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Nonlinear Optical Studies of Defects and Domain Structures in Perovskite-Type Dielectric Ceramics

David J. Ascierno
The Graduate Center, City University of New York

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NONLINEAR OPTICAL STUDIES OF DEFECTS AND

DOMAIN STRUCTURES IN PEROVSKITE-TYPE DIELECTRIC CERAMICS

by

DAVID J. ASCIENZO

A dissertation submitted to the Graduate Faculty in Physics in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York

2017
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and Domain Structures in Perovskite-type Dielectric Ceramics

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David J. Ascienzo

This manuscript has been read and accepted by the Graduate Faculty of Physics
in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

_________________________  ____________________________
Date  Professor Yuhang Ren
      (Chair of Examining Committee)

_________________________  ____________________________
Date  Professor Igor L. Kuskovsky
      (Executive Officer)

Supervisory Committee:

Professor Steven Greenbaum

Professor Ying-Chih Chen

Professor Jun Ouyang

Professor Yu Zhang

THE CITY UNIVERSITY OF NEW YORK
Abstract

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In order to improve future generations of ceramic capacitors, a deeper understanding of voltage-induced dielectric breakdown and electrical energy storage limitations in these materials is required. This dissertation presents the use of far-field optical second harmonic generation (SHG) polarimetry, as well as photoluminescence and confocal Raman spectroscopy, for investigating: 1) dc electric field-induced structural distortions at undegraded Fe-doped SrTiO$_3$ (Fe:STO) electrode interfaces, 2) structural defect and strain formation due to oxygen vacancy migration in electrodegraded Fe:STO single crystals, and 3) mixed tetragonal and rhombohedral phases in ferroelectric Zr-doped BaTiO$_3$ (BZT) thick films exhibiting high energy densities and efficiencies.

First, electric field-induced second harmonic generation (EFISHG) and photoluminescence spectroscopy were used to study local structural changes at electrode interfaces in reduced and oxidized Fe:STO single crystals at room temperature. Results show that ionic displacements along the applied field axis lead to electrostrictive distortions which are described by Fe:Ti-O bond stretching and bending effects in Fe:Ti-O$_6$ octahedra. Differences in the EFISHG responses of the oxidized and reduced crystals are explained by the Schottky barriers and built-in electric fields at their metal-dielectric interfaces which depend strongly on local oxygen vacancy concentrations.
The built-in electric field in the interfacial depletion region is revealed to be greater in oxidized Fe:STO compared to reduced Fe:STO, leading to stronger structural changes at low dc voltages in the reduced crystal compared to the oxidized one. Structural differences between the reduced and oxidized Fe:STO cathodes are indicated by both EFISHG and photoluminescence measurements, showing that the clustering of oxygen vacancies at the reduced cathode leads to deviations from tetragonal (4mm) symmetry.

Second, structural defect and strain formation in electrodegraded reduced and oxidized Fe:STO single crystals were investigated using optical SHG and confocal Raman measurements. SHG revealed structural inhomogeneity resulting from the formation of Fe$^{4+}$/oxygen ion and Fe$^{3+}$/oxygen vacancy aggregation sites along the degraded anode and cathode interfaces, respectively. It is also shown that mixed Fe$^{3+}$/Fe$^{4+}$ states and strain are generated across the electrocoloration boundaries, or color fronts, in both crystals. These results, as well as oxygen sublattice variations between the anodic and cathodic bulk shown by confocal Raman data, depict the creation of a structural interface along the color front. In comparing both electrodegraded oxidized and reduced Fe:STO crystals, we reveal that structural strain is higher across the oxidized crystal’s color front compared to the reduced crystal, although this strained region is slightly wider in the reduced crystal compared to the oxidized one. We further indicate that structural and electrochemical inhomogeneity has a dependence on the distance between electrodes due to the finite size of the strained region across both color fronts.

Third, optical SHG polarimetry was used in the reflection and transmission geometries to characterize heterophase polydomain structures in Zr-doped BaTiO$_3$ (BZT) ferroelectric films exhibiting high energy storage densities and efficiencies. Under a compressive film-substrate misfit strain, tetragonal and rhombohedral phases can coexist in these films as elastic domains. In
the reflection geometry, the SHG signal arises primarily from compressive strain-induced tetragonal domains growing along the thickness of the film. In the transmission geometry, the SHG signal arises from rhombohedral domains and the SHG contributions from tetragonal domains effectively vanishes. Rhombohedral symmetry is shown to increase with film thickness as a result of strain relaxation away from the tetragonal film-substrate interface. Greater misfit strains are shown to lead to a higher degree of tetragonal symmetry in the films. In addition, the presence of mixed rhombohedral and tetragonal phases is supported by transmission electron microscopy (TEM) and x-ray diffraction (XRD) measurements. The high energy performance of the films is directly connected to these mixed tetragonal and rhombohedral polydomain structures which serve to decrease remnant polarizations and help delay saturation of the dielectric’s polarization.
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Chapter 1: Introduction and Motivation

Linear and nonlinear dielectric ceramics are a linchpin in modern technologies as core components of capacitive devices designed for the storage of electric charge and energy. Due to their fast charge-discharge speeds and high dielectric strengths, dielectric capacitors have the potential to out-perform batteries, fuel cells, and electrochemical capacitors in the next generation of electrical energy devices [1]. Although these materials are capable of storing and supplying electricity with very high energy and power densities, their lifetime, reliability, and overall performance are limited by the onset of voltage-induced dielectric breakdown mechanisms as well as device underachievement from high remnant polarizations and early polarization saturation.

The voltage-induced breakdown mechanisms which wreak havoc on the insulating properties of electroceramics are multifaceted and heavily influenced by both electronic and ionic transport processes across the dielectric’s bulk and metal-dielectric interfaces. Of equal importance to the performance of these materials is the electromechanical coupling between imposed electrical fields and structural strain which leads to electrostriction, a property of all dielectric materials in which the applied electric field distorts the crystal lattice. Furthermore, the formation of structural defects and inhomogeneities is exasperated by the mass transport and accumulation of ionic and electronic defects in these materials, further contributing to dielectric degradation [2].

During recent years, we have successfully utilized optical second harmonic generation (SHG), with the support of other techniques, to investigate \( dc \)-bias induced local structural distortions and defects in fresh and electrodegraded \( Fe \)-doped \( SrTiO_3 \) (Fe:STO) single crystals. Our study of electric field-induced and ionic defect-induced structural change in perovskite-type electroceramics has advanced the community’s knowledge of voltage-induced dielectric
breakdown. In addition, we have worked on the characterization of heterophase polydomain structures in domain-engineered ferroelectric thick films exhibiting pseudo-linear \( P-E \) hysteresis curves which showcase high energy densities and efficiencies. In light of these accomplishments, the primary focus of this dissertation is to relay our investigations of voltage-induced structural changes in perovskite-type dielectric single crystals and heterophase polydomain structures in perovskite-type ferroelectric thick films. These studies have directly contributed to the understanding of voltage-induced dielectric ceramic breakdown and the strain-engineering of domain structures for improved dielectric ceramic energy performance.

