of surface displacement (measured as an amplitude
signal on the lock in amplifier) and a physical displacement of the surface at a particular frequency.

In general, the frequency of the oscillating probe voltage at the tip plays a very important role in determining the amplitude and contrast of measurements in PFM. Choosing the proper frequency can enhance or minimize contrast in the image, or even null a contrast completely. Labardi examined the influence of frequency on the measurement technique, attributing most of the variation in oscillation to a complex resonant structure determined by the tip and sample surface in contact with each other.\textsuperscript{27,42} Unfortunately, most papers on PFM do not pay close attention to the frequency and this may explain the wide variety of image contrasts and image wall widths measured in the literature.

Frequency scans of the sample were made by keeping the probe over a uniform domain area in lithium niobate and varying the frequency of the applied voltage and plotting the resulting cantilever amplitude and the phase between applied voltage and surface response. These plots are shown in Figure 3-2. The phase shows a continual increase in angle (the general slope in Figure 3-2(a)), which indicates a frequency dependent background term.\textsuperscript{42} Most images in this paper were taken between 30-35 kHz at a relatively flat area in the amplitude and phase as shown in Figure 3-2(b).
There are several different origins of the signal in a vertical PFM image. The net amplitude, $A$, of the oscillating surface is given by the sum of all the contributing factors

$$A = A_{pi} + A_{es} + A_{nl}$$ \hspace{1cm} 3-7

where $A_{pi}$ is the electromechanical (piezoelectric) amplitude, $A_{es}$ is the electrostatic amplitude,\textsuperscript{10,43} and $A_{nl}$ is the non-local contribution due to capacitive interaction between the sample surface and the cantilever assembly.\textsuperscript{44} Discussion of the magnitudes of each factor in Equation 3-7 are discussed in detail in papers by Hong\textsuperscript{45} and Kalinin.\textsuperscript{30} Any signal observed on a sample, then, must be thought of as the sum of all these interactions.
The mechanism for piezoelectric signal is as shown in Figure 3-3(a). Here, the amplitude of the vertical oscillations ($A_{pi}$) should be the same on either side of the domain wall and be related to the piezoelectric coefficient $d_{33}$. The phase, which is the delay between the applied signal and the surface displacement, contains information about the polarization direction. For example, in lithium niobate, where the piezoelectric $d_{33}$ coefficient is positive, the application of positive tip bias to the $+P_s$ surface of a domain (i.e. positive end of the polarization, $P_s$), results in a contraction of the sample surface (negative displacement of cantilever, $-A_{pi}$) as shown in Figure 3-3(a). Therefore, the surface oscillation is $\pi$ out of phase with the oscillating tip bias. The case is reversed above a $-P_s$ surface of a domain (i.e. negative end of the polarization, $P_s$) in Figure 3-3 (b) where the surface oscillation is in phase with the oscillating tip bias.

The electrostatic response, also called the “Maxwell stress”, arises from electrostatic forces acting between a conductive cantilever tip and a charged ferroelectric
surface as shown in Figure 3-3(c,d). The net charge of the surface, due to screening of the spontaneous polarization, can be either net positive or negative. For a partially screened surface, a net positive charge will be on the $+P_s$ surface and net negative charge on the $-P_s$ surface. In the case of an over-screened surface, where the spontaneous polarization is over-compensated by surface charges, a net negative charge will be on the $+P_s$ surface and net positive charge on the $-P_s$ surface. Partially or completely screened surfaces are the likely state of ferroelectric surfaces in air$^{17}$, while over screening is observed on electrically poled samples like PZT thin films.$^{46,47}$ We note that the phase relation between the applied voltage and the tip displacement is the same for the piezoelectric mechanism and the over-compensated surface. The phase relation is opposite for the partially screened case.

On a piezoelectric surface, all contrast mechanisms are active. To test for the dominant mechanism for a given sample, the relative phase delay above a domain of known orientation must be found. Using a lock-in amplifier, we have experimentally verified that above the $+P_s$ surface in lithium niobate, the oscillation of the sample is phase shifted $180^\circ$ from the input oscillating voltage and in-phase above a $-P_s$ surface. This indicates two possibilities: (1) the signal is primarily electromechanical in nature or (2) the $-P_s$ surface has a net negative charge and the $+P_s$ surface has a net positive charge, which indicates an over-screened surface. Both of these contributions could be occurring simultaneously and will be analyzed in the discussion section. As pointed out before, the frequency of the imaging voltage can cause a large variation in signal amplitude and
phase, so care must be taken to avoid frequencies close to resonant peaks or the dominant mechanism can be incorrectly identified.

In addition to the local tip-surface interactions, there is also a long range electrostatic interaction due to capacitive cantilever assembly-surface interactions, $A_{nl}$. If this interaction is strong enough it can obscure important image characteristics, like the phase shift between adjacent domains.\(^4\) It depends inversely on the spring constant of the cantilever and can be minimized by using very stiff spring constant cantilevers. Measurements were made with cantilevers of stiffness varying between 2 and 20 N/m. It was found that for stiffness less than ~12 N/m a proper 180° phase shift between adjacent domains could not be seen regardless of the imaging frequency. All images in this paper were taken with cantilevers of spring constant 14 N/m.

### 3.3.2 Vertical Imaging Mode Piezoelectric Response

PFM images a variety of interactions at the domain wall - mechanical, electro-mechanical, and electro-static. Therefore, the wall width found in PFM images, as determined by the amplitude, is actually the \textit{interaction width}, which we note, is \textit{not} to be confused with the explicit domain wall width over which the polarization reverses. The latter has been measured by Bursill to have an upper limit of 0.28 nm using high-resolution TEM images in lithium tantalate (isomorphous to lithium niobate).\(^4\)

The interaction widths, $\omega_i$, of all images presented in this paper are defined as the full width at half maximum (FWHM) corresponding to the amplitude change from the
minimum point to where the value increased to half the full value on either side. We should note that the FWHM, $\omega_o$, is different than $x_o$ used in the expression $A = A_o \tanh(x/x_o)$. At $\pm \omega_o/2$ the amplitude is $A = \pm 0.5 \ A_o$, compared to positions at $\pm x_o$ where the amplitude $A = \pm 0.76 \ A_o$. For a symmetric curve, the interaction width (FWHM), $\omega_o$, is related to the half wall width, $x_o$, as $x_o = 0.91 \omega_o$.

Bermudez et al. imaged Czochralski grown periodically poled congruent lithium niobate with a variety of techniques including PFM. They did not measure the interaction width of the domain wall but rather measured the amplitude of oscillation in a uniform domain area. J. Wittborn imaged room temperature periodically poled lithium niobate and determined the interaction width (FWHM) to be ~150 nm. Gruverman measured the interaction width in electrically poled domains in lithium tantalate to be 120 nm. However, the data presented in the last two papers lack important details of the images, especially the signal used to determine the interaction width (amplitude, phase, or $X=\text{amplitude} \times \cos(\text{phase})$ signal) or the frequency of the applied voltage, which limits the comparison of these papers with the current work.

Shown in Figure 3-4 are the topography, amplitude and phase images of a region containing a domain wall in congruent LiNbO$_3$. A topographic step across the domain wall was not measured on any crystal, which is attributed to the presence of residual polishing scratches of approximately 2-3 nm visible in Figure 3-4(a). Non-local electrostatic interaction in the image has been minimized as evidenced from the similar vertical displacement amplitude on either side of the wall (Figure 3-4(e)) and a proper
180° phase change across the wall (Figure 3-4(f)). There is very little cross talk between the topography image and the PFM image.

Measurements were then taken of the interaction widths in unannealed congruent crystals. After a domain wall was located, consecutive images were taken on the same area, zooming in on the domain wall. The time constant on the lock-in amplifier was made as small as possible (30 µs) and scans were taken very slowly (scan rates < 2000 nm/s) to achieve the highest resolution of the interaction width.

Figure 3-4: Images on congruent lithium niobate. (a), (d) are topography images and a cross section; (b),(e) are vertical amplitude and cross section, and (c),(f) are phase image and cross section, respectively. V is the virgin side; R is the domain-reversed area. Distances in (a), (b), and (c) are in nanometers.

Close analysis of the vertical amplitude PFM signal scans of the congruent domain wall shows an asymmetry as shown in Figure 3-4(e) and in Figure 3-5. The long tail region in the signal is always present on the domain-reversed side (R) which is
created by electric fields at room temperature and contains frustrated defect dipoles. Scan artifacts have been eliminated as a source of asymmetry by comparing images obtained by scanning in both forward and reverse directions as well as scanning with the cantilever perpendicular (0°) and parallel (90°) to the domain wall. As shown in Figure 3-5 the asymmetry is still present. To eliminate leveling or background artifacts, several correction functions have been applied to the profiles. For example, using a hyperbolic tangent correction \( y = A_o \tanh(x/x_o) \) where \( A \) and \( y \) are fitting parameters with the \( x=0 \) set to be the minimum of the experimental amplitude) mimic leveling artifacts leaves the asymmetric profile unchanged as shown in Figure 3-5(b).

![Figure 3-5](image_url)

Figure 3-5: (a) Eliminating tip geometry and scan artifacts from images on vertical amplitude scans of congruent lithium niobate. Forward and reverse amplitude signals overlaid along with images obtained with cantilever parallel (0°) and perpendicular (90°). (b) Congruent image correction using a hyperbolic tangent. V indicates virgin area; R indicates domain-inverted area.

Since this asymmetry is not an artifact of leveling or scanning, it indicates the presence of local structure around the domain wall. This asymmetry could be related to the intrinsic nonstoichiometric defects present in the material. This is further supported by a comparison of near-stoichiometric lithium niobate crystals to congruent crystals as
shown in Figure 3-6(a). The asymmetry is almost completely absent in the near-stoichiometric crystals. The interaction width was found from the amplitude images of several samples and different domain sizes. If the amplitude was not the same on either side, the width was found from the minimum point to where the value increased to half the full value on either side. The smallest interaction width in congruent lithium niobate was ~140 nm, and in near-stoichiometric lithium niobate, ~113 nm. The near-stoichiometric crystal width is ~20% less than the congruent crystal indicating the influence of defect dipoles. Narrower interaction widths have been measured using other scanning force techniques and on other materials using PFM (see Table Table 3-1). The narrower interaction widths measured with PFM is due to different material properties (i.e. dielectric and piezoelectric constants) as well as the sample thicknesses. This will be revisited in Section 3.5.1 and in the discussion Section 3.6.

Figure 3-6: Effects of nonstoichiometry on vertical PFM signal. (a) Comparison of congruent and near-stoichiometric lithium niobate vertical amplitude images. Notice the asymmetry in congruent case. (b) Comparison of annealed and unannealed crystals in congruent crystals.
Further support for the role of nonstoichiometric point defects as the origin of the asymmetry is obtained by comparing measurements taken before and after annealing of the congruent crystals at 200°C for 24 hours. This anneal allows for the reorientation of the frustrated defect dipoles in the domain state R. Looking at the same domain wall, the interaction width is found to decrease slightly as shown in Figure 3-6(b), reducing from ~140 nm in the unannealed crystal to ~120 nm in the annealed crystal.

The asymmetry could also be related to a mechanical clamping of the inner domain, as it is effectively embedded in a matrix of oppositely oriented domain. However, this has been eliminated as a possibility, by examining many walls of domains of varying sizes. Even in very large domains sizes, such as a 4 mm domain in a sample of 10 mm, the asymmetry was still present. Far away from the domain wall, the amplitude of oscillation was similar on either side, but upon approaching the wall there was always a diminished response on the domain inverted region.

The preceding analysis assumes that the domain wall is perfectly vertical and smooth. While it is energetically favorable to have vertical smooth domain walls that minimize the divergence of the polarization, it is possible that the numerous pinning sites at crystal defects can allow a tilted or jagged domain wall to be the stable configuration. A jagged domain wall, as pictured in Figure 3-7(a), could be the origin of the asymmetry in the image, as the piezoelectric response of a jagged domain wall will not be symmetric. This could also explain the presence of the asymmetry in the congruent crystals, which contain many nonstoichiometric point defects to act as pinning sites, compared to the symmetric response in the stoichiometric crystal, which does not
contain the nonstoichiometric defects and theoretically a smoother domain wall. A tilted domain wall as pictured in Figure 3-7(b) will still give a symmetric response, although it will be broader than the perfectly vertical domain wall. The third possibility is a tilted and jagged domain wall, which will be both broadened and asymmetric. These possibilities will be discussed in further in Section 3.6.1.

![Figure 3-7: Exaggerated examples of (a) uneven domain wall caused by nucleation or pinning sites not on the surface of the crystal (b) non-vertical domain wall. The vertical dotted line is the approximate center of the domain wall in each case.](image)

Finally, the contribution to the asymmetry can arise from the electrostatic state of the crystal surface, indicating perhaps a gradient in the charge compensation mechanism across the domain wall. This possibility will be further discussed in Section 3.6. The exact nature of this distribution will be probed using complementary electrostatic imaging techniques in Section 3.4.

It should be noted here that while the measured values in this work (110-140 nm) are similar to the values reported in literature (120-150 nm25,49) much smaller interaction widths have been measured in other materials. Reported values of the wall widths of single crystal TGS measured by PFM are in the range of 40-110 nm.21,27 However, 8 nm widths have been measured in TGS by friction force microscopy and UHV non-contact dynamic force microscopy.18,19 This points to the inherent spatial limitations of using
PFM to study ferroelectric surfaces. Due to the electric field distribution, the tip probes a very small but finite volume of the sample which depends upon the tip radius and the dielectric constants of the sample. For LiNbO$_3$ imaged with a 50 nm radius tip biased with 5 volts, this volume extends ~50 nm into the sample surface and will be discussed in greater length in 3.5.1.

### 3.3.3 Lateral Imaging Mode Piezoelectric Response

Lithium niobate belongs to point group $3m$, and the domains form with the crystallographic $y$-directions parallel to the domain walls as shown in Figure 3-8(a). The lateral image can then probe information in two different planes. When the cantilever arm is parallel to the domain wall as shown in Figure 3-8(b) and (d), the distortions in the crystallographic $x$-$z$ plane are probed. This will be referred to as a $0^\circ$ lateral scan for the remainder of this thesis. On crossing from one domain orientation to the other across the domain wall in the $x$-$z$ plane, the $z$- and $y$- crystallographic axes changes direction (from $-z$ (-y) to $+z$ (+y)) through a two-fold rotation about the $x$-axis. Wittorn$^{25}$ proposed that the contrast comes mainly from a distortion of the sample surface near a domain wall as one side expands up and the other shrinks down, giving a sloping surface at the domain wall as pictured in Figure 3-8(b). In this case, only the domain wall region will show a maximum in the lateral signal.
When the cantilever arm is perpendicular to the wall as shown in Figure 3-8(c,e), distortions and torsions in the y-z plane are probed. This will be referred to as a 90° lateral scan for the remainder of this thesis.

The profiles with the cantilever parallel to the domain wall (0° scan) are shown in Figure 3-9. They indeed show a peak in the amplitude image as expected and also contain a slight asymmetry. The measured interaction length in the lateral 0° amplitude image was found to be 211 nm in congruent crystals and 181 nm in near-stoichiometric crystals, which is wider than the vertical signal widths. The amplitude of the images in congruent or near-stoichiometric crystals is always similar in magnitude. Amplitude calibration in the lateral direction to a physical distance is not possible with this sample geometry, although recent work by Li et al. examining singular islands of PZT material and investigations of ZnO nanobelts by Zhao et al. indicate that the torsional response...
of the cantilever can be related to the $d_{31}$ coefficient under specific orientations. The lateral phase image contains too much noise to be of any use.

![Images of PFM images and amplitude profiles](image)

Figure 3-9: Left-right PFM image (a),(b) and cross section (c),(d) for cantilever parallel to domain wall (0°). Congruent lithium niobate (a),(c) and near-stoichiometric lithium niobate (b), (d).

Shown in Figure 3-10 is the lateral image for the cantilever perpendicular to the domain wall (90° scan). This is a difficult image to obtain, mainly because the signal is small – about a tenth of the signal in the 0° scan – and because the measurement is very sensitive to the angle of the cantilever with respect to the domain wall. As the cantilever rotates from the perpendicular position to the wall, the signal amplitude begins to increase until the same shape and amplitude profile of the 0° scan is obtained at roughly
10° of rotation from the perpendicular position. The cross sectional curves are shown in Figure 3-10(c,d).

Figure 3-10: Left right images in nm (a,b) and cross section (c,d) for cantilever perpendicular to domain wall (90°). Congruent lithium niobate (a,c) and near-stoichiometric lithium niobate (b,d).

The origin of the non-zero lateral 90° signals as evidenced in Figure 3-10(a) and (b) far from the domain wall is of unclear origin. One would expect the lateral signal to disappear far from the wall, as experimentally observed for the lateral 0° signals in Figure 3-11(a) and (b). The much weaker signal level of the 0° scans means the measurements are much more susceptible to some of the inherent problems in using a cantilever deflection scheme, since all degrees of motion of the cantilever are in some way coupled. This non-zero signal far from the wall appears to be a step like distribution
in the signal superimposed on an anti-symmetric distribution present at the wall. The exact origin of the step-like contrast is unknown and requires further examination of the influence of other coupling effects. Considering the complex frequency response present for the vertical signal as in Figure 3-2, investigation of this lateral signal might give clues as to its origin. Future work should fully calibrate the torsional modes of the cantilever in the manner set forth by Koleski et al.\textsuperscript{52} However in this paper, we limit our discussion to the anti-symmetric distribution present at the wall and not on this step-like distribution.

This surprising local structure at the domain wall in the lateral 90° images in Figure 3-10(c,d) could have its origin in highly localized strains or distortions at the wall or be related to the defect dipoles. A further series of images was collected to show how local defect related fields could give rise to the contrast observed. As shown in Figure 3-11 (a), a congruent crystal is poled from the virgin state (state 1) to a partially poled state (state 2), which is the state for most of the crystals imaged in this paper. In this situation, the reversed domains, R, contain defect dipoles with a less stable configuration than in the surrounding matrix virgin state, V. If we now partially reverse domains within the R state to a state $V_2$, we now have the original domain orientation similar to the virgin crystal, V, while the matrix domain state, R, has the unstable defect configuration. As shown in the schematic of Figure 3-11, this process creates domain walls separating domain states V and R, and well as walls separating states R and $V_2$ ($\equiv V$). As shown in Figure 3-11(b) and (c), the features observed in anti-symmetric behavior of the 90° lateral scans reverse their contrast in going from V-to-R versus going from R-to-$V_2$, clearly suggesting that these features arise from the presence of the frustrated defect dipoles. As mentioned before, a step-like signal is present in these images which appear to be larger
in Figure 3-11(a) than (b). The origin of the step height is unclear, but it cannot be explained with the defect model and is more likely related to inherent cross coupling of the cantilever motion to another type of cantilever motion.

![Figure 3-11](image)

Figure 3-11: Left right images for cantilever perpendicular to domain wall (90°) for two poling cases in congruent lithium niobate. (a) (1)-(4) shows the sequence of domain reversal in sample with (1) virgin state, (2) partial forward poling, (3) full forward poling under electrode, and (4) partial reversal where virgin state 2 is the same as the virgin state V with the addition of a poling cycle history. The domain walls circled in step (2) and (4) are imaged in (b) and (c) respectively.

In summary, the differences between the near-stoichiometric and congruent piezoelectric responses at the domain walls support the premise that frustrated defects in the reversed domain (R) state affect the local electromechanical properties across a wall. The substantial reduction in the measured interaction widths between near-stoichiometric and congruent crystals indicates that the frustrated defects interact with the domain wall. The asymmetry always tails into the domain-reversed (R) area. Asymmetries in the vertical signal in congruent crystals are reduced with annealing and disappear in near-stoichiometric crystals where frustrated defects exist. In the lateral images, the
differences between congruent and near-stoichiometric crystals are pronounced and of presently unclear origin. Next, we attempt to understand these PFM images more quantitatively using modeling.

### 3.4 Electrostatic Imaging

SSPM and EFM imaging were preformed on a Digital Instruments Dimension 3000 NS-III using metal coating cantilevers of various resonance frequencies from ~60 kHz up to ~315 kHz. The lift height for both imaging techniques were varied between 10-200 nm above the sample surface. EFM measurements were taken with a series of bias voltages from -12 to 12 volts and the SSPM images were taken with an oscillating voltage of 5 volts peak. The domain wall appeared as a faint dark band in the optical microscopy used to focus and position the AFM cantilever which allowed domain walls to be located. High resolution non-contact mode images of the sample surface could be achieved as shown in Figure 3-12(a).

The results of the EFM and SSPM measurement are inconclusive. The collected phase image showed no contrast and imaged only topographic artifacts as shown in Figure 3-12(b). The SSPM image showed almost no contrast as shown in Figure 3-12(b).
To establish the limit of the resolution, the EFM was calibrated by scanning an interdigital electrode biased by voltages as small as 5 mV using a Fluke 701 calibrating power supply. Using the same 150 kHz cantilever used in the acquisition of Figure 3-12, the cantilever was line scanned repeatedly over an electrode pad as the bias was increased. The threshold where a signal could be obtained in the EFM image was ~50 mV. This is shown in a scan of the electrode edge as the bias is increased in Figure 3-13.

Figure 3-12: Non-contact images near a domain wall in LiNbO$_3$ (a) topography, (b) EFM image (-12 V bias, 50 nm lift height), (c) SSPM image (5 V oscillating voltage, 20 nm lift height). The dotted line in (a) is the approximate location of the domain wall observed through the optical vision system of the microscope. Resonant frequency of cantilever was 150 kHz. Each scan is 20 µm x 20 µm.

Figure 3-13: Scan of electrode pad biased by different voltage. (a) topography and (b) EFM image.
No electrostatic measurement on pure congruent LiNbO$_3$ has previously been reported. Tsunekawa et al. examined surface acoustic wave (SAW) grade LiNbO$_3$ wafers and observed microdomains on the surface of the crystals with cantilever deflections of about 2 nm, although force calibration was not performed. SAW grade crystals are grown in reducing atmospheres and are generally more conductive, optically opaque, much diminished in pyroelectric charging with temperature changes, and have numerous grain boundaries and defects than optical grade crystals, so they are not an appropriate comparison to optical grade LiNbO$_3$. Bluhm et al. used EFM to image a periodically poled lithium niobate surface layer of 2 µm thickness created by Ti diffusion. They measured a cantilever deflection contrast of 2 nm corresponding to an 8 nN force. Similar forces where measured by Bermudez et al. using EFM on the surface of Er doped periodically poled lithium niobate created during the crystal growth process. They obtained an image contrast and measured force of 6 nN when the cantilever was biased with -12 V. However, they determined the contrast was not due to static surface charges, but instead to a change in the dielectric constant. The latter two studies were preformed on modified LiNbO$_3$ so exact comparisons to congruent LiNbO$_3$ cannot be made.

The potential difference between two adjacent $c+$ and $c-$ domains has been measured as 155 mV in BaTiO$_3$ and 40 mV in KTP. The difference in the work function between $c+$ and $c-$ surfaces has been measured in LiNbO$_3$ using electron emission to be 400 mV, although the difference measured using scanning force microscopy is expected to be less. Within the limits of the experiments preformed, the measured value of 50 mV is taken as a rough approximation to the upper limit of the potential difference across a domain wall, although further, more conclusive
measurements should be performed. Measurements of potential screening on BaTiO$_3$ and charged grain boundaries in SrTiO$_3$ indicate that the lateral resolution is limited to ~300 nm related to the non-contact nature of the measurements. Similar limitation would be present in measurements on LiNbO$_3$ as well, so higher resolution than the PFM measurements presented in Section 3.3.2 would not be possible by this technique.

3.5 Modeling Piezoelectric Response in PFM

3.5.1 Electric Field Distribution at the Tip

One of the primary unknowns in understanding a PFM image is the distribution of the electric field under an AFM tip with a small radius of curvature that is in contact with a ferroelectric surface (0.1 to 1 nm separation) idealized in Figure 3-14.

![Figure 3-14: Geometry of idealized AFM tip over anisotropic dielectric material.]

The approach taken in this paper is to use analytical solutions that describe an ideal electrostatic sphere-plane model. The limitations to this approach are discussed near the end of this section. However, these estimations are still useful and will be used
as the input for the modeling in the next section. The first step is to determine the capacitance between a charged sphere and a dielectric material, given in der Zwan 57 as

\[ C = R \sinh \alpha \sum_{n=0}^{\infty} \left( \frac{\sqrt{\varepsilon_r \varepsilon_e - \varepsilon_1}}{\sqrt{\varepsilon_r \varepsilon_e + \varepsilon_1}} \right)^n \frac{1}{\sinh (n+1)\alpha} \] \quad 3-8

and

\[ \alpha = \cosh^{-1} \frac{R + d}{R} \] \quad 3-9

where units are CGS, and \( R \) is the radius of the sphere, \( d \) is the separation between the sphere and surface, \( \varepsilon_r \) and \( \varepsilon_z \) are the dielectric constants in the radial and \( z \) direction respectively and \( \varepsilon_1 \) is the exterior dielectric constant (air in this case). Using the calculated value for capacitance the necessary charge, \( Q \), for a given voltage can be found from \( Q = CV \). The voltage and electric field distribution within the anisotropic dielectric sample can be found using the model given by Mele 58 as

\[ E_z(r, z) = \frac{2Q}{\varepsilon_0 (\sqrt{\varepsilon_r \varepsilon_z} + 1)} \frac{1}{\gamma \left( R + d \right)} \frac{z / \gamma - (R + d)}{\left( r^2 + z / \gamma - (R + d) \right)^{3/2}} \] \quad 3-10

\[ V(r, z) = \frac{2Q}{\varepsilon_0 (\sqrt{\varepsilon_r \varepsilon_z} + 1)} \frac{1}{\sqrt{r^2 + (z / \gamma - (R + d))^2}} \] \quad 3-11

\[ \gamma = \sqrt{\frac{\varepsilon_z}{\varepsilon_r}} \] \quad 3-12

where \( E_z \) is the electric field in the \( z \) direction, \( r \) is the distance coordinate parallel to the surface, \( z \) is the distance into the sample, \( Q \) is the calculated charge from the previous step, \( \varepsilon_r \) and \( \varepsilon_z \) are the dielectric constants of the anisotropic material in the radial and \( z \) direction respectively, \( R \) is the radius of the AFM tip, and \( d \) the separation between the sphere and surface.
Using values found in the literature and specifics for our tip geometry, with \( \varepsilon_r = 28.1 \), \( R = 50 \text{ nm} \), \( d = 1 \text{ nm} \), the capacitance is calculated as \( 1.44 \times 10^{-17} \text{ F} \). With an imaging voltage of 5 volts, the resulting charge is \( 7.20 \times 10^{-17} \text{ C} \). From this value, the maximum electric field and voltage directly under the tip is \( 1.738 \times 10^7 \text{ V/m} \) and 0.51 V respectively. The distance into the sample where the field falls to \( 1/e^2 \) value is 52 nm in the depth \((z \text{ direction})\), and 88 nm on the surface \((r \text{ direction})\). The overall normalized field \((E/E_o, \text{ where } E_o \text{ is the maximum field})\) and voltage \((V/V_o, \text{ where } V_o \text{ is the maximum field})\) in the sample is shown in Figure 3-15. These show the effect of field enhancement due to the small radius of curvature, as well as the quickly falling potential for even short distances from the tip. It is interesting to note that even a small imaging voltage of 5 volts results in a large electric field in the sample. The peak field generated in the sample using this model is only slightly below the coercive field of the congruent material \( (2.2 \times 10^7 \text{ V/m}) \). If one considers a similar distribution in near-stoichiometric crystals, the coercive field \( (4.0 \times 10^6 \text{ V/m}) \) is actually exceeded for a finite volume of crystal. This volume is an oblate spheroid with radius on the surface of 66 nm and penetrating into crystal a depth of 32 nm.

However, domain reversal is not occurring during the imaging process. When the maximum imaging DC voltage \( (5 \text{ V}) \) is applied to the sample through the tip for periods of time up to 1 hour, no domain creation is observed. Similarly, Terabe has reported AFM tip poling of stoichiometric lithium niobate, and demonstrated that the process requires a time of at least one second to form stable domains for even a very high DC voltage \( (40 \text{ V}) \) across a 5 \( \mu \text{m} \) thick crystal which generates a field 8 times higher than
used in our imaging \(1.4 \times 10^8\) V/m under the tip.\(^{59}\) This switching time required is therefore much longer than the time for which the peak imaging voltage of 5 volts is applied to the sample (<25 µs). The coercive fields at such frequencies are unknown but trends show that coercive field increases with increasing frequency.\(^{60}\)

![Figure 3-15: Normalized voltage \((V/V_o)\) and field distributions \((E/E_o)\) on sample for imaging voltage of 5 volts separated 1 nm from dielectric surface where \(V_o=0.51\) V and \(E_o=1.74 \times 10^7\) V/m. Sample surface (a) and cross section (b).](image)

There are several limitations to this distribution model. Recently, in several papers by Kalinin\(^{30,61}\), the imaging process in PFM can be separated into two distinct regions, the weak indentation limit, where the contact region between the sharply curved cantilever tip and the sample surface is a point contact, and strong indentation limit, where significant indentation of the sample surface by the tip increases the contact area and give rise to similar tip and surface potentials. Fields in the sample immediately under the tip in the strong indentation limit are most likely higher than in the plane-sphere model used here. However, the modeling in this paper is assumed to follow the weak indentation limit for FEM modeling simplicity. We feel this is justified considering the set point deflection of the PFM feedback loop for the images taken in the study were set
to 0, and that the field distribution for models which includes indentation effects reduces to the point charge model for larger separations from the tip. The inclusion of the electromechanical coupling effects would improve the modeling, but for the initial FEM modeling the sphere-plane model is a good first approximation.

In addition to the modeling uncertainty, the exact nature of the fields in the sample can be affected by surface and material properties. Issues include bound polarization charges, water, or other adsorbents on the surface, as well as a possible reconstructed surface layer with different properties than the bulk material (the so called “dead” layer). Since the exact nature of the surface is currently unknown, the proposed model here will be used as the maximum “ideal” field and will be used in the finite element modeling in following sections. The actual piezoelectric surface displacements calculated can then be treated as the “maximum” displacements that can be expected corresponding to these fields. The qualitative behavior of the piezoelectric responses across a wall can be predicted and compared with experiments.

The confinement of the electric field in the material is determined mainly by the tip radius, \( r \), and the ratio of the dielectric constants \( \varepsilon_z \) to \( \varepsilon_r \). The electric field in the radial direction at the surface (setting \( z = 0 \) in Equation 3-10) gives a distribution that is only dependent upon the radius, \( r \), times a constant for a given material. The \( 1/e^2 \) value of the field in the radial direction at the surface is then the same for any material as shown in Figure 3-16(a). Examination of Equation 3-10 also shows that the ratio of the dielectric constants \( \varepsilon_z \) to \( \varepsilon_r \) (\( \gamma \) in Equation 3-12) determines the confinement of the electric field in the \( z \) direction - as \( \gamma \) gets smaller the electric field falls quicker in the \( z \)
direction. Therefore, it can be expected that smaller tip radius can improve lateral resolution while higher dielectric constants in the sample can improve the depth resolution. This is shown in Figure 3-16 for a variety of anisotropic crystals given in Table 3-2.

Table 3-2: Dielectric Constants of Some Anisotropic Crystals and Ceramics

<table>
<thead>
<tr>
<th>Material</th>
<th>$\varepsilon_z$</th>
<th>$\varepsilon_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNbO$_3$</td>
<td>28.1</td>
<td>84.1</td>
</tr>
<tr>
<td>Triglycine sulphate (TGS)</td>
<td>43</td>
<td>8.6/5.7*</td>
</tr>
<tr>
<td>Lead zirconate titanate (PZT-4)</td>
<td>1350</td>
<td>1475</td>
</tr>
<tr>
<td>Barium titanate (BaTiO$_3$)</td>
<td>200</td>
<td>4600</td>
</tr>
<tr>
<td>Guanidinium aluminum sulfate hexahydrate (GASH)</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>$\alpha$-Quartz (SiO$_2$)</td>
<td>4.5208</td>
<td>4.6368</td>
</tr>
</tbody>
</table>

* in TGS $\varepsilon_{11} \neq \varepsilon_{22}$

Note: all $z$ crystallographic axes along $z$ axis in Figure 3-14

Figure 3-16: (a) the $1/e^2$ field distribution for a variety of crystals using the presented electric field model. The left side of (a) shows the contour plot of the field distribution in LiNbO$_3$. (b) the $1/e^2$ field depth, capacitance between tip and sample surface, and $\gamma$ values for the different materials in (a). Tip radius of 50 nm in all cases.
3.5.2 Finite Element Modeling

The finite element method has been used to solve a number of complex field problems from many diverse fields as heat and fluid flow, mechanical failure, structural analysis, antenna theory, electromagnetic waves, biomechanics, and geology.\textsuperscript{68} It is a well developed theory with many of the first seminal papers published in the 1960\textquotesingle s,\textsuperscript{69,70} and solutions of the coupled elastic and electric field problems (piezoelectric) analyzed since the 1970\textquotesingle s.\textsuperscript{71} This technique provides numerical solutions to field problems by dividing the calculation domain into a number of elements interconnected by a number of nodes. The elements and nodes are then represented by a system of equations, where the nodal solutions to these equations give the spatial variation of the field in any node. Computational demands of FEA are so extensive that computer implementation is mandatory with analyses involving more than a million degrees of freedom not uncommon.\textsuperscript{68,72}

Figure 3-17: Log10 of the electric field for the top surface of the lithium niobate used in finite element method modeling: \(x\), \(y\), and \(z\) components of electric field in (a), (b), and (c) respectively. Each plot is 2000 x 2000 nm.
Finite element modeling (FEM) of the sample surface under an electric field applied through an AFM tip was performed using the commercial software ANSYS. Using a 10-node tetrahedral coupled field element with four degrees of freedom per node, the voltage and displacement in the $x$, $y$, and $z$ directions in a slice of lithium niobate material under an applied electric field was simulated. The field distribution simulated a 50 nm tip separated 0.1 nm from the surface with a bias of was a ±5 volts, which is the same radius of curvature for the tips used in imaging. The material properties necessary for the simulation were the piezoelectric coefficients (18), elastic coefficients (21), unclamped dielectric constants (3), and the density, all found in the literature. The physical dimensions of the simulated slice of material were 8 x 8 x 4 µm in the $x$, $y$, $z$ directions respectively. The voltage distribution on the top and bottom surfaces was determined using the model described in the previous section and is shown in Figure 3-17, with a boundary condition on the bottom surface of zero net-displacement in the $z$ direction. In each simulation, approximately a 13,000-element 19,000-node mesh was used in the solution, with the elements right below the applied voltage about 0.1 nm across. Although actual PFM experiments are performed with an alternating voltage (~35 kHz), only the static case was considered, i.e. the maximum displacements of the sample surface at peak imaging voltage (+/− 5 V). The FEM solution provides displacements of the sample surface at each node, $U_x$, $U_y$, and $U_z$. From these values, the distortion of the sample surface can be determined. A sample batch file for simulation of the model in ANSYS is included in Appendix B.1.
Two cases were modeled: the case of the field applied to (1) a uniform domain area on the surface of the sample and (2) a sample with the introduction of a single domain wall as shown in Figure 3-18. To model the domain wall, a solid block of material was divided into an up (+$P_s$) and a down (-$P_s$) domain by applying a coordinate system transformation to one half of the block as shown in Figure 3-18. The down-domain is obtained by rotating the crystallographic coordinate system of the up-domain by 180° about the $x$-axis in the orthogonal coordinate system, (2-fold rotation) thus resulting in $x \rightarrow x$, $y \rightarrow -y$, and $z \rightarrow -z$. This corresponds to the loss of the two fold axis parallel to $x$ with the transition from $\overline{3}m \rightarrow 3m$. The boundary between the two domains (at $x=0$) is a domain wall plane across which the properties change stepwise. It is important to note that this is a perfectly vertical and smooth domain wall.

Figure 3-18: Finite element modeling of the piezoelectric response across a domain wall in LiNbO$_3$. Probe is moved a distance, $S$, perpendicular to domain wall and displacement vectors describing surface displacements, $U_x$, $U_y$, and $U_z$, are determined.
A series of simulations were performed as the fixed tip voltage was moved a distance, $S$, as shown in Figure 3-18, perpendicular to the domain wall for distances between −200 and 200 nm. Shown in Figure 3-19 are the surface distortions $U_x$, $U_y$, and $U_z$ calculated by FEM for 3 cases: (1) uniform domain with $S=0$, (2) a domain wall at $x=0$ and tip at $S=0$, and (3) domain wall at $x=0$ with tip at $S=100$ nm. Upon introduction

Figure 3-19: Finite Element Method (FEM) calculations of surface displacements for +5 volts applied to the $+P_z$ surface for: a uniform domain with source at $S=0$ in (a,b,c), domain wall at $x=0$ and source at $S=0$ in (d,e,f), and domain wall at $x=0$ with source at $S=100$ in (g,h,i). Distortion $U_x$ is shown in column 1 (a,d,g), $U_y$ in column 2 (b,e,h), and $U_z$, in column 3 (c,f,i) with all distortions in picometers shown in common color bar on the right. Crosshairs indicate the position of tip, and the dotted vertical line indicates the domain wall. Each figure is 2000 x 2000 nm.
of the domain wall in (d,e,f), the distortion on left and right sides of domain wall reverse compared to that in (a,b,c). The distortions become more complicated on moving the source away from the wall in (g,h,i). The tip was assumed to stay in the same position on the distorted surface, i.e. a tip at position \((x_1, y_1, z_1)\) moves to \((x_1 + U_{x1}, y_1 + U_{y1}, z_1 + U_{z1})\) where \(U_{x1}, U_{y1}, U_{z1}\) are the distortion of the sample surface at the initial location of the tip.

3.5.3 Simulation of Vertical Signal and Experimental Comparison

To find the vertical piezoelectric signal from the FEM data the maximum expansion of the sample surface, \(U_z\), underneath the tip was found for different positions, \(S\), from the wall and is shown in Figure 3-20(a). This qualitatively mimics the PFM measurement as the distortion of the sample surface displaces the cantilever either up or down, and the lock-in amplifier measures this displacement. The amplitude signal measured in PFM is the peak-to-peak value of the sample displacement as shown Figure 3-20(b). It shows the expected result that away from the domain wall, surface expansion is the greatest and as the tip approaches the domain wall the magnitude of the oscillation goes through a minimum. The curves in Figure 3-20(a) were fit to curves of the form \(A_o \tanh(x/x_o)\) with a half wall width of \(x_o = 58\) nm. This curve was chosen and will be used for future curve fitting because it is identical in form to the change in polarization across the wall as given in Lines.\(^5\) The minimum in the displacement at the domain wall is due to the mechanical interaction between the two oppositely distorting domains. The full-width-at-half-maximum of the FEM data gave an interaction width,
$ \omega_o $, of the domain wall as 64 nm. Far away from the wall, as simulated in the uniform domain case, the maximum amplitude of surface displacement was found to be 6.72 pm. The peak-to-peak amplitude oscillation value found by FEM is therefore $ 2 \times 6.72 = 13.4 $ nm.

The FEM modeling technique considers strictly the electromechanical behavior of the material. It is important to note that the concept of nonstoichiometry is completely neglected in the FEM simulation – all the simulation variables are the bulk material properties and the voltage distribution. Therefore, a comparison was made between the near-stoichiometric measurements and the FEM modeling.

![Figure 3-20](image1.png)

**Figure 3-20:** Displacement $ U_z $ underneath tip in FEM simulation as tip is moved across domain wall located at 0 nm. Each point represents the tip position relative to wall and maximum displacement of the surface. A best fit curve of the form $ A_o \tanh(x/x_o) $ is plotted as well. In (b) the absolute value of the difference between the two curves in (a) is plotted along with the absolute difference of the two best-fit curves in (a).

Shown in Figure **3-21** is the measured vertical signal in near-stoichiometric LN along with the results from the FEM simulation. The magnitude of oscillation in simulation and measurement are very similar. The amplitude of oscillation experimentally measured away from the domain wall on both congruent and near-
stoichiometric LN measure between 20-30 pm. This is of similar order-of-magnitude as the maximum oscillation predicted by simulation ~13.4 pm. If the separation is decreased to 0.1 nm (which increases the field in the sample) the static surface expansion would increase to 9 nm giving an oscillation of ~18 pm. The similarities of these results indicate that the electric field model and the finite element simulations give reasonable order-of-magnitude predictions. The forms of both curves in Figure 3-21 are similar, showing a dip in the signals at the domain wall returning to equal amplitudes on either side. However, the interaction widths, defined here as full width half maximum, are very different. The FEM simulation gives an interaction width, $\omega_o$, of 64 nm compared to the experimental $\omega_o$ of 113 nm.

![Graph showing vertical amplitude signal on near-stoichiometric LN along with FEM simulation results with domain wall located at 0 nm. The simulation width is 65 nm compared to the experimental width of 113 nm.](image)

Figure 3-21: Vertical amplitude signal on near-stoichiometric LN along with FEM simulation results with domain wall located at 0 nm. The simulation width is 65 nm compared to the experimental width of 113 nm.
3.5.4 Simulation of the Lateral Piezoelectric Signal and Experimental Comparison

The lateral signal for the cantilever parallel to the domain wall (0° lateral scan), shown in Figure 3-8(b) and (d), measures the torsion of the cantilever in the x-z plane, given by the slope of the sample surface in the x-z plane under the tip is shown in Figure 3-22(a). The results for a variety of tip positions, S, are shown in Figure 3-22(b). As the tip is moved toward the domain wall, the surface under the tip ceases to be flat, and starts to tilt as one side expands up and the other side expands down as pictured in Figure 3-22(a). When the voltage reverses polarity, the slope tilts the other way. In this way, a maximum in the lateral signal is measured in the domain wall area. The FEM data fit to the form \( A_o \tanh(x/x_o) \) gave the interaction width, \( \omega_o \), as 59 nm, which is very close to the interaction width found from the z displacement analysis above (64 nm).

![Figure 3-22](image)

Figure 3-22: FEM simulation of the lateral image amplitude with cantilever parallel to domain wall located at 0 nm (0° lateral scan). Shown in (a) are surface cross sections for -5V applied at 3 different tip positions (S = -100, 0, 100) and the slope of the surface at the tip position indicated by a circle. Shown in (b) is the slope of the surface under the tip for different tip positions, S, from the domain wall with a fit function of \( A_o \tanh(x/x_o) \).
A comparison of the $0^\circ$ lateral scan results between simulation and experiments is shown in Figure 3-23. Although the forms of the curves are similar, (both showing a peak in signal at the domain wall), the FEM model predicts the interaction width, $w_0$, to be 45 nm compared to ~180 nm for the measurement. Since the experimental lateral signal cannot be calibrated, quantitative comparisons in the amplitudes cannot be made between simulation and measurement.

Figure 3-23: Lateral amplitude signal for tip parallel to domain wall on near-stoichiometric lithium niobate along with FEM simulation results. The fit to the simulation data is the difference of the curves in Figure 3-22(b). Every 10$^{th}$ point of the experimental data is marked by a circle.

The lateral signal for the cantilever perpendicular to the domain wall, ($90^\circ$ lateral scan) as shown in Figure 3-8(c) and (e), measures the torsion of the cantilever in the $y$-$z$ plane. The $y$-axis switches orientation by $180^\circ$ on crossing the domain wall. This tends to inhibit distortion in the $y$-$z$ plane at the domain wall itself. Shown in Figure 3-24 is the evolution of the surface distortion in the $y$-$z$ plane as the tip position, $S$, is moved away
from the domain wall. At the wall, shown in Figure 3-24(a), distortion is minimal, and the slopes of the surface are also small. On moving away from the domain wall, the surface begins to distort again, mainly due to the movement in the z direction. The distortion in the y-direction is a pinching motion towards the tip when the surface expands up and an expansion away from the tip when the surface contracts down. At $S=30$ nm, shown in Figure 3-24(b), the surface is beginning to expand, with concave and convex bulges under the tip. The slopes of the surfaces are still small. For distances $S=40$ and larger shown (Figure 3-24 (c,d)), the concave and convex bulges disappear, and the surface expands fully. When the surface expands, the tip is on top of a peak and measures the maximum slope as the tip is strongly influenced by displacements in the y direction that cause torsioning of the tip. However, when at the bottom of the depression, displacements in the y direction have less of an effect because the tip in a trough, and cannot easily torsion. Even though the electric field is symmetric about the x- and y- axes, the resulting distortions are not symmetric about the x or y-axis due to the 3-fold symmetry. An example is shown in 3-19(b) where the displacement in y has three lobes. Any slice along this surface along the y direction will yield slightly more displacement on the upper half of the slice than on the lower side. This gives a net “bulge” along the y direction shown in Figure 3-24(c,d). The tip then follows the slant of this bulge, which tilts the cantilever at the peak preferentially toward one side for a given bias, and opposite for the opposite bias.
The slopes of the surface in the $y$-$z$ plane are plotted in Figure 3-25. They are very different between the positive and negative bias voltage, showing a peak above the down-domain for positive bias, and peak above the up-domain for negative bias. Since an oscillating bias is used in PFM imaging, the resulting signal from the expansion is shown in Figure 3-25(c) that shows a minimum at the wall and peaks slightly away from the wall.

The lateral $90^\circ$ signal for simulation and measurement is shown in Figure 3-26. Although the FEM simulation data is noisy, a trend can be seen of a double peak with a minimum at the domain wall. This form is qualitatively similar to the data from the experimental measurement. The FEM simulation suggests that the signal measured in this
direction is due to asymmetric bulging in the y-z plane that switches orientation on either side of the domain wall.

Figure 3-25: FEM simulation of the lateral image with tip perpendicular to domain wall (90° lateral scan) located at x=0 nm for +5 V (a) and –5 V (b). Shown in diamonds with drop lines are the slopes to the surfaces shown in Figure 21. Shown in (c) is the magnitude of the difference between the two curves in (a) and (b) that is measured by experiment.

Figure 3-26: Lateral image amplitude signal for tip perpendicular to domain wall (90°-lateral scan) on near-stoichiometric LN along with FEM simulation results. Every 10th point of the experimental data is marked by a circle.
3.5.5 Accuracy and Validity of Modeling

The material model was verified by applying uniform voltages to the $+z$ and $-z$ surfaces of a rectangular slice of material. The simulated surface displacements were verified by comparison to the linear relation $\varepsilon_{33} = d_{33}E_3$, where $d_{33}$ is the piezoelectric coefficient, $\varepsilon_3$ is the strain along the $z$ direction, and $E_3$ is the applied electric field.

For each of the PFM imaging simulations, a 13,000-element 19,000-node mesh was used in the solution, with the elements right below the applied voltage about 0.1 nm across. This was automatically split into elements and meshed by the software, with specific refinement in areas near the tip. To confirm the convergence of the model, similar displacements near the tip were found when increasing the number of elements by 2 and 4 times which gives confidence in the model.

Since the imaging mechanism is an alternating signal, simulation of a positive and negative voltage on the surface at each point $S$ from the domain wall was performed. The final imaging curve is therefore a combination of these two separate curves. The PFM simulation curve must be thought of as a composite curve, with each individual point representing the difference between two FEM simulations (positive and negative biases). Each individual simulation is smooth and continuous, but because several different simulation curves are used in the generation of a single imaging curve, this causes a certain amount of noise in the simulations. When comparing this to the experimental data, which is taken from a continuous smooth curve, the simulation data appears noisy.

For the vertical curve only the displacement, $U_z$, which is a primary output of the simulation, was used to determine the curves. As shown in Figure 3-20(a) there is some
noise point to point which is slightly amplified when the curves are subtracted in Figure 3-20(b) but is fit well by the $A_o \tanh(x/x_o)$ curve. Compare Figure 3-20(b) to the lateral signals in Figure 3-23 and Figure 3-26, which are derived from tangents to the distorted surface, not the displacements themselves, and therefore have larger associated errors than the vertical signal. In these cases, aside from the inherent numerical errors due to discretization of continuous functions into finite elements, the majority of error came from sampling. First, the slope of the distorted surfaces at the probe point is required, which is the tangent to the surface at one point. While the displacements themselves are continuous, the first derivative of the surface displacements are not necessarily continuous and are very sensitive to conditions around the point sampled. Several node points were considered in the determination of the tangent values. In the case of the lateral 90°-signal plane (Figure 3-26), the distortions are so small in the $y$ direction that behavior is dominated by the $z$-signal. Amplifying the $y$ displacement by a factor of ten allows a trend be seen in the data. In this way, the $y-z$ signal data should only be used to illustrate a possible trend and is the noisiest of the three imaging types.

3.6 Discussion

3.6.1 Comparison of Measurements to FEM Modeling

In order to place the comparisons in proper context, there are several limitations and assumptions present in the finite element model that need to be discussed. The first
is that the voltage and electric field in the sample surface are assumed to be identical to
the analytical solution given in the previous section. This is an idealization of the
physical reality, since the absolute field values at the surface depend on the surface
structure and conditions that are not precisely known. In addition, it is assumed that the
physical properties of the sample determined from a bulk crystal (i.e. piezoelectric
coefficients) apply at very small length scales and are valid for describing small volumes
near or on the surface. The actual imaging technique uses an oscillatory voltage that can
introduce resonance effects into the measurements, whether in the cantilever, sample
surface, or both. The static FEM simulations ignore these effects.

Despite these limitations, the FEM simulations can be used to determine two
pieces of information: the magnitude of the sample oscillations and the interaction width
of the wall. The quantitative surface displacements can be considered to be the
maximum values that the surface can possibly expand. Their values are of the same order
of magnitude as the measured displacements (13.4 pm compared to ~20-30 pm).

The measured interaction width at a domain wall (~113 nm) in the experimental
PFM images is twice as large as the FEM model (~ 64nm). There are several factors that
contribute to the interaction width of the wall. This width should be thought of as the
upper limit of the interactions at the wall and include contributions from the applied field
(magnitude and distribution), tip geometry (radius), surface effects (charge distribution),
domain wall smoothness and angle of the domain wall relative to the polarization
direction, and sample properties (dielectric, piezoelectric, and elastic constants). Of
these, the FEM simulation only models the electromechanical behavior of the sample;
therefore the dip in amplitude at the domain wall in the simulation is due only to the electric field distribution, the strain compatibility, and the mechanical coupling of the two oppositely expanding domains. We next explore some of these contributions.

One limiting factor to the interaction width of the domain wall is the inherent mechanical coupling present between the oppositely expanding domains. The width of the transition from full expansion to full contraction depends on some intrinsic combination of the elastic and electromechanical constants of the material. An exact analytical solution to this problem can be approached using Ginzburg-Devonshire-Landau theory;\textsuperscript{75,76} however, consideration of the sample surface and field distribution complicates this problem greatly.\textsuperscript{77-79} To get a numerical solution from FEM, a uniform electrode was defined on both the top and the bottom surfaces of the finite element model discussed earlier, so that there was a uniform field distribution in the bulk of the material. This uniform field is a simulation of the limiting case where the tip radius $R \rightarrow \infty$. It was found from FEM modeling that for a uniform electric field, the inherent electromechanical width across a single 180° wall is independent of the applied electric field for a sample of constant thickness as shown in Figure 3-27(a). While the maximum surface displacement increases linearly with the field as expected, the electromechanical width remains the same for a given crystal thickness. Also, the electromechanical width is linearly related to the sample thickness as shown in Figure 3-27(b) for a fixed uniform electric field value. This scaling factor in LiNbO$_3$, which relates the electromechanical width to the sample thickness ($t$), has a value of $\omega_{pl} / t \sim 0.16$. (Note that $\omega_{pl}$ is the FWHM wall width). For the 300 µm thick crystals as used in this study, the intrinsic
electromechanical width for a uniform field is extrapolated to ~49 µm. This value, while quite wide, is supported by X-ray synchrotron measurements taken of a single domain wall in LiNbO$_3$.\textsuperscript{80,81} It was observed in a 300 µm thick crystal contained several large reversed domains that the strain field around a domain wall when the sample was under a bias extended to ~50 µm in width. Also, interaction widths scaling with the sample thicknesses have been experimentally observed in PZT thin films imaged by PFM where larger interaction widths were measured for thicker films.\textsuperscript{37,82} The scaling factor calculated from these PZT thin film measurements is ~0.09. Both the simulations and the experimental observations point to an ultimate limit to the resolution that is related to the electromechanical response of the material and the sample thickness.

![Figure 3-27](image.png)

**Figure 3-27:** FEM simulations of the electromechanical interaction width (FWHM), $\omega_{pl}$, under uniform electric field applied to samples for (a) varying electric field and constant thickness of 4 µm and (b) varying sample thickness and fixed electric field.

By using a PFM tip electrode on one face, much higher PFM wall resolution is possible in thicker crystals due to the highly localized electric fields produced by the tip near the surface, thus *effectively* reducing the thickness of the crystal. To examine the influence of the tip radius and electric field effects in the sample, the FEM modeling was
performed for a variety of tip radii using the electric field model for a 5 V imaging voltage. The results of these simulations are shown in Figure 3-28(a). For tips larger than the 50 nm radius used in this study, the interaction width predicted by the FEM model is relatively insensitive to the radius. As the radius gets smaller than 50 nm, there is a sharp reduction in the measured interaction width.

In an attempt to understand Figure 3-28(a), the electric field distribution was found for a variety of tip radii. The cutoff value, below which the electric field in the sample did not give rise to measurable displacement, was experimentally determined by finding the minimum applied voltage (0.6 V peak) that generated a signal the lock-in amplifier could measure. Using this voltage value, the peak field under the tip calculated from the analytical model is $2.9 \times 10^6$ V/m which is used as the cutoff value for determining the electric field distribution of the oblate spheroid with a radius, $r$, on the surface and penetrating into crystal a depth, $d$, into the surface with a total volume, $V$.

Figure 3-28: (a) FEM simulations of interaction width, $\omega_0$, for a variety of tip radii, $R$. (b) normalized values of the maximum electric field under the tip and the field distribution for varying tip radii where the field falls to the experimentally determined cutoff value of $2.9 \times 10^6$ V/m. For normalization, $E_{\text{max}} = 5.88 \times 10^7$ V/m, $d_{\text{max}} = 69.6$ nm, $R_{\text{max}} = 183$ nm, and $V_{\text{max}} = 2.81 \times 10^{-21}$ nm$^3$ are used.
These values are normalized to the maximum values for each curve and are shown in Figure 3-28 (b). The trends show the expected results that the peak electric field is enhanced for smaller radius tips and the distribution becomes more diffuse for increasing tip radii.

From Figure 3-28(b) the sharp drop off in the FEM calculated interaction widths do not correlate exactly with any of the calculated field distributions. The maximum field, \( E \), under the tip is enhanced for smaller tip radii, \( R \); however, this is unlikely to contribute to increased wall resolution because it is the distribution of the field that is important. The flat region of Figure 3-28(a) roughly correlates with the depth data in Figure 3-28(b), which is in the range of \( R=60-200 \) nm with a mean value of \( \omega_0 \sim 70 \) nm.

One may now pose an interesting question: from a PFM domain wall resolution viewpoint, is it better to lower the effective probe depth in a bulk crystal through decreasing the tip radius (Figure 3-28(a)) or is it better to decrease the crystal to an equivalent thickness and employ uniform electric fields across the sample, as in Figure 3-27(b)? For example, from Figure 3-28(a), if we take the effective probe depth under a tip radius of \( R \sim 125 \) nm to be \( d \sim 70 \) nm, then for a crystal of the same thickness of \( t=70 \) nm, and using the thickness scaling factor \( \omega_{pi} / t \sim 0.16 \) from Figure 3-27(b), we calculate the extrapolated electromechanical PFM wall width for a uniform electrode geometry to be \( \sim 11 \) nm, which is much narrower than the simulated width of \( \sim 65 \) nm for the tip geometry. This would suggest, at face value, that as we go from a thick crystal to a thin crystal or film, the intrinsic wall width under uniform electrodes transitions from being much larger to significantly smaller than the PFM wall width measured by a tip that
produces the same effective probe depth in a thicker crystal. To verify if such a
counterintuitive scaling effect is true would require a careful set of measurements of a
single domain wall, comparing different thickness of the same single crystal material
under controlled PFM imaging conditions. However, one may instead discover that this
is not true and it may then point to the inadequacy of using the scaling for a uniform field
to a region with highly non-uniform fields. Other limitations of the sphere-plane
analytical model as discussed in Section 3.5.1, especially ignoring the piezoelectric
indentation of the sample surface, should also be borne in mind.

In conclusion to the wall width issues, we can state that there exists a thickness
dependent intrinsic electromechanical width to an antiparallel domain wall under uniform
electrodes. This width can be substantially modified by choosing non-uniform fields
using PFM tip geometry. Therefore, in a PFM measurement of antiparallel domain walls,
which of these effects dominates depends, in general, on the tip geometry and the sample
dimensions.

The possibilities of the larger interaction width in the PFM experiments as
compared to the modeling could be related to surface effects not accounted for in the
FEM modeling. If there were a “dead” layer on the surface that is paraelectric, caused by
surface reconstruction or diminishing spontaneous polarization near the surface, this
would introduce a distance between the voltage source and the piezoelectric material that
would act to decrease the electric field in the piezoelectric portion of the sample.
Similarly, the presence of a thin film of water on the sample surface would cause a
broadening of the electric field. This was observed by Avouris in the oxidation of silicon
surfaces with an AFM tip where it was necessary to replace the tip radius with much wider meniscus of water to model their results.\footnote{83} Both of these situations then broaden the electric field distribution. While the FEM model predicts relative insensitivity to broader electric field values, this none-the-less could be the origin of the broadening in the actual measurement.

Another possibility of the broadening of the domain wall could be a domain wall that is not perfectly vertical and is pictured in Figure 3-7(b). While the vertical case is more energetically favorable by reducing the divergence in the polarization, defects can stabilize the domains in other orientations. Growth of domains are usually in dagger shapes originating at the $+z$ face and propagate toward the $-z$ face. The angle of the growing domain wall, as measured from cross-sectional analysis of the domain walls by Gopalan and Mitchell, gives the maximum angle of the domain wall with respect to the polarization direction as $\sim 2.1^\circ$.\footnote{84} In a 300 $\mu$m thick crystal, this translates to an 11 $\mu$m transition distance on the sample surface. However, since the electric field distribution from the tip only samples a small depth near the surface (within $\sim 50$ nm), the signal will be broadened but it is not exactly clear to what degree. Additional FEM simulations on an angled domain wall should be performed to determine the nature of the change.

The final possibilities for the domain broadening and asymmetry could be the electrostatic distribution on the surface around a domain wall. If we assume that compensation of the ferroelectric polarization is at least partially accomplished by surface charges adsorbed from the environment then there is a charged double layer on the surface. There would then be a diminishing or enhancement of the amplitude due to electrostatic interaction of the tip by the charged surface. The sign of this charge changes
across a domain wall and would introduce a gradient in the electrostatic signal that would be present in the interaction width. We will examine two simple cases of screening – an under-screened surface, meaning net bound polarization charge remains on the surface, or over-screened surface, meaning net bound polarization is over-screened by the surface layer, as shown in Figure 3-3(c) and (d) respectively.

Let us examine a simple model of a domain wall at \( x=0 \) being scanned by a positively charged tip and only consider the spatial distribution the piezoelectric and electrostatic amplitudes, \( A_{pi}(x) \) and \( A_{es}(x) \), respectively. The variation of the signal on crossing a domain is given as a hyperbolic tangent which was used to fit the simulated vertical data in Figure 3-20(a). The total amplitude signal, \( A_{o}(x) = A_{pi}(x) + A_{es}(x) \), as a function of distance, \( x \), is then given as

\[
A_{o} \tanh(x/x_o) = A_{pi} \tanh(x/x_{pi}) + A_{es} \tanh(x/x_{es}) e^{i\theta}
\]

where \( \theta \) gives the phase relation between the electrostatic amplitude and the positively charged tip, and \( x_o, x_{pi}, \) and \( x_{es} \) are domain wall half width widths. These are related to the interaction widths (FWHM) by \( x_o=0.91\omega_o, x_{pi}=0.91\omega_{pi}, \) and \( x_{es}=0.91\omega_{es} \). There are two different types of electrostatic signals, one from an over-screened surface, \( A_{es}=A_{ov} \), and one from an under-screened surface, \( A_{es}=A_{un} \). The phase, \( \theta \), is \( \pi \) for an under-screened surface and 0 for an over-screened surface. The variation across the wall for the piezoelectric and electrostatic signals is shown in Figure 3-29(a) where \( A_{pi} > A_{es} \).

If the domain regions are under-screened, the electrostatic signal, \( A_{un} \), will be contrary to the piezoelectric signal (\( \theta=\pi \)). Summing the two signals for an under-screened surface gives the net amplitude (the absolute value of equation 9) as shown in
Figure 3-29(b). The net amplitude acquires a ridge around the wall, caused by adding the contrary signals. This ridge structure is not experimentally observed.

If we let the surface be over-screened, the phase difference $\theta=0^\circ$ in Equation 3-13, and the resultant amplitude is shown in Figure 3-29(c). One can notice that the combined signal is wider than just the piezoelectric signal alone. The amplitude and transition width of the over-screened electrostatic signal can cause broadening of the net signal observed in PFM measurements. Plotting ratios of the amplitudes of the signals ($A_{ov}/A_{pi}$) and to the interaction widths ($\omega_{ov}/\omega_{pi}$) gives different values of the interaction width as shown in Figure 3-30. A variety of ratios can give a net interaction width equal to the experimentally measured width (~110 nm) assuming the piezoelectric interaction width is given by the finite element method simulation result (~65 nm). For example, if $A_{ov}$ is equal to $A_{pi}$, then the $\omega_{ov}$ is approximately twice as wide as $\omega_{pi}$. Although over-screening can explain signal broadening, the mechanism for an overscreened surface is presently
An over screened surface has been observed on reduced SAW grade LiNbO$_3$, although comparison to congruent optical grade wafers is not easy due to the severely modified electrical nature of the reduced samples.

An estimation of the ratios of the signals can be made using the threshold observed value of the electrostatic distribution on the sample surface of 50 mV measured in Chapter 3.4. Following the formulation of Hong, the amplitudes of the piezoelectric signal, $A_{pi}$, and electrostatic signal, $A_{es}$, are given by

$$A_{pi} = d_{33} V_{ac} \quad 3-14$$

$$A_{es} = -\frac{1}{k} \frac{dC}{dz} V_{e} V_{ac} \quad 3-15$$

Figure 3-30: Contours in nanometers of the full-width-at-half-maximum for the combined piezoelectric and over-screened electrostatic signals versus the ratios of the electrostatic to the piezoelectric amplitude ($A_{ov}/A_{pi}$) and transition widths ($\omega_{ov}/\omega_{pi}$). The dark line indicates the experimentally measured interaction width ($\omega_{o}$~110 nm) on stoichiometric lithium niobate.
where \( d_{33} \) is the piezoelectric coefficient, \( V_{ac} \) is the applied oscillating imaging voltage, \( k \) is the cantilever spring constant, \( dC/dz \) is the capacitance between the tip-cantilever system and the sample surface, \( V_c \) is the surface potential measured using SSPM. Using the electric field model in Section 3.5.1, the \( dC/dz \) term can be numerically calculated as \(-1.73 \times 10^{-9} \, \text{F/m}\) at 0.1 nm tip separation. If \( V_c \) is equal to the upper limit of 50 mV estimated using EFM and \( k \) is 12 N/m, the upper limit value of \( A_{es}/V_{ac} \) is \(~3.60 \, \text{pm/V^2}\). This value is \(~60\%\) the value \( A_{ps}/V_{ac} = 6 \, \text{pm/V^2} \). From the data collected in Section 3.4 the nature of the surface screening cannot be determined. However, if we assume over screening and use the model above, the ratio \( A_{ov}/A_{pi} \) is 0.6 which gives a ratio \( \omega_{ov}/\omega_{pi} \) of \(~8\). This gives an estimation of the lower limit of the electrostatic signal width as \(~500 \, \text{nm} \) (\( 8 \times 65 \, \text{nm} \)). However, when \( A_{ov}/A_{pi} < 1 \) there is large variation of \( \omega_{ov}/\omega_{pi} \) for small variation of \( A_{es} \) which makes the estimation of the electrostatic signal particularly prone to large errors. This is especially true since \( A_{es} \) is itself an estimation. Therefore, the electrostatic signal width is still an uncertain quantity.

### 3.6.2 Asymmetry in PFM measurements

Finally, the issue of the asymmetry in the PFM images will be examined. Any asymmetry in the electrostatic distribution across a wall could give rise to asymmetry in the vertical signal in a way discussed above. Higher resolution measurements of the electrostatic distribution than presented in Chapter 3.4 should be performed using non-contact methods, although the inherent long range nature of these measurements might
not provide the spatial resolution needed to resolve the issue.\textsuperscript{9,15,16,85} Also, as discussed in Section 3.3.2, a jagged domain wall could introduce asymmetry into the signal.