1.1 \textit{dc} Electric Field-induced Degradation in Perovskite-type Dielectrics

Over recent years, industrial needs have been demanding further miniaturization of electroceramic devices resulting in thinner dielectric layers [2, 3]. As a result of smaller material scales, greater electrical stresses are being applied across dielectrics and leading to accelerated device failure rates. From the combined effects of high electrical and thermal stresses, dielectric ceramics undergo a common breakdown process known as voltage-induced resistance degradation [4-7]. Over time, the insulation resistance of the ceramic decreases and leads to a significant increase in leakage current. This degradation process inevitably results in device failure since the dielectric loses its insulating properties. Thus, it is crucial to fully understand the factors contributing to the voltage-induced resistance degradation process in order to improve electroceramic device lifetime and reliability.
Due to its well-defined defect chemistry and similar properties to the popular ferroelectric barium titanate ($\text{BaTiO}_3$), strontium titanate ($\text{SrTiO}_3$) has served researchers as an excellent model for studying the causes and effects of voltage-induced degradation in perovskite-type dielectric ceramics. After years of extensive research, it was established that resistance degradation in electroceramics depends strongly on the defect chemistry of the material. In particular, evidence pointed to the electric field-driven migration of oxygen vacancies as a dominative cause for the phenomenon [5-12]. Under an imposed $dc$ electric field, the initially uniform distribution of oxygen vacancies in the material changes as vacancies migrate towards the cathode while oxygen ions move towards the anode. This so-called demixing process results in the formation of an ionic and electronic defect concentration gradient, as well as an oxidation state gradient for central B-site cations in the perovskite lattice. The concentration of oxygen vacancies and conduction electrons becomes largest at the cathode and lowest at the anode [13, 14]. Consequently, an electrochemical $p$-$n$ junction is induced, where the anodic region becomes $p$-type conducting and the cathodic region becomes $n$-type conducting, as a result of local electronic equilibria changes made in an attempt to conserve charge neutrality (a.k.a electroneutrality) across the crystal [5-7]. This electrochemical $p$-$n$ junction is forward biased and ultimately leads to an increase in leakage current.

The model for oxygen vacancy demixing was first described in a series of papers on $dc$ electric field-induced degradation in perovskite-type titanates by Waser et al. (1990) and Baiatu et al. (1990) [5-7]. In formal terms, the model presents a $dc$ electric field-induced stoichiometry polarization based on the mixed electronic and ionic conductivity in electroceramics. For example, consider a typical parallel-plate capacitor, as shown in Fig. 1.1, with metal electrodes deposited on opposite crystal faces of the electroceramic for $dc$ electric field application.
Figure 1.1: Illustration of oxygen vacancy migration in a typical parallel-plate, metal-dielectric-metal, capacitor. The initially uniform distribution of oxygen vacancies changes in response to the dc electric field.

During poling, one electrode is positively charged and acts as the anode while the other electrode is negatively charged and acts as the cathode. This charging process results in an induced polarization across the bulk of the electroceramic. Positively charged oxygen vacancies will begin to travel towards the negatively charged electrode at a rate dependent on the temperature, i.e. the higher the temperature, the faster the diffusion. Since the metal electrodes have a blocking effect (For temperatures less than ~400°C[15, 16]) on the migration of ionic charge carriers, an accumulation of oxygen ions and vacancies at the anode and cathode interfaces occurs, respectively.

By analyzing STO’s defect chemistry, Baiatu et al. (1990) produced oxygen vacancy concentration profiles across electrodegraded STO crystals based on defect structure constants and
a numerical solution to the general diffusive transport equation for mixed electronic-ionic conducting perovskite-type titanates. Their results showed good agreement with experimentally observed electrocoloration boundaries in electrocolored STO. From their phenomenological electrodegradation studies, they were also able to investigate the time evolution of the electric field distribution as well as the electrocoloration boundary across STO. In addition, Waser et al. (1990) investigated resistance degradation rates as functions of dopant concentration, temperature, and imposed dc voltage in STO ceramics. From their data, they concluded that: 1) The migration of oxygen vacancies across ceramic grain boundaries is electrodegradation rate-limiting. 2) The electrical potential drop per ceramic grain boundary is crucial for comparing electrodegradation rates in ceramics of similar chemical compositions with different mean grain sizes. 3) Internal electric fields are concentrated at ceramic grain boundaries during electrodegradation. 4) The electrodegradation rate has a power law dependence on the three interrelated parameters, electrical voltage, electric field, and dielectric thickness. 5) Under a constant dc electric field, the time required for electrodegradation is proportional to the dielectric thickness since the distance migrated by oxygen vacancy defects increases proportionally with dielectric thickness. 6) There is no correlation between the acceptor dopant concentration and the electrodegradation rate, which suggests ceramic grain boundaries aren’t affected by dopant concentration. 7) The type of acceptor dopant has a strong influence on the electrodegradation rate and activation energies for oxygen diffusion. 8) Electrodegradation is typically limited, resulting in a stabilization of the leakage current density, i.e. leakage currents do not increase indefinitely. 9) Time-dependent studies of the electric field distribution and electrocoloration boundaries support the electromigration of oxygen vacancies as being essential for the electrodegradation process. 10) Electrodegradation has no obvious dependence on the ambient oxygen partial pressure.
Later, Wang et al. (2016) [4] would expand on the quantitative modeling of voltage-induced resistance degradation in acceptor-doped STO by investigating the temporal evolution of electrical conductivities under a \textit{dc} electrical field. To do so, they numerically solved the transport equations for ionic and electronic defects coupled with the defect reaction equilibrium equations. They discussed how local electron and hole concentrations are controlled by the local electronic defect equilibria. It was shown how the \textit{dc} electric field-induced migration of oxygen vacancies results in a subsequent, instantaneous reformation of local electronic defect equilibria which leads to resistance degradation. They further demonstrated that, under long-term \textit{dc} electrical field application, resistance degradation and charge defect distributions are strongly influenced by crystal annealing oxygen partial pressures, and imposed \textit{dc} voltages and ambient temperatures during electrodegradation.

Furthermore, Rodewald et al. (2000) [17] was also able to verify the spatially resolved conductivity distributions in Fe:STO single and poly crystals under \textit{dc} electric field stresses using micro-contact impedance spectroscopy. Liu et al. (2008) [18, 19] performed thermally stimulated depolarization current measurements on Fe:STO crystals to investigate the relationship between depolarization effects and degradation phenomena. They were able to study dielectric relaxations of polarized dipoles, charge traps, and oxygen vacancies in Fe:STO crystals. Wojtyniak et al. (2013) [20] analyzed electrodegradation and resistive switching in Fe:STO crystals. In their work, they investigated the electrocoloration of STO single crystals with different Fe dopant concentrations and found that extended defects and oxygen vacancy diffusion pathways formed between the metal electrodes. Furthermore, they showed that the migration of oxygen ions towards the anode interface resulted in the trapping of oxygen gas bubbles between the crystal surface and electrode. Yang et al. (2004) [13, 14] combined impedance spectroscopy, transmission electron
microscopy, and electron energy-loss spectroscopy to look into the microchemical and microstructural causes of resistance degradation in BTO capacitors. They observed that oxygen vacancy concentrations increased towards the cathode. They also showed that more linear defects in the BTO grains formed towards the cathode side, resulting from the clustering of oxygen vacancies. Their analysis showed that microstructural modulations to crystal lattice planes corresponded with asymmetric oxygen distributions across highly degraded capacitors. Moballegh et al. (2015) [21] employed electron microscopy, diffraction, and spectroscopy in order to investigate the local evolution of microstructure and microchemistry at interfaces during electrodegradation in TiO$_2$ single crystals. They observed the accumulation of sub-stoichiometric point defects at the cathode interface. They also discussed the effect of stoichiometry on insulation-resistance, providing evidence that lower defect concentrations lead to higher resistivity. In short, multiple findings support that the $dc$ electric field-induced redistribution of oxygen vacancy defects plays a critical role in the resistance degradation of perovskite-type electroceramics.