Another consideration is that the asymmetry could be due to changes in the material properties in the area of the domain wall. These stressed and distorted regions around the domain wall could have different physical properties from the bulk values. It has been shown by scanning-nonlinear-dielectric microscopy in periodically poled lithium niobate that very strong residual stresses or electric fields remain in the crystal that reduce the nonlinear dielectric constant in the region of the wall.\textsuperscript{86} The asymmetry could be explained by a change in the wall region of any of the physical coefficients important to this measurement: the dielectric, piezoelectric, or elastic constants.

![Figure 3-31: FEM simulations of a domain wall with the d_{33} coefficient of the right side of a 180° domain wall (at x=0) reduced to 75% of the full value on the left side. Shown in (a) is the vertical signal and in (b) the lateral signal 90° to the wall.]

As an exaggerated example, FEM simulations were performed which arbitrarily reduced the d_{33} coefficient on one side of the domain wall to 75% of the other side. The simulated results are shown in Figure 3-31(a). It shows that the vertical signal has some asymmetry because the right side of the domain wall does not expand as much as the left,
as one would expect. Similar results can be drawn for the lateral signal in Figure 3-31(b) as well. This step-like large reduction of $d_{33}$ across a domain wall is perhaps a less likely scenario than a more realistic gradient of the value of $d_{33}$ across the wall. Such FEM calculations are more difficult with present commercial codes and require further work. Measurements made using the PFM setup give the same amplitude of the oscillation in an up and a down domain when measured far from the domain wall ($>100 \ \mu m$), which indicates that any changes must be in a highly localized region around the domain wall. The piezoelectric $d_{33}$ coefficient was chosen in this study for modeling simplicity, but modification of other piezoelectric coefficients, as well as the dielectric or the elastic constants are also possibilities.

3.7 Conclusions

The local piezoelectric response at a single ferroelectric $180^\circ$ domain wall is measured in congruent and near-stoichiometric LiNbO$_3$ single crystals. Unexpected asymmetry in piezoresponse across the wall was observed, which is found to correlate to the crystal stoichiometry. The measured electromechanical interaction widths in congruent crystals are wider than in the near-stoichiometric values: for the vertical signal, $\omega_v=140 \ \text{nm}$ compared to $113 \ \text{nm}$, and for the lateral signal, $211 \ \text{nm}$ compared to $181 \ \text{nm}$. Finite element modeling of the electromechanical response of the domain wall shows excellent qualitative agreement with experimental images for near-stoichiometric compositions. The amplitude of oscillation in vertical piezoresponse mode also showed
an excellent agreement between modeling (13.4 nm) as compared to the measured (20-30 nm) values. Detailed analysis shows that the PFM resolution of a single antiparallel wall is determined both by intrinsic electromechanical width as well as tip size.

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Chapter 4

Phenomenological Theory of Domain Walls

A key objective of this thesis is to create and precisely control the orientation of ferroelectric domains in lithium niobate and lithium tantalate. These domain walls, however, have certain low energy configurations which ultimately control the orientations of the domain walls. Understanding these orientations and studying the key differences between the two materials can help in the design of optical devices by elucidating the controlling factors and the reasons of any differences. In this chapter, a phenomenological treatment of domain wall orientations based on the Ginzburg-Landau-Devonshire theory is developed in lithium niobate and lithium tantalate.

The outline of the chapter is as follows: In Section 4.2 the theoretical framework is explained. Section 4.3 will go through the theoretical expansion of the free energy for two cases: a homogeneous case for uniform domain orientation and an inhomogeneous case for a system with a domain wall of arbitrary orientation. Analytical expressions are developed which are analyzed numerically to determine the minimum polarization, strain, and energy configurations of the domain walls in Section 4.4. Domains created at higher temperatures will be analyzed in the current framework and discussed in Section 4.5. Key differences will be highlighted and discussed in Section 4.6.
4.1 Introduction

From a fundamental viewpoint, the domain wall structure and shapes observed in these materials highlight interesting issues relating to preferred domain wall orientations, wall strains, the wall width, and defect mediated changes in the local structure of these domain walls. For example, when domains are created in a single crystal of LiNbO$_3$ or LiTaO$_3$ by external electric fields, one observes a variety of naturally preferred crystallographic shapes exhibited by these crystals depending on slight variations in crystal stoichiometry. Figure 4-1 summarizes two primary shapes preferred by these crystals. The stoichiometric crystals of both LiNbO$_3$ and LiTaO$_3$ exhibit six sided polygonal shapes, with domain walls parallel to the crystallographic $c$-glide planes ($yz$-plane), termed as $y$-walls. With lithium deficiency in the crystals, the shape of the domains in congruent LiTaO$_3$ changes to triangular domains with domain walls parallel to the crystallographic $xz$-planes, termed $x$-walls. This change in domain shape with stoichiometry changes is not seen in congruent LiNbO$_3$. It is also important to note that with increasing lithium deficiency in the crystals, the regions adjoining domain walls show increased optical birefringence,$^1$ strains,$^2$ and local electric fields that extend over microns.
The above observations are driven by both crystallographic considerations and defect-mediated changes. Towards separating these effects, this chapter addresses the following question: what are the energetically favored orientations of domain walls in stoichiometric LiNbO$_3$ and LiTaO$_3$ purely from a crystallographic viewpoint. We will assume that there is no external electric field applied and the crystal is unclamped. Both LiTaO$_3$ and LiNbO$_3$ show a second order phase transition from a higher temperature paraelectric phase with space group symmetry $R\overline{3}c$ to a ferroelectric phase of symmetry R3c at Curie temperatures $T_c$ of $\sim$690$^\circ$ C and $\sim$1190$^\circ$C, respectively. The approach is to minimize the invariant Ginzburg-Landau-Devonshire (GLD) free energy for a crystal in the presence of a single 180$^\circ$ domain wall. This yields the strains, wall width, and the minimum energy orientations of this wall, which can then be compared with the experimental observations. General conclusions can also be drawn regarding the possible reasons for domain shape changes introduced by the addition of defects.

Figure 4-1: Piezoelectric force microscopy phase contrast images of domain shapes in (a) congruent LiTaO$_3$ and (b) congruent LiNbO$_3$. Black indicates a down domain, white indicates an up domain. The left image is 35x35 µm and the right image is 70x70 µm. Stoichiometric compositions of both LiNbO$_3$ and LiTaO$_3$ show hexagonal domains at room temperature as shown in (a).
4.2 Theoretical Framework

We base our analysis on the Ginzburg-Landau-Devonshire (GLD) theory.\textsuperscript{3-6} According to the Landau theory, the phase transition from the paraelectric phase to the ferroelectric phase occurs as a result of a symmetry change. In LiTaO\textsubscript{3} and LiNbO\textsubscript{3}, the paraelectric phase belongs to the space group $R\overline{3}c$ (point group $\overline{3}m$) and the ferroelectric phase belongs to the space group $R3c$ (point group $3m$) corresponding to a loss of the inversion symmetry at the transition point. The symmetry breaking results in the evolution of a primary order parameter in the low symmetry ferroelectric phase. In the case of LiTaO\textsubscript{3} and LiNbO\textsubscript{3}, the primary order parameter is the polarization along the crystallographic $z$ direction, $P_z$.

The fields of interest are the macroscopic strains and the macroscopic polarization. The six strain components and the two orthogonal components of the polarization other than the primary order parameter are coupled to the primary order parameter and are treated as secondary order parameters in this analysis.

Since we are interested in the macroscopic fields, we are only interested in the $\Gamma$ point (zone center) in the Brillouin zone. Thus, the symmetry considerations for the free energy reduce to the considerations of the symmetry of the point group of the prototype phase $\overline{3}m$. The presence of domain walls can be considered as perturbations in the vicinity of the $\Gamma$ point. This is reflected in the free energy that corresponds to the gradient in the order parameters in the GLD theory.

All the energy terms in the ferroelectric phase have to satisfy the point group symmetries of the prototype paraelectric phase, namely: 3 fold rotation about the
polarization direction, a mirror plane in the \( y-z \) plane along the \( c \)-glide plane, and the inversion symmetry. The energy terms cannot change when the coordinates are transformed using an allowed symmetry (in other words, energy terms should be invariant). To examine the tensor properties in the hexagonal system, it is convenient to transform the real \( x \) and \( y \) axes into complex axes \( \xi \) and \( \eta \) by using the transform\(^7,8\)

\[
\begin{bmatrix}
\xi \\
\eta \\
\zeta
\end{bmatrix} =
\begin{bmatrix}
i & -1 & 0 \\
i & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
x \\
y \\
z
\end{bmatrix}.
\]

This can be used to transform the three fold rotation, the mirror, and the inversion operations from the \([x,y,z]\) coordinate system to the \([\xi,\eta,z]\) coordinate system as

\[
R_3 = \begin{bmatrix}
\cos\left(\frac{2\pi}{3}\right) & \sin\left(\frac{2\pi}{3}\right) & 0 \\
-\sin\left(\frac{2\pi}{3}\right) & \cos\left(\frac{2\pi}{3}\right) & 0 \\
0 & 0 & 1
\end{bmatrix}
\Rightarrow R_3' = \begin{bmatrix}
e^{-(2\pi i/3)} & 0 & 0 \\
0 & e^{(2\pi i/3)} & 0 \\
0 & 0 & 1
\end{bmatrix}
\tag{4-2}
\]

\[
M = \begin{bmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\Rightarrow M' = \begin{bmatrix}
0 & -1 & 0 \\
-1 & 0 & 0 \\
0 & 0 & 1
\end{bmatrix}
\tag{4-3}
\]

\[
I = \begin{bmatrix}
-1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & -1
\end{bmatrix}
\Rightarrow I' = \begin{bmatrix}
-1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & -1
\end{bmatrix}.
\tag{4-4}
\]

Notice that the transformation in Equation 4-1 makes the three fold rotation into a diagonal matrix in Equation 4-2. By using these transformations, the symmetry invariant energy terms for the transition \( \overline{3}m \rightarrow 3m \) can be more easily derived. Sample terms from each energy type in Section 4.3 are derived using this method and included in Appendix C.1.
The approach used for the derivation of the free energy will be as follows. First the free energy that must be invariant under the prototype point group symmetry operations will be derived in Section 4.3. This free energy with the polarization components as variables with the constraint that the crystal is stress-free will be minimized to give the equilibrium values of polarization and strain in 4.3.1. Using the homogeneous values of the polarization and the strain components, an infinite 180° domain wall at some angle to the crystallographic x-z plane will then be introduced in Section 4.3.2. The structure of the domain wall is obtained using variational minimization of the total free energy under the constraints of strain compatibility and mechanical equilibrium. The polarizations, strains, and energies as a function of domain wall angle will be presented in Section 4.4 and additional analysis as a function of temperature will be presented in Section 4.5. The discussion and conclusions will given in Sections 4.6 and 4.

4.3 Free Energy

The general form of the free energy of a ferroelectric material is given by

$$F(P_i, P_{i,j}, \varepsilon_k) = F_L(P_i) + F_{el}(\varepsilon_k) + F_c(P_i, \varepsilon_k) + F_G(P_{i,j})$$

where $P_i$ are the polarization components, and $\varepsilon_k$ are the strains in Voigt’s notation. In particular, LiNbO$_3$ and LiTaO$_3$ belong to the $\overline{3}m$ point group. In the following analysis, the crystallographic uniaxial direction is denoted as z-axis. The y-axis is chosen such that the y-z plane coincides with a crystal-glide plane as shown in Figure 1-2. The x-axis is
chosen such that the $x$, $y$ and $z$ axes form a right-handed Cartesian coordinate system. The free energy form that is invariant under the point group $\overline{3}m$ consists of the following terms: The first term is the Landau-Devonshire free energy describing a second order phase transition, and is given by

\[
F_L(P) = \frac{-\alpha_1}{2} P_z^2 + \frac{\alpha_2}{4} P_z^4 + \frac{\alpha_3}{2} (P_x^2 + P_y^2)
\]

where $\alpha_i$ is temperature dependent and positive in the ferroelectric phase, while $\alpha_2$ and $\alpha_3$ are positive. The $\alpha_i$ are given in Table 4-2 which are related to the dielectric constants given in Table 4-1. The elastic free energy of the system is given by

\[
F_{el}(\varepsilon) = \beta_1 \varepsilon_3^2 + \beta_2 (\varepsilon_1 + \varepsilon_2)^2 + \beta_3 [(\varepsilon_1 - \varepsilon_2)^2 + \varepsilon_6^2]
\]

where, following Voigt’s notation, $\varepsilon_1 = u_{1,1}$, $\varepsilon_2 = u_{2,2}$, $\varepsilon_3 = u_{3,3}$, $\varepsilon_4 = u_{2,3} + u_{3,2}$, $\varepsilon_5 = u_{1,3} + u_{3,1}$, and $\varepsilon_6 = u_{1,2} + u_{2,1}$, and $u_i$ are the lattice displacements. The $\beta_i$ given in Table 4-2 are related to the elastic constants given in Table 4-1. The third term in Equation 4-5 is the electrostrictive coupling between the polarization and strain components and is given by

\[
F_e(P, \varepsilon) = \gamma_1 (\varepsilon_1 + \varepsilon_2) P_z^2 + \gamma_2 \varepsilon_3 P_z^2 + \gamma_3 [(\varepsilon_1 - \varepsilon_2) P_y + \varepsilon_6 P_x P_z] + \\
\gamma_4 (\varepsilon_5 P_x P_z + \varepsilon_4 P_y P_z) + \gamma_5 (\varepsilon_1 + \varepsilon_2) (P_x^2 + P_y^2) + \gamma_6 \varepsilon_3 (P_x^2 + P_y^2) + \\
\gamma_7 [(\varepsilon_1 - \varepsilon_2) (P_x^2 - P_y^2) + 2 \varepsilon_6 P_x P_y] + \gamma_8 \varepsilon_4 (P_x^2 - P_y^2) + 2 \varepsilon_5 P_x P_y
\]
where the $\gamma_i$ are listed in Table 4-2 which are related to the electrostrictive and elastic constants given in Table 4-1. The final term in Equation 4-5 is the gradient energy of the lowest order compatible with the $\overline{3}m$ symmetry, and is given by

$$F_G(P_{i,j}) = g_1(P_{z,1}^2 + P_{z,2}^2) + g_2(P_{z,3}^2)$$  \(4-9\)

Here, $g_1$ and $g_2$ are the gradient coefficients. To keep the mathematical complexity tractable at this stage, we neglect the energy contribution from the gradient of the secondary order parameters. We will neglect the electrostrictive coupling energy terms from Equation 4-8 that do not involve the primary order parameter, $P_z$. Later in Section 4.6 we show that gradient terms of the type $P_{n,n}$ play an important role in determining the domain shape as well.

![Figure 4-2: Orientation of the rotated coordinate system ($x_n, x_t, z$) with respect to the crystallographic coordinate system ($x,y,z$). Also noted is the domain wall orientation, which is parallel to the $x_t$ axis.](image)

In the presence of a domain wall at a variable orientation to the $x$-axis or $y$-axis, it is convenient to work in a rotated coordinate system as shown in Figure 4-2. This new coordinate system is obtained by a proper rotation of the $x$-axis and $y$-axis about the $z$-axis, such that $x \rightarrow x_n$ and $y \rightarrow x_t$ and $(x_n, x_t, z)$ forms a right handed coordinate system.
The subscripts \( n \) and \( t \), respectively, refer to the coordinates normal and parallel to the domain wall. The free energy in the new coordinate system is then given by

\[
F(P_i, \varepsilon_k, P_{j,t}) = -\frac{\alpha_1}{2} P_{z}^2 + \frac{\alpha_2}{4} P_{z}^4 + \frac{\alpha_3}{2} (P_n^2 + P_t^2) \\
+ \beta_1 \varepsilon_3^2 + \beta_2 (\varepsilon_n + \varepsilon_t)^2 + \beta_3 (\varepsilon_n - \varepsilon_t)^2 + \varepsilon_6^2 \\
+ \beta_4 (\varepsilon_n + \varepsilon_t) \\
+ \gamma_1 (\varepsilon_n + \varepsilon_t) P_{z}^2 + \gamma_2 \varepsilon_3 P_{z}^2 + \gamma_3 (\varepsilon_n - \varepsilon_t) P_{t} P_{z} + \varepsilon_6 P_{n} P_{z} \\
+ \gamma_4 (\varepsilon_5 P_{n} P_{z} + \varepsilon_4 P_{t} P_{z}) + g_1 (P_{z,n}^2 + P_{z,t}^2) + g_2 (P_{z,3}^2)
\]

where \( \theta \) is the angle between the \( x \) and \( x_n \) coordinate axes. Following Voigt’s notation,

\[
\varepsilon_n = u_{n,n}, \quad \varepsilon_t = u_{t,t}, \quad \varepsilon_3 = u_{3,3}, \quad \varepsilon_4 = u_{t,3} + u_{3,t}, \quad \varepsilon_5 = u_{n,3} + u_{3,n}, \quad \text{and} \quad \varepsilon_6 = u_{t,n} + u_{n,t}, \quad \varepsilon_i
\]

are the lattice displacements, and \( P_n \) and \( P_t \) are polarizations along the \( n \) and \( t \) axes, respectively. The following analysis will use the free energy in Equation 4-10.
Table 4-1: Relevant Physical Constants of LiNbO$_3$ and LiTaO$_3$

<table>
<thead>
<tr>
<th></th>
<th>LiTaO$_3$ $^{9-12}$</th>
<th>LiNbO$_3$ $^{9-11,13}$</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_s$</td>
<td>50-55</td>
<td>70-75</td>
<td>µC/cm$^2$</td>
</tr>
<tr>
<td>$\varepsilon_{11}$</td>
<td>52.7 ± 1.1</td>
<td>84.3 ± 0.8</td>
<td>-</td>
</tr>
<tr>
<td>$\varepsilon_{33}$</td>
<td>44.0 ± 0.7</td>
<td>28.9 ± 0.7</td>
<td>-</td>
</tr>
<tr>
<td>$c_{11}$</td>
<td>2.3305 ± 0.0004</td>
<td>1.9886 ± 0.0003</td>
<td>$\times 10^{11}$ N/m$^2$</td>
</tr>
<tr>
<td>$c_{12}$</td>
<td>0.4644 ± 0.0006</td>
<td>0.5467 ± 0.0004</td>
<td>$\times 10^{11}$ N/m$^2$</td>
</tr>
<tr>
<td>$c_{13}$</td>
<td>0.8358 ± 0.0063</td>
<td>0.6726 ± 0.0093</td>
<td>$\times 10^{11}$ N/m$^2$</td>
</tr>
<tr>
<td>$c_{33}$</td>
<td>-2.7414 ± 0.0104</td>
<td>2.3370 ± 0.0152</td>
<td>$\times 10^{11}$ N/m$^2$</td>
</tr>
<tr>
<td>$c_{14}$</td>
<td>-1.067 ± 0.0004</td>
<td>0.0783 ± 0.0002</td>
<td>$\times 10^{11}$ N/m$^2$</td>
</tr>
<tr>
<td>$c_{44}$</td>
<td>0.9526 ± 0.0002</td>
<td>0.5985 ± 0.0001</td>
<td>$\times 10^{11}$ N/m$^2$</td>
</tr>
<tr>
<td>$Q_{31}$</td>
<td>-0.00485 ± 0.0002</td>
<td>-0.003</td>
<td>m$^4$/C$^2$</td>
</tr>
<tr>
<td>$Q_{33}$</td>
<td>0.016 ± 0.007</td>
<td>0.016</td>
<td>m$^4$/C$^2$</td>
</tr>
<tr>
<td>$Q_{42}$</td>
<td>0.016 ± 0.0001</td>
<td>-0.003 ± 0.03</td>
<td>m$^4$/C$^2$</td>
</tr>
<tr>
<td>$Q_{44}$</td>
<td>0.056 ± 0.005</td>
<td>0.0375 ± 0.03</td>
<td>m$^4$/C$^2$</td>
</tr>
</tbody>
</table>
4.3.1 Homogeneous Case: Single Domain Wall

We first consider the homogeneous case where the material exists in a single domain state and apply the following constraints

\[
\frac{\partial F}{\partial P_i} = 0, \quad 4-11
\]

\[
\frac{\partial F}{\partial \varepsilon_i} = \sigma_i = 0 \quad 4-12
\]

<table>
<thead>
<tr>
<th>Expression</th>
<th>LiTaO(_3)</th>
<th>LiNbO(_3)</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha_1)</td>
<td>(\frac{1}{2\varepsilon_{33}})</td>
<td>1.256</td>
<td>2.012</td>
</tr>
<tr>
<td>(\alpha_2)</td>
<td>* derived from 4-15</td>
<td>5.053</td>
<td>3.308</td>
</tr>
<tr>
<td>(\alpha_3)</td>
<td>(\frac{1}{\varepsilon_{11}})</td>
<td>2.22</td>
<td>1.345</td>
</tr>
<tr>
<td>(\beta_1)</td>
<td>(\frac{1}{2} C_{33})</td>
<td>13.55</td>
<td>12.25</td>
</tr>
<tr>
<td>(\beta_2)</td>
<td>(\frac{1}{2} (C_{11} + C_{12}))</td>
<td>6.475</td>
<td>6.4</td>
</tr>
<tr>
<td>(\beta_3)</td>
<td>(\frac{1}{2} (C_{11} - C_{12}))</td>
<td>4.925</td>
<td>3.75</td>
</tr>
<tr>
<td>(\beta_4)</td>
<td>(C_{13})</td>
<td>7.4</td>
<td>7.5</td>
</tr>
<tr>
<td>(\beta_5)</td>
<td>(\frac{1}{2} C_{44})</td>
<td>4.8</td>
<td>3</td>
</tr>
<tr>
<td>(\beta_6)</td>
<td>(C_{14})</td>
<td>-1.2</td>
<td>0.9</td>
</tr>
<tr>
<td>(\gamma_1)</td>
<td>(\frac{1}{2} (C_{11} + C_{12}) Q_{31} + \frac{1}{2} C_{13} Q_{33})</td>
<td>-0.202</td>
<td>0.216</td>
</tr>
<tr>
<td>(\gamma_2)</td>
<td>(\frac{1}{2} C_{33} Q_{31} + \frac{1}{2} C_{13} Q_{31})</td>
<td>1.317</td>
<td>1.848</td>
</tr>
<tr>
<td>(\gamma_3)</td>
<td>(2 C_{14} Q_{44} - \frac{1}{2} (C_{11} - C_{12}) Q_{42})</td>
<td>-2.824</td>
<td>-0.33</td>
</tr>
<tr>
<td>(\gamma_4)</td>
<td>(C_{44} Q_{44})</td>
<td>4.992</td>
<td>3.9</td>
</tr>
<tr>
<td>(\lambda_1)</td>
<td>Equation 4-17</td>
<td>6.418</td>
<td>9.359</td>
</tr>
<tr>
<td>(\lambda_2)</td>
<td>Equation 4-18</td>
<td>-0.157</td>
<td>-0.4874</td>
</tr>
</tbody>
</table>
where \(\sigma_i\) is the stress. Constraint 4-11 specifies uniform homogeneous polarization values in the material and 4-12 specifies that the material is stress free. These constraints result in the following homogeneous strains and polarizations:

\[
\varepsilon_4 = \varepsilon_5 = \varepsilon_6 = 0
\]

\[
P_n = P_t = 0
\]

\[
P_z = P_h = \pm \left[ \frac{\alpha_1}{\alpha_2 + 4(\beta_1\psi_1^2 + 4\beta_2\psi_1^2 + 2\beta_4\psi_1\psi_2 + 2\gamma_2\psi_1 + \gamma_2\psi_2)} \right]^{1/2}
\]

where the subscript \(h\) refers to the homogeneous case and

\[
\psi_1 = \frac{2\gamma_1\beta_1 - \gamma_2\beta_4}{2(\beta_4^2 - 4\beta_1\beta_2)} \quad \text{and} \quad \psi_2 = \frac{2\gamma_2\beta_2 - \gamma_1\beta_4}{\beta_4^2 - 4\beta_1\beta_2}
\]

Using the homogeneous value \(P_z = P_h\) of \(z\)-axis polarization, we obtain the spontaneous dilatory strains as

\[
\varepsilon_n = \varepsilon_t = \lambda_1 = \psi_1 P_h^2
\]

\[
\varepsilon_3 = \lambda_2 = \psi_2 P_h^2
\]

It can be seen that in the homogeneous case, there is no polarization in the \(n-t\) plane and that the shear strains are zero. There are two possible orientations for the homogeneous polarization, \(P_h\). Note that \(P_h\) is equal to the spontaneous polarization value, \(P_s\), as found in the literature. The coefficient \(\alpha_2\) in Table 4-2 was determined using Equation 4-15 and the known experimental values of \(\alpha_i\) and \(P_h\) at room temperature for LiNbO\(_3\) and LiTaO\(_3\). The values of \(\lambda_1\) and \(\lambda_2\) are, respectively, \(\lambda_1 = 6.4 \times 10^{-4}\) and \(\lambda_2 = -1.6 \times 10^{-3}\) (for LiTaO\(_3\)) and \(\lambda_1 = 9.36 \times 10^{-4}\) and \(\lambda_2 = -4.8 \times 10^{-3}\) (for
LiNbO$_3$), indicating that there is a homogeneous tensile strain in the $x$-$y$ plane and a homogeneous compressive strain in the $z$-direction.

### 4.3.2 Inhomogeneous Case: Single Infinite Domain Wall

We now introduce an infinite 180° domain wall in the crystal. The position of the wall in the rotated coordinate system is shown in Figure 4-2. The $x_r$-$z$ plane corresponds to the plane in the domain wall where the $z$-component of the polarization vanishes. Far away from the domain wall, we assume that the polarizations take a homogeneous value of $-P_h$ in the $-x_n$ direction and $+P_h$ in the $+x_n$ direction. The angle $\theta$ between the normal to the domain wall, $x_n$ with the crystallographic $x$-axis defines the orientation of the wall in the $x$-$y$ plane. We will seek a quasi-one dimensional solution, where the polarization and strain fields are functions of only the coordinate normal to the wall (i.e. the coordinate $x_n$). In a defect free material, the St. Venant’s strain compatibility condition must hold

$$\nabla \times \nabla \times \mathbf{\varepsilon} = 0 \tag{4-19}$$

where $\mathbf{\varepsilon}$ in the above equation is the strain tensor.\textsuperscript{14} Noting that the strains are a function of $x_n$ only, and taking the homogeneous values far away from the wall, Equation 4-19 yields

$$\tilde{\varepsilon}_4 = 0, \ \varepsilon_r = \lambda_1, \ \varepsilon_3 = \lambda_2 \tag{4-20}$$
Note that these strain values are valid throughout the material including the wall region. In addition, the divergence of stress must be zero to ensure mechanical equilibrium, i.e.

\[ \nabla \cdot \bar{\sigma} = 0 \] \hspace{1cm} (4-21)

where \( \bar{\sigma} \) represents the stress tensor. Noting that the stresses are a function of \( x_n \) only, and vanish far away from the wall, Equation (4-21) yields

\[ \sigma_n = \bar{\sigma}_5 = \bar{\sigma}_6 = 0 \] \hspace{1cm} (4-22)

Defining \( \Delta \varepsilon_n = \varepsilon_n - \lambda_1 \), as the deviation of the normal strain \( \varepsilon_n \) from the homogeneous value \( \lambda_1 \), Equation (4-22) gives,

\[ \begin{bmatrix} \Delta \varepsilon_n \\ \bar{\varepsilon}_5 \\ \bar{\varepsilon}_6 \end{bmatrix} = \begin{bmatrix} m_{ij} \end{bmatrix} \begin{bmatrix} P_z^2 - P_h^2 \\ P_z P_n \\ P_z P_r \end{bmatrix} \] \hspace{1cm} (4-23)

The strains \( \bar{\varepsilon}_5 \) and \( \bar{\varepsilon}_6 \) can also be considered as deviations from their homogeneous values, recalling that their homogeneous values are zero from Equation 4-13. In Equation (4-23), the matrix \( [m_{ij}] = [a_{ij}]^{-1}[b_{ij}] \), where

\[ [a_{ij}] = \begin{bmatrix} 2(\beta_2 + \beta_3) & \beta_6 \sin(3\theta) & 0 \\ \beta_6 \sin(3\theta) & 2\beta_5 & \beta_6 \cos(3\theta) \\ 0 & \beta_6 \cos(3\theta) & 2\beta_3 \end{bmatrix} \] \hspace{1cm} (4-24)

and

\[ [b_{ij}] = \begin{bmatrix} -\gamma_1 & -\gamma_3 \sin(3\theta) & -\gamma_3 \cos(3\theta) \\ 0 & -\gamma_4 & 0 \\ 0 & -\gamma_3 \cos(3\theta) & \gamma_3 \sin(3\theta) \end{bmatrix}. \] \hspace{1cm} (4-25)
Now we minimize the total free energy $F$ with respect to the polarizations $P_n$ and $P_t$ as follows

$$\frac{\partial F}{\partial P_i} = 0, \quad (i=n,t) \quad 4-26$$

where, for the present, the gradient terms $P_{n,n}$ and $P_{t,t}$ have been ignored. Equation 4-26 in combination with Equation 4-20 and Equation 4-23-22 yields relationships between the polarizations $P_n$, $P_t$, and $P_z$ as follows:

$$\begin{bmatrix} P_n \\ P_t \end{bmatrix} = \frac{P_z (P_z^2 - P_h^2)}{\alpha_3^2 + \alpha_3 (\mu_{11} + \mu_{22}) P_z^2 + (\mu_{11} \mu_{22} - \mu_{12} \mu_{21}) P_z^4} \begin{bmatrix} \nu_1 \alpha_3 + (\nu_1 \mu_{22} - \nu_2 \mu_{12}) P_z^2 \\ \nu_2 \alpha_3 + (\nu_2 \mu_{11} + \nu_1 \mu_{21}) P_z^2 \end{bmatrix} \quad 4-27$$

The constants $\nu_i$ and $\mu_{ij}$ are listed in Appendix C.1.

From Equation 4-27, we see that the polarizations $P_n$ and $P_t$ depend on $P_z$ in a highly nonlinear manner. In order to simplify these relations for further progress, we estimate the relative magnitudes of different terms in the denominator of the prefactor in Equation 4-27 for $0 \leq \theta \leq 2\pi$ and $|P_z| \leq P_h$. Using the values of physical constants given in Table 4-2 and 4-1 for LiNbO$_3$ and LiTaO$_3$, we find that $\alpha_3^2 \sim 10^{19}$ N$^2$m$^4$C$^{-4}$, $|\alpha_3 (\mu_{11} + \mu_{22}) P_z^2| \leq 10^{18}$ N$^2$m$^4$C$^{-4}$, and $|\mu_{11} \mu_{22} - \mu_{12} \mu_{21}) P_z^4| \leq 10^{16}$ N$^2$m$^4$C$^{-4}$.

Therefore, we retain only the $\alpha_3^2$ term in the denominator of the prefactor in Equation 4-27. The polarizations $P_n$ and $P_t$ simplify to odd functions of $P_z$ and vanish at $P_z = P_h$. From Equation 4-23, we note that the strains $\Delta \varepsilon_n$, $\tilde{\varepsilon}_5$, and $\tilde{\varepsilon}_6$ are even functions of $P_z$ and vanish at $P_z = P_h$. Relationships for the polarizations $P_n$ and $P_t$ and strains $\Delta \varepsilon_n$, $\tilde{\varepsilon}_5$, and $\tilde{\varepsilon}_6$ are given as
where the matrices \([p_{ij}]\) and \([\phi_{ij}]\) are listed in Appendix C.1.