Despite all of this extensive research performed to understand the underlying origins of voltage-induced insulation-resistance degradation, oxygen vacancy demixing, and electrical conductivity changes in perovskite-type electroceramics [5-7, 9, 10], the correlated structural changes due to ionic and electronic defect migration and $dc$ electrical stress in these materials is not well understood. In this dissertation, both pristine and electrodegraded $Fe$-doped $SrTiO_3$ (Fe:STO) single crystals were studied in order to investigate the effects of $dc$ electrical stress and electronic and ionic defect electromigration on the perovskite structure. Using far-field optical second harmonic generation (SHG) polarimetry, supported by confocal Raman and photoluminescence spectroscopy, we were able to effectively investigate: 1) Local structural changes at Fe:STO electrode interfaces resulting from oxygen vacancy migration and $dc$ electrical
stress; 2) The formation of structural defects, strain, and inhomogeneities at electrode interfaces and bulk regions in electrodegraded Fe:STO single crystals.

First, we revealed that the application of a dc electrical stress across pristine Fe:STO leads to a quadratic straining of the local lattice near the electrode interface. This straining is a result of electrostrictive deformations from ionic displacements along the electrical field axis. Furthermore, the use of platinum (Pt) metal electrodes led to the formation of Schottky barriers which influenced structural changes occurring in the probed interfacial depletion regions. Sample annealing allowed us to perform a comparison of these structural deformations in electrochemically reduced and oxidized Fe:STO single crystals. We found that the local oxygen vacancy concentration and poling direction greatly affected the rate and strength of the electrostrictive distortions. Our results ultimately showed that oxygen vacancies lower the Schottky barrier height and weaken the insulating properties of interfacial depletion regions, resulting in greater structural deformation under low dc voltage stress.

Next, we investigated electrically degraded reduced and oxidized Fe:STO single crystals and observed a high degree of structural inhomogeneity to occur along the interfaces. This inhomogeneity was concluded to be a direct result of the formation of ionic defect aggregation sites along each interface. The anodic and cathodic bulk regions were shown to be dominated by two different kinds of oxygen bond distortions, resulting in the formation of a structural interface at the electrocoloration boundary. We further reveal the formation of a structural strain field across this boundary. By comparing strain across the oxidized and reduced crystals, we conclude that oxygen vacancies play an important role in both strain relaxation and electroneutrality during the electrodegradation process. Our results clearly show that oxygen vacancy demixing results in the formation of structural defects and long-range structural strain.
1.2 Strain Field-tuning of Perovskite-type Ferroelectric Films

The international need to replace fossil fuel energy resources with clean, renewable energy sources has led to a very high demand for electronic and microelectronic devices which can efficiently store and release large amounts of electricity. The most promising candidates for such power applications are dielectric ceramics exhibiting high energy storage densities and energy efficiencies. In accordance with a rising industrial need for high energy performance electroceramics, this dissertation presents the characterization of heterophase polydomain structures ferroelectric Zr-doped $\text{BaTiO}_3$ (BZT) thick films using optical second harmonic generation. These epitaxially strained BZT films exhibit high energy densities (50 to 170 J/cm$^3$) and efficiencies (up to ~96%) proposed to have been made possible by the presence of mixed tetragonal and rhombohedral phases as elastic domains throughout the film lattice. This heterophase polydomain structure lowers remnant polarizations and delays saturation of the polarization within the ferroelectric films, allowing them to store more electrical energy while maintaining low charge-discharge loss. By varying the thickness of the film, strain relaxation can be taken advantage of and the ratio between tetragonal and rhombohedral domains becomes tunable. An understanding of how domain structure is affected by lattice misfit strains resulting from the substrate species and strain relaxation due to increased dielectric thickness will ultimately lead to a greater understanding of ferroelectric film engineering for high energy storage applications.

The strain tuning of ferroelectric films has been reviewed by Schlom et al. (2007) [22]. The effects of biaxial strain on the electrical properties of epitaxially grown ferroelectric films and
superlattices are discussed in detail. Theoretical approaches, including first principle methods, thermodynamic analysis, and phase-field models are applied to biaxially strained ferroelectric films. Important experimental techniques for characterizing the properties of strained ferroelectric films and superlattices, as well as the ideal substrates to grow films on are also talked about. The use of strain for tuning the capabilities of ferroelectric films revolves around manipulating the coupling between the electrical and mechanical properties of the material. In a ferroelectric crystal, there is a spontaneous polarization which can be reoriented, or poled, through the application of an external electric field. The spontaneous polarization can be altered by strain effects since a strong quadratic coupling exists between polarization and strain. At the unit cell scale, spontaneous electric dipole moments are formed from relative displacements between the ions composing the lattice, as shown in Fig. 1.2.

**Figure 1.2**: Comparison between a non-polar (cubic SrTiO₃) perovskite unit cell and a polar (tetragonal BaTiO₃) perovskite unit cell (Graphic made in Avogadro 1.1.1[23]).

Over large volumes, these polar unit cells combine to form polarized crystal grains, or domains, which results in the stabilization of macroscopic polarization fields across the bulk of the material. By straining the crystal lattice, the ions composing the material can be coerced into alternative
positions, thus effectively modifying polar ordering and changing the overall domain structure. The domain morphology of a ferroelectric plays a critical role in governing the energy storage properties of the material.

The energy storage performance of a ferroelectric crystal can be determined from measuring the response of its polarization to an external electric field, *i.e.* measuring its *P*-*E* hysteresis loop. The *P*-*E* hysteresis loop of a typical ferroelectric film exhibits a large remnant polarization (*P_r*) and a slightly larger saturation polarization (*P_s*) under an applied electric field. As a result, the *P*-*E* hysteresis loop is wide, as shown in Fig. 1.3a.

**Figure 1.3:** Polarization-electric field (*P*-*E*) hysteresis loops, as shown by Cheng et al.[24]. (a) Typical ferroelectric hysteresis loop; (b) Example of a slim hysteresis loop; (c) Partially shown hysteresis curves near their respective saturation points. Delayed saturation results in a higher energy density. For all figures, the green area represents the discharged energy density (*W_d*), while the brown area is the energy loss (*W_{loss}*).

The energy storage characteristics of the *P*-*E* hysteresis loop can be determined by the shaded areas in the plot since the green areas represent discharged energy densities (*W_d*), while the brown areas represent energy losses (*W_{loss}*). The sum of the two regions is equal to the charged energy...
density ($W_c$). It becomes evident that, although a typical ferroelectric has a higher charged energy density ($W_c = W_d + W_{loss}$) compared to a linear dielectric, its energy efficiency ($\eta = \frac{W_d}{W_c}$) is lower which results in large energy losses during charge-discharge cycles. In addition, the electrical breakdown of a ferroelectric is expected to occur shortly after the onset of polarization saturation, leading to lower applicable electric fields compared to linear dielectrics. To improve the energy performance of ferroelectric films, a higher energy density and efficiency must be achieved by decreasing the remnant polarization ($P_r$) and delaying polarization saturation ($P_s$) such that a slim $P-E$ hysteresis loop can be measured, as shown in Fig. 1.3b. This allows the ferroelectric film to withstand higher electric fields and store more electrostatic energy with higher efficiencies. There are several popular approaches used to “slim down” the $P-E$ hysteresis loop of a ferroelectric film such as using relaxor ferroelectrics [25, 26] or compositions near phase boundaries [27], utilizing space-charges [28] or interfaces [29], and the inclusion of a dead layer [30].

A promising approach for improving the energy density and efficiency of ferroelectric films was recently used by Cheng et al. [24]. In their work, a rhombohedral BaZr$_{0.2}$Ti$_{0.8}$O$_3$ (BZT) solid solution and substrate misfit strain are used to create competing polydomain structures in order to tune the energy performance parameters in ferroelectric films, i.e. “slim down” their $P-E$ hysteresis loops. A topical review on polydomain structures in ferroelectric and ferroelastic films has been published by Roytburd et al. [31], overlaying thermodynamic models, phase field modeling, and experimental studies of such domain structures in epitaxial films. The resulting ferroelectric BZT thick films were found to exhibit coexisting tetragonal and rhombohedral phases at room temperature, allowing a delay of polarization saturation as well as lower remnant polarizations. So far, heterophase polydomain structures have only been observed and reported in BiFeO$_3$ (BFO)[32-35] and Pb(Zr,Ti)O$_3$ (Zr:PTO)[36] ferroelectrics. These BZT polydomain films
demonstrate high energy storage densities and efficiencies compared to single-phase polydomain ferroelectrics. Furthermore, superior dielectric performances with excellent field and frequency stabilities are achieved in these films. The key idea behind these favorable properties lies in the engineering of ultra-adaptive nanoscale domains which can adjust in response to an applied electrical field. Here, we present the use of optical second harmonic generation polarimetry for probing these epitaxial ferroelectric BZT thick films in order understand the domain distributions which govern their high energy performances.

Transmission electron microscopy (TEM) and X-ray diffraction (XRD) measurements on these BZT thick films verified the presence of mixed rhombohedral and tetragonal phases as elastic domains. Here, we used polarization-resolved SHG to probe the coexisting tetragonal and rhombohedral domains within the films. In the reflection geometry, SHG signals were found to arise predominantly from tetragonal domains growing along the thickness of the films, i.e. perpendicular to the film-substrate interface. The appearance of rhombohedral signatures in the reflected SHG intensity profiles with increasing thickness demonstrates symmetry reductions resulting from strain relaxation as rhombohedral domains become more prevalent. In the transmission geometry, SHG contributions from the tetragonal domains vanish and signals from the rhombohedral domains become dominative. Complex transmitted SHG profiles are observed as a result of elastic rhombohedral polydomains along the thickness of the film. Transmission SHG measurements provide further evidence of rhombohedral domain growth with increasing film thickness. We thus provide supporting evidence for the coexistence of mixed tetragonal and rhombohedral phases as elastic domains in epitaxially strained BZT films at room temperature and clearly demonstrate an increase in rhombohedral domains with increasing film thickness. These
heterophase polydomain nanostructures are directly responsible for the lowered remnant polarizations and delayed polarization saturations observed in the epitaxial films.

1.3 Scope of Dissertation

Chapter 1 provides a coherent introduction and motivation for our investigation of *dc* electric field-induced structural changes at Fe:STO electrode interfaces, structural defect and strain formation in electrodegraded Fe:STO single crystals, and coexisting tetragonal and rhombohedral phases in ferroelectric BZT thick films.

Chapter 2 discusses the relevant theoretical foundations and concepts required for understanding and analyzing the experimental results presented in later chapters. In particular, we discuss the prevalence of perovskite-type dielectric ceramics, defect chemistry and resistance degradation of Fe:STO single crystals, strain-field tuning of elastic domains in BZT films, and the theoretical foundations of optical nonlinearity and SHG.

Chapter 3 provides experimental details on samples, equipment, and optical setups. In particular, this chapter discusses sample preparation, our femtosecond laser systems and relevant laser physics principles and parameters, far-field optical SHG polarimetry setups, the confocal Raman spectroscopy setup, and the photoluminescence spectroscopy setup.

Chapter 4 presents our investigation of local structural changes due to the *dc* electric field-induced migration of oxygen vacancies at oxidized and reduced Fe:STO interfaces using optical SHG in the reflection geometry and photoluminescence spectroscopy. Optical SHG measurements were used to analyze changes to the second-order susceptibility components while
photoluminescence was used to measure fluorescence changes resulting from electronic orbital transitions.

Chapter 5 presents our study of structural defect and strain formation in electrodegraded Fe:STO single crystals due to oxygen vacancy migration. Optical SHG in the reflection geometry was employed to study structural defect accumulation and inhomogeneity across electrodegraded interfaces. Optical SHG in the transmission geometry and confocal Raman spectroscopy were used to study structural defect and strain formation across electrocolored bulk regions.

Chapter 6 presents our investigation of coexisting tetragonal and rhombohedral phases in ferroelectric BZT thick films using optical SHG in the reflection and transmission geometries. In the reflection geometry, changes to the second-order susceptibility were used to verify an increase in rhombohedral symmetry signatures with increasing film thickness. In the transmission geometry, changes in the $d$-polarized SHG intensities were used to further verify an increase in rhombohedral symmetry signatures with increasing film thickness.

Chapter 7 summarizes the findings of this dissertation as well as the short-term outlook of each study.

Any published work or argumentations have been cited accordingly.
Chapter 2: Theoretical Background

This chapter goes over relevant theoretical concepts helpful for understanding the experimental results presented in research chapters 4, 5, and 6. Section 2.1 discusses perovskite-type dielectrics and how structure plays an important role in determining electrical properties. Section 2.2 discusses the defect chemistry of Fe:STO while section 2.3 describes the causes and effects $dc$ voltage-induced resistance degradation in Fe:STO. Section 2.4 provides a brief discussion of how heterophase polydomain structures in BZT are engineered using epitaxial strain. Section 2.5 discusses the theoretical concepts behind optical SHG. It should be noted that for section 2.5, we will only be considering second harmonic radiation from electric dipole sources. However, quadrupolar and magnetic sources of second harmonic radiation can become significant in other material systems [37].

2.1 Structure and Dielectric Properties

A dielectric is any insulating material which can be polarized by an imposed electric field. It is this property which makes dielectric materials ideal for capacitive energy-storage devices. For a linear, isotropic dielectric the induced polarization across the material can be expressed as:

$$
P = \varepsilon_0 \Pi_e E$$ \hspace{1cm} (2.1)

Here, $\varepsilon_0$ is the permittivity of free space and $\Pi_e$ is the electrical susceptibility of the dielectric material. The electrical susceptibility measures how easily the dielectric can be polarized in
response to an applied electric field. In general, the electrical susceptibility must be described in full as a tensor such that Eq. 2.1 would formally become:

\[
P = \varepsilon_o \begin{pmatrix}
\Pi_{xx} & 0 & 0 \\
0 & \Pi_{yy} & 0 \\
0 & 0 & \Pi_{zz}
\end{pmatrix} \mathbf{E}
\] (2.2)

Here the indices \(x, y,\) and \(z\) represent an orthogonal set of pseudo-cubic directions and to reproduce Eq. 2.1 we take \(\Pi_{xx} = \Pi_{yy} = \Pi_{zz} = \Pi_e\). The electric susceptibility components serve as proportionality constants and thus influence the strength of the dielectric’s polarization field. If we are to achieve high energy storage under low applied fields then it becomes necessary to choose materials with large susceptibilities. Although high susceptibilities are needed in certain devices, such as the use of high-\(k\) materials in semiconductor industry, in general linear dielectrics with high susceptibilities are more vulnerable to break down when exposed to high electrical stress. In order to improve dielectric energy performance, we may take advantage of the electrical properties of nonlinear dielectrics.