So far, we have minimized the total free energy, \(F\), with respect to \(P_n\) and \(P_t\) (Equation 4-26) under the constraints of strain compatibility (Equation 4-19) and mechanical equilibrium (Equation 4-21). This has enabled us to obtain the expressions for the secondary order parameters \((P_n, P_t, \text{ and } \varepsilon_i)\) in terms of the primary order parameter, \(P_z\). We now perform variational minimization of the total free energy, \(F\), with respect to the primary order parameter, \(P_z\) under the boundary conditions that \(P_z\) approaches \(\pm P_h\) far away from the domain wall. This gives us the Euler-Lagrange equation,

\[
\frac{\partial F}{\partial P_z} - \frac{\partial}{\partial x_n} \left( \frac{\partial F}{\partial P_{z,n}} \right) = 0
\]

The partial derivative \(\partial F / \partial P_z\) is a polynomial in odd powers of \(P_z\) as follows:

\[
\frac{\partial F}{\partial P_z} = -\zeta_1 P_z + \zeta_3 P_z^3 + \zeta_5 P_z^5 + \zeta_7 P_z^7 + \zeta_9 P_z^9 + \zeta_{11} P_z^{11}
\]

The first two coefficients \(\zeta_1\) and \(\zeta_3\) are given by
For further analysis of the order parameter, we truncate the polynomial in Equation 4-31 after the $P_z^3$ term. On substituting for the physical properties of LiNbO$_3$ and LiTaO$_3$ from Table 4-2, it is found that for all values of $0 \leq \theta \leq 2\pi$, $|\xi_1| \sim 10^9$ Nm$^{-2}$C$^{-2}$, 

$$|\xi_3 P_h^2| \sim 10^9$ Nm$^{-2}$C$^{-2}$, $|\xi_5 P_h^4| \sim 10^3$ Nm$^{-2}$C$^{-2}$, $|\xi_7 P_h^6| \sim 10^2$ Nm$^{-2}$C$^{-2}$, $|\xi_9 P_h^8| \sim 0.1 - 1$ Nm$^{-2}$C$^{-2}$.

Therefore the truncation of Equation 4-31 is justified.

With this truncation, Equation 4-31 can be rewritten as

$$2g_1P_{z,nn} = -\xi_1 P_z + \xi_3 P_z^3$$

4-34

The solution to this equation is the kink solution, given by

$$P_z(x_n) = \frac{\xi_1}{\xi_3} \tanh \left( \frac{x_n}{2} \sqrt[3]{\frac{\xi_1}{g_1}} \right)$$

4-35

where $x_n$ is the coordinate parallel to the domain wall normal $n$. The domain wall half-width, $x_o$, is defined as $x_o = 2 \sqrt[3]{\frac{g_1}{\xi_1}}$. Substituting the expression for $P_z(x_n)$ into Equations 4-28 and 4-29, we get the variation of strains and in-plane polarizations, $P_n$ and $P_t$ as a function of $x_n$. Substituting these expressions into Equation 4-10, we get the total inhomogeneous free energy $F_{inh}$. As a cautionary note, although in deriving Equation 4-35, we neglected the higher order terms in $P_z$ in Equation 4-31, one cannot do so in calculating the total free energy, $F_{inh}$. As will be seen further on, the variation of
the free energy, $F_{DW}$ calculated from Equation 4-34 as a function of the domain wall angle $\theta$ is small as compared to the mean value itself. Therefore, the truncation of higher order polarization terms in Equation 4-29 should be carried out with care, if at all. The average domain wall energy per unit volume, $F_{DW}$, due to the addition of a domain wall to the homogeneous single domain state can then be calculated as

$$F_{DW} = \frac{1}{\Delta x} \int_{-\Delta x/2}^{+\Delta x/2} (F_{inh} - F_{h}) dx$$ 4-36

where $F_{inh}$ and $F_{h}$ are the total free energy Equation 4-10 for the inhomogeneous and the homogeneous states, respectively. The integration window, $\Delta x$, was chosen across the wall as $\Delta x = 4x_o$, where $x_o$ is the wall half width. This window corresponds to where the energy drops to 2.2% of the peak value at the domain wall. Integration over a larger window does not significantly increase the integrated energy. We note that after performing the integration in Equation 4-36, the $F_{DW} \propto \sqrt{g_1}$, where the other gradient term $g_2$ is ignored as before.

4.4 Polarizations, Strains, and Energy Predictions

Using the material constants listed in Table 4-1, the variation of the free energy, polarization, and strains as a function of domain wall orientation was calculated for both LiNbO$_3$ and LiTaO$_3$. This was implemented using Matlab and the codes are included in Appendix C.1. These results are presented and discussed below.
Equation 4-3 shows a plot of the gradient term, \( g_1 \) as a function of the wall width, \( x_o \). The domain wall width, the distance over which the polarization reverses, has been measured by Bursill et al. to have an upper limit of 0.28 nm using high-resolution TEM images in lithium tantalate (isomorphic to lithium niobate). Taking this as the wall width, \( 2x_o \), for both materials, the upper limit for the gradient term is estimated as \( 3.98 \times 10^{-11} \text{Nm}^4/\text{C}^2 \) and \( 2.53 \times 10^{-11} \text{Nm}^4/\text{C}^2 \) for LiNbO\(_3\) and LiTaO\(_3\), respectively.

Since the theory does not include any energy contributions from non-stoichiometry related defects, a direct comparison of the properties calculated below can be made only with the stoichiometric compositions of these materials.

![Graph showing gradient coefficient, \( g_1 \), as a function of wall half width, \( x_o \).](image)

**Figure 4-3:** Gradient coefficient, \( g_1 \), as a function of wall half width, \( x_o \)

![Hexagonal wall orientations with wall normals for (a) \( y \)-walls and (b) \( x \)-walls.](image)

**Figure 4-4:** Hexagonal wall orientations with wall normals for (a) \( y \)-walls and (b) \( x \)-walls
Two types of walls are of special interest in these materials: The six “y-walls” lying in the crystallographic y-z planes with wall normals at $\theta = m\pi/3$ as shown in Figure 4-4(a), and the six “x-walls” lying in the crystallographic x-z planes with wall normals at $\theta= (\pi/6+m\pi/3)$ as shown in Figure 4-4(b), where $m$ is an integer from 0-5. The stoichiometric crystals of both LiNbO$_3$ and LiTaO$_3$ possess domain orientations with y-walls. It is important to note that the angular dependence always refers to the orientation of the normal to the domain wall within the x-y plane.

4.4.1 Polarizations

Figure 4-5 shows the spontaneous polarization $P_s$ as a function of normalized distance, $x_n/x_0$, perpendicular to a domain wall according to Equation 4-35. This variation is the same for all orientations $\theta$ of the domain wall in the x-y plane. The saturation polarization $P_s$ far from the domain wall is $\pm 0.5$ C/m$^2$ for LiTaO$_3$ and 0.75 C/m$^2$ for LiNbO$_3$.

In the absence of a domain wall, the polarizations in the x-y plane, $P_n$ and $P_t$, do not exist. However, they are non-zero in the vicinity of a domain wall, and disappear away from the wall. The divergence of the polarization also gives rise to strain in the region around the domain wall as discussed in Section 4.4.2. While consistent mathematically, the physical nature of these in-plane polarizations in not clear and will be discussed at greater depth in Section 4.6.
The magnitude and direction of these in-polarizations, \( P_n \) and \( P_t \), are dependent on the normal to the wall orientation, \( \theta \). This is shown in a quiver plot in Figure 4-6(a) for LiTaO\(_3\) and Figure 4-6(b) for LiNbO\(_3\), where the in-plane polarization \( P_{\text{in-plane}} = \sqrt{P_n^2 + P_t^2} \) is plotted as arrows. The length and direction of the arrows represent the magnitude and direction, respectively, of the vectors \( \vec{P}_{\text{in-plane}} \) in the \( x-y \) plane. The circle in the plot represents the schematic of a hypothetical circular domain wall. Figure 4-6(c) is a polar plot of the maximum amplitude of \( \vec{P}_{\text{in-plane}}(\theta) \) for LiNbO\(_3\) and LiTaO\(_3\).
It is seen in Figure 4-7(a) that and the \( x \)-walls have \( \vec{P}_{\text{in-plane}} = \vec{P}_n \) and in Figure 4-7(b) the \( y \)-walls have \( \vec{P}_{\text{in-plane}} = \vec{P}_t \). This is shown in Figure 4-7 for LiTaO\(_3\) but is also true for LiNbO\(_3\). In addition, these in-plane polarizations can also form in-plane antiparallel domain walls in the \( x-y \) plane. The \( \vec{P}_n \) and \( \vec{P}_t \) vectors reverse directions on crossing such a domain wall along the \( x_n \) direction. The variation of \( \vec{P}_n \) and \( \vec{P}_t \) as a function of \( x_n \) is shown in Figure 4-8(a) and (b), respectively, for LiTaO\(_3\). Again,
Figure 4-8 is valid for LiNbO$_3$ as well by changing the sign and magnitudes of $\vec{P}_n$ and $\vec{P}_t$ for each of the curves in accordance with Figure 4-6(c).

A significant feature of these plots is that the in-plane polarizations at the $x$-walls are perpendicular to the wall, and are oriented in a head-to-head or tail-to-tail
configuration across the walls. These domain walls must therefore be *electrically charged walls*. On the other hand, the $y$-walls have in-plane polarizations that are parallel to these walls, thereby creating *uncharged* walls. Therefore, the $x$-walls must have additional electrostatic wall energy as compared to $y$-walls; the energy arising from the divergence of in-plane polarization at the wall. This is a significant feature that is further discussed in Section 4.4.3.

**4.4.2 Strains**

In the absence of a domain wall (the homogeneous case), the spontaneous strains in LiNbO$_3$ and LiTaO$_3$ are (1) an isotropic strain $\varepsilon_n=\varepsilon_t=\lambda_1$ in the crystallographic $x$-$y$ plane (see Equation 4-17), and (2) a normal strain $\varepsilon_z=\lambda_2$ in the $z$-direction (see Equation 4-18). No shear strains exist (Equation 4-13).

In the presence of a single infinite domain wall, the strains in the domain wall region are different from the homogeneous strains far away from this wall. Since the domain wall plane $t$-$z$ is considered infinite in both the $t$ and the $z$-coordinate axes, the normal strains $\varepsilon_t$ and $\varepsilon_z$ and the shear strain $\tilde{\varepsilon}_4$ in the $t$-$z$ plane of the domain wall do not change from their homogeneous values (see Equation 4-17, 4-18, and 4-20). However, the strain $\varepsilon_n$ (strain normal to the domain wall in the direction $x_n$), shear strain in the $n$-$z$ plane, $\tilde{\varepsilon}_5$, and shear strain in the $n$-$t$ plane, $\tilde{\varepsilon}_6$, change from their homogeneous values by amounts given by Equation 4-29.
The change in the normal strain, $\Delta \varepsilon_n(\theta)$, for both LiNbO$_3$ and LiTaO$_3$ is shown in Figure 4-9(a) and (b), respectively. The strains $\tilde{\varepsilon}_5(\theta)$ and $\tilde{\varepsilon}_6(\theta)$ at the center of the wall ($x_n = 0$) are shown as polar plots in Figure 4-10(a) and (b), respectively.

![Figure 4-9: Change in the normal strain, $\Delta \varepsilon_n$, at the wall ($x_n = 0$) for (a) LiNbO$_3$ and (b) LiTaO$_3$.](image1)

![Figure 4-10: Strains at the wall ($x_n = 0$) for (a) $\tilde{\varepsilon}_5$ and for (b) $\tilde{\varepsilon}_6$. Note the circle in both figures represents zero strain.](image2)

The variation of these strains as a function of the normalized coordinate $x_n/x_0$ perpendicular to the domain wall in LiTaO$_3$ is plotted in Figure 4-11(a) and (b) for $x$-
walls and y-walls, respectively. The corresponding plots for LiNbO3 are shown in Figure 4-12.

Figure 4-11: The strain in LiTaO3 at (a) x-walls, where curve 1 is $\Delta \varepsilon_n$ for $\theta = 30$ and 90°, curve 2 is $\tilde{\varepsilon}_5$ for $\theta = 90^\circ$, curve 3 is $\tilde{\varepsilon}_5$ for $\theta = 30^\circ$, and curve 4 is $\tilde{\varepsilon}_6$ for $\theta = 30$ and 90°. The y-walls are shown in (b), where curve 1 is $\Delta \varepsilon_n$ for $\theta = 0$ and 60°, and curve 2 is $\tilde{\varepsilon}_5$ and $\tilde{\varepsilon}_6$ for $\theta = 0$ and 60°. Every 10th point is marked.

Figure 4-12: The strain in LiNbO3 at (a) x-walls, where curve 1 is $\Delta \varepsilon_n$ for $\theta = 30$ and 90°, curve 2 is $\tilde{\varepsilon}_5$ for $\theta = 90^\circ$, curve 3 is $\tilde{\varepsilon}_5$ for $\theta = 30^\circ$, and curve 4 is $\tilde{\varepsilon}_6$ for $\theta = 30$ and 90°. The y-walls are shown in (b), where curve 1 is $\Delta \varepsilon_n$ for $\theta = 0$ and 60°, and curve 2 is $\tilde{\varepsilon}_5$ and $\tilde{\varepsilon}_6$ for $\theta = 0$ and 60°. Every 10th point is marked.
Some significant features are revealed in Figures 4-11 and 4-12 for both the $x$-walls and the $y$-walls.

(1) The shear strain $\varepsilon_{6}^{\sim}=0$ in the $n-t$ plane for the $x$-walls as well as the $y$-walls for both materials.

(2) The shear strain $\varepsilon_{5}^{\sim}$ (shear strain in the $n-z$ plane) is zero for the $y$-walls in both materials. However, this strain is non-zero for the $x$-walls. In addition, the sign of the shear strain $\varepsilon_{5}^{\sim}$ changes from positive for the three $x$-walls at $\theta=(\pi/2+2m\pi/3), m=0-2$ to negative for the three $x$-walls at $\theta=(\pi/6+2m\pi/3), m=0-2$. This is shown in Figure 4-13. Although the calculations are done for domain walls that are infinite in the lateral extent (along the $t$-axis), if we imagine the formation of a hexagonal domain by bringing together the six $x$-walls, every adjacent hexagonal face will have a different sign for the shear strain, $\varepsilon_{5}^{\sim}$. The above discussion is valid for both materials.

(3) The change in the normal strain $\Delta \varepsilon_{n}$ is negative for LiTaO$_3$ and positive for LiNbO$_3$ for all orientations of the domain wall. Since the homogeneous strain $\varepsilon_{n}$ in both
materials is positive (net tensile strain; see Section 4.3.1), this indicates that the normal tensile strain $\varepsilon_n$ in the domain wall region is lower than the bulk value (by ~34% at the domain wall) in LiTaO$_3$ and higher in the domain wall region (by ~64% at the domain wall) in LiNbO$_3$ compared to the bulk value.

### 4.4.3 Free Energy Anisotropy

The free energy of the domain wall, $F_{DW}$, is numerically calculated from Equation 4-10 in combination with Equation 4-36. This requires a knowledge of the gradient term $g_1$, which is not experimentally known, but was estimated earlier as $g_1 \leq 3.98 \times 10^{-11}$ Nm$^4$/C$^2$ by using $x_o = 2 \sqrt{\frac{g_1}{\zeta_1}}$ where $x_o$ is the transition width measured from atomic positions in the TEM$^{16}$ and $\zeta_1$ is given in Equation 4-32. For further calculations, we assume a value of $g_1 = 4 \times 10^{-11}$ Nm$^4$/C$^2$. While the absolute magnitude of free energy depends on the magnitude of the gradient term, the results discussed below deal with the energy anisotropy as a function of domain wall orientation angle, $\theta$. This energy anisotropy is characterized by the quantity $\Delta F_{DW} = [F_{DW}(\theta) - F_{DW}(0^\circ)]$ which is calculated with respect to the minimum free energy which occurs at the $y$-walls. The symmetry of the dependence of $\Delta F_{DW}$ on the angle $\theta$ is found to be independent of the absolute value of the gradient term.
Figure 4-14: Energies of domain walls in LiTaO₃ relative to 0°. (a) shows the normalized change in free energy, $\Delta F_{DW}$, (b) shows the depolarization energy, $\Delta F_D$ and (c) is the normalized change in the total energy, $\Delta F_{total} = \Delta F_{DW} + \Delta F_d$. Note that (b) and (c) have the same scale, while (a) does not. Units in all plots are J/m³. The dotted hexagon represents the low energy domain wall configuration for each plot.

Figure 4-15: Energies of domain walls in LiNbO₃ relative to 0°. (a) Shows the normalized change in free energy, $\Delta F_{DW}$, (b) shows the depolarization energy, $\Delta F_D$ and (c) is the normalized change in the total energy, $\Delta F_{total} = \Delta F_{DW} + \Delta F_d$. Note that (b) and (c) have the same scale, while (a) does not. Units in all plots are J/m³. The dotted hexagon represents the low energy domain wall configuration for each plot.

Figure 4-14(a) and Figure 4-15(a) show a polar plot of the free energy $\Delta F_{DW}$ calculated by combining Equation 4-10 and 4-36 as a function of domain wall normal orientation, $\theta$, with respect to the crystallographic $x$ axis for LiTaO₃ and LiNbO₃, respectively. The variation of domain wall energy is $\Delta F_{DW}/F_{mean} \sim 10^{-7}$, where $F_{mean} = \langle F_{DW}(\theta) \rangle$. Though small in magnitude, it was confirmed that the angular variation of $\Delta F_{DW}$ shown in Figure 4-14 is not a numerical artifact, since the polar symmetry of the energy plot was found to be insensitive to large variations in input
parameters. Changing each of the physical constants individually in Table 4-1 did not change the symmetry of $\Delta F_{DW}/F_{mean}$. For example, changing the coefficients $c_{11}$, $c_{13}$, $c_{33}$, $c_{14}$, $q_{33}$, $q_{42}$, $q_{44}$, or $e_{11}$ by a factor 0.01 to 30 slightly changed the magnitude but did not change the symmetry of the free energy. The free energy was more sensitive to the coefficients $c_{12}$, $c_{13}$, $q_{31}$, and $e_{33}$, with the symmetry changing only if the coefficients were multiplied by a factor less than 0.6 or greater than 1.5. These values are summarized in Table 4-3. However, the changes in the physical constants needed to induce symmetry changes are very large and unphysical. Further, our calculations have a higher precision than the observed variation – the numerical variation is $\sim 10^2$ while calculations are carried out to $10^{-16}$.

Table 4-3: Range of Material Constants for Symmetry Stability of the Free Energy.

<table>
<thead>
<tr>
<th></th>
<th>LiTaO$_3$</th>
<th>LiNbO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>$\varepsilon_{11}$</td>
<td>0.01</td>
<td>30</td>
</tr>
<tr>
<td>$\varepsilon_{33}$</td>
<td>0.01</td>
<td>11</td>
</tr>
<tr>
<td>$c_{11}$</td>
<td>0.01</td>
<td>30</td>
</tr>
<tr>
<td>$c_{12}$</td>
<td>0.4</td>
<td>4</td>
</tr>
<tr>
<td>$c_{13}$</td>
<td>0.01</td>
<td>3.5</td>
</tr>
<tr>
<td>$c_{33}$</td>
<td>0.01</td>
<td>30</td>
</tr>
<tr>
<td>$c_{14}$</td>
<td>0.01</td>
<td>30</td>
</tr>
<tr>
<td>$c_{44}$</td>
<td>0.4</td>
<td>7.5</td>
</tr>
<tr>
<td>$Q_{31}$</td>
<td>0.02</td>
<td>12</td>
</tr>
<tr>
<td>$Q_{33}$</td>
<td>0.01</td>
<td>30</td>
</tr>
<tr>
<td>$Q_{42}$</td>
<td>0.01</td>
<td>30</td>
</tr>
<tr>
<td>$Q_{44}$</td>
<td>0.01</td>
<td>30</td>
</tr>
</tbody>
</table>

Multiplication of each of the material properties given in Table 4-1 within the range specified results in change of the free energy, but not the symmetry of the free energy.

The change in free energy, given in Figure 4-14(a) and Figure 4-15(a) for LiNbO$_3$ and LiTaO$_3$, exhibits a six-fold symmetry with six energy minima at $\theta = (\pi/6 + m\pi/3)$
where \( m = 0 \) to 5. These orientations correspond to \( x \)-walls, domain walls in the crystallographic \( x-z \) planes with the wall normal in the \( \pm y \) directions. Note that the six-fold symmetry of the lobes preserves the mirror symmetry about the three crystallographic \( y \)-axes. We note that the six-sided hexagonal domain that can be formed with these six minimum energy domain wall configurations does not correspond to the actual domain wall shapes observed experimentally in stoichiometric \( \text{LiNbO}_3 \) and \( \text{LiTaO}_3 \), as shown in Figure 4-1.

One of the energy contributions missing in Equation 4-10 is the depolarization energy at a domain wall introduced by the variation of in-plane polarization \( P_n \) across the domain wall in the direction \( x_n \). In other words, an additional depolarization energy term proportional to \( P_{n,n}^2 \), which was originally ignored, needs to be accounted for. This energy as a function of distance normal to the domain wall, \( x_n \), is calculated starting from Gauss’s law given as

\[
E(x_n) = -\frac{P_n(x_n)}{\varepsilon_0} \quad 4-37
\]

where \( E(x_n) \) is the depolarizing field arising from the polarization, \( P_n(x_n) \).\(^{17}\) For a one dimensional case, where the electric field and polarization are zero at \( \pm \infty \) for the normal components of electric field and polarization, the energy per unit area for a wall length of \( dx \) at \( x \) is

\[
\frac{\varepsilon_0}{2} E^2(x_n) \, dx = \frac{P_n^2(x_n)}{2\varepsilon_0} \, dx . \quad 4-38
\]

The depolarization energy per unit volume of the wall at \( x \) is given by
with units of J/m³. The integration window, \( \Delta x = 4x_{cw} \), was chosen as in Equation 4-36. The depolarization energy in Equation 4-39 is calculated numerically from the normal polarization, \( P_n \), as shown in Figure 4-8 as a function of distance, \( x_n \), from the wall.

Figure 4-14(b) and Figure 4-15(b) shows the depolarization energy, \( \Delta F_d = F_d(\theta) - F_d(0º) \). It can be seen from these plots that the minimum energy is rotated 60º from the minimum energy configuration shown in Figure 4-14(a) and Figure 4-15(a). The depolarization energy favors \( y \)-domain walls in the crystallographic \( y-z \) planes with the wall normal in the \( \pm x \) directions. Since the change in the depolarization energy is larger than the change in the domain wall free energy, the resulting total energy, \( \Delta F_{total} = \Delta F_{dw} + \Delta F_d \), has symmetry that favors \( y \)-walls as shown in Figure 4-14(c) and Figure 4-15 (c).

Figure 4-16 shows the plot of total free energy as a function of the gradient coefficient \( g_1 \). Using the upper limit on the width of the domain wall as 0.28 nm in \( \text{LiTaO}_3 \), the gradient energy is \( 2.53 \times 10^{-11} \text{ Nm}^4/\text{C}^2 \). Using this value, the calculated domain wall energy, \( \sigma_{cw} \), in \( \text{LiTaO}_3 \) is \( \sim 60 \text{ mJ/m}^2 \). Experimental estimates of domain wall energy vary. Using the activation field for the experimentally measured exponential energy.
dependence of sideways domain velocity in an applied electric field in congruent LiTaO$_3$, and following the Miller-Weinreich theory$^{18}$, Gopalan et al. have estimated the wall energy to be $\sim 35$ mJ/m$^2$. Following this analysis and using data for the wall velocity in stoichiometric crystals$^{20}$, the wall energy in stoichiometric composition crystals (which is the correct material composition for comparison with the presented calculations) is calculated as $\sim 9$ mJ/m$^2$. This estimate considers only the polarization and depolarization energies, and ignores strain, coupling and gradient energies. On the other hand, using the curvature of a pinned domain wall under an external field in congruent LiTaO$_3$, and modeling the process as a tradeoff between a decrease in polarization energy and an increase in domain wall energy, Yang and Mohideen estimated the wall energy as $\sigma_w \sim 200-400$ mJ/m$^2$. Yet another estimate based on optical birefringence at the domain wall over a 3 µm width in congruent LiTaO$_3$ yields an electrostatic energy of $\sim 240$

Figure 4-16: Domain wall energy per unit area, $F_{DW}$, as a function of the gradient coefficient $g_1$. The inset of the figure is an expansion of the plot near zero and the vertical line is the upper estimate of $g_1$ calculated from the domain wall width from the literature.
mJ/m².¹ The estimation of wall energy in this study is near the lower end of experimental estimations.

4.5 Influence of Temperature on Domain Wall Orientation

As seen in Chapter 2.3.5, the domain shapes in both LiNbO₃ and LiTaO₃ show a strong correlation to the temperature at which they are created. In congruent LiTaO₃ at room temperature, the domain walls favor a triangular set of χ-walls. However, domain walls created at higher temperatures favor hexagonal and trigonal χ-walls. The series of wall orientations with temperature are shown in Figure 4-17. In congruent LiNbO₃, the temperature change is not as dramatic. The shapes change from hexagonal at room temperature to a mixture of hexagonal and triangular domain shapes at 150°C and are summarized in Figure 4-18.

To try to understand these changes, simulations were performed using the previously developed framework replacing the physical coefficients with the values measured at higher temperatures. The stiffness and the dielectric constants have been measured for both of the congruent materials as a function of temperature in the range of 25-200°C,²²,²³ and are plotted as functions of temperature in Figure 4-19 for congruent LiNbO₃ and in Figure 4-20 for congruent LiTaO₃. The change in the electrostriction coefficients in this temperature range has not been directly measured. However, since even at 200°C we are not close to the transition temperature in either material, we will assume that the electrostrictive coefficients do not change significantly as function of
temperature. This has measured in Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN) ceramics and in triglycine sulfate (TGS) crystals.$^{24,25}$

Figure 4-17: Change in domain wall orientation in LiTaO$_3$ with temperature. (a) $x$ walls at 25ºC, (b) hexagonal $y$ walls at 125ºC, and (c) trigonal $y$ walls at 165ºC.

Figure 4-18: Change in domain wall orientation in LiNbO$_3$ with temperature. Hexagonal $y$ walls at (a) 25ºC and (b) 125ºC, and (c) trigonal and hexagonal $y$ walls at 150ºC.
The spontaneous polarization as a function of temperature is given by

\[ P_s^2 = \frac{\alpha_1}{\alpha_2} = \frac{\alpha_0 (T_c - T)}{\alpha_2} \]  

where \( \alpha_1 \) and \( \alpha_2 \) are given in Equation 4-6. Using the spontaneous polarization value at room temperature, \( P_{s,RT} \), the values at higher temperatures can be estimated by
where RT is room temperature ($25^\circ$C) and $T_c$ is the Curie temperature in degrees Centigrade. This expression agrees well with the measured change in the spontaneous polarization for LiNbO$_3$ and LiTaO$_3$ in the temperature range from 25-400$^\circ$C.\textsuperscript{27,28} These variations are shown in Figure 4-21. The polarization decrease is 6\% in LiNbO$_3$ and 14\% in LiTaO$_3$ from 25$^\circ$C to 200$^\circ$C.

![Figure 4-21](image)

**Figure 4-21**: Change in the spontaneous polarization with temperature. Curves calculated from the data of Savage\textsuperscript{27} and Iwasaki.\textsuperscript{28}

The strains $\varepsilon_5$, $\varepsilon_6$, and $\Delta\varepsilon_n$, decrease from the values at room temperature. From 25$^\circ$C to 200$^\circ$C, the decrease for LiNbO$_3$ for $\varepsilon_5$, $\varepsilon_6$, and $\Delta\varepsilon_n$ at the wall center is $\sim$10\%, $\sim$10\%, and $\sim$12\%, respectively. For LiTaO$_3$, the decrease in $\varepsilon_5$, $\varepsilon_6$, and $\Delta\varepsilon_n$ at the wall center is $\sim$20\%, $\sim$5\%, and $\sim$22\%, respectively. However, the forms of the plots vary only in magnitude and keep the same symmetry as shown in Figures 4-9 and 4-10 for all temperature regions.
The free energy, $\Delta F_{DW} = F_{DW}(\theta) - F_{DW}(0^\circ)$, the depolarization energy, $\Delta F_d = F_d(\theta) - F_d(0^\circ)$, and total energy, $\Delta F_{total} = \Delta F_{DW} + \Delta F_d$, are shown as a function of temperature in Figure 4-22 for LiTaO$_3$ and Figure 4-23 for LiNbO$_3$. One can see that all the energies decrease as compared to their room temperature values. As the temperature is changed from 25°C in LiTaO$_3$, the change in variation of the total energy, $\Delta F_{total}$, decreases by 51% by 125°C and 77% by 200°C. In LiNbO$_3$, the change in variation of the total
energy, $\Delta F_{\text{total}}$, decreases by 22% by 125°C and 39% by 200°C. The values of the mean domain wall energy, $F_{\text{total,mean}} = \langle F_{\text{total}}(\theta) \rangle$, is given in Table 4-4.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$F_{\text{total,mean}}$ (in J/m$^3$)</th>
<th>$F_{\text{total,mean}}$ (in J/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>1.9x10$^8$</td>
<td>5.37 x10$^7$</td>
</tr>
<tr>
<td>200°C</td>
<td>1.67x10$^7$</td>
<td>3.95 x10$^7$</td>
</tr>
<tr>
<td>Change</td>
<td>-1.73 x10$^8$</td>
<td>-1.42 x10$^7$</td>
</tr>
</tbody>
</table>

It is clear that as the temperature increases, the free energy contributions decrease primarily as a consequence of the primary order parameter, $P_s$, decreasing. The thermal energy can be estimating using the simple model of $3kT$ energy per atom in a three dimensional solid, where $k$ is Boltzmann’s constant and $T$ is the temperature in Kelvin.\textsuperscript{29} Using the unit cell volumes and number atoms per unit cell (30), the thermal energy for LiNbO$_3$ and LiTaO$_3$ is $\sim$3.9x10$^6$ J/m$^3$ at room temperature and $\sim$6.22 x10$^6$ J/m$^3$ at 200°C. This simple estimation gives the thermal energy as two orders of magnitude lower than the wall energies in Table 4-4.

However, when considering the anisotropy of the wall free energy (deviation of the wall energy with angle, $\Delta F_{\text{total}}$, on the order of $\sim$20-400 J/m$^3$), the thermal energies are much greater. This indicates that there are stabilizing factors not accounted for in the present model. This could be due to domain wall pinning arising from surface effects in a finite sized crystals or from bulk defects, which are not accounted for in the present model. Regardless, it is clear that the domain wall free energy decreases with temperature while the thermal energy increases with temperature. This entropic increase with temperature would favor less faceted domain walls as the temperature increases.
4.6 Discussion

At the onset, it is important to note the limitations of this model. We calculate the energy anisotropy of an infinite domain wall in an infinite block of material. The surfaces are completely neglected which profoundly influence the behavior of ferroelectrics. The proposed domain wall shapes predicted in this model are then taken from the low energy configurations of the infinite wall which neglect the interactions of multiple walls as well as intersections of walls. Contributions from defects are also neglected. Also, at the onset, we made an a priori assumption that it is possible to generate in-plane polarization near a wall. It is mathematically consistent in the scope of this model and allows for the determination of the domain wall orientations. However, it is not evident why these in-plane polarizations should arise from a crystallographic perspective. On crossing the domain wall, the polarization switches direction by changing the magnitude through zero ($P \rightarrow -P$ and vice versa) but not by rotation of the polarization. These in-plane components of the polarization cannot then be generated due to the polarization transition. These in-plane polarizations are intimately linked to the in-plane strains, although how physically both these in-plane components are generated is not clear. Despite these limitations, the model has some predictive value although these limitations cannot explain all the variety of domain wall properties seen in the actual material.

Although differences between lithium niobate and lithium tantalate in the preceding analysis are slight, we find it important to highlight the major differences. With respect to polarizations, each material shares the same symmetry, with charged domains walls for $x$-wall orientations and uncharged walls for $y$-wall orientations.
However, in addition to differences in the magnitudes of the polarization, the sign of each is different with polarization in head-to-head configuration in LiTaO$_3$ with domain wall normals at 30º, 150º, and 270º, and in LiNbO$_3$ at 90º, 210, and 330º. The change in the normal strain, $\Delta \varepsilon_n$, is negative for LiTaO$_3$ and positive for LiNbO$_3$ for all orientations. This normal strain is lowest for $x$-wall orientations in LiTaO$_3$ and $y$-wall orientations in LiNbO$_3$ (see Figure 4-9).

By combining information from the polarizations, strains, and energies of the domain walls as functions of wall angle, comments can be made on preferred orientations. Considering only the free energy contribution as in Equation 4-10 it is found that the minimum energy configuration is for the $x$-wall orientations as shown in Figure 4-14(a) and Figure 4-15(a). However, the $x$-walls are charged domain walls due to head-to-head or tail-to-tail in-plane polarization configurations on crossing the domain wall. This in-plane polarization leads to high depolarizing energy for the $x$-walls, giving the total energy of the domain walls a minimum for $y$-wall orientations for both LiTaO$_3$ and LiNbO$_3$ as shown in Figure 4-14(c) and Figure 4-15(c).