For a nonlinear dielectric, the induced polarization can be expanded as a power series with respect to an applied electric field [38]:

\[
P = \varepsilon_o \left( \Pi_e^{(1)} \mathbf{E} + \Pi_e^{(2)} \mathbf{E} \mathbf{E} + \Pi_e^{(3)} \mathbf{E} \mathbf{E} \mathbf{E} + \ldots \right)
\] (2.3)

Whether or not the dielectric polarization exhibits higher order, nonlinear susceptibilities at higher electric fields depends on structural properties of the material, which in turn are determined by chemical composition and electromechanical conditions.
Ferroelectric ceramics are one of the most important groups of nonlinear dielectrics used for high energy-storage. These insulating materials are composed of polar unit cells which can be reoriented by an external field, resulting in the polarization switching and reversal effects observed in $P-E$ hysteresis loops. Over large volumes these dipolar unit cells form regions of uniform, macroscopic polarization fields known as electric domains. The boundaries between neighboring electric domains are known as domain walls. Electric domain formation is a consequence of the lattice seeking to conserve charge neutrality and minimize the total electrostatic energy of the system. Since each unit cell is polar, local charge carriers reposition themselves to try and oppose the intrinsic polarity of the material, leading to boundaries between groups of unit cells which ultimately form domain structures. Electric domains can also be formed as a result of large pinning polarization fields due to the accumulation of mobile ionic defects, such as oxygen vacancies. This is known as defect domain stabilization and can lead to breakdown mechanisms such as aging. In section 2.4, we will discuss how strain effects may lead to the formation of additional domains, known as elastic domains.

Ferroelectricity in ceramic materials is inseparable from structural symmetry since it is only allowed in non-centrosymmetric crystal point groups. The 21, non-centrosymmetric point groups are well-documented: $1, 2, m, 222, mm2, 4, 4 \overline{2} 2, 4 mm, \overline{4} 2 m, 3, 32, 3 m, 6, \overline{6}, 622, 6 mm, \overline{6} 2 m, 23, 432,$ and $\overline{4} 3 m$ [39, 40]. The possible polar domain variants, or domain polarization directions, accessible within a ferroelectric can be determined from its crystal point group symmetry. As an example, Fig. 2.1 shows cubic ($Pm3m$), tetragonal ($4 mm$), and rhombohedral ($3 m$) unit cells with their possible polar axes shown as red arrows [41]. Due to centrosymmetry, the cubic cell is non-polar and does not exhibit an electric dipole moment. For tetragonal symmetry, the polarization can point towards any of the 6 pseudo-cubic faces of the unit
cell depending on the position of the tetragonal $c$-axis. For rhombohedral symmetry, the polarization can point towards any of the 8 pseudo-cubic corners of the unit cell depending on the tilt directions. In general, the lower degree of symmetry, the more possible polarization directions there are. These symmetries also determine domain wall formation, since these boundaries form between neighboring electric domains. Materials exhibiting tetragonal symmetry can only form 90° and 180° electric domain walls, while materials exhibiting rhombohedral symmetry, a trigonal structure, will typically form 180° electric domain walls.

![Figure 2.1](image)

**Figure 2.1:** Examples of polar domain variants in ferroelectric materials exhibiting tetragonal (4mm) and rhombohedral (3m) symmetry. On the left a centrosymmetric cubic unit cell is shown for reference. In the middle, a non-centrosymmetric tetragonal unit cell is shown where the solid arrow points in the direction of the $(100)$ polarization and dashed arrows point in other 5 possible directions. On the right, a non-centrosymmetric rhombohedral unit cell is shown where the solid arrow points in the direction of the $(111)$ polarization and dashed arrows point in the other 7 possible directions.
2.1.1 Perovskite-type Ceramics

Historically, the term perovskite refers to a structural class of crystallographic compounds which share the ABO$_3$ structure of calcium titanate, CaTiO$_3$ [42]. In Fig. 2.2, a typical perovskite arrangement is shown in the form of cubic ($Pm\bar{3}m$) SrTiO$_3$.

![Perovskite Lattice Composition](image)

**Figure 2.2:** Depiction of a typical perovskite lattice composition using SrTiO$_3$. Four Sr cations (green A-sites) sit at the corners of the cubic unit cell, six oxygen anions sit (red O-sites) at the corners of a central octahedron, and a central titanium cation (grey B-site) sits inside the oxygen octahedron.

It is interesting to note that most electroceramics being studied today can be classified as perovskites. The perovskite structure is very versatile and, when engineered using different chemical compositions, showcases a wide array of crystal phases and functions as shown in Fig. 2.3[42].
Figure 2.3: Examples of various perovskite-type ceramics and their multiple functions [42].

To understand this multi-faceted functionality, one may look at the stability of the perovskite structure itself. The robustness of the perovskite structure can be examined according to Goldschmidt’s tolerance factor [42-44]:

\[
t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)}
\]  \hspace{1cm} (2.4)

In Eq. 2.4, \(R_A\), \(R_B\), and \(R_O\) are the radii of the ions which comprise the perovskite \(\text{ABO}_3\) compound. As an exemplary perovskite, cubic \(\text{SrTiO}_3\) has a tolerance factor very close to 1, with \(R_A = 1.44\) Å, \(R_B = 0.605\) Å, and \(R_O = 1.40\) Å [45]. Substituting other ions with different sizes onto the lattice shifts the tolerance factor, causing structural distortions. A tolerance factor of 1 is considered perfect cubic symmetry, while the accepted range for a stable, pseudo-cubic symmetry is \(0.8 \leq t \leq 1\). For \(t > 1\), A-site cations are too big or B-site cations are too small, leading to the formation of hexagonal or tetragonal symmetry. For \(t < 0.8\), the A-site cations become too small, or B-site
cations become too large, leading to the formation of orthorhombic and rhombohedral symmetries. For \( t < 0.7 \), A-site and B-site ions have similar radii and result in various trigonal symmetries [46]. Thus, the tolerance factor can be used to predict the symmetry and stability of perovskite-type ceramics [47]. In other words, the perovskite structure acts as a stable framework in which different ions can be fitted. The chemical composition and structural phase of the resulting perovskite determine its functionality.