Considering the strain, either domain wall orientation ($x$-wall or $y$-wall) has a zero $\tilde{\varepsilon}_6$ component, which is the shear strain in the $x_t$-$x_n$ plane. However, the $\tilde{\varepsilon}_5$ strain, strain in the $x_n$-$z$ plane, is non-zero for the $x$-walls and contrary in sign for adjacent hexagonal faces and is as pictured in Figure 4-13. The vertices of a hexagon formed by these $x$-walls would therefore be high-energy points, requiring a screw-like defect at that site to accommodate the change in the sign of this shear strain. On the other hand, there are no
such restrictions at the vertices of a hexagonal domain formed by the $y$-walls and lower energy vertices result.

![Diagram of hexagonal and triangular domain walls](image)

Figure 4-24: Two possible sets of triangular $x$-walls. The dotted walls in each case outline the hexagonal $x$-wall configuration for clarity.

The free energy and strain analysis of the crystallographic contributions therefore supports the physical reality of $y$-walls being preferred over $x$-walls in stoichiometric crystals of both lithium niobate and lithium tantalate.

This analysis, however, ignores non-stoichiometric defect complexes present in the crystal structure. These defects drastically change the poling kinetics, and in the case of lithium tantalate, also change the preferred domain wall orientation. In this case, instead of hexagonal $y$-wall domain shapes seen in the stoichiometric crystals, triangular $x$-walls are preferred in congruent composition of Li$_{0.95}$Ta$_{1.01}$O$_3$ at room temperature, as shown in Figure 4-1(a). It is clear that these defects in combination with the previously highlighted differences between the crystals, favor formation of triangular domains formed by one of two sets of $x$-walls, as shown in Figure 4-24. However, neglecting for the moment both the non-stoichiometric defects and the interactions of domain walls, it is
interesting to think about the $x$-wall orientations. Domains with $x$-wall orientations have in-plane polarization normal to the domain wall and non-zero strain, $\tilde{\varepsilon}$, in the $x_n$-$z$ plane. Since the sign of this strain is contrary on adjacent faces (as in Figure 4-13), triangles composed of every other domain wall orientation have the same sign of stress on all adjacent faces eliminating the high strain points at the corners of a hexagon formed by $x$-walls.

Therefore, one can conclude that within this theoretical framework, if the $x$-walls are preferred at all, they should occur as triangles, unless there are screw-like dislocations at the vertices of a hexagon to facilitate a hexagonal domain composed of $x$-walls. Nevertheless, the two sets of $x$-walls are degenerate in energy within the free energy described, and therefore they might be expected to occur with equal probability. However, in congruent crystals, one of these sets (Type I) is clearly preferred over the other (Type II). The presence of non-stoichiometric defects therefore appears to prefer one set over the other. In order to understand this preference, one will have to better understand the nature of these organized point defects and their contribution to the free energy, which is expected to be anisotropic as well. We note that many higher order gradient energy terms exist and in the preceding analysis, we have only considered the lowest order energy terms (Equation 4-9). Two such higher order terms with the proper 3-fold and 6-fold symmetries are given as

$$F_{G3\text{-}fold}(P_{i,j}) = g_2 \left( P_{z,3}^2 \right) + g_3 \left( 6P_{z,x}^2 P_{z,y} - 2P_{z,y}^3 \right)$$  \hspace{1cm} 4-42

$$F_{G6\text{-}fold}(P_{i,j}) = g_2 \left( P_{z,3}^2 \right) + g_6 \left( 2P_{z,y}^6 - 2P_{z,x}^6 + 30P_{z,x}^4 P_{z,y}^2 - 30P_{z,x}^2 P_{z,y}^4 \right)$$  \hspace{1cm} 4-43
where $g_3$ and $g_6$ are the 3-fold and 6-fold gradient coefficients and $P_{a,b}$ indicates the derivative $\frac{\partial P_a}{\partial b}$. It was noted that these terms, when included in time-dependent Ginzburg-Landau (TDGL) simulations, can result in the evolution of hexagonal or trigonal domain shapes. If the 3-fold term dominates, triangular domains evolve. Similarly, hexagonal domains evolve if the 6-fold energy term dominates. One possibility is that the non-stoichiometric point defects influence these higher order energy terms to give rise to symmetries not obvious in the one-dimensional analysis presented in this paper. The presented model is valuable, however, in understanding the intrinsic structure of a domain wall expected without the presence of extrinsic defects, external fields, or higher order energy terms whose coefficients are not known experimentally.

The importance of the defects to the observed domain features is further supported by the temperature effects observed in the LiTaO$_3$ system, where at higher temperatures the y walls are the favored orientation. Aside from the decrease in the magnitude of the strains and energies, no dramatic shift in the curves is observed. This indicates the change in domain shape could be either the influence of thermal energy overcoming the crystal anisotropy energy, or the decrease or disappearance of the influence of the defect dipoles. Following the proposed defect structure as discussed in Chapter 1.2, the defect complex of Nb or Ta antisites ($\text{Nb}_{Li}^{****}$ or $\text{Ta}_{Li}^{****}$) surrounded by lithium vacancies ($\text{V}_{Li}'$) with a charge balance of $4[\text{Nb}_{Li}^{****}] = [\text{V}_{Li}']$. At temperatures above 150ºC, the internal field related to these lithium vacancies has been shown to quickly reorient and assume a low energy configuration. At room temperature (25ºC) however, these defects are frozen and form aggregated defect dipole complexes. One of
the clear correlations therefore is that changes in domain shapes in congruent LiTaO$_3$ with temperature are accompanied by changes in defect complexes with temperature. In congruent LiNbO$_3$, these charges in defects do not appear to be strong enough to change the domain shapes.

4.7 Conclusions

The preferred domain wall shapes of ferroelectrics LiNbO$_3$ and LiTaO$_3$ have been analyzed by taking into account the free energy of the system. A theoretical framework has been developed to analyze the polarizations, strains, and energies associated with a domain wall of arbitrary orientation in both lithium niobate and lithium tantalate. It was found that $x$-walls are charged domain walls due to head-to-head or tail-to-tail in-plane polarizations, maximum strains, and maximum total free energy. In contrast, the $y$-walls show a minimum in strains, zero head-to-head or tail-to-tail in-plane polarization, and a minimum in the total free energy. The $y$-walls are therefore the preferred orientations in stoichiometric compositions and this is supported by experimental observations of such hexagonal domains composed of $y$-walls in the stoichiometric compositions of these materials. This analysis does not directly consider the interaction of multiple domain walls as well as the influence of non-stoichiometric point defects present in the congruent compositions of these materials. These point defects have been proposed to be organized into defect complexes,$^{20}$ and probably have different defect symmetries that lead to triangular domains in congruent lithium tantalate. The exact mechanism of defect-domain wall interactions is presently unknown in these materials and will require understanding.
the structure and symmetry of defects themselves on the atomic scale. It was found that
domains formed at temperatures higher than 165ºC in LiTaO$_3$ formed domains composed
of y-walls favored by the stoichiometric crystals, instead of forming x-walls normally
seen at 25ºC. This indicates that the nature of the influence of the defects on the wall
orientations is changing with temperature.

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Chapter 5

Domain Micro-engineered Devices

5.1 Introduction

The advent of the laser in the early 60’s brought a surge of interest in techniques to modify, deflect, and change the frequency of laser light. These functions are extensively used today in such technological applications such as displays, telecommunications, analog to digital conversion, printing, and data storage devices. Of the many competing technologies, integrated optical devices fabricated in lithium niobate and lithium tantalate offer a versatile solid-state platform to do all of these functions integrated seamlessly in the same device.\(^1\)

The ability to precisely pattern the domain structure in these materials allows for the creation of integrated optical devices. If the domains are patterned into the shape of lenses or prisms, light passing through the crystal can be focused and deflected through the electro-optic effect.\(^2-4\) By patterning these crystals into periodic gratings, the wavelength of light can be converted to different wavelengths through nonlinear optical effects to create new laser sources not readily available (details in Appendix A).\(^5,6\) This chapter will be laid out as follows: electro-optic device theory will be laid out in Section 5.2. Device fabrication will be discussed in Section 5.3 followed by device testing in
Section 5.4. Specific device designs and performance will be discussed in Section 5.5 followed by the conclusions in Section 5.6.

5.2 Device Theory

5.2.1 Electro-optic Effect and Domain Reversed Devices

When a light wave propagates through an optical medium, the oscillating electromagnetic field exerts a polarizing force on all of the electrons comprising the medium. Since the inner electrons of the atoms are tightly bound to the nuclei, the majority of the polarizing effect is exerted on the outer valence electrons. In an isotropic medium the general relation between the polarization, $P$, and the electronic field, $E$, is expressed as a series expansion, namely,

$$P_i = \varepsilon_0 \left( \chi^{(1)}_{ij} E_j + \chi^{(2)}_{ijk} E_j E_k + \chi^{(3)}_{ijkl} E_j E_k E_l + \ldots \right)$$ \hspace{1cm} \text{(5-1)}

where $\chi^{(1)}_{ij}$, $\chi^{(2)}_{ijk}$, $\chi^{(3)}_{ijkl}$ and so on are the nonlinear susceptibility tensors and $\varepsilon_0$ is the permittivity of free space.

The linear electro-optic effect, also called the Pockel’s effect, is a linear change in the indices of refraction (which is the ratio of the speed of light through the medium compared to the speed through a vacuum) with an externally applied static electric field. The linear electro-optic effect exists only in crystals that lack an inversion center. In all materials, the application of an electric field to the crystal causes a change in the
polarization, $P_i$, as given in Equation 5-1. For all even terms in Equation 5-1, changing the direction of one of the electric field, say $E_j \rightarrow -E_j$, changes the polarization, $P_i$, from $\chi^{(2)}_{ijkl} E_j E_k \rightarrow -\chi^{(2)}_{ijkl} E_j E_k$. If the material possesses a center of inversion symmetry, the two induced polarizations directions ($P_i$ and $-P_i$) are equivalent, which means that all components of $\chi^{(2)}_{ijkl}$ vanish. In a non-centrosymmetric material, the generalization of the linear electro-optic effect only is given by

$$P_i = \chi^{(2)}_{ijkl} E_j^0 E_k^0$$

where $E_j^0$ is an optical field and $E_k^0$ is a static DC field. The quadratic susceptibility tensor, $\chi^{(2)}_{ijkl}$, is a 27 element tensor.

The linear electro-optic effect is usually characterized as the electric field dependence of the index ellipsoid. For a plane-polarized wave propagating in any given direction in a uniaxial crystal, there are two allowed polarizations, one along the optical axis and the other perpendicular to it. The total phase velocity of a wave propagating in an arbitrary direction depends on both the velocities of waves polarized along the directions of the principal axes and on the direction of the propagation of the wave. The directions of polarization of the two allowed waves and their phase velocities can be found through the index ellipsoid, a mathematical entity written as

$$\frac{x^2}{n_x^2} + \frac{y^2}{n_y^2} + \frac{z^2}{n_z^2} = 1.$$  

Mathematically, the electro-optic effect can be represented as a deformation of the index ellipsoid due to an external electric field. For a beam propagating along the $z$-axis
(n_x=n_y=n_0 and n_z = n_e) in the presence of an externally applied electric field, the ellipsoid becomes

\[
\begin{align*}
\left[\frac{1}{n_x^2} + \Delta\left(\frac{1}{n_x^2}\right)_{1}\right] x^2 & \left[\frac{1}{n_y^2} + \Delta\left(\frac{1}{n_y^2}\right)_{2}\right] y^2 & \left[\frac{1}{n_z^2} + \Delta\left(\frac{1}{n_z^2}\right)_{3}\right] z^2 & + 2\Delta\left(\frac{1}{n_x^2}\right)_{4} yz & + 2\Delta\left(\frac{1}{n_y^2}\right)_{5} xz & + 2\Delta\left(\frac{1}{n_z^2}\right)_{6} xy & = 1
\end{align*}
\]

where

\[
\Delta\left(\frac{1}{n^2}\right)_{ij} = r_{ij} E_k
\]

and where \( E_k \) is the externally applied electric field and \( r_{ijk} \) are the linear electro-optic coefficients. The electro-optic coefficients are related to \( \chi^{(2)}_{ijk} \) by

\[
\begin{align*}
\begin{bmatrix}
0 & -r_{22} & r_{13} \\
0 & r_{22} & r_{13} \\
0 & 0 & r_{33} \\
0 & r_{51} & 0 \\
r_{51} & 0 & 0 \\
-r_{22} & 0 & 0
\end{bmatrix}
\end{align*}
\]

\[
5-6
\]

Customarily, the 27 elements of the linear electro-optic coefficients are reduced to 18 elements by using matrix notation so \((ij) \neq h\) and \( r_{ijk} \) becomes \( r_{hk} \). Crystal symmetry dictates which coefficients are present and which are zero.

Using this notation, we can express Equation 5-6 for \( \text{LiTaO}_3 \) and \( \text{LiNbO}_3 \) in matrix form as

\[
5-7
\]

If an electric field is applied along the polar \( c \) or 3 axis, the index ellipsoid in Equation 5-4 reduces to
For an extraordinarily polarized light beam traveling along the $x$-axis in a $z$-cut crystal, the index is given as

$$\frac{1}{n_e^*} = \frac{1}{n_e^2} + r_{33} E_3$$

Equation 5-9

implying

$$\Delta \left( \frac{1}{n_e^2} \right) = r_{33} E_3$$

Equation 5-10 can be rewritten in the common form of the electro-optic coefficient as

$$\Delta n_e = -\frac{1}{2} n_e^3 r_{33} E_3.$$ 

Equation 5-11

The change of index given in Equation 5-11 is dependent upon the crystallographic orientation. Both lithium niobate and lithium tantalate have two allowed domain orientations, one pointing in the positive direction along the $c$ crystallographic axis (up domain), or oriented 180° to this direction pointing along the $-c$ crystallographic axis (down domain). The sign of the electro-optic coefficient, $r_{ij}$, depends upon the orientation of these domains, so light propagating through the crystal under an uniform electric field ($+E_z$) will see a decrease in the index of refraction ($n_e - \Delta n_e$) in an up domain and an increase ($n_e + \Delta n_e$) in the down domain orientation, and a change in the index of $2\Delta n_e$ at the domain wall. By patterning domains in these materials into particular shapes, active deflection and shaping of laser beams can be achieved.
Another third rank tensor effect, namely piezoelectricity, was neglected in the above analysis. When a field is applied to electro-optic crystals, a strain resulting from the inverse piezoelectric effect is also present. The generalization of Equation 5-5 becomes

$$\Delta \left( \frac{1}{n^2} \right)_j = P_{ij}^e \cdot S_j + r_{ij} \cdot E_j \tag{5-12}$$

where $P_{ij}^e$ is the elasto-optic coefficient measured under constant electric field and $S_j$ is the strain tensor arising from the piezoelectric response. At high frequencies, inertia prevents the material from straining, and in this case the first term in equation 5-12 is zero, but at lower frequencies the first term in general cannot be ignored. However, the piezoelectric effect in both lithium niobate and lithium tantalate is fairly weak and typically does not influence the index change as long as mechanical resonances are avoided.

### 5.2.2 Electro-optic Lenses

Patterning domains in the shape of lenses can create lens stacks to focus and diverge beams passing through the crystal. If the domains are patterned into a stack of simple thin lenses, the power, $\phi$, of the combined lens is given by

$$\phi = \frac{1}{f} = N \left( \frac{n_2 - n_1}{n_1} \right) \left( \frac{2}{R} \right) = N \left( \frac{2\Delta n_e}{(n_e - \Delta n_e)} \right) \left( \frac{2}{R} \right) \tag{5-13}$$
where N is the number of lenses in the stack, f is the focal length, R is the radius of curvature of the front and back face, and the indices inside and outside the lenses are given by \( n_1 = (n_e - \Delta n_e) \) and \( n_2 = (n_e + \Delta n_e) \), respectively. The lens power is then electrically field tunable. Such a device can be used to modify a beam size, or can be used to collimate a rapidly diverging beam, like the output from a waveguide of fiber optic cable. Yamada and Saitoh first demonstrated a stack of 50 identical domain inverted cylindrical lenses in LiNbO\(_3\) that created a focal point at 8.5 mm at 0.5 kV/mm.\(^2\)

A lens stack composed of 7 identical plano-convex lenses in LiTaO\(_3\) was demonstrated by Kawas which demonstrated a 150 mm focal length change with an applied bias of 3 kV/mm.\(^1\)

![Figure 5-1:](image)

Figure 5-1: (a) a biconvex lenses formed by two hemispherical surfaces with radius of curvature, \( R_c \). (b) a collimating lens stack composed of cylindrical domain inverted lenses collimating input \( \omega_i \) to output \( \omega_o \)

The lens stacks designed in this work are used to collimate a specified input beam size to a specified output beam size. The lens stack is composed of a series of biconvex lenses formed by two cylindrical surfaces. As shown in Figure 5-1, there are three parameters for these lenses: the radius of curvature, \( R_c \), the width, \( D \), and thickness, \( t \). To minimize the total length of the scanner stack, the width of the lenses should be made
just larger than the waist of the focusing beam at any point along the stack length. The width of the first lens is given by

\[ D = 2\delta \omega_o \left[ 1 + \left( \frac{\lambda s}{\pi \omega_o^2} \right)^2 \right]^{1/2} \]  

where \( \omega_o \) is the waist at the output of the waveguide, \( s \) is the distance from waist to the first lens, \( \lambda \) is the wavelength of light, and \( \delta \sim 1.2 \) is a design parameter which specifies how much larger the width of the lens is compared to \( 1/e^2 \) waist of the beam. From the dimensions of the first lens, subsequent lens diameters are determined by the ABCD transfer matrix methods to compute the beam diameter as it propagates through the lens stack.\(^{11,12}\)

### 5.2.3 Electro-optic Scanners

Solid-state electro-optic deflectors based in domain inverted ferroelectrics have several advantages over mechanical and other systems including the non-inertial scanning, small device sizes, and high operating speeds. These analog deflectors allow control over the angular deflection of a laser beam. The first concept of electro-optically controlled deflectors was given by Lopseitch in 1968.\(^{13}\) The designs were first realized beginning in the early 1970’s in polished and stacked ferroelectric crystals arranged with alternating polarization directions,\(^{14}\) or using single crystals with prism electrode geometries.\(^{15-17}\) These initial devices generally has low deflection angles typically on the order of 0.1-1°/kV.\(^{18}\) Domain inverted devices were first realized in waveguide
geometries using diffusion induced near surface polarization in LiNbO$_3$ in 1994 with a deflection angle of 0.45° and deflection of 0.46°/kV.\textsuperscript{19} Electrically poled domain engineered devices first appeared in 1996 by Yamada et al. fabricated in LiNbO$_3$ capable of 5° scanning angle.\textsuperscript{2} This design was improved upon by Fang et al. which demonstrated a horn shaped scanner capable of 5° scanning angle and deflection of 5.2°/kV.\textsuperscript{20}

![BPM simulation of different electro-optic scanner designs in LiTaO$_3$: (a) rectangular, (b) horn-shaped, and (c) cascaded horn-shaped. Deflection angles (one way) are 5.25°, 8.45°, and 14.77° respectively. Each device has the same length (15 mm), operating field (15 kV/mm), interface number (10), and beam size (100 µm). Domain orientation inside the triangles is 180° opposite to that of the surrounding areas. All dimensions are in mm.](image)

The most basic geometry for deflecting light is by use of an optical prism. In the paraxial approximation, where the deflection angles are small, one can use a series of prisms in sequence, each prism successively deflecting the light beam further and further
from the optical axis. The simplest design is a *rectangular scanner*, first proposed by Lotspeich in 1968, which consists of \( N \) identical prisms placed in sequence, each with a base \( l \) and height \( W \), such that the total length of the rectangular scanner is \( L = Nl \) and width is \( W \). Such a scanner is shown in Figure 5-2(a) as simulated by the beam propagation method (BPM), which is an iterative simulation technique for structures which have small index variations (<0.3).\(^{21,22}\) For details of the beam propagation method see Appendix D.1. For all the simulations in this chapter unless otherwise stated, the input light is polarized in the extraordinary direction, the index of refraction for \( \text{LiTaO}_3 \), \( n_e \), is taken as 2.1818, and the \( r_{33} \) value for \( \text{LiTaO}_3 \) is taken as 30.5 pm/V for light at 632.8 nm from tabulated data.\(^{23,24}\)

The total deflection angle, \( \theta_{\text{int}} \), at the output for a light beam incident along the axis, \( L \), of the rectangular scanner is given by

\[
\theta_{\text{int}} = \frac{\Delta n \ L}{n \ W} \tag{5-15}
\]

where \( n \) is the index of refraction of the material, and \( \Delta n \) is the index difference between the prism and the surrounding matrix, where \( \Delta n < n \). If these prisms are fabricated in an electro-optic medium, the \( \Delta n \) is electric field tunable and therefore results in an electric field controlled deflection angle, \( \theta_{\text{int}} \). When the deflected light beam exits the electro-optic material (index, \( n \)) into air (index, 1), the output deflection is enhanced further by Snell’s law as

\[
\theta_{\text{ext}} = \sin^{-1}\left[n \sin(\theta_{\text{int}})\right].
\]

Such rectangular scanners have been demonstrated in \( \text{LiTaO}_3 \).\(^{3,4,19}\) Equation 5-15 shows that the longer the device, \( L \), and narrower the width, \( W \), the higher the deflection angle, \( \theta_{\text{int}} \). However, closer examination illustrates the competing effects of design
parameters. The width, $W$, of the scanner should be as small as possible to increase the deflection angle, but large enough to completely enclose the trajectory of the beam inside the device. Noting that the pivot point for deflection in a rectangular scanner lies at the center of the rectangle, the maximum deflection angle is limited to

$$\theta_{\text{int, max}} = \tan^{-1} \left( \frac{(W - 2\omega)}{L} \right)$$

where $\omega$ is the radius of the light beam at the output of the scanner. This second constraint reflects that the maximum deflection angle, $\theta_{\text{max}}$, for a rectangular scanner is proportional to $W/L$, which therefore imposes restrictions on reducing the width and simultaneously increasing the length indefinitely for achieving higher deflection.

The deflection angle could be enhanced if the width was decreased to be as small as permitted by the beam diameter at the input, but was gradually increased to just accommodate the trajectory of the beam. This is the so-called horn-shaped scanner and is shown in Figure 5-2(b). Assuming that the length of the scanner is large relative to the width ($L \gg W$) and the maximum change in the index is small compared to $n_e$ ($\Delta n \ll n_e$), the lateral position of the beam $x(z)$ from the optic axis is determined as a function of propagation distance $z$ as

$$\frac{d^2x}{dz^2} = \frac{\Delta n}{n_e} \frac{1}{W(z)}$$  \hfill 5-16

where the scanner width $W(z)$ for a Gaussian beam is given as

$$\frac{W(z)}{2} = x(z) + w_o \sqrt{1 + \left( \frac{\lambda_o(z - z_o)}{\pi n_e w_o^2} \right)^2}$$  \hfill 5-17
where $\lambda_o$ is the free space wavelength, $\omega_o$ is the beam waist, and $z_o$ is the position of the beam waist.$^{20}$

Although the horn shaped scanner significantly improves deflection angles, it too has limitations on beam deflection. The amount of deflection becomes diminished near the end of the scanner, as shown in Figure 5-3(a) and (b) which shows the displacement and its derivative, respectively, of the beam in the horn-shaped scanner in Figure 5-2. The derivative curve, which shows the change in deflection angle per length, flattens out near the end of the scanner.

![Figure 5-3](image_url): Performance of the horn-shaped scanner in Figure 5-2(b) showing (a) the displacement and (b) derivative of the displacement.

To further increase the deflection angle for a given length, a new device concept called a *cascaded scanner* has been designed. This design takes advantage of the efficient deflection near the beginning of a horn shaped scanner where the width of the scanner is narrow. The cascaded scanner consists of a series of individual scanners...
aligned so that subsequent scanners in the stack are aligned to the previous scanner’s peak deflection. Each subsequent scanner is fabricated in the same piece of electro-optic crystal but operated with a different power supply. A schematic of a 2-stage cascaded scanner is shown in Figure 5-2(c). At peak operating field, the first stage scanner first deflects the beam along a given direction. A second set of scanners is oriented along the maximum deflection direction of the first stage scanner, so that when the first stage is at its maximum deflection, a field is applied to the second scanner which further deflects the beam. By cascading a series of horn-shaped scanners such that each successive scanner builds upon the deflection of the previous scanner, one can effectively increase the scan angle arbitrarily. The advantage of this design is twofold. First, additional stages can be appended until a final target deflection is achieved, or second, the field requirements can be reduced for a given required scan angle (by increasing the number of stages). The trade off is in more complex drive controllers, as each scanner must work in tandem with the others.
A comparison of the three scanner designs is shown in Figure 5-2. For the same scanner length (15 mm), number of interfaces (10), input beam size (100 µm), and operating field (15 kV/mm), the rectangular, horn, and cascaded scanners deflect 5.25º, 8.45º, and 14.77º, respectively. The scan angle is increased by a factor of 2.8 by going from a rectangular to a cascaded scanner. A comparison of the beam trajectories and derivatives is shown in Figure 5-4.

Scanners are characterized in terms of the total angular displacement called the scan angle. However, this value can be manipulated by focusing optics. A true measure of a deflector is given by the number of resolvable spots in the far field, which is given by

\[ N = \frac{\theta_{tot}}{2\theta_{div}} \]
where \( \theta_{\text{tot}} \) is the total deflection angle (peak-to-peak) and \( \theta_{\text{div}} \) is the far-field divergence angle given by

\[
\theta_{\text{div}} = \frac{\lambda}{\pi \omega_0}
\]  \hspace{1cm} 5-19

where \( \lambda \) is the wavelength of light and \( \omega_0 \) is the waist at the focal point of the beam.

### 5.2.4 Beamlet Scanner Device

The ultimate limitation of the electro-optic beam scanners as detailed in the previous section is the strict requirements on beam waist – both in the vertical (thickness) direction and in the plane of the device – limited to 50-500 \( \mu \text{m} \) for achieving reasonable steering angles. While thicker crystals are desired to increase the aperture size, this leads to higher operating voltages for a given operating field (typically \( \sim 2-15 \text{ kV/mm} \)). In the plane of the device, the deflection angle is inversely related to the width of the domain prisms, which leads to a tradeoff between aperture size and deflection angle.

While this is not a problem for small, low power beams, larger beam sizes used in military and sensing applications cannot be adequately deflected by these scanner designs. Furthermore, focused high power density beams will exceed the damage threshold of the crystal. What is needed, therefore, is a way to increase the aperture size without degrading the scan angle or increasing the voltage requirements.
The method for steering wide aperture beams in the device plane is to split the beam into many smaller beamlets that are scanned separately by an array of individual prism scanners as shown in Figure 5-5. Each individual channel is deflected separately, and each deflected beam is recombined to form a single large beam in the far-field. The path length of each of the beamlets through the device is designed to be exactly equal, resulting in equal relative phase shifts upon deflection. Any small differences in phase can be adjusted using an electro-optic phase shifter for each beamlet. This approach is similar to the phased array scanning where the beam is separated and delayed in the individual channels so that resultant beam has a shifted phase front.\textsuperscript{26-28}

Each individual scanner can be composed of any of the scanner design discussed in the previous section, the only requirement being that each beamlet channel must not overlap any other channel. This limits the application of the horn-shaped scanner due to
the increasing scanner width. A rectangular or cascaded rectangular scanner can be
designed for the appropriate deflection.

To accommodate wide beams in the thickness direction, several separate domain
patterned crystals can be stacked in a head to head fashion, so that in each layer the
spontaneous polarization direction is opposite of that in features just below and above it.
A bias can be applied to the properly electroded shared interface, with bias and ground on
alternating layers. This allows a much thicker beam to be scanner without an increased
voltage.

The convergence of the individual beamlets to form a coherent beam of larger
diameter in the far field for arrays of polished prism defectors and phased optical
antennas has been shown previously.\textsuperscript{14,29} The exact pattern in the far field is shown to be
a function of the beamlet number, spacing, and channel width. The phases of the
beamlets converging to an angle $\theta$ (in the far field) from two adjacent channels separated
by $D$ are normally shifted by the amount $kD\theta$ where $k$ is the wave number. This gives rise
to an interference pattern and a modulation of the intensity. However, the component
waves can be brought back into phase by integrating small phase shifting electro-optic
patches prior to each steering channel as shown in Figure 5-5.
5.3 Device Fabrication

5.3.1 Micro-Pattered Devices

The fabrication of electro-optic devices starts with commercially available z-cut congruent lithium niobate or lithium tantalate single crystals of thickness typically between 0.3 and 0.5 mm thick. After dicing to the appropriate dimensions, a photoresist pattern of the device is defined on the \( +z \) face of the crystal surface with conventional contact photolithography as shown in Figure 5-6(a). This pattern is then over-sputtered with metal (Ta or Cr/Au) and the underlying photoresist dissolved away, leaving a metal pattern on the top surface.
A photoresist coating (Shipley 1811 photoresist) is then deposited uniformly on the surface of the sample, across both the electrode and crystal features and hard baked (box oven 120ºC for 2 hours) to remove any solvents. This layer has been found to improve selectivity of the domain reversal process by inhibiting domain reversal beyond electrode edges by suppressing surface conduction. The positive electrode is the Ta-film pattern on the +z face, while a uniform water electrode is used on the -z face as the ground. For domain inversion, ~21kV/mm electric field is applied across the crystal while the transient current is monitored and domain nucleation and growth is monitored in situ. The details of the poling method are in Chapter 2.2.

After poling, the device is then annealed at temperatures greater than 200ºC for several hours to remove the index and strain distribution caused by the domain inversion
224

process. This leads to the relaxation of the frustrated defects dipoles in the material. After slowly cooling to room temperature to avoid the creation of microdomains through the pyroelectric effect, the crystal is end polished by hand down to 0.05 μm finish using diamond media and colloidal silica. For the electro-optic devices, uniform electrodes are then sputtered on both faces and contact to the electrode pads is made by copper tape. The entire device with the exception of input and output faces is then encapsulated in silicone to prevent arcing across the edges of the device.

5.3.2 Crystal Ion Sliced Electro-optic Devices

Recently, an ion-implantation-based technique called crystal ion slicing (CIS), has been reported for making thin slices of ferroelectric materials including lithium niobate. CIS allows a free standing micron-thick single crystal film to be fabricated from a bulk crystal. In CIS, ion implantation is used to define a damaged sacrificial layer several microns below the surface. This sacrificial layer is then etched away by immersion in a dilute hydrofluoric acid solution. During the etching process there is lithium diffusion out of the sample which is replaced by fluorine ions. However, despite this leaching, the CIS films have been measured to have the same index of refraction, electro-optic coefficients, and second order non-linearity. The large etch selectivity of the damage layer over the rest of the crystal allows for the lifting off of a thin film, whose thickness is well controlled by the implantation energy. By crystal ion
slicing of domain-engineered devices fabricated on wafers, operating voltages can be significantly reduced in the device.

This bulk device with patterned domain is then ion implanted with a dose of $5 \times 10^{16}$ ions/cm$^2$ He$^+$ ions at an energy of 3.8 MeV with the temperature of the sample kept below $12^\circ$C during implantation. This was carried out at the Oak Ridge National Lab Ion Implantation facility. The input faces of the implanted devices are then end polished to 0.25 μm finish. After polishing, rapid thermal annealing at $450^\circ$C for 40 s in flowing forming gas (5% H$_2$, 95% Ar) was used to enhance the etch selectivity between sacrificial layer and the rest of the sample. The device was then encapsulated in an HF resistant wax, which was used to protect the film’s top surface and polished ends. Finally the device is immersed in dilute HF (10%) until it is completely detached.
An intermediate annealing step is required to improve the quality of the films and to decrease the lift off time. This is believed to occur by promoting the diffusion of helium into the implantation induced micro voids and the buildup of an internal pressure in the sacrificial layer.\(^{40}\) The annealing conditions were optimized by testing small pieces (1.5 mm x 5 mm) of LiNbO\(_3\) implanted at the same energy for various conditions. In general, samples with rapid thermal annealing temperatures lower than 450ºC took longer to lift off as shown in Figure 5-7(a). For example, the lift-off times were 6 hours

**Figure 5-7:** (a) Lift off time increased for higher processing temperatures. (b) Etch depth was found to scale linearly with exposure to acid

**Figure 5-8:** AFM images of lift off surface. (a) 400ºC in N\(_2\) lift off for 16 hours with etch depth of 50.52 nm. (b) 450ºC in forming gas lift off for 6 hours with etch depth of 20.31 nm. Etch lines in (a) and (b) are somewhat aligned with the y crystallographic axes.
at 450°C, ~12 hours for 400°C, and >24 hours with no annealing. Annealing temperatures higher than 450°C tended to cause spalling and cracking of the CIS layer. Other annealing atmospheres, such as Ar, N₂ and air, caused longer lift off times. The liftoff face showed etch lines that were characterized by contact force microscopy as shown in Figure 5-8. The optimal lift conditions yielded an average etch depth of 20.3 ± 2.4 nm, which was much better than the >40 nm for other processing conditions. The density of the etch lines was found to have no clear relation between process atmosphere, temperature, or exposure time to acid. This annealing step in the liftoff process using the optimized conditions (40 second anneal at 450°C in forming gas), allows relatively large sample areas (2 mm x 10 mm) to be lifted off in ~16 hours.