### 2.2 Defect Chemistry in Fe:STO

Mobile charge defects such as oxygen vacancies, holes, and electrons contribute to the conductivity and polarization of acceptor-doped SrTiO\(_3\) crystals. For Fe-doped SrTiO\(_3\) (Fe:STO) in the dilute doping regime, where \([\text{Ti}] \gg [\text{Fe}]\), Ti sites are partially filled by Fe atoms exhibiting mixed \(\text{Fe}^{3+}\) and \(\text{Fe}^{4+}\) valence states such that one can take the following mass conservation condition[4, 48]:

\[
[F\text{e}]_{\text{total}} = [F\text{e}^{3+}] + [F\text{e}^{4+}] \tag{2.5}
\]

In Eq. 2.5, \([\text{Fe}^{3+}]\) and \([\text{Fe}^{4+}]\) represent the concentrations (number density) of \(\text{Fe}^{3+}\) and \(\text{Fe}^{4+}\) ions in the crystal, respectively. Due to the mixed valence states of the acceptor-dopant Fe, charge neutrality of the unit cell is not always conserved. For example, consider both tetravalent and trivalent Fe-doped SrTiO\(_3\) unit cells. We have the following two charge conservation equations:

\[
4S\text{r}^{2+} + F\text{e}^{4+} + 6O^{2-} \rightarrow 0 \tag{2.6a}
\]
\[ 4Sr^{2+} + Fe^{3+} + 6O^{2-} \rightarrow -1 \]  
(2.6b)

In order to maintain charge neutrality with respect to the crystal lattice, oxygen vacancies form in the first coordination shell of Fe\(^{3+}\) defect centers, and we obtain the following charge equation:

\[ 4Sr^{2+} + Fe^{3+} + 5O^{2-} \rightarrow +1 \]  
(2.6c)

Due to this net positive charge, excess electrons in the crystal will tend to crowd oxygen vacancy defects to compensate. Thus, the following conservation condition appears for the crystal:

\[ 2[V_o^\circ] + [h] = [Fe^{3+}] + [e] \]  
(2.7)

In Eq. 2.7, \([V_o^\circ]\), \([h]\), and \([e]\) are the concentrations of oxygen vacancies, holes, and free electrons in the crystal. The symbol for the doubly ionized oxygen vacancy, \(V_o^\circ\), comes from Kröger-Vink notation where the V stands for vacancy, the O stands for the oxygen site, and the two dots represent that the point defect has an effective charge of +2 with respect to the lattice. Singly ionized oxygen vacancies, \(V_o\), with an effective charge of +1 can also form by accepting free electrons when free electron concentrations are high. In common cases where free electronic carrier concentrations are very low, Eq. 2.7 can be simplified [4, 48]:

\[ 2[V_o^\circ] \approx [Fe^{3+}] \]  
(2.8)

As a result, the oxygen vacancy concentration within the crystal at low temperatures \((T \lesssim 400^\circ C)\) can be estimated based on the Fe-doping concentration [7, 49, 50].
Fe:STO is a mixed ionic and electronic conductor and its total conductivity can be expressed as follows:

$$\sigma_{\text{total}} = \sigma_{v_0} + \sigma_e + \sigma_h$$  \hfill (2.9)

In Eq. 2.9, $\sigma_{v_0}$, $\sigma_e$, and $\sigma_h$ represent the oxygen vacancy, electron, and hole conductivities, respectively. These conductivities have been shown to exhibit a strong dependence on annealing oxygen partial pressure and temperature[15, 16]. The defect chemistry of an Fe:STO single crystal can thus be tuned according to both of these annealing parameters for electrochemical reduction and oxidation treatments. Fe:STO contains much higher oxygen vacancy concentrations compared to electronic carriers at nearly all temperatures, resulting in oxygen vacancies playing an unrivaled role during dc electric field-induced degradation compared to other mobile point defects[10, 15, 16, 51].

The concentration of oxygen vacancy defects as a function of temperature in the crystal can be approximated by considering the Gibbs free energy of the system [44, 52]:

$$\mathcal{G} = H - TS$$  \hfill (2.10)

In Eq. 2.10, $\mathcal{G}$ is the Gibbs free energy, $H$ is the total enthalpy of the crystal, $T$ is the temperature, and $S$ is the entropy of the crystalline system. The entropy consists of a vibrational (phonon entropy) and configurational (configurational entropy) term such that:

$$S = S_{\text{vib}} + S_{\text{conf}}$$  \hfill (2.11)
Here, the enthalpy and vibrational entropy can be taken to be proportional to the number of vacancies, and the configurational entropy is a function of the number of vacancies such that we can transform Eq. 2.10 as follows:

\[
\Delta G = N_v (\Delta H - T \Delta S_{vib}) - T \Delta S_{conf}(N_v) \tag{2.12}
\]

Here, \(N_v\) represents the number of vacancies in the crystal lattice. The configurational entropy can be expressed by considering the total number of arrangements between vacancies and oxygen sites in the crystal, \(W = \binom{N}{N_v} = \frac{N!}{(N-N_v)! N_v!}\). Thus, the configurational entropy can be expressed as:

\[
S_{conf}(N_v) = k_b \ln \left( \frac{N!}{(N-N_v)! N_v!} \right) \tag{2.13}
\]

Here, \(k_b\) represents Boltzmann’s constant and \(N\) is the total number of vacancies and oxygen sites in the crystal. In the thermodynamic limit \((N >> 1)\), \(S_{conf}(N_v)\) can be simplified using Stirling’s approximation, \(\ln(N!) \approx N \ln(N) - N\). Eq. 2.13 becomes:

\[
S_{conf} = N k_b \ln \left( \frac{N}{N - N_v} \right) - N_v k_b \ln \left( \frac{N_v}{N - N_v} \right) \tag{2.14}
\]

Now, in order to find the equilibrium condition for the number of vacancies, we must solve for the Gibbs free energy minimum by differentiating and setting the expression to zero:

\[
\frac{d \Delta \tilde{G}}{d N_v} = (\Delta H - T \Delta S_{vib}) - T \frac{d S_{conf}}{d N_v} = 0 \tag{2.15}
\]
With care, the derivative of the configurational entropy with respect to the vacancy number becomes:

$$\frac{dS_{conf}}{dN_v} = \frac{d}{dN_v} \left\{ Nk_b \ln \left( \frac{N}{N-N_v} \right) - N_v k_b \ln \left( \frac{N_v}{N-N_v} \right) \right\} = -k_b \ln \left( \frac{N_v}{N-N_v} \right) \quad (2.16)$$

And Eq. 2.15 can be written as:

$$\frac{N_v}{N-N_v} = e^{\frac{S_{vib}}{k_b} e^{\frac{-\Delta H}{k_bT}}} \quad (2.17)$$

Since the number of vacancies is typically much less than the total number of lattice sites in a crystal, $\frac{N_v}{N-N_v}$ can approach the concentration of oxygen vacancies, $\frac{N_v}{N-N_v} \approx \frac{N_v}{N} \approx [N_v]$. If the vibrational entropy and enthalpy of the system are known, then the equilibrium concentration of oxygen vacancies at a specified temperature can be estimated. The two significant enthalpies for oxygen vacancies are the so-called generation and migration enthalpies [53, 54]. The generation enthalpy corresponds to the potential energy required for the formation of an oxygen vacancy while the migration enthalpy corresponds to the potential energy required for a vacancy to hop from one site to another, which is how diffusion occurs within the lattice. At higher temperatures, additional thermal energy facilitates site hopping for oxygen vacancies in the system, thus increasing their mobility. Measured $\Delta H_{mig}$ values typically range between ~0.6–0.7 eV in STO[55] and dilutely-doped STO[15, 16] single crystals.
2.2.1 Structural Defects

The substitution of Ti with the acceptor-dopant Fe not only introduces ionic and electronic defects into the SrTiO$_3$ lattice, but also creates structural defects at the unit cell level. These ionic defects alter electronic orbital structure by modifying the potential energy landscape around them, causing the formation of structural distortions in the crystal lattice. The three most common Fe defect centers within Fe:STO are the tetragonal distortion, Jahn-Teller distortion, and the doubly ionized oxygen vacancy defect complex, all of which exhibit tetragonal (4mm) symmetry, i.e. $a = b \neq c$, as shown in Fig. 2.4 (Graphics made using Avogadro 1.1.1[23]).

Figure 2.4: Fe:Ti-O$_6$ octahedral centers found throughout the Fe:STO crystal lattice. (a) Cubic Ti$^{4+}$ center (uncharged). (b) Tetragonal Fe$^{3+}$ defect center (-1 charge). (c) Jahn-Teller distortion of the Fe$^{4+}$ defect center (uncharged). (d) Oxygen vacancy formation near an Fe$^{3+}$ defect center (+1 charge). Fe-defect centers (b), (c), and (d) portray tetragonal (4mm) symmetry. Dashed black arrows show the stretching or compression of crystal physics axes, $a$ and $c$. 
It is important to note that for both undegraded STO and Fe:STO, unit cells transition from cubic ($Pm\bar{3}m$) symmetry to tetragonal ($4mm$) symmetry near surfaces due to atomic displacements along the normal axis[56, 57]. Fe:Ti valence state changes and local oxygen ion migrations govern the formation of structural defects in Fe:STO during oxygen vacancy migration. In the tetragonal distortion, shown in Fig. 2.4b an Fe$^{3+}$ cation occupies a Ti$^{4+}$ site and fully coordinates itself to six nearest oxygen neighbors in the octahedron. This defect is negatively charged with respect to the crystal lattice. In the Jahn-Teller distortion, an Fe$^{4+}$ cation occupies a Ti$^{4+}$ site and fully coordinates itself to six nearest oxygen neighbors in the octahedron. In order to avoid electronic $d$-orbital degeneracies around the Fe$^{4+}$ cation, the octahedron undergoes a geometric deformation which results in oxygen bond expansion and contraction along the $c$- and $a$-axis, respectively, as shown in Fig. 2.4c[58, 59]. This defect has a neutral charge with respect to the surrounding crystal lattice. We note that Fe$^{4+}$ cations may also occupy Ti$^{4+}$ sites without introducing a Jahn-Teller distortion. For the oxygen vacancy defect complex, as shown in Fig. 2.4d, an Fe$^{3+}$ cation occupies a Ti$^{4+}$ site and coordinates itself with five nearest oxygen neighbors and one vacancy. The vacancy results in a displacement of the central Fe$^{3+}$ cation and bending of the $a$-axis oxygen bonds. This defect is positively charged with respect to the crystal lattice [4, 60-62]. As a result of oxygen vacancy demixing in Fe:STO, local Fe$^{4+}$ valence states reduce to Fe$^{3+}$ valence states in the cathode region. Meanwhile, oxygen ions and holes pile up near the anode and lead to the local oxidation of Fe$^{3+}$ valence states to Fe$^{4+}$ valence states. Thus, Fe$^{4+}$ structural defects, such as tetragonal and Jahn-Teller distortions, form in the anode region while oxygen vacancy defect complexes form in the cathode region.
2.3 Resistance Degradation in Fe:STO

2.3.1 Reduction Model

In the reduction model, the high mobility and concentration of oxygen vacancies are described as the dominating contributors to voltage-induced resistance degradation in Fe:STO[7, 10, 17, 63]. Under the influence of a dc electrical field, positively charged oxygen vacancies migrate towards the cathode while oxygen ions migrate towards the anode. Due to the electrodes blocking effect on ionic currents at low temperatures (T ≲ 400°C), oxygen vacancies pile up. Consequently, an electrochemical p-n junction is formed, where the anodic region becomes p-type conducting and the cathodic region becomes n-type conducting, as a result of local electrons compensating the accumulation of vacancies at the cathode in an attempt to conserve charge neutrality [5-7]. The rise in electronic conductivity at the electrochemically reduced cathode leads to a decrease in insulation-resistance. An increase in leakage current across the dielectric ceramic by two orders of magnitude occurs, diminishing the materials capacitive ability.

2.3.2 Electrocoloration

A process known as electrocoloration also occurs in Fe:STO as a result oxidation state changes to the transition metal, Fe, in the anodic region. As the external electric field drives oxygen vacancies away from the anode, the Fe$^{4+}$ concentration increases significantly due to a loss of local electronic carriers. The increased concentration of Fe$^{4+}$ in the anode leads to a visible darkening of the anodic region due to local increases in optical absorption[64]. This process has been shown experimentally to be reversible by reversing the electrical field for STO with various transition
metal dopants such as Ni, Mo, and Al [65]. It has also been shown that the ambient oxygen pressure has no effect on the electrocoloration process [20].

2.3.3 Electrostriction

In addition to driving oxygen vacancy migration, dc electrical stress also induces forces on the crystal lattice which cause a structural deformation known as electrostriction[66]. Electrostriction is an electromechanical effect which results from the coupling between strain and an electrical field[38, 67-69]. When electrostrictive strain occurs in a dielectric ceramic, the material typically undergoes a lattice expansion along the applied electric field axis as a result of field-induced ionic displacements. The elastic properties of the ceramic can also lead to constrictive deformations perpendicular to the applied field axis[67]. The combined effects of defect accumulations at the anode and cathode and electrostrictive distortions in the material lead to a redistribution of structural strain, especially over electrocoloration boundaries which separate electrochemically reduced and oxidized bulk regions. Computational studies have provided strong evidence for increased oxygen vacancy mobility due to structural symmetry breaking and strain. Density Functional Theory (DFT) calculations have shown that strain compromises oxygen bond strengths and can lead to decreases in both oxygen vacancy defect formation energies and migration energy barriers [70, 71]. To this point, structural defect and strain formation in Fe:STO are predicted to increase vacancy mobility, ultimately contributing to the resistance degradation process.
2.3.4 Metal-dielectric Interface

Metal-dielectric interfaces, also known as electrode interfaces, also have a strong effect on voltage-induced resistance degradation. The widely accepted model for resistance degradation, first proposed by Baiatu et al.[5-7], describes the electric field-driven migration of oxygen vacancies as the dominative cause for conductivity increases. In this model, the mixed ionic and electronic conducting properties of the material leads to a migration of oxygen ions and vacancies towards the anode and cathode, respectively. This process is typically studied at high temperatures (T > 400°C) since higher oxygen vacancy mobilities decrease degradation times [9, 10, 14, 17, 20]. However, at low field and room temperature ranges, oxygen vacancy demixing cannot occur on short time scales. Instead, the dc electric field can generate local oxygen vacancy migrations and electrostrictive structural changes near the electrode interfaces where charge defect accumulation is strongest [66, 72].

Structural symmetry is inherently broken at the metal-dielectric interface as a result of an asymmetric electronic distribution across the junction. The Jellium model[73] can be used to describe this asymmetry by treating the electron density in the metal electrode as an electron gas bounded by the dielectric layers. The simplest solutions for the electron density at the interface become [74]:

\[
n(z) = n_+ \left(1 - \frac{1}{2} e^{\beta(z-z_0)} \right), \quad z < z_o \tag{2.18a}
\]

\[
n(z) = n_+ \left(\frac{1}{2} e^{-\beta(z-z_0)} \right), \quad z > z_o \tag{2.18b}
\]
In Eq. 2.18, $\beta$ is a scaling parameter to be determined, $z_o$ is the position where the electronic density is half of its bulk value, and $n_+$ is the ionic density in the bulk of the metal electrode. The electron density inside the metal tends to the ionic density in order to conserve charge neutrality within the bulk of the metal, although this is not true at the surface of the metal. Fig. 2.5 shows the electron distribution between the metal electrode and dielectric layers which results in symmetry breaking along the $z$-axis.

![Figure 2.5: Electronic distribution at a metal-dielectric interface, approximated using Eq. 2.18. The light grey shaded region represents the metal electrode, while the white region represents the dielectric. The red solid curve signifies the electronic density across the junction.](image)

The electronic distribution and electrical response of the metal-dielectric interface are further complicated according to what kind of conducting contact is formed. For example, if the metal is platinum (Pt) and the dielectric is Fe-doped or undoped SrTiO$_3$ then, due to work function differences existing between the electrode and dielectric layers, the formation of a Schottky junction will take place [75]. An energy barrier, known as the Schottky Barrier, forms between the
metal and dielectric which leads to a rectifying behavior [76]. In addition, the Schottky Barrier also leads to the formation of an interfacial depletion region. The depletion region is a thin insulating region which becomes depleted of electronic carriers, leaving behind only ionic defects. Intrinsic electric fields can form across this region as a result of electronic carrier build up on opposite ends of the region. Under the influence of an external electric field, the depletion region can break down, quenching the intrinsic electric field at the interface.

2.4 Domain Structures in BZT Films

At room temperature, barium titanate (BaTiO$_3$, BTO) films exhibit tetragonal ($4mm$) symmetry, with in-plane and out-of-plane lattice parameters of $a = 3.992$ Å and $c = 4.036$ Å, respectively. Within the BTO unit cell, the central Ti$^{4+}$ cation is displaced with respect to the surrounding oxygen octahedron, resulting in the formation of an electric dipole moment, as previously shown in Fig. 1.2. Thus, BTO is a ferroelectric ceramic with tetragonal ($4mm$) symmetry at room temperature. Through the use of zirconium (Zr$^{4+}$) as a B-site dopant, the equilibrium phase of BZT can be transitioned to rhombohedral ($3m$) symmetry. The BZT equilibrium phase as a function of Zr-doping amount is shown in Fig. 2.6, according to the solid lines.
**Figure 2.6:** Plot shown from Cheng et al.[24]. Equilibrium phase of Ba(Zr$_x$Ti$_{1-x}$)O$_3$ as a function of Zr-doping with (Dashed line) and without (Solid line) compressive strain. The room temperature equilibrium bulk phase transforms from tetragonal (4mm) in undoped BTO to rhombohedral (3m) in 20% Zr-doped BTO (BaZr$_{0.2}$Ti$_{0.8}$O$_3$).

The ionic radius of Zr$^{4+}$ is larger than that of Ti$^{4+}$ which results in a strong shift of the perovskite’s Goldschmidt tolerance factor. Although BZT exhibits rhombohedral bulk symmetry at room temperature, the coexistence of mixed tetragonal (4mm) and rhombohedral (3m) phases can be achieved through the stabilization of a strain-induced morphotropic phase boundary. The dashed lines in Fig. 2.6 show the BZT equilibrium phase as a function of Zr-doping amount under compressive strain. This compressive strain leads to coexisting tetragonal and rhombohedral phases as elastic domains. Just as electric domains form to minimize the electrostatic free energy, these elastic domains form to minimize the energy of long-range mechanical stress fields in the material.
2.4.1 Heterophase Polydomain Structures

Phase refers to the structural symmetry of the crystalline unit cell while domain refers to the orientation of the electrical polarization. Thus, ferroelectric films exhibiting heterophase polydomain structures consist of multiple polar domain variants of more than one crystalline phase. The ferroelectric BZT thick films discussed in this dissertation exhibit heterophase polydomain structures due to their coexisting rhombohedral ($3m$) and tetragonal ($4mm$) crystal phases. Rhombohedral phases have 8 pseudo-cubic ⟨111⟩ polar domain orientations while tetragonal phases have 6 pseudo-cubic ⟨001⟩ polar domain orientations, as shown previously in Fig. 2.1. Evidently, heterophase polydomain structures have valuable energy storage properties as a result of how they respond to external $dc$ electrical stress. During field application, heterophase polydomain structures can absorb additional electrical energy by transitioning into single phase structures, thus delaying the saturation of their polarization. This delay leads to larger applicable electric fields and, consequently, higher breakdown field strengths. As a result, energy densities in films exhibiting heterophase polydomain structures are expected to surpass the energy densities of single phase films. The energy storage properties of ferroelectric films exhibiting heterophase polydomain structures can be tuned even further by taking advantage of mechanical stresses. Since these domain structures are elastic in nature, $i.e.$ stabilized as a result of the minimization of elastic energy, mechanical constraints such as film thickness and substrate species have a strong effect on the equilibrium bulk structures formed during epitaxial growth[32, 33, 77]. Consequently, tuning the domain architecture results in a tuning of the remnant and saturation polarization and, by extension, the energy storage properties of the film.
2.4.2 Strain-field Tuning of Domain Structures

BZT has intrinsic electrical properties well-suited for applications as a dielectric capacitor, such as a large dielectric constant and a slim hysteresis loop[78, 79]. However, these properties can be further improved by taking advantage of strain effects to tune the elastic domain structure of the film. BZT epitaxial films of different thicknesses (nanometer to micrometer range) can be grown on a variety of cubic and pseudo-cubic single crystal substrates. The substrate species chosen is a crucial mechanical constraint and governs how strong the misfit strain on the film is. Consider the following case for a ferroelectric film grown on a pseudo-cubic, or tetragonal, substrate. The match between the in-plane lattice parameter of the film ($a_f$) and substrate ($a_s$) in this case decides the degree and type of misfit strain[31]. The misfit strain is defined as follows:

\[ \varepsilon_M = \frac{a_f - a_s}{a_s} \quad (2.19) \]

Three different film-substrate misfit strains are shown in Fig. 2.7.
**Figure 2.7:** Shows different misfit strains which can form between the epitaxial ferroelectric film and the tetragonal substrate. (a) The case where $a_f = a_s$ doesn’t result in a misfit strain; (b) The case where $a_f > a_s$ leads to a compressive strain on the film; (c) The case where $a_f < a_s$ leads to an expansive tensile strain on the film. Short-dashed lines mark the interface sites for clarity.

Fig. 2.7a shows the homoepitaxial growth scenario, when $a_f = a_s$ and the misfit strain is zero. The lack of a misfit strain has no effect on the structure of the film. Fig. 2.7b and Fig. 2.7c show the two heteroepitaxial growth scenarios where $a_f \neq a_s$ and the misfit strain can result in a compressive or tensile strain on the film lattice. Under compressive strain, the film lattice squeezes along the in-plane direction to minimize mechanical stresses from the substrate. In contrast, under a tensile, or expansive, strain the film lattice elongates along the in-plane direction to minimize such stresses. Due to the tensor nature of mechanical stresses, compressive straining of the film lattice leads to expansion along the film’s thickness while tensile straining of the film leads to a compression along the film’s thickness. In this work, compressive misfit strains were utilized since the in-plane lattice parameter of BZT is approximately $a = 4.12$ Å, while the lattice parameters of the SrTiO$_3$ (STO), LaAlO$_3$ (LAO), and (La,Sr)(Al,Ta)O$_3$ (LSAT) substrates are 3.905 Å, 3.79 Å