Figure 5-9: (a) A side view of device during liftoff where slice is to the left and bulk crystal is to the right, and (b) shows a top view of a 10 mm x 2 mm x 6 µm CIS electro-optic scanner on z-cut LiNbO₃. The triangles visible in (b) are oppositely oriented domain states with a base of 1000 µm and height of 775 µm.

Figure 5-9(a) shows the device during the lift off process, where the CIS piece is in the process of detaching itself from the bulk piece on the right. Figure 5-9 shows an optical micrograph of the successfully lifted off device. The domain structures patterned in the crystal before the implantation, annealing, and lift off steps are still present in the crystal. Figure 5-9(b) also shows some of the inherent difficulties in lifting off large size devices using etchant. Notice the large chip out of the input face and damage to the
output face. If these chips are in the entrance or exit path for the scanner channel, no light could be coupled. Additionally, the lifted off scanners tended to show curvature in the plane. This curvature caused cracking and breaking of the sample in subsequent processing steps, like electrode coating and mounting.

5.4 Device Testing

The device is placed in the path of a He-Ne laser with a wavelength of 632.8 nm as shown in Figure 5-10. A polarizer selects either the extraordinary or ordinary beam. Focusing lenses are placed in the path of the beam so that appropriate beam waist in the horizontal plane is achieved and the beam passes through the wafer in the vertical plane without being clipped by the input faces. A CCD camera placed at the output of the device is used to monitor the intensity profile of the beam.

The scanning angle was determined as a function of the applied voltage using the testing apparatus shown in Figure 5-10. To determine the deflection angle of the scanner, the change in the position of the centroid of the Gaussian intensity distribution in the horizontal plane of the camera is found at two distances from the output edge of the device, $D_1$ and $D_2$. For a centroid displacement of $\Delta x_1$ at the $D_1$ camera position and $\Delta x_2$ at the $D_2$ camera position, the deflection angle is given by $\theta = \tan^{-1} (\Delta x_2 - \Delta x_1)/(D_2 - D_1)$. The deflection angle is measured as a function of the applied voltage and at different input polarizations. The number of resolvable spots is the angular scan range divided by the angular diffraction spread.
To characterize the performance of the lens stack, the location and diameter of the input beam is first characterized by recording a series of images over a range of distances from the waist to exactly determine the input beam parameters. The lens stack is then inserted in the beam in a similar manner to Figure 5-11. A series of images is obtained for a range of distances between the input waist and the device entrance face, \( d_i \), for a given output distance, \( d_o \), as shown in Figure 5-11. The measured output waists as a function of applied bias can then be fit to device geometry by using ABCD transfer matrix methods.\(^{11,12}\) The transfer matrix for the entire device, \( T \), is calculated as

\[
T = \begin{pmatrix} 1 & d_i \\ 0 & 1 \end{pmatrix} M \begin{pmatrix} 1 & d_o \\ 0 & 1 \end{pmatrix}
\]  

\(^{5-20}\)
where $d_1$ and $d_2$ are the distance from the entrance face to the first lens and last lens and output face, $n$ and $\Delta n$ are the index and change of the index of refraction, $N$ is the total number of lenses in the stack, and $R_k$ is the radius of curvature of the $k^{th}$ lens. From this the waist at the output of the device, $\omega_o$ can be calculated using

$$ q_i = i \frac{\pi \omega_o^2 n}{\lambda} \quad 5-22 $$

$$ q_f = \frac{T_{11}q_i + T_{12}}{T_{21}q_i + T_{22}} \quad 5-23 $$

$$ \omega^2 = \omega_o^2 \left[ 1 + \left( \frac{\text{real}(q_f)}{\text{imag}(q_f)} \right)^2 \right] \quad 5-24 $$

where $q_i$ is the Gaussian parameter, $q$, at the input to the device, $q_f$ is the $q$ after the lens stack, $T_{ij}$ is the transfer matrix given in Equation 5-20, $\omega_o$ is the initial beam radius at a distance $d_i$ from the input face, $\lambda$ is the wavelength of the light, and $n$ is the index of the incident media. The terms $\text{real}(q_f)$ and $\text{imag}(q_f)$ refer to the real and imaginary parts of the Gaussian parameter $q_f$. 

\[ M = \begin{pmatrix} 1 & d_1 \\ 0 & 1 \end{pmatrix} \prod_{k=1}^{N} \begin{pmatrix} 1 & 0 \\ \frac{n - \Delta n}{R_k \Delta n} & 1 \end{pmatrix} \begin{pmatrix} 1 & R_k \frac{2n - \Delta n}{R_k \Delta n} & 0 \\ \frac{\Delta n - n}{R_k \Delta n} & 1 \end{pmatrix} \begin{pmatrix} 1 & d_2 \\ 0 & 1 \end{pmatrix} \quad 5-21 \]
5.5 Device Design and Performance

5.5.1 Integrated Lens and Horn-Shaped Scanners

An integrated device composed of a stack of bi-convex parabolic lenses and a horn-shaped scanner was fabricated in a single piece of lithium tantalate crystal and is shown in Figure 5-12 (a). The lens component is designed to collimate and focus light from a point-source, waveguide, or fiber. The scanner section is designed to scan the output beam in one dimension.

Figure 5-12: (a) Integrated lens and scanner device below penny for scale. Left and right rectangles on device are the lens and scanner, respectively. (b) and (c) are BPM simulations of extraordinary polarized light at 632.8 nm propagating through the structure. (b) shows the fabricated lens stack at 8 kV/mm collimating a point source to an output beam of 1/e² beam radius of 50 µm and (c) the fabricated scanner stack at 15 kV/mm deflecting the beam 8.1° from the optic axis. The polarization direction of the crystal is perpendicular to the page, with the area enclosed by the lenses or triangles opposite in spontaneous polarization ($P_s$) than the rest of the device.
The stack consists of 32 bi-convex lenses shown in a beam-propagation simulation (BPM) in Figure 5-12(b). It shows a diverging 4 µm radius input beam, the output from a typical fiber optic cable, collimated to a 50 µm radius beam for input to the scanner section of the device with an applied field of 8 kV/mm. Detailed dimensions of the individual lenses (see Figure 5-1) are given in Table 5-1.

Table 5-1: Dimensions of Lenslets in the Collimating Lens Stack

<table>
<thead>
<tr>
<th>Lens Number</th>
<th>D/2 (µm)</th>
<th>Lens Number</th>
<th>D/2 (µm)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>50.0</td>
<td>17</td>
<td>65.8</td>
</tr>
<tr>
<td>2</td>
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<tr>
<td>5</td>
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<td>21</td>
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</tr>
<tr>
<td>6</td>
<td>50.0</td>
<td>22</td>
<td>74.8</td>
</tr>
<tr>
<td>7</td>
<td>50.0</td>
<td>23</td>
<td>76.0</td>
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<td>8</td>
<td>50.0</td>
<td>24</td>
<td>77.0</td>
</tr>
<tr>
<td>9</td>
<td>50.0</td>
<td>25</td>
<td>77.8</td>
</tr>
<tr>
<td>10</td>
<td>50.0</td>
<td>26</td>
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<tr>
<td>11</td>
<td>50.9</td>
<td>27</td>
<td>78.7</td>
</tr>
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<td>28</td>
<td>78.8</td>
</tr>
<tr>
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<td>56.2</td>
<td>29</td>
<td>78.8</td>
</tr>
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<td>14</td>
<td>58.7</td>
<td>30</td>
<td>78.8</td>
</tr>
<tr>
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</tr>
<tr>
<td>16</td>
<td>63.5</td>
<td>32</td>
<td>78.8</td>
</tr>
</tbody>
</table>

Images of the focused beam are shown in Figure 5-13 with the performance of the lens shown in Figure 5-14(a). Notice for a fixed relative position between the beam waist and the device input face, different applied voltages focus the output beam.
This scanner is designed for an input beam of $<150 \mu m$ diameter and operates at $\pm 15 \text{ kV/mm}$, which translates to $\pm 4.29 \text{ kV}$ across the 286 $\mu m$ thick z-cut LiTaO$_3$ crystal. The designed scanner had 10 prism sections and is shown in Figure 5-12(c). The input and output widths are 250 and 1450 $\mu m$, respectively, and the total length of the device is 15 mm.

Figure 5-13: Images of the focused beam for applied voltage of (a) 0 V, (b) 1.2 kV, (c) 2.4 kV.

Figure 5-14: (a) The beam waist for different voltages as a function of different device positions relative to the laser focal point along with best fits from ABCD theory. (b) Deflection as a function of applied voltage for ordinary and extraordinary polarized input light. The circles are measured data and the straight line is a Beam Propagation Method prediction.
The scanning angle was determined as a function of applied voltage using the testing method pictured in Figure 5-10. The deflection angle is measured as a function of applied voltage and different input polarizations and is plotted in Figure 5-14(b). For extraordinary polarized input light (parallel to the ferroelectric polarization direction), the measured voltage dependence of the deflection angle is 1.845°/kV and the maximum deflection angle is ±7.3° (a total of 14.6°) at ±4.05 kV. A theoretical estimate as determined by BPM simulation is plotted on the same graph. Simulation gives a voltage dependence of the deflection angle 2.01°/kV with a maximum deflection of ±8.1° (total 16.2°) at ±4.05 kV. The measured values are ~0.17°/kV lower than the expected performance from BPM. For ordinary polarized incident light (perpendicular to ferroelectric polarization direction), the measured voltage dependence of the deflection angle is 0.503°/kV with a maximum deflection of ±2.04° (a total of 4.07°) at ±4.05 kV. The BPM simulations for ordinary light ($r_{13} = 8.4$ pm/V and $n_o = 2.1763$ at 632.8 nm) shows a deflection angle voltage dependence of 0.60°/kV with a maximum deflection of ±2.43° (total 4.86°) at ±4.05 kV. The experimentally measured values are 0.045°/kV lower than expected from BPM simulations. This discrepancy is most likely due to imperfect hand polishing of the input and output faces resulting in rounding and skewing of these faces. The estimated curvature of the output face should have a radius of curvature of ~16.7 cm (about 10 times the length of the device) to explain the discrepancy between the measured and predicted scan performance.
A multiple-exposure image of the beam profile is shown in Figure 5-15 for extraordinary polarized light. The voltage for each exposure was varied incrementally from –3820 to +3820V such that each profile was separated by approximately one spot diameter with a maximum angular deflection of approximately 13.75º. One observes a total of 17 resolvable spots which amounts to 2.23 spots/kV. Theoretical estimations based on BPM simulation of total number of resolvable spots give 18.49 spots or 2.43 spots/kV. This in practice translates to only 17 full spots with the rest as partial spots, about ~0.75 spots on either side.

While the intrinsic response of the electro-optic effect is known to be in the GHz range\(^{41,42}\), the ultimate speed performance of the device is limited by the large voltage requirements (neglecting piezoelectric resonances). When driven at high frequencies, these devices are essentially parallel plate capacitors with current requirements (when driven by a sine wave) given by

\[
i = \omega C_\omega V_{\text{peak}} \cos(\omega t) \tag{5-25}\]

where \(C_\omega\) is the capacitance of the device at the drive frequency, \(V_{\text{peak}}\) is the peak voltage applied to the device, and \(\omega\) is the angular frequency of the applied signal. Notice the \(\omega\) term scales the required current linearly with frequency, which makes driving these
devices at high frequency primarily a driver issue. The capacitance of the horn shaped section of the scanner was measured using an HP4198 impedance analyzer and measured to be 27.5 nF at 1 kHz. The testing power supply has a 2 µA current limit. Using Equation 5-25, the calculated maximum frequency using this power supply is 0.58 kHz driven at 4000 V and 4.66 kHz for 500 V. The 4.66 kHz frequency is very close to experimentally observed maximum frequency of 4.42 kHz, where increasing the driving frequency reduces the scan angle.

The propagation losses of this device were not directly measured. However, estimation of the losses can be made by considering the amount of reflection at each interface in the device, where reflection from one interface is given by

$$R = \frac{\cos\theta - \sqrt{\left(\frac{n_1}{n_2}\right)^2 - \sin^2\theta}}{\cos\theta + \sqrt{\left(\frac{n_1}{n_2}\right)^2 - \sin^2\theta}}$$  \hspace{1cm} 5-26

where $n_1$ and $n_2$ are the index of original and new medium, respectively, and $\theta$ is the normal angle with respect to the boundary. Most reflection losses occur at the input and output faces with a ~13% reflection loss at each interface. The 30 interfaces in the scanner device (assumed to be perfectly smooth) only have a calculated reflection loss of $1.2 \times 10^6$ at each interface even at full bias ($\Delta n$ is small). The theoretical loss for this device is therefore only 1.3 dB and could be reduced further with anti-reflection coatings. The actual losses are most likely higher due to scattering losses at the domain walls (see Figure 2-15). However, scattering losses from the domain walls are very likely a small amount considering the line scan in Figure 5-15, which shows the intensity of the
transmitted beam as a function of applied bias, does not measurably decrease as the operating bias is increased.

5.5.2 Cascaded Horn Shaped Electro-optic Scanner

A 2 stage cascaded electro-optic scanner has been designed and fabricated in a single piece of LiTaO$_3$. The device layout and BPM simulation is pictured in Figure 5-16. It is designed for an input beam of $<70$ µm diameter and operating field of $\pm 11$ kV/mm, which translates to ±1.1 kV across the 100 µm thick $z$-cut LiTaO$_3$ crystal used in this study. The device shown consists of three scanners, A, B, and C. Scanner A forms the stage-1, and operates under an oscillating field of $\pm 11$ kV/mm, and deflects the beam through a maximum angle of ±6.6°. The second stage can further deflect the beam by an additional ±6.4°. Since at any time instant scanners A, A+B, or A+C handle the beam, scanners B and C can have the same electrode and voltage supply. Thus scanner A would form stage-1 and scanners B and C would form stage-2.
The scanner was designed to work in conjunction with a high-speed voltage supply with peak output voltages of 1.1 kV. This operational field (11 kV/mm) is well below the coercive fields of ~21 kV/mm for congruent z-cut LiTaO$_3$ crystals that would reverse and destroy the domain pattern. Figure 5-17(a) shows how the first and second stage scanners would work in tandem. Peak deflection is reached when both the first and the second scanners are at peak voltages. For continuous scanning, one needs a voltage driver that seamlessly applies the appropriate voltage waveforms to both stages. A specially designed arbitrary waveform signal generation based in a field programmable gate array (FPGA) which outputs to high voltage amplifiers was built in collaboration with the University of Delaware.  

Figure 5-16: A BPM simulation of the multi-section scanner showing peak deflection from both scanners at 11 kV/mm. The two large rectangles represent the electrode pads. The peak deflection is 13.04° in one direction, 26.08° total.
The deflection angle is measured as a function of applied voltage and is plotted in Figure 5-17 (b). For extraordinary polarized input light (along the ferroelectric polarization direction), the measured voltage dependence of the deflection angle is 5.84 °/kV for scanner 1 and 5.7°/kV for scanner 2 and the maximum deflection angle for the device is ±12.7° (a total of 25.4°) with ±1.1 kV on both scanner stages. A theoretical estimate as determined by the BPM simulation is plotted on the same graph. The simulation predicts a voltage dependence of the deflection angle is 104.7 mrad/kV for scanner 1 and 102.2 mrad/kV for scanner 2 with a maximum total deflection of ±13.04° (total 26.8°) for peak fields on both scanners. The maximum number of resolvable spots for this device was estimated as 29.75 spots at maximum total deflection. Finally, the scanner operation was also tested up to 5 kHz. A picture of the scanned beam projected

Figure 5-17: (a) The driving waveforms for optimal operation. The bottom trace shows the voltage placed on the stage 1 (scanner A). While at peak voltage, the voltage for stage 2, scanners B,C (middle trace) is ramped. The top trace shows the deflection of the beam. (b) Performance of high angle scanner. The upper row of voltages refers to the first stage voltage and the lower row refers to the second stage voltage. The inset shows the high-speed scan (5 kHz) showing full 25.4°. The beam is projected on a flat screen and imaged from the side. The two vertical lines indicate different scan areas.
on a screen is shown in the inset of (b). No noticeable degradation of the scan angle was observed, and higher scan speeds should be possible with higher power drivers.

The reason for the discrepancy of 1.2° between the measured (25.4°) and predicted (26.8°) values of the deflection is mostly accounted for by the fact that the maximum applied field across any scanner was $1.1\text{kV/(104±1\text{μm})}=10.57±0.1\text{kV/mm}$, instead of the design specification of 11 kV/mm. This would reduce the overall scan angle by 0.8-1.28°. This is also the primary reason why the beam coupling from the first to the second stages of the scanner is not optimal with our 1.1kV driver, resulting in the scan brightness being slightly less intense for the B and C arms of the scanner as compared to the central arm, A (see inset in Figure 5-17(b)).

5.5.3 Beamlet Devices

A single 5-stage cascaded rectangular scanner device with 13 beamlet channels was designed and fabricated to deflect a 1064 nm IR laser beam a total of 10° as proof of concept. The input beam was divided into 13 separate channels separated by 0.5 mm by an array of cylindrical lenses of 50 mm focal length. Shown in Figure 5-18 is a BPM simulation of the designed device with 5 kV/mm applied to each scanner element with the index of refraction, $n_e$, taken as 2.1403, and the $r_{33}$ value is taken as 29.14 pm/V for light at 1064 nm from tabulated data. Specification of each of the individual scanners is given in Table 5-2. Notice the width of each scanner decreases slightly to accommodate the width of the focused beam in each scanner channel.
These beamlets are focused into a single EO device and were steered using an applied voltage of $V_{\text{max}} \sim 1.51$ kV across the crystal. This corresponds to a field of 5.39 kV/mm. This cascaded scanner requires a synchronized bias supply needed for a continuous steering operation of the laser beam, since the bias fields should be applied incrementally, with each successive scanner stage ramped from 0 bias to peak bias only after the previous stage is at full bias (see previous section). A 5 stage compact programmable voltage driver was designed and fabricated in a previous study and detailed in the literature, but was unavailable for this study.\(^{43}\) However, the device was

Figure 5-18: BPM simulation of 5-stage 13-beamlet scanner showing full deflection at 5 kV/mm. The polarization direction of the crystal is perpendicular to the page, with the area enclosed by the triangles opposite in spontaneous polarization ($P_s$) than the rest of the device. The peak deflection is 10.3° in one direction.

Table 5-2: Specification of Beamlet Scanner

<table>
<thead>
<tr>
<th></th>
<th>Stage 1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Width, $D$ (mm)</td>
<td>0.444</td>
<td>0.410</td>
<td>0.383</td>
<td>0.362</td>
<td>0.348</td>
<td>8.31</td>
</tr>
<tr>
<td>Length, $L$ (mm)</td>
<td>11.16</td>
<td>10.209</td>
<td>9.45</td>
<td>8.852</td>
<td>8.41</td>
<td>50</td>
</tr>
<tr>
<td>Field (kV/mm)</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Internal deflection (°)</td>
<td>0.69</td>
<td>0.95</td>
<td>0.94</td>
<td>0.93</td>
<td>0.92</td>
<td>4.72</td>
</tr>
<tr>
<td>External deflection (°)</td>
<td>2.06</td>
<td>2.04</td>
<td>2.02</td>
<td>2.00</td>
<td>1.98</td>
<td>10.13</td>
</tr>
</tbody>
</table>

These beamlets are focused into a single EO device and were steered using an applied voltage of $V_{\text{max}} \sim 1.51$ kV across the crystal. This corresponds to a field of 5.39 kV/mm. This cascaded scanner requires a synchronized bias supply needed for a continuous steering operation of the laser beam, since the bias fields should be applied incrementally, with each successive scanner stage ramped from 0 bias to peak bias only after the previous stage is at full bias (see previous section). A 5 stage compact programmable voltage driver was designed and fabricated in a previous study and detailed in the literature, but was unavailable for this study.\(^{43}\) However, the device was
tested with the following configurations: stage 1 only, stages 1+2, stage 1+2+3, stages 1+2+3+4, and stages 1+2+3+4+5. The maximum deflection for each stage and for the total device were measured and compared with the theory.

Figure 5-19: Actual images of beamlet steering for applied voltages for wavelength of 1.064 µm. Color indicates intensity.

The scanning was tested in a continuous manner for the first stage and is shown in Figure 5-19. The measured deflection angle versus voltage for Stage 1 agrees well with theory, as shown in Figure 5-20(a). Figure 5-20(b) shows a plot of the deflection angle as a function of the number of activated stages. The experiments were performed at 5.39 kV/mm, which gives a slight increase of 4.7% in the observed deflection angle over the designed value at 5kV/mm. This increase in deflection for fields above the designed value of 5 kV/mm is because the scanner channel widths were designed to be 60% larger than the focused beam waist as calculated from Gaussian optics using the specified focal
length of the lens array. This allows slightly higher fields than the design specified field to be applied. This deflection angle is ~4% smaller than the expected calculated value for a field of 5.39 kV/mm. However, applying a voltage higher than 5.27 kV/mm causes the beams to leave the scanner channels, so any bias above 5.27 kV/mm gives no additional deflection.

Figure 5-20: (a) deflection angle versus applied voltage across only stage 1 of the beamlet device. (b) deflection angle versus the number of steering stages activated in the beamlet device.

There is no limit to the number of beamlets, and hence no limits on the incident beam size in the crystal plane in using this design approach. Demonstration of this beamlet scanner is a critical step towards realizing large-aperture, large-angle beam steering. Further device design improvement can potentially increase these steering angles to 30-40°. Stacking several such scanners devices in the thickness direction will allow large aperture beams in the thickness direction as well.
5.6 Conclusions

The theory, design, and fabrication of several devices have been performed in ferroelectric LiNbO$_3$ and LiTaO$_3$. These include the fabrication of an integrated lens and scanner device, a cascaded electro-optic device, and a new beamlet scanner concept. The further development of these devices can be used in next-generation optical devices and systems, including space based communication systems where non-inertial beam deflection is required. The ability to integrate many diverse shapes in the same ferroelectric material can allow for many an exciting way to integrate several important optical functions, including beam deflection, beam shaping, and frequency doubling, all seamlessly integrated on the same optical chip. Future device challenges include reducing the operating voltages and reducing further the sizes of the created domains. These issues can be addressed with better device design. Also, crystal ion slicing of domain engineered devices has been demonstrated, opening a door for low voltage devices. However, further processes issues need to be addressed relating to film warping and cracking.

References


Chapter 6

Summary and Conclusions

This thesis has investigated how to create and shape domain walls in ferroelectric LiNbO$_3$ and LiTaO$_3$ and used the developed techniques to create domain microengineered devices for integrated optics. The heart of many of the issues in this thesis involve the \textit{intrinsic nonstoichiometric defects} which originate at the atomic scale, and exert influence from nanoscale all the way to the macroscale properties.

6.1 Summary of Major Findings

The conclusions derived in this thesis can be divided into three categories: those related to the electrostatic and electromechanical properties of the domain wall as imaged with scanning force microscopy, those related to creation and shaping of domain walls, and those related to domain wall applications.

6.1.1 Electromechanical and electrostatic properties of domain wall

1. The measured electromechanical interaction widths in congruent crystals are wider than in the near-stoichiometric crystals. For the vertical signal, $\omega_v=140$ nm for the
congruent compared to 113 nm for the near stoichiometric, and for the lateral $x$-$z$ signal, 211 nm (congruent) compared to 181 nm (near stoichiometric). [Chapter 3.3.2]

2. There was an asymmetry in the vertical signal of the PFM response in the congruent crystals which was not observed in the near-stoichiometric crystals. Further, annealing the crystals causes the asymmetry to be diminished. The difference between the near-stoichiometric and congruent crystals supports the premise that frustrated defects in the reversed domain state affect the local electromechanical properties across the wall. The mechanism of this is unclear. [Chapter 3.3.2]

3. The electrostatic distribution around the domain wall is still an unknown quantity. Both electrostatic force microscopy measurements and scanning surface potential microscopy measurements could not detect the domain wall for a variety of lift heights, biases, and cantilevers. [Chapter 3.4]

4. Finite element method simulations were performed for each of the measured PFM signals. The vertical displacement predicted by FEM (13.4 pm) agreed well with the experimentally measured value of ~20-30 pm. Qualitative forms of the displacement were found for the $x$-$z$ and $y$-$z$ planes. The FEM results showed no asymmetry and can be compared to the near-stoichiometric measurements. The interaction widths calculated in the FEM modeling are much narrower than the experimental measurements. [Chapter 3.5]

5. The finite element method predicts an inherent electromechanical width of a domain that depends upon the material properties and the thickness of the sample. Within the limits of the electrostatic distribution model, the FEM predicted width of the
domain wall width is relatively insensitive to the tip radii in the range of radii 50-200 nm. [Chapter 3.6]

6.1.2 Creation and shaping of domain walls

1. Methods were developed for creating controllable domain features in both LiNbO₃ and LiTaO₃ congruent crystals. The constant domain wall motion and high nucleation density in LiTaO₃ allows for controlling the motion by keeping the current at a constant experimentally determined level. In LiNbO₃, because of the variable and high domain wall velocity and inhomogeneous nucleation rates, features can be created by applying a variety of pulses of varying amplitude and duration to the crystal. [Chapter 2.2]

2. Periodically poled gratings with domain periods of 6.7 μm in 300 μm thick crystals (aspect ratio of 45) were created using backswitching and single long duration pulse techniques. However, uniformity over the entire sample surface is still a challenge. The major limitation to poling of the congruent crystals was identified as nucleation density. [Chapter 2.2.5]

3. Examination of arbitrary shapes created in LiNbO₃ and LiTaO₃ indicate that the domain wall shapes follow specific wall orientations. Due to the large number of pinning sites in LiTaO₃, the domain walls are better able to fit to arbitrary domain wall shapes than in LiNbO₃. [Chapter 2.2.6]
4. Ginzburg-Landau-Devonshire theory predicts the formation of y-walls in both LiTaO₃ and LiNbO₃ when considering energy, strain, and in-plane polarizations. [Chapter 4.4]

4. The coercive fields decrease by ~48% in LiTaO₃ and ~51% in LiNbO₃ at elevated temperatures in the range from 25-200°C. Switching time and nucleation density both increase at higher temperatures. An unexpected and anomalous transient current were measured in each of these materials, with pronounced increases in charge for LiNbO₃. The exact nature of this phenomenon is unknown but experiments indicate the formation of stable charged domain walls in the material. [Chapter 2.3.4]

5. Creation of devices at higher temperatures offers techniques to create higher aspect ratio domains. Demonstrations of poling at high temperature showed that they can be used to create high fidelity domain gratings, although further work must be done to achieve uniformity in the thickness and the plane of the device. [Chapter 2.3.6]

6.1.3 Applications of domain walls

1. Several types of domain microengineered devices were demonstrated in LiNbO₃ and LiTaO₃. These include an integrated lens and scanner, a cascaded electro-optic scanner, and a beamlet device. These results are compared to the literature and given in Table 6-1. [Chapter 5.5]

2. Cascaded electro-optic scanners offer higher scanner angles for a fixed device length or a lower operating voltage. Beam deflection of 25.4° was demonstrated for such a device, the highest reported to date in this technology. [Chapter 5.5.2]
3. A new beamlet concept was introduced which was used to scan a large 7.5 mm diameter beam through 10° deflection. [Chapters 5.5.3]

4. Crystal ion slicing techniques have been demonstrated on domain inverted devices. The domains survive the liftoff process intact. While CIS may not be a practical device technology as of yet, studying domains in these thin slices of material using scanning force microscopy can offer insights into the material and offer the ability to study in-situ domain kinetics with an AFM probe. [Chapter 5.3.2]

Table 6-1: Comparison of Domain Engineered Electro-Optic Scanning Devices

<table>
<thead>
<tr>
<th>Scanner Type</th>
<th>Input Aperture (µm)</th>
<th>Max Angle (°)</th>
<th>Displacement (°/kV)</th>
<th>Resolvable Spots</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waveguide *</td>
<td>750</td>
<td>0.45</td>
<td>0.458</td>
<td>7</td>
<td>Chen¹</td>
</tr>
<tr>
<td>Rectangular †</td>
<td>500</td>
<td>0.70</td>
<td>0.70</td>
<td>11</td>
<td>Gahagan²</td>
</tr>
<tr>
<td>Horn Shaped †</td>
<td>100</td>
<td>14.6</td>
<td>1.8</td>
<td>17</td>
<td>Chapter 5.5.1</td>
</tr>
<tr>
<td>Cascaded †</td>
<td>70</td>
<td>25.4</td>
<td>11.5</td>
<td>30</td>
<td>Chapter 5.5.2</td>
</tr>
<tr>
<td>Beamlet †</td>
<td>6500</td>
<td>10.4</td>
<td>2.08</td>
<td>-</td>
<td>Chapter 5.5.3</td>
</tr>
</tbody>
</table>

* indicates diffusion induced polarization reversal
† indicates electric field induced polarization reversal

6.2 Connecting Theme of the Thesis: Influence of Defects

The focus of materials of this thesis, congruent LiNbO₃ and LiTaO₃, has been primarily due to their excellent nonlinear optical properties and because of their commercial availability and technological importance. The congruent crystals are unusual crystals however, as tremendous amount of effort has been invested in growing high quality uniform crystals of that are essentially non-stoichiometric. These crystals,
by virtue of their nonstoichiometry, possess inherent and pervading defects in the crystal structure which dominate the materials behavior.

These defects are observed at the nano and microscale where the nonstoichiometric defects are observed to influence the local electromechanical properties of the domain wall. These defects give rise to an asymmetry in the induced piezoelectric distortions around a domain wall as well as changes in interaction widths as compared to stoichiometric crystals.

The influence of these nonstoichiometric defects extends to the macroscale where it is manifest in the preferred domain wall orientations. In both LiNbO$_3$ and LiTaO$_3$, simulations of wall orientations by Ginzburg-Landau-Devonshire theory predict hexagonal domain walls that are parallel to the $y$-axis ($y$-walls). These predictions agree well with the stoichiometric crystals of LiTaO$_3$ and LiNbO$_3$ and the congruent crystals of LiNbO$_3$. However, in congruent LiTaO$_3$ crystals triangular domains are preferred with $x$-axis orientations. This is clearly an influence of the nonstoichiometric point defects. When the domains are created at temperatures $>100^\circ$C, where the lithium vacancies can start to rearrange, the congruent crystals of LiTaO$_3$ form domain shapes predicted by theory, namely hexagonal $y$-wall orientations.

These defects have a strong influence on the poling properties of the material as well. The coercive field in congruent materials is very high, about 21-22 kV/mm. These coercive fields are an order of magnitude larger than in the stoichiometric compositions. This is both an advantage and a disadvantage in terms of optical devices which exploit the nonlinear optical effects. The high coercive field means that very high electric fields can be applied to devices composed of structured domain walls. This is an advantage for
electro-optic devices in which a much larger change in the index of refraction can be induced in the crystal before the domain structures are destroyed. This is a disadvantage because these high fields make the creation of high aspect ratio domain shapes (thickness to width ratio) difficult. These high aspect ratio devices are necessary for high power laser frequency conversion or for UV light creation in quasi-phase matched structures.

6.3 Open Scientific Issues and Future Work

The initial high temperature poling experiments unearthed a wide variety of questions. The temperature mediated domain shape change in LiTaO$_3$ can be studied to give insight into the nature of the defect dipoles and how they influence the domain wall properties. The specifics on the domain kinetics at higher temperatures are unknown, although it is clear that at higher temperatures, nucleation density is higher and wall velocity is lower. Experiments looking explicitly at switching times for applied step voltages as a function of temperature should be performed. This can give a temperature dependent value to $\delta$ in the expression $t = t_o \exp(\delta/(E - E_c))$ and can be used to determine the relative contribution of nucleation and growth. Further detailed studies involving in-situ observation of domain walls at elevated temperatures should be performed to give visual confirmation. The anomalous charge generated during poling at high temperatures is still an open question. While this is thought to originate due to the movement of charged domain walls, further experiments and theory needs to be developed. In general, the ferroelectric fatigue in these materials has been little studied.
for electrodes other than water. As a first step, experiments should investigate formation of charged domain walls at room temperature using different electronic and ionic conductors. Once charged domain walls are formed, experiments should be performed to determine if the charged walls can be destroyed with electrode removal, poling, or annealing treatments. This will help in the understanding of the mechanisms of stabilization. Once the mechanism of charged wall formation is established at room temperature, whether due to injected charge, oxygen vacancies, etc., the origin at higher temperatures can be deduced. The origin of the anomalous charge can be determined by measuring the evolved charge as a function of LiNbO$_3$ and LiTaO$_3$ crystal thickness and temperature.

From a device perspective, poling at elevated temperatures has been shown to offer possibilities of creating finer features than room temperature poling. Additionally, temperature mediated domain wall configurations can be utilized to create better patterns in congruent LiTaO$_3$. However, the pinning of the domain wall and the formation of charged domain walls need to be further investigated to see if this will adversely affect device performance. Additional work needs to be done to see if these walls are formed with other electrodes; perhaps other conducting oxide electrodes like SrRuO$_3$ or ionic conductors could eliminate this problem entirely. Interface and fatigue effects in general have not been studied in LiNbO$_3$ and LiTaO$_3$, and could help elucidate some of the mechanisms of the polarization locking after forward poling. Nucleation of domains at higher temperatures followed by room temperature poling should be investigated.

The origin of many of the issues raised in this thesis involve the intrinsic nonstoichiometric defects. The current defect dipole model of a polar cluster gives a very
good physical description of some of the material and poling properties, but detailed
modeling of the defects starting from atomic scale is necessary to accurately describe the
nature of the defects and how they interact with macroscale properties like the domain
wall. Potential simulation methods should including molecular-dynamics calculations
which have been used in the simulation of the ferroelectric transitions in LiNbO$_3$\textsuperscript{3} or
pseudo-potential methods.\textsuperscript{4}

Further scanning probe studies should be performed on single ferroelectric
domain walls. These studies provide very basic information as to the nature of the
piezoelectric distortions on nanoscale structures. Simulations and measurements indicate
that there are many competing effects in measuring feature sizes at these small scales: the
intrinsic electromechanical width determined by the physical constants of the material,
the sample thickness, and the electric field distribution determined by the probe tip.
Understanding the interplay between them will determine the ultimate spatial resolution
of the PFM technique and is vital for the future progress in the field. Experiments
investigating the interaction width in LiNbO$_3$ should be performed for a series of crystal
thickness ranging from thinned crystals or CIS slices with thickness of ~10 µm through
to bulk crystals with thicknesses ~500 µm with a number of different tip radii (10-100
nm). This would establish the exact nature of tip and thickness scaling effects. Further
refinements of the FEM simulations should be performed. Specifically, future work
should simulate the effect of tilted and jagged boundaries on the broadening and
asymmetry of signal.

The applications of domain microengineered devices are very diverse. The ability
to fabricate numerous functions on the same chip leads to a large array of conceivable
devices. The limitations for the scanner technology are the high driving fields as well as the tight beam conditioning required to pass the light through the crystals. However, the beamlet concept introduced in this thesis is one possible solution to these problems. Other promising areas of future uses include high speed analog to digital conversion where, for example, high speed analog electrical signals are fed into microstrip electrodes which modulate a domain engineered deflector to generate digital signals.

There are exciting possibilities in the technology of quasi-phase matching for creating new laser wavelength sources. The future, however, of quasi-phase matched devices probably does not lie in congruent crystals of either LiNbO$_3$ or LiTaO$_3$. Future uses include high power sources, which require domain structures in much thicker crystals, and UV light generation, which requires very small domain gratings (<1 µm domain size). Both congruent compositions show significant photorefractive damage which requires the device to be operated at temperatures higher than 120ºC. This coupled with the high coercive fields make creating and operating QPM structures difficult in the congruent crystals. Additional markets in display technology are currently of great interest in industry, where infrared light from inexpensive laser diode technologies are frequency converted to red, green, and blue sources. The highest aspect ratio domains have been demonstrated in MgO doped LiNbO$_3$ or in stoichiometric crystals. Future developments in QPM structures are most promising in these materials as they show a reduction in both the coercive field and photorefractive damage. However, significant material development must be preformed to get these crystals to the level of uniformity present in the congruent crystals.
References


Appendix A

Quasi Phase Matching

A.1 Quasi-Phase Matched Wavelength Conversion

Second harmonic generation (SHG) is a nonlinear optical conversion method that can create laser light at different frequencies and offers ways to generate coherent light in regions where compact and efficient lasers are unavailable. This conversion of light to smaller wavelengths can lead to miniaturization and higher data storage densities. Most importantly, conversion of light into higher frequencies can provide new laser sources from the UV to the IR.

Suppose two identical optical fields with frequency, $\omega$, given by $E_j = E_o \cos(\omega t)$, are traveling though a nonlinear crystal. Using Equation 5-1 in Chapter 5.2.1, which relates induced polarization to the applied electric field, and keeping only second order terms, we get\(^{1,2}\)

$$P_i = \chi^{(2)}_{ijk} E_j E_j = E_o^2 \cos^2(\omega t) \quad \text{A-1}$$

After manipulation Equation A-1 becomes

$$P_i = \frac{1}{2} \chi^{(2)}_{ijk} E_o^2 + \frac{1}{2} \chi^{(2)}_{ij} E_o^2 \cos(2\omega t) \quad \text{A-2}$$
The first term in Equation A-2 indicates there is a static DC polarization field established in the medium, while the second term indicates there is a polarization in the medium that is oscillating at twice the input frequency $\omega$. This phenomenon is called second harmonic generation (SHG). Any input light to a crystal with significant $\chi^{(2)}$ effects will exhibit second harmonic generation. As with any 3rd rank tensor, only crystal systems that do not possess a center of symmetry will exhibit these effects (neglecting surface symmetry-breaking artifacts).

Because of the dispersive nature of solids, the speed at which light moves through a medium is dependent upon the wavelength of the light. In general, the index of refraction, $n$, is not the same at two different wavelengths. Therefore, when a material exhibits SHG, the fundamental frequency and the second harmonic frequency travel at different speeds though the crystal. This will cause the fundamental and secondary waves to go into and out of phase as it propagates through the crystal, and will cause constructive and destructive interference of the two beams. This significantly reduces the efficiency, as energy flows back and forth between the fundamental and secondary waves.

An easy way to look at these interacting waves is to examine the wave vectors in the material, given by $k_i = 2\pi n_i / \lambda_i$, where $n_i$ is the index at the wavelength $\lambda_i$. The relative phase difference between the fundamental waves (two of them) and the harmonic wave is given by

$$\Delta k = k_{2\omega} - k_{\omega} - k_{\omega} = k_{2\omega} - 2k_{\omega}$$

A-3
where \( k_\omega = 2\pi n_\omega / \lambda_\omega \) and \( 2\pi n_{2\omega} / \lambda_{2\omega} \).

To see the effect of wave vector mismatch using Maxwell’s equations and Equation A-3, one arrives at

\[
\frac{dE_{2\omega}}{dz} = -i\omega \sqrt{\frac{\mu}{\varepsilon}} d (E_\omega)^2 e^{-i\Delta k z} \quad \text{A-4}
\]

which relates the input \( E \) field at frequency \( \omega \) with the generated second harmonic electric field at frequency \( 2\omega \). Note that \( d \) is the second harmonic tensor, a 3rd rank tensor equal to \( 2\chi^{(2)}_{ijk} \). This equation assumes two things: one that there is no absorption of input laser light and that depletion of the input wave at \( \omega \) due to conversion to \( 2\omega \) is negligible so that \( E_\omega \) is independent of position along \( z \).

Integrating Equation A-4 over the length of a crystal of length \( l \) yields

\[
I(l) \propto E_{2\omega}(l) E_{2\omega}^*(l) = \omega^2 \left( \frac{\mu}{\varepsilon} \right) d^2 (E_\omega)^4 l^2 \frac{\sin^2(\Delta kl/2)}{(\Delta kl/2)^2} \quad \text{A-5}
\]

The last term in Equation A-5 reduces the overall efficiency. This is an interference term and is identical to the sinc function seen in Young’s experiment. The main peak and the first zero of this interference pattern is called the coherence length and is given by

\[
L_c = \frac{\pi}{\Delta k} = \frac{\lambda}{4(n_{2\omega} - n_\omega)} \quad \text{A-6}
\]

which is a measure of the maximum crystal length that is useful in producing the second-harmonic power when there is a non-zero phase match.
Quasi-phase matching (QPM) is a powerful technique used to generate second harmonic light when phase matching is not possible through birefringence. It is the repeated and periodic alternations of the sign of the SHG coefficient, so that instead of the signal decaying beyond the coherence length, \( L_c \), it will continue to build. This is shown in Figure A-1.

With periodic domain reversal, a periodic modulation of the \( d \) coefficient is possible. Letting \( d \) become a periodic function of propagation distance, \( z \), it can be expanded in a Fourier series as

\[
d(z) = d_{\text{bulk}} \left( \sum_{m=-\infty}^{\infty} a_m \exp \left( im \frac{2\pi}{\Lambda} z \right) \right)
\]  

where \( \Lambda \) is the period of \( d(z) \) and \( a_m \), is given by

\[
a_m = \frac{1}{\Lambda} \int_0^\Lambda d(z) \exp \left( im \frac{2\pi}{\Lambda} z \right) dz
\]

Now Equation A-4 becomes Equation A-9
\[ \frac{dE_{2\omega}}{dz} = -i\omega \sqrt{\frac{\mu}{\varepsilon}} \omega_{bulk} (E_{\omega})^2 a_{m} \exp \left[ iz \left( \frac{2\pi}{\lambda} + \Delta k \right) \right] \quad A-9 \]

In this case the phase matching condition becomes

\[ m \frac{2\pi}{\lambda} = \Delta k \quad A-10 \]

where \( m \) is some integer greater than or equal to one.\(^5\) Shown in Figure A-1 are the efficiencies of birefringence phase matching and first order (\( m=1 \)) and third order (\( m=3 \)) QPM.

Combining Equation A-3 and Equation A-10 yields

\[ \omega = \frac{m \lambda_{\omega}}{2(n_{2\omega} - n_{\omega})} \quad A-11 \]

which can be used to find appropriate gratings for frequency doubling input light when the refractive indices are known.

Similar equations and phase matching conditions can be found for optical parametric oscillations, which is the conversion of one input beam to two output beams of different frequencies.\(^1,2\) In this case, the pump beam at \( \omega_p \) is converted to beams at \( \omega_i \) and \( \omega_s \), called the idler and signal, such that \( \omega_p = \omega_i + \omega_s \) instead of the pump signal producing two 2 identical beams at twice the frequency as in SHG. The phase matching of Equation A-3 then becomes,

\[ \Delta k = k_p - k_i - k_s \quad A-12 \]

where \( k_p, k_i, \) and \( k_s \) are the wave vectors of the pump, idler and signal, respectively. The grating size, \( \Lambda \), can then be found from
A.2 Quasi-Phase Matched Devices

There are several ways to achieve QPM in materials. Some methods include stacking plates of materials oriented so that alternating plates have opposite signs of the nonlinear polarization or using periodic electrodes to induce a periodic sign changes in nonlinear liquid crystal. However, the most successful method is the periodic alternation of ferroelectric domains in crystals like LiNbO$_3$ and KTP, either in material growth or by periodically poling the domain structure. An example of a QPM device formed by periodic poling in is shown in Figure A-2

\[ \theta = \frac{2m\pi}{(k_p - k_i - k_s)} \]

Figure A-2: QPM device formed by a grating of alternating polarization. A portion of input pump beam at $\omega_p$ is converted to the signal and idler beams at $\omega_s$ and $\omega_i$. For SHG, $\omega_s = \omega_i$ so that the pump at $\omega_p$ is converted to a signal at $2\omega_p$.

The periodic poling of lithium niobate and lithium tantalate has been intensely researched since the early 1990’s. The poling techniques and the device conversion efficiency and lifetime have improved. However, as laser sources push toward the UV,
the grating period, $\Lambda$, must get smaller. For example to frequency double light to 400 nm in lithium niobate (LiNbO$_3$), gratings with periods of 2.6 $\mu$m must be created uniformly along 5-6 cm of crystal as well as through the crystal thickness. The aspect ratio of the domains, the ratio of crystal thickness to inverted domain size, currently determines the limits of devices. Current state of the art devices have aspect ratios approaching 500. High ratios (>500) are needed for the next generation of optical devices. These include short period devices for UV generation, as well as high power devices where thick (>2 mm) crystals are required. Additionally, the uniformity of the domains in the thickness and grating direction is critical to device conversion efficiency.

References


Appendix B

Supplemental Material for Chapter 3

B.1 ANSYS Batch Files

This program is run in batch mode (not graphical) mode of ANSYS 7.0. Prior to running this program, a file ‘JunctionStart.db’ should be created and saved in the graphical mode. This file should include the two field distributions ‘TopV’ and ‘BotV’ which are descriptions of the electric fields from Chapter 3.5.1. This file can be easily modified to change the position of the tip relative to the domain wall. Once the program has completed running, the results can be opened and viewed in the ANSYS graphical mode.

B.1.1 Sample Batch File

This program will create a file name QP_200 that is the simulation of the tip at 200 nm from the domain wall.

! Start ---------------------------------------------------------------
Start 1
/CLEAR
/Filename, QP_200,1

!load file with loads programmed graphically already in it
RESUME,JunctionStart,db

/PREP7  ! Preprocessor Section ----------------------------------

! Format + Material Properties
ET,1,SOLID98,3
MP,DENS,1,4640e-27
TB,PIEZ,1
TBDATA,2,-2.43, 0.23
TBDATA,5,2.43, 0.23
TBDATA,9,1.33
TBDATA,10,-2.43
TBDATA,14, 3.76
TBDATA,16, 3.76
MP,PERX,1,84.1e9
MP,PERY,1,84.1e9
MP,PERZ,1,128.1e9
TB,ANEL,1
TBDATA,1,2.03e2, 0.573e2, 0.752e2, 0, 0.085e2
TBDATA,7,2.03e2, 0.752e2, 0, -0.085e2
TBDATA,12,2.424e2
TBDATA,16,0.728e2, 0, .085e2
TBDATA,19,0.595e2, 0, 0.595e2

! start building stuff
BLOCK, -4000, 0, -4000, 4000, 0, -4000
BLOCK, 0, 4000, -4000, 4000, 0, -4000
! VPLOT, all

VGLUE, ALL
VGEN, 1, ALL, , , -200, 0, 0, 0, 1, 1  ! move by displacement

! Define 2 coordinate systems
LOCAL, 11, 0, 1000, 0, 0, 0, 0, 0, ,
LOCAL, 12, 0, -1000, 0, 0, 0, 180, 0, ,

! create cylinder
CYLIND, 400, , 0, 400, ,

VSEL, ALL
VGLUE, ALL

VSEL, NONE
VSEL, ALL
VLIST, ALL
!select the cylinder
VSEL, S, VOLU, ,4,4, ,1
VSEL, ALL
VLIST, ALL
VSEL, NONE

!delete areas 8, 18, 19
ASEL, S, AREA, ,8,8, ,1
ASEL, A, AREA, ,18,19, 1
ADELE, ALL

!assign areas different coordinate systems first pick then assign
VSEL, S, VOLU, ,5,5, ,1
VATT, 1, ,1,11
VSEL, S, VOLU, ,6,6, ,1
VATT, 1, ,1,11
VSEL, NONE

!apply loads
DA, 21, VOLT, %TopV%
DA, 11, VOLT, %TopV%
DA, 17, VOLT, %TopV%
DA, 22, VOLT, %TopV%
DA, 1, VOLT, %BotV%
DA, 13, VOLT, %BotV%
DA, 1, UZ, 0
DA, 13, UZ, 0

!now mesh
VSEL, ALL
MSHAPE, 1, 3D
SMRTSIZE, 1, , , , , , , , , ,
VMESH, ALL
ASEL, S, AREA, ,11, 11, ,0
ASEL, A, AREA, ,17, 17, 0
AREF, ALL, 1, 1, ,
ASEL, NONE

!Now Solve
/SOLU
SOLVE
SAVE, , , ,ALL
FINISH
Appendix C

Supplemental Material For Chapter 4

C.1 Sample Derivations of Energy Terms

A sample invariant energy term for each type of energy in Equation 4-5 will be derived using the coordinate transformations given in Equations 4-1 to 4-4. The Ginzburg-Laudau terms given in Equation 4-6 will be analyzed first. We begin by transforming the real \((x,y,z)\) axes to the complex \((\xi,\eta,z)\) axes using Equation 4-1. This changes the terms \(P_x, P_y, \text{ and } P_z \) to \(P'_\xi, P'_\eta, \text{ and } P'_\zeta\). The transforms in Equation 4-2 to 4-4 are then used to operate on each of the transformed free energy terms. Because the resulting energy terms must be invariant with the symmetry transformations, any terms not identical to the initial term after transformation is equal to zero. Those terms that are invariant are then transformed back to the real axes \((x,y,z)\). This series of procedures are summarized in Table C-1.

Table C-1: Sample Invariant Energy Derivation of Ginzburg-Landau Terms

<table>
<thead>
<tr>
<th>Initial Term</th>
<th>Symmetry Tranformations</th>
<th>Transformed Term</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P'<em>\xi P'</em>\zeta)</td>
<td>3 fold (e^{i\frac{2\pi}{3}} P_\zeta P_\eta = 0)</td>
<td>(P_\zeta P_\eta)</td>
</tr>
<tr>
<td>(P'<em>\xi P'</em>\eta)</td>
<td>(P_\xi P_\eta)</td>
<td>(P_\xi P_\eta)</td>
</tr>
</tbody>
</table>
Following the same procedure, the other energy terms can be derived. Sample elastic energy terms in Equation 4-7 are transformed in Table C-2, and sample coupling energy terms in Equation 4-8 are transformed in Table C-3.

**Table C-2:** Sample Invariant Energy Derivation of Elastic Energy Terms

<table>
<thead>
<tr>
<th>Initial Term</th>
<th>Symmetry Transformations</th>
<th>Transformed Term</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_{\xi\xi}\partial_{\xi}$</td>
<td>3 fold Inversion Mirror Complex Real</td>
<td></td>
</tr>
<tr>
<td>$e_{\xi\xi}$</td>
<td>$e^{-i\frac{2\pi}{3}}e_{\xi\xi}$</td>
<td>$e_{\eta\eta}$</td>
</tr>
</tbody>
</table>

**Table C-3:** Sample Invariant Energy Derivation of Coupling Energy Terms

<table>
<thead>
<tr>
<th>Initial Term</th>
<th>Symmetry Transformations</th>
<th>Transformed Term</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{\eta}^{\xi}P_{\xi}^{\eta}e_{\xi\xi}$</td>
<td>3 fold Inversion Mirror Complex Real</td>
<td></td>
</tr>
<tr>
<td>$P_{\eta}^{\xi}P_{\xi}^{\eta}$</td>
<td>$e^{-i\frac{2\pi}{3}}P_{\eta}^{\xi}P_{\xi}^{\eta}$</td>
<td>$P_{\eta}^{\xi}P_{\eta}^{\eta}$</td>
</tr>
</tbody>
</table>

The gradient energy terms $P_{ij}$ (or $\frac{\partial P_i}{\partial j}$) is a covariant tensor. Because the $(\xi, \eta, z)$ axes are Cartesian, the gradient energy terms can be transformed in a similar method as the other energy terms above.1

**Table C-4:** Sample Invariant Energy Derivation of Gradient Energy Terms

<table>
<thead>
<tr>
<th>Initial Term</th>
<th>Symmetry Transformations</th>
<th>Transformed Term</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{\xi,\xi}$</td>
<td>3 fold Inversion Mirror Complex Real</td>
<td></td>
</tr>
<tr>
<td>$P_{\xi,\xi}$</td>
<td>$e^{\frac{i2\pi}{3}}P_{\xi,\xi}$</td>
<td>$P_{\xi,\xi}$</td>
</tr>
</tbody>
</table>

---

C.2 Supplemental Equations

The constants $v_i$ and $\mu_{ij}$ used in Equation 4-27 are

\begin{align*}
v_1 &= -\gamma_3 m_{31} \cos(3\theta) - \gamma_3 m_{11} \sin(3\theta) - \gamma_4 m_{21} \quad \text{C-1} \\
v_2 &= -\gamma_3 m_{11} \cos(3\theta) + \gamma_3 m_{31} \sin(3\theta) \quad \text{C-2} \\
\mu_{11} &= \gamma_3 m_{32} \cos(3\theta) + \gamma_3 m_{12} \sin(3\theta) + \gamma_4 m_{22} \quad \text{C-3} \\
\mu_{12} &= \gamma_3 m_{33} \cos(3\theta) + \gamma_3 m_{13} \sin(3\theta) + \gamma_4 m_{23} \quad \text{C-4} \\
\mu_{21} &= \gamma_3 m_{12} \cos(3\theta) - \gamma_3 m_{32} \sin(3\theta) \quad \text{C-5} \\
\mu_{22} &= \gamma_3 m_{13} \cos(3\theta) - \gamma_3 m_{33} \sin(3\theta). \quad \text{C-6}
\end{align*}

The matrices $[\rho_{ij}]$ in Equation 4-28 are

\begin{align*}
\rho_{11} &= -\frac{v_1 P_h^2}{\alpha_3} \quad \text{C-7} \\
\rho_{12} &= \frac{v_1}{\alpha_3} - \frac{(v_1 \mu_{22} - v_2 \mu_{12}) P_h^2}{\alpha_3^2} \quad \text{C-8} \\
\rho_{13} &= \frac{v_1 \mu_{22} - v_2 \mu_{12}}{\alpha_3^2} \quad \text{C-9} \\
\rho_{21} &= -\frac{v_2 P_h^2}{\alpha_3} \quad \text{C-10} \\
\rho_{22} &= \frac{v_2}{\alpha_3} + \frac{(v_1 \mu_{21} - v_2 \mu_{11}) P_h^2}{\alpha_3^2} \quad \text{C-11} \\
\rho_{23} &= \frac{v_2 \mu_{11} - v_1 \mu_{21}}{\alpha_3^2}. \quad \text{C-12}
\end{align*}
The matrices \( \phi_{ij} \) in Equation 4-29 are

\[
\phi_{i1} = -m_{i1} p_h^2, \quad (i=1,2,3) \tag{C-13}
\]

\[
\phi_{i2} = m_{i2} + m_{i2} p_{11} + m_{i3} p_{21}, \quad (i=1,2,3) \tag{C-14}
\]

\[
\phi_{i3} = m_{i2} p_{12} + m_{i3} p_{22}, \quad (i=1,2,3) \tag{C-15}
\]

\[
\phi_{i4} = m_{i2} p_{13} + m_{i3} p_{23}, \quad (i=1,2,3). \tag{C-16}
\]

### C.3 Matlab Implementation

The code in this section is in two parts. The first section will generate the polarizations, strains, and energies of the system and save the data in a data file. The data is then loaded and manipulated in a second program.

To simulate the materials, first run the program ‘GDL StandardGen.m’ (which is given in Section C.3.2). This will automatically generate two files ‘LNstandard’ and ‘LTstandard’ which contain all the simulation data including free energy, depolarization energy, strains \( \bar{\varepsilon}_5, \bar{\varepsilon}_6, \) and \( \Delta \varepsilon_n \), and the polarizations \( P_z, P_n, \) and \( P_t \). Next, run ‘GDL FreeEnergy’ (which is given in Section C.3.3) which will normalize and plot the free, depolarization, and total energy. Similar programs can be derived to plot the strain and polarizations distributions.
C.3.1 Data Generation

%GDL implementation of domain wall orientation in LiNbO3 and LiTaO3

clear clc close all fig=0;

materialarray = [1,2]; %1 for LN, 2 for LT

for scrim = 1:length(materialarray)
    material = materialarray(scrim);

    % specifications for calculation points
    divsteps = 151; % number steps across the domain wall must be odd!!
    spread = 4; % spread * wo - width on either side to calculate
    Energyspread = 2; % * wo on either side - how much to normalize the free
    energy by

    % input parameters - wall width and gradient ----------------------
    g_or_w = 0; % 0 = gradient specified, 1 = width specified

    % --- material properties ----------------------------------------
    epsilon_0=1/(9e9*4*pi); % permittivity in si units
    e0 = epsilon_0;
    if material == 1 % Lithium Niobate !!! -----------------------
        ps=0.75; % C/m2
        gr1=3.9770e-011; % gradient term in Nm4/C2

        % elastic constants in N/m2 (c)
        c11=2.03e11; c12=0.53e11; c13=0.75e11;
        c33=2.45e11; c14=0.09e11; c44=0.60e11;

        % electrostrictive coefficients Q in m4/C2
        q31=-0.003; q33=0.016; q42=0.020; q44=0.065;

        % dielectric constants in C2/(Nm2)
        e11=84.1*epsilon_0; e33=28.1*epsilon_0; e22=e11; % Constant stress
        e11=46.5*epsilon_0; e33=27.3*epsilon_0; e22=e11; % Constant strain
        e11=84.1*epsilon_0; e33=28.1*epsilon_0; e22=e11; % Constant stress
        % y walls

        PlotTitle = 'Lithium Niobate Standard Settings';

    elseif material == 2 % Lithium Tantalate !!! -----------------------
        ps=0.5; % ps=0.5;
        gr1=2.5278e-011; % gradient term in Nm4/C2

        % elastic constants in N/m2
        c11=2.28e11; c12=0.31e11; c13=0.74e11;
        c33=2.71e11; c14=-0.12e11; c44=0.96e11;

        % elastic constants in N/m2
        c11=2.28e11; c12=0.31e11; c13=0.74e11;
        c33=2.71e11; c14=-0.12e11; c44=0.96e11;
%electrostrictive coefficients Q in m^4/C^2
q31=-0.0047; q33=0.011; q42=0.016; q44=0.052;

%dielectric constants in C^2/(Nm^2)
e11=53*epsilon_0; e33=44*epsilon_0; e22=e11; %Constant stress
e11=41*epsilon_0; e33=42*epsilon_0; e22=e11; %Constant strain
e11=53*epsilon_0; e33=44*epsilon_0; e22=e11; %Constant stress

PlotTitle = 'Lithium Tantalate Standard Settings';
end

%The pre-multipliers beta in elastic energy terms
b1=c33/2;
b2=(c11+c12)/4;
b3=(c11-c12)/4;
b4=c13;
b5=c44/2;
b6=c14;

%the premultipliers gamma in the electrostrictive coupling energy terms
g1=(c11+c12)*q31/2+c13*q33/2;
g2=c33*q33/2+c13*q31/2;
g3=2*c14*q44-(c11-c12)*q42/2;
g4=c44*q44;

%premultipliers alpha in the polarization energy terms
a1=1/(2*e33);
a3=1/e11;
s1=(2*g1*b1-g2*b4)/(2*(b4^2-4*b1*b2)); %eq (4.16)
s2=(2*g2*b2-g1*b4)/(2*(b4^2-4*b1*b2)); %eq.(4.16)
a2=(a1/ps^2)-4*(b1*s2^2+4*b2*s1^2+2*b4*s1*s2+2*g1*s1+g2*s2); %from Eq 4.15

%homogeneous strains, lambda1 and lambda2
l1=s1*ps^2; % perpendicular to z-axis (4.17)
l2=s2*ps^2; % parallel to the z-axis (4.18)

%start calculations ----------------------------------------------

%the variable t is angle from 0 to 2pi degrees
% number of theta; numtheta=1 for t=pi/6.
% So t=-pi/6+(numtheta-1)*pi/60 and numtheta=round(t*60/pi+11)
numtheta=1;

for t=-pi/6:pi/60:pi/2-pi/60; % changing value of theta

% The aij, bij, and the mij matrices
aij=[2*(b2+b3), b6*sin(3*t), 0; b6*sin(3*t), 2*b5 , b6*cos(3*t); 0 ,
b6*cos(3*t), 2*b3]; %Eq. (4.24)
bij=[-g1, -g3*sin(3*t), -g3*cos(3*t); 0, -g4, 0; 0, -g3*cos(3*t),
g3*sin(3*t)]; %Eq. (4.25)
mij=inv(aij)*bij;

% the nu terms 4.26-4.27
n1=-g3*mij(3,1)*cos(3*t)-g3*mij(1,1)*sin(3*t)-g4*mij(2,1); % (4.26)
\[ n_2 = \frac{g_3 \cdot m_{ij}(1,1) \cdot \cos(3t) + g_3 \cdot m_{ij}(3,1) \cdot \sin(3t)}{2}; \quad (4.27) \]

% the muij matrix (Eqs (4.28-4.31)
\[
\mu = [g_3 \cdot m_{ij}(3,2) \cdot \cos(3t) + g_3 \cdot m_{ij}(1,2) \cdot \sin(3t) + g_4 \cdot m_{ij}(2,2),
\]
\[
g_3 \cdot m_{ij}(3,3) \cdot \cos(3t) + g_3 \cdot m_{ij}(1,3) \cdot \sin(3t) + g_4 \cdot m_{ij}(2,3),
\]
\[
g_3 \cdot m_{ij}(1,2) \cdot \sin(3t) - g_3 \cdot m_{ij}(3,2) \cdot \cos(3t),
\]
\[
g_3 \cdot m_{ij}(1,3) \cdot \sin(3t) - g_3 \cdot m_{ij}(3,3) \cdot \cos(3t)];
\]

% The rho-ij and the phi-ij matrices (see appendix for definitions)
\[
\rho = [-n_1 \cdot \psi^2 / a_3, n_1 / a_3 - (n_1 \cdot \mu(2,2) - n_2 \cdot \mu(1,2)) \cdot \psi^2 / a_3^2, (n_1 \cdot \mu(2,2) - n_2 \cdot \mu(1,2)) / a_3^2 - n_2 \cdot \psi^2 / a_3, n_2 / a_3 + (n_1 \cdot \mu(2,1) - n_2 \cdot \mu(1,1)) \cdot \psi^2 / a_3^2, (n_2 \cdot \mu(1,1) - n_1 \cdot \mu(2,1)) / a_3^2];
\]
\[
\phi(:,1) = -m_{ij}(:,1) \cdot \psi^2;
\]
\[
\phi(:,2) = \text{mij}(:,1) + \text{mij}(:,2) \cdot \rho(1,1) \cdot \text{mij}(:,3) \cdot \rho(2,1);
\]
\[
\phi(:,3) = \text{mij}(:,2) \cdot \rho(1,2) + \text{mij}(:,3) \cdot \rho(2,2);
\]
\[
\phi(:,4) = \text{mij}(:,2) \cdot \rho(1,3) + \text{mij}(:,3) \cdot \rho(2,3));
\]

% squiggle (4.36) and (4.37)
\[
sq_1 = a_1 - 4 \cdot g_1 \cdot l_1 - 2 \cdot g_2 \cdot l_2 - g_3 \cdot (\phi(1,1) \cdot \rho(2,1) + \phi(3,1) \cdot \rho(1,1)) \cdot \cos(3t) - g_3 \cdot (\phi(1,1) \cdot \rho(1,1) - \phi(3,1) \cdot \rho(2,1)) \cdot \sin(3t) - g_4 \cdot \phi(2,1) \cdot \rho(1,1);
\]
\[
sq_3 = a_2 + 2 \cdot g_1 \cdot \phi(1,2) + g_3 \cdot (\phi(1,1) \cdot \rho(2,2) + \phi(1,2) \cdot \rho(2,1) + \phi(3,1) \cdot \rho(1,2) + \phi(3,2) \cdot \rho(2,1)) \cdot \cos(3t) + g_3 \cdot (\phi(1,1) \cdot \rho(1,2) + \phi(1,2) \cdot \rho(1,1) - \phi(3,1) \cdot \rho(2,2) - \phi(3,2) \cdot \rho(2,1)) \cdot \sin(3t) + g_4 \cdot (\phi(2,1) \cdot \rho(1,2) + \phi(2,2) \cdot \rho(2,1)) \cdot \rho(1,1));
\]

% homogeneous strains and polarizations
\[
e_{4h} = 0; \quad e_{5h} = 0; \quad e_{6h} = 0; \quad \% equations 4.9 strains are tilda quantities \]
\[
e_{nh} = l_1; \quad e_{th} = l_1; \quad e_{3h} = l_2; \quad \% equations 4.13, 4.14 \]
\[
P_{nh} = 0; \quad P_{th} = 0; \quad \% polarizations, 4.10 \]
\[
P_{zh} = \psi; \quad \% sentence above 4.13
\]

% Inhomogeneous situation-----------------------------------------------------------

% specify either gradient energy or width
if g_or_w == 0    \% 0 = gradient specified
    width(numtheta)=2/sqrt(sq1./gr1); \% domain wall width
elseif g_or_w == 1  \% 1 = width specified
    width(numtheta)=wall_width;
    gr1 = (0.5*width(numtheta))^2 * sq1;
end

% define calculation steps perpendicular to domain wall, xn
if g_or_w == 0
    xlo = -spread*width(numtheta);
    dx=(2*spread*width(numtheta))/(divsteps+1);
    xhi=spread*width(numtheta);
elseif g_or_w == 1
    xlo = -spread*wall_width;
    xhi=spread*wall_width;
    dx = spread*wall_width/(divsteps+1);
end
x = [xlo:dx:xhi];

e4=0; et=11; e3=12; \% 4.16 -- 4.18, strains with tilda on top
% Polarizations for inhomogeneous case (4.39) and (4.25)
Pzmatrix(numtheta,:)=sqrt(sq1./sq3).*tanh(x.*0.5.*sqrt(sq1./gr1));
%4.39
Pz=Pzmatrix(numtheta,:);
Pnmatrix(numtheta,:)=Pz.*((Pz.^2-ps^2).*((n1*a3+(n1*mu(2,2)-
n2*mu(1,1)))/a3^2*a3*(mu(1,1)+mu(2,2))).*Pz.^2+(mu(1,1)*mu(2,2)
-mu(1,2)*mu(2,1)).*Pz.^4);
Pn=Pnmatrix(numtheta,:);
Ptmatrix(numtheta,:)=Pz.*((Pz.^2-
ps^2)*((n2*a3+(n2*mu(1,1)+n1*mu(2,1)))/a3^2*a3*(mu(1,1)+mu(2,2)
).*Pz.^2+(mu(1,1)*mu(2,2)-mu(1,2)*mu(2,1)).*Pz.^4);
Pt=Ptmatrix(numtheta,:);

% Strains for inhomogeneous case (4.21)
denmatrix(numtheta,:)= mij(1,1).*(Pz.^2-
ps^2)+mij(1,2).*Pz.*Pn+mij(1,3).*Pz.*Pt; % delta-epsilon-n=epsilon-n minus lambda-1
den=denmatrix(numtheta,:);
enmatrix(numtheta,:)= 11+den;
en=enmatrix(numtheta,:);
e5matrix(numtheta,:)= mij(2,1).*(Pz.^2-
ps^2)+mij(2,2).*Pz.*Pn+mij(2,3).*Pz.*Pt; % epsilon-5-tilda
e5=e5matrix(numtheta,:);
e6matrix(numtheta,:)= mij(3,1).*(Pz.^2-
ps^2)+mij(3,2).*Pz.*Pn+mij(3,3).*Pz.*Pt; % epsilon-6-tilda
e6=e6matrix(numtheta,:);

% Free energy differences between inhomog. and homog. cases-----------
% see equation (4.6)
% Polarization energy difference dF1 = Fl,i - Fl,h
Fp(numtheta,:)=-0.5*a1.*(Pz.^2-ps^2)+0.25*a2*(Pz.^4-
ps^4)+0.5*a3*(Pn.^2+Pt.^2);
% Strain energy difference dF1 = Fs,i - Fs,h
%Fs2(numtheta,:)=2*b2.*(en+et).*den+b3.*(den.^2+e6.^2)+b4.*e3.*den+b5.*
e5.*e6.*cos(3*t)+b6.*den.*e5.*sin(3*t); %amits expression
Fs(numtheta,:)= (b4.*den.*e3)+(b2.*den.*(den+4.*en)) +
(b6.*den.*e5.*sin(3*t)) + b5.*e5.^2 + (b6.*e5.*e6.*cos(3*t)) +
b3.*(den.^2+e6.^2);
% Coupling energy difference - expressions the same.....
%Fc2(numtheta,:)=g1.*(den.*Pz.^2+11.*(Pz.^2-ps^2))+g2.*e3.*(Pz.^2-
ps^2)+g3.*(den.*Pt.*Pz+e6.*Pn.*Pz).*cos(3*t)+g3.*(den.*Pn.*Pz-
e6.*Pt.*Pz).*sin(3*t)+g4.*e5.*Pn.*Pz; %amit
Fc(numtheta,:)=-ps^2.*(g2.*e3+2.*g1.*en) +
Pz.*2.*(g2.*e3+g1.*den+2.*en) + Pz.*(Pt.*g3.*(den.*cos(3*t)-
e6.*sin(3*t)))+Pn.*(g4.*e5+Pn.*(g4.*e5+g3.*(den.*sin(3*t)+e6.*cos(3*t))
)));
% Gradient energy difference
Fg(numtheta,:)=(gr1.*(gradient(Pz,dx)).^2;
% DW energy difference (eq. 4.40) as a function of distance xn
\[ dF(\text{numtheta},:) = Fp(\text{numtheta},:) + Fs(\text{numtheta},:) + Fc(\text{numtheta},:) + Fg(\text{numtheta},:) ; \]

% Integrated free energy difference and polarization
area(\text{numtheta}) = 0; % integrated free energy difference
area1(\text{numtheta}) = 0;
area2(\text{numtheta}) = 0;
area3(\text{numtheta}) = 0;
area4(\text{numtheta}) = 0;
depol_F(\text{numtheta}) = 0; % depolarization energy
int_Pn(\text{numtheta}) = 0; % integrating Pn vs xn; need for calculating depolarization energy
depol_F2(\text{numtheta}) = 0; % integrating Pn vs xn; need for calculating depolarization energy
G = gradient(Pn, dx);

\[ Pn2 = Pn.^2; \]

% Numerical integration of the energy
for qq = 1:(length(x)-1) % integrate along xvector from -spread*width to spread*width

    index_x = qq;

    area(\text{numtheta}) = area(\text{numtheta}) + (dF(\text{numtheta}, index_x) + dF(\text{numtheta}, index_x+1)) .* 0.5 .* dx; % integrated free energy difference

    area1(\text{numtheta}) = area1(\text{numtheta}) + (Fp(\text{numtheta}, index_x) + Fp(\text{numtheta}, index_x+1)) .* 0.5 .* dx; % integrated polarization energy difference

    area2(\text{numtheta}) = area2(\text{numtheta}) + (Fs(\text{numtheta}, index_x) + Fs(\text{numtheta}, index_x+1)) .* 0.5 .* dx; % integrated strain energy difference

    area3(\text{numtheta}) = area3(\text{numtheta}) + (Fc(\text{numtheta}, index_x) + Fc(\text{numtheta}, index_x+1)) .* 0.5 .* dx; % integrated coupling energy difference

    area4(\text{numtheta}) = area4(\text{numtheta}) + (Fg(\text{numtheta}, index_x) + Fg(\text{numtheta}, index_x+1)) .* 0.5 .* dx; % integrated gradient energy difference

    int_Pn(\text{numtheta}) = int_Pn(\text{numtheta}) + (Pn(index_x) + Pn(index_x+1)) .* 0.5 .* dx; % integrated polarization normal to wall

    depol_F(\text{numtheta}) = depol_F(\text{numtheta}) - 0.5 .* G(index_x) .* int_Pn(\text{numtheta}) .* dx / epsilon_0; % depolarization energy

end

disp(sprintf('ratio of depol1 to depol2 %.5e', (depol_F/depol_F2)));

% Units in before integration J/m3, after integration J/m2, so divide by dx value to get volume
DF(\text{numtheta}) = (depol_F(\text{numtheta}))./(2 * Energyspread.*width(\text{numtheta})); % depolarization energy - correct one!
DF2(numtheta) = (area(numtheta))./(2*Energyspread.*width(numtheta));
% integrated free energy difference
DF3(numtheta) = (depol_F2(numtheta))./(2*Energyspread.*width(numtheta));

% quantities for the second 120 degree slice
totN = length([-pi/6:pi/60:pi/2-pi/60]);

Pzmatrix(numtheta+totN,:) = Pzmatrix(numtheta,:);  % Polarizations along z
Pnmatrix(numtheta+totN,:) = Pnmatrix(numtheta,:);  % Polarizations along n
Ptmatrix(numtheta+totN,:) = Ptmatrix(numtheta,:);  % Polarizations along t
denmatrix(numtheta+totN,:) = denmatrix(numtheta,:);  % strain of some type
e5matrix(numtheta+totN,:) = e5matrix(numtheta,:);  % strain along 5 (xz)
e6matrix(numtheta+totN,:) = e6matrix(numtheta,:);  % strain along 6 (xy)
enmatrix(numtheta+totN,:) = enmatrix(numtheta,:);  % strain normal
Fp(numtheta+totN,:) = Fp(numtheta,:);  % Polarization energy difference
Fs(numtheta+totN,:) = Fs(numtheta,:);  % Strain energy difference
Fc(numtheta+totN,:) = Fc(numtheta,:);  % Coupling energy difference
Fg(numtheta+totN,:) = Fg(numtheta,:);  % Gradient energy difference
dF(numtheta+totN,:) = dF(numtheta,:);  % DW energy as a function of distance xn
DF(numtheta+totN) = DF(numtheta);  % depolarization energy
DF2(numtheta+totN) = DF2(numtheta);  % integrated free energy difference

% quantities for the third 120 degree slice
Pzmatrix(numtheta+2*totN,:) = Pzmatrix(numtheta,:);
Pnmatrix(numtheta+2*totN,:) = Pnmatrix(numtheta,:);
Ptmatrix(numtheta+2*totN,:) = Ptmatrix(numtheta,:);
denmatrix(numtheta+2*totN,:) = denmatrix(numtheta,:);
e5matrix(numtheta+2*totN,:) = e5matrix(numtheta,:);
e6matrix(numtheta+2*totN,:) = e6matrix(numtheta,:);
enmatrix(numtheta+2*totN,:) = enmatrix(numtheta,:);
Fp(numtheta+2*totN,:) = Fp(numtheta,:);
Fs(numtheta+2*totN,:) = Fs(numtheta,:);
Fc(numtheta+2*totN,:) = Fc(numtheta,:);
Fg(numtheta+2*totN,:) = Fg(numtheta,:);
dF(numtheta+2*totN,:) = dF(numtheta,:);
DF(numtheta+2*totN) = DF(numtheta);
DF2(numtheta+2*totN) = DF2(numtheta);

numtheta = numtheta + 1;  % increment counter
end  %..of the for-loop for the t value
numtheta = numtheta - 1;

% end variation loop - save data of interest
position_x = 0;
dwp = round(1+(position_x-xlo)/dx);  % index - at 0 along x
variation = 1;
straine5(variation,:) = e5matrix(:,dwp)';
straine6(variation,:) = e6matrix(:,dwp)';

%End Calculations===============================================

%plotting
theta=pi/6;
index_t=round(theta*60/pi+11);
position_x=0;
index_x=round(1+(position_x-xlo)/dx); %index - at 0 along x
dwp = index_x; %domain wall position
tmatrix=[-pi/6:pi/60:11*pi/6-pi/60]; %matrix of 2 pi radians
tmatrix3=-pi/6:pi/60:(2*pi-pi/6-pi/60);
xvector=x/1e-9;

wo = width(1);
lambda1 = l1;
depolE = DF;
freeE = DF2;
depolE2 = DF3;

%Save data for next time......
if material == 1
    save LNstandard Pnmatrix Ptmatrix Pzmatrix e5matrix e6matrix
denmatrix enmatrix tmatrix3 xvector wo lambda1 dF depolE freeE depolE2;
    disp('saved LN');
elseif material == 2
    save LTstandard Pnmatrix Ptmatrix Pzmatrix e5matrix e6matrix
denmatrix enmatrix tmatrix3 xvector wo lambda1 dF depolE freeE depolE2;
    disp('saved LT');
end

end

C.3.2 Data Generation

C.3.3 Manipulation

%polar plots and 3d plots
clear clc close all fig=0;

%load data!!
load LNstandard; %old values 8 x0
depLN = depolE;
depLN2 = depolE2;
freeLN = freeE';

wLN = wo/1e-9;

load LTstandard;

depLT = depolE;
depLT2= depolE2;
freeLT = freeE';

ww = round(length(xvector)/2);

%consider only at the wall
theta = tmatrix3*180/pi;
index = find(theta > 0);
ang0 = index(1);
index = find(theta > 30);
ang30 = index(1);
ans = ang0; %normalize with respect to x = 0

%normalize Free Energy
freeLNn = (freeLN - freeLN(ang))';
freeLTn = (freeLT - freeLT(ang))';

%normalize Depolarization Energy
depLNn = (depLN - depLN(ang));
depLTn = (depLT - depLT(ang));

%normalize combo
comboLN = (freeLN+depLN')';
comboLNn = comboLN - comboLN(ang);
comboLT = (freeLT+depLT')';
comboLTn = comboLT - comboLT(ang);

%plot magnitudes of each energy
fig=fig+1;
figure(fig)
subplot(3,1,1);
plot(theta, freeLN);
ylabel('free');
subplot(3,1,2);
plot(theta, depLN);
ylabel('depol');
subplot(3,1,3);
plot(theta, depLN+freeLN');
ylabel('free+depol');
suptitle('LN');

fig=fig+1;
figure(fig)
subplot(3,1,1);
plot(theta, freeLT);
ylabel('free');
subplot(3,1,2);
plot(theta, depLT);
ylabel('depol');
subplot(3,1,3);
plot(theta, depLT+freeLT');
ylabel('free+dep');
suptitle('LT');
Appendix D

Supplemental Material for Chapter 5

D.1 Beam Propogation Method

The beam propagation method (BPM) is an iterative electromagnetic wave simulation technique that requires an initial index profile, field distribution, and calculation widow as inputs. It was first used by Feit and Fleck to calculate wave propagation in optical fibers and through the atmosphere.\(^1\)\(^2\) This calculation technique is especially well suited to computer calculations by taking advantage of fast Fourier transformations algorithms. This method is called Fast Fourier Transform Beam propagation method (FFT-BPM).\(^3\)\(^4\)

Briefly, for a two dimensional problem the electromagnetic waves described by the BPM are approximate solutions of the Helmholtz equation given as

\[
\left( \frac{d^2}{dx^2} + \frac{d^2}{dz^2} \right) E(x,z) + k_o^2 n(x,z)^2 E(x,z) = 0
\]

which is a plane wave propagating in the z-direction where \(k_o\) is the wave vector. This can be described as

\[
E(x,z) = A(x) \exp\left[ -i \beta(z) z \right]
\]
where $A(x)$ is the complex amplitude and $\beta(z)$ is the propagation constant. We will assume that the change in $n(x,z)$ in $z$ is gradual compared to the wavelength of the light, then $\beta(z)$ is constant over small distance in $z$ and Equation D2 can be written as

$$E(x,z + \Delta z) = \exp[-i \beta(z) z] E(x,z)$$  \hspace{1cm} \text{D3}

Substituting Equation D1 into Equation D2 yeilds

$$\left[ \frac{d^2}{dx^2} - \beta^2(z) + k_o^2 n^2(x,z) \right] E(x,z) = 0. \hspace{1cm} \text{D4}$$

One of the key assumptions in FFT-BPM is that the change in the refractive index $\Delta n(x,y,z)$ from a background value, $n_o$ is small and can be represented by

$$n(x,z) = n_o + \Delta n(x,z) \hspace{1cm} \text{D5}$$

Using this, and manipulating Equation D4 we arrive at

$$\beta(z) = (\nabla_i^2 + k_o^2 n^2(x,z))^{1/2} \equiv \frac{\nabla_i^2}{(\nabla_i^2 + k_o^2 n_o^2)^{1/2} + k_o n_o} + k_o (n_o + \Delta n(x,z)) \hspace{1cm} \text{D6}$$

where $\nabla_i^2 = (d^2 / dx^2)$. Substituting Equation D6 into Equation D3 yields

$$W(x,z + \Delta z) = \exp\left[ -i \Delta z \left( \frac{\nabla_i^2}{(\nabla_i^2 + k_o^2 n_o^2)^{1/2} + k_o n_o} + k_o (n_o + \Delta n(x,z)) \right) \right] W(x,z) \hspace{1cm} \text{D7}$$

where $W(x,z)$ is a new function that describes the propagation through the background medium with index $n_o$ given by

$$W(x,z) = E(x,z) \exp[i k_o n_o z]. \hspace{1cm} \text{D8}$$
At the core of the FFT-BPM is a manipulation of Equation D7. With some mathematical approximations,\(^4\) this equation is split into three parts as

\[
W(x, z + ?.z) = \exp \left[ -i \frac{\Delta z}{2} \left( \frac{\nabla_i^2}{(\nabla_i^2 + k_o^2 n_o^2)^{1/2} + k_o n_o} \right) \right]
\times \exp \left[ -i \Delta z k_o \Delta n(x, z) \right]
\times \exp \left[ -i \frac{\Delta z}{2} \left( \frac{\nabla_i^2}{(\nabla_i^2 + k_o^2 n_o^2)^{1/2} + k_o n_o} \right) \right] W(x, z)
\]

where \(\nabla_i^2\) is an operator. The first line of Equation D9 it the propagation through the homogeneous medium with index \(n_o\) a distance of \(\Delta z/2\), the second line is the phase correction due to the variation of the index \(\Delta n(x, y, z)\), and the third line is another propagation of distance \(\Delta z/2\).

Equation D9 is particularly easy to implement on a computer when it is realized that in optical systems, propagating through distances is a simple multiplication in Fourier space while a phase correction is a simple multiplication in real space.\(^5\)

Numerically this is given by

\[
\omega(m, z + \frac{z}{2}) = \exp \left[ -i \frac{\Delta z}{2} \left( \frac{-k_{xm}}{(-k_{xm}^2 + k_o^2 n_o^2)^{1/2} + k_o n_o} \right) \right] \omega(m, z)
\]

\[
W_+ \left(x, z + \frac{z}{2}\right) = \exp \left[ -i \Delta z k_o \Delta n(x, z) \right] W_- \left(x, z + \frac{z}{2}\right)
\]

where Equation D10 is the k-space propagation through distance \(\Delta z/2\) and Equation D11 is the phase correction in real space. The value \(\omega\) is the Fourier transform of \(W\), given by

\[
\mathcal{F}\left(\omega(m, z + \frac{z}{2})\right) \rightarrow W(w, z + \frac{z}{2}).
\]
propagation can be efficiently calculated. This is pictured graphically in Figure D-1. The total propagation distance, $z$, is broken into segments, $\Delta z$.

**Figure D-1:** Iterative process for the calculation of fast Fourier transform BPM.

### D.1.1 Main Program

The main propagation program is the uppermost program which calls the device structure, builds the calculation window, determines the index distribution, and does the iterative calculations.

```plaintext
clear; clc; home;
disp('Beam Propagation Program for scanner geometries');
disp('');
```
Portion=1;
xvar=0;
nvar=0;

t=input('database filename? ','s');
waveguide = input('Show waveguide? y/n [y] ','s');
colour = input('Bright color pallet for lenses? y/n [n] ','s');
BandW = input('Black and white? y/n [n] ','s');
if isempty(colour)    pallette=0; end
if colour == 'y'      pallette = 1; else    pallette = 0; end
if isempty(waveguide) drawWG=1; end
if waveguide == 'y'   drawWG=1; else    drawWG=0; end
if isempty(BandW)     BW=0; end
if BandW == 'y'       BW=1; else    BW=0; end

outname=strcat(t,'_out');
bwpic=strcat(t,'_bw.ps');
clrpic=strcat(t,'_clr.ps');
pl='y';

if (pl=='y'),
    close all;
    ssz = get(0,'ScreenSize');
    imageplot=figure('Position',[ssz(3)*.1 ssz(4)*.5 ssz(3)*.85 ssz(4)*.4],
                      'PaperPosition',[2.75 2.5 4 6],'Name','Image');
    intensityplot=figure('Position',[ssz(3)*.1 ssz(4)*.05 ssz(3)*.4
                                    ssz(4)*.3],'Name','Intensity Profile');
    end;

eval(t);  % initialize variables and define database

disp(sprintf('Filename where Ef stored: %s',outname));
dnv=zeros(1,Xpoints);
%compute number of databases
DBnum=size(DB,3);

% x and z values
% Length and Width are the dimensions of the grid, defined in the
x=[0:Xpoints-1]/(Xpoints-1)*Width-Width/2;
z=[0:Zpoints-1]/(Zpoints-1)*Length+Zstart;

% mode at the input
Ep=gaussian_mode(lam,no,wo,x,z(1));
Ep=squash(4*deltax,Ep,x);       %squash field
Ein=Ep;
svb=bord(3,.01*i,x);            %absorbing border
svb=svb+bord(2,.05*i,x);
svb=svb+bord(1,.1*i,x);

alpha=deltaz/deltax;
gamma=deltax*ko*no;
Pv=propv(Xpoints,alpha,gamma);

if Xdisprange>Width, Xdisprange=Width; end
% Setup output matrix for field and waveguide images
nx=xres;
if nx>Xpoints, nx=Xpoints; end;
nz=zres;
if nz>Zpoints, nz=Zpoints; end;
newz=0;
Ef=zeros(nz,nx);
Wg=uint8(zeros(nz,nx));
Efmax=zeros(1,Zpoints);
Efmax_where=zeros(1,Zpoints);
xsamp=round(interp1(x,[1:Xpoints],([0:nx-1]/(nx-1)-1/2)*Xdisprange));
xaxis=interp1(x,xsamp);
zsamp=round(interp1(z,[1:Zpoints],(min(z)+[0:nz-1]/(nz-1)*Length)));
zaxis=interp1(z,zsamp);

% get variation structure
svv=vstruct(z);
if (pl=='y'),
figure(imageplot);
figure(intensityplot);
plot(xaxis,interp1(Ein,xsamp).^2);
kevclock('cmInit','Start');
end;

% Main Propagation Loop – build structure, propogates
zndx=1;
for zi=1:Zpoints,
    dnv=svb;
    % Generate structure
    for DBndx=1:DBnum,
        sv(DBndx,:)=gstruct (DB(:,,:,:DBndx),x,z(zi));
        % Compute output matrix
        if ((z(zi) >= eb(DBndx,3)) & (z(zi) <= eb(DBndx,4)))
            dnv=sv(DBndx,:)*dn(DBndx)*2-dn(DBndx)+svb;
        end
    end
    if(zi==zsamp(zndx)),
        newz=zndx;
        Ef(newz,:)=abs(interp1(Ep,xsamp));
        newWg=zeros(1,nx);
        for DBndx=1:DBnum,
            newWg=newWg+interp1(sv(DBndx,:),xsamp);
        end
        Wg(newz,:)=newWg;
        zndx=zndx+1;
    end
end
% lens correction
Lv = lens(alpha, gamma, no, dnv);

% save max field value and position
[Efmax(zi), Efmax_where(zi)] = max(abs(Ep).^2);

% Propagate one step forward
Ep = Lv.*fft(ifft(Ep).*Pv);
end

if(pl=='y'),
  kevclock('cmClose','End');
end;
if(pl~='y'),
close all;
ssz = get(0,'ScreenSize');
set(0, 'DefaultSurfaceEdgeColor', 'none');
imageplot = figure('Position', [ssz(3)*.1 ssz(4)*.5 ssz(3)*.85
  ssz(4)*.4], 'PaperPosition', [2.75 2.5 4 6], 'Name', 'Image');
intensityplot = figure('Position', [ssz(3)*.1 ssz(4)*.05 ssz(3)*.4
  ssz(4)*.3], 'Name', 'Intensity Profile');
end;

figure(intensityplot);
% prepare data for output as image and intensity
Eout = Ep;
pa = angle(Eout);
lpa = length(pa);
pa(lpa+1) = pa(lpa);
pau = unwrap(pa);
dpu = diff(pau)/deltax;
pra = dpu/ko/no*180/pi;

Emax = max(max([abs(Ein) abs(Eout)]));
Pmax = ceil(max(abs(pra)));

EEmin = Pmax*((abs(Ein)/Emax).^2*1.6-1);
EEout = Pmax*((abs(Eout)/Emax).^2*1.6-1);

axis([-Width/2 Width/2 -Pmax Pmax]);
plot(xaxis, interp1(pra, xsamp), ...
    xaxis, interp1(EEmin, xsamp), ...
    xaxis, interp1(EEout, xsamp));
axis;

disp('Generating Waveguide outline');
if drawWG == 1
  Wg(1:nz-1, 1:nx-1) = (Wg(1:nz-1, 1:nx-1) ~= Wg(2:nz, 2:nx));
  Wg(nz,:) = zeros(1, nx);
  Wg(:, nx) = zeros(nz, 1);
else
  Wg = uint8(zeros(nz, nx));
end

disp('Generating Image');
Emax = max(max(Ef));
D.1.2 Sample Device Program

This is a sample structure run by the main code above to generate a simple rectangular scanner.

```matlab
figure(imageplot);
map=colormap;
map(1,:)=[1 1 1];
colormap(map);
N=max(size(colormap));
Image=uint8((round((Ef/Emax).^2*(N-2))+1).*(1-double(Wg))+1);
image(zaxis/1000,xaxis,transpose(double(Image)));
set(gcf,'Color',[1 1 1]);
set(gca,'Color',[0.5 0.5 0.5]);
set(gca,'YTick',[])
set(gca,'XTick',[])

initalize parameters and set the structure
%basic parameters of laser
lam=.6328;
wo=50;
ko=2*pi/lam;
disp(sprintf('lambda = %.4fum
two = %.1fum',lam,wo));

%basic material parameter LiNbO_3
no=2.174; %extraordinary refractive index
r33=30.3e-6; %electro-optic coefficient (microns/Volt)
V=1000; %applied voltage (Volts)
t=100; %thickness of sample in microns
dn(1)=.5*no^3*r33*V/t;

%number of points in propagating mode, must be power of 2 for Xpoints
Xpoints=2^12;
Zpoints=2^13;

%size of BPM grid
Width=6.0e3;
Xdisprange=Width;
Length=30.0e3;
entmarg=0;

deltaz=Length/(Zpoints-1);
deltax=Width/(Xpoints-1);
```
disp('');

%Start propagating here
Zstart=-500;
xres=300;zres=900;

% database file
DB1=[]; DB2=[];

%definition of Rectangular lenses
TriNumber=10; %10
Height=((75+840)/2)*2;
Total_length=20000;

%calculations of 1st triangle
Tri_length=Total_length/TriNumber;
x1=-Height/2;
z1=entmarg;
x2=Height/2;
z2=z1+(Tri_length/2);
x3=-Height/2;
z3=z1+(Tri_length);
zposition=z1;

%z1=entmarg; %set first lens in from margin %add lenses to database
for ndx=1:TriNumber
    DB1=adbase(DB1,'TRI_ANY',x1,z1,x2,z2,x3,z3,zposition);
    zposition=zposition+Tri_length;
    z1=z1+Tri_length;
    z2=z2+Tri_length;
    z3=z3+Tri_length;
end

eb(1,:)=[-Width/2 Width/2 -250 Length-750];
DB=[];
DB(1:size(DB1,1),:,:)=DB1;

D.1.3 Supporting Programs

Below are miscellaneous programs called by the main program routine or the structure program.

function soln=lens(alpha,gamma,no,dnv)
%Create lens vector given the parameters alpha and gamma and the core index no and the change from core index dnv (vector)
const=i*alpha*gamma/no;
soln=exp(const*dnv);
% find the edges of a triangle for input into the adbase command
function soln=tri_any(x1,z1,x2,z2,x3,z3,z)
% Create triangle with corners (x1,z1), (x2,z2), (x3,z3)
% z1,z2,z3 should be in ascending order, i.e. z1<=z2<=z3
if (z<=z3) & (z>=z1),
    soln(1)=x1+(z-z1)*(x3-x1)/(z3-z1);
    if (z==z2),
        soln(2)=x2;
    elseif (z<z2),
        soln(2)=x2+(z-z2)*(x1-x2)/(z1-z2);
    else
        soln(2)=x2+(z-z2)*(x3-x2)/(z3-z2);
    end;
    if soln(1)>soln(2),
        temp=soln(1);
        soln(1)=soln(2);
        soln(2)=temp;
    end;
else
    soln=[0 0];
end;

function soln=adbase(DB,struct,p1,p2,p3,p4,p5,p6,p7)
% This creates a structure to be read by gstruct and displays output
to screen. End result will be variable DB1 to be a vector where rows
represent separate elements (i.e. triangle) and the values in the
columns refer to struct, p1, etc. specific information about the
element. So if scanner has 13 triangles, DB1 should have 10 rows
% Add a structure to the data base DB
% struct is a string specifying element type
% (CIRCLE, RECT, LINE, TAPER, ARC, TRI, ELLIPS, PLCV, TRI_ANY)
% p1-p7 are optional parameters
%initialize variables
scode=0;
sp1=sprintf('Nothing');
sp2=sprintf('Nothing');
sp3=sprintf('Nothing');

sz=size(DB);
xpos=sz(1)+1;

if (nargin<=8), p7=0; end;
if (nargin<=7), p6=0; end;
if (nargin<=6), p5=0; end;
if (nargin<=5), p4=0; end;
elseif strcmp(struct,'TRI_ANY'),
scode=9;
disp([sp1 sp2 sp3]);

DBV(1)=scode;
DBV(2)=p1;
DBV(3)=p2;
DBV(4)=p3;
DBV(5)=p4;
DBV(6)=p5;
DBV(7)=p6;
DBV(8)=p7;

DB(nxpos,:)=DBV;
soln=DB;

function soln=gstruct(DB,x,z)
%gstruct(DB,x,z)
%Generate structure vector by imaging database DB given the x vector and the z coordinate
S=[0 0];
sdb=size(DB);
lsdb=size(DB(1));
sv=zeros(1,length(x));

for js=1:lsdb,
stype=DB(js,1);
p1=DB(js,2);
p2=DB(js,3);
p3=DB(js,4);
p4=DB(js,5);
p5=DB(js,6);
p6=DB(js,7);
if (stype==1), [S]=circle(p1,p2,p3,p4,z);
elseif (stype==2), [S]=rect(p1,p2,p3,p4,z);
elseif (stype==3), [S]=line(p1,p2,p3,p4,p5,z);
elseif (stype==4), [S]=taper(p1,p2,p3,p4,p5,p6,z);
elseif (stype==5), [S]=arc(p1,p2,p3,p4,p5,p6,z);
elseif (stype==6), [S]=tri(p1,p2,p3,p4,z);
elseif (stype==7), [S]=ellips(p1,p2,p3,p4,z);
elseif (stype==8), [S]=pln_cvx(p1,p2,p3,p4,z);
elseif (stype==9), [S]=tri_any(p1,p2,p3,p4,p5,p6,z);
elseif (stype==10), [S]=poscyllens(p1,p2,p3,p4,p5,p6,z);
elseif (stype==11), [S]=parabolic(p1,p2,p3,p4,p5,p6,z);
end;

sv=astruct(sv,S,x);
end;
soln=sv;
References

VITA

David Scrymgeour was born March 23, 1975 in Marion, Ohio. After living in various locales in the western United States, he began his undergraduate education at the University of Utah. After jumping majors several times, he decided to choose a course of study that encompassed aspects of all of his previous majors and decided to study Materials Science. In the winter of 1996, he transferred to The Pennsylvania State University and started coursework in Ceramic Science. During the summer of 1997 he worked at the Idaho National Engineering Laboratory where a heady mix of outdoor recreation and material science made him realize that research would be a good occupation. He completed his Bachelor’s Degree in Ceramic Science and Engineering in May, 1998, and then, swearing never to return, headed to parts unknown.

During the next year he went to work for four months the Idaho National Engineering Laboratory and for 8 months at General Electric Corporate Research and Development Center in Schenectady, New York. Having his fill of being a scientific peon, he returned to school in the Fall of 1999 again at the Pennsylvania State University where he enrolled in the Intercollege Materials Program. He was awarded an NSF Graduate Research Fellowship in Spring of 2001 which clinched his decision to stay for a PhD. His thesis work was on optical materials and optical devices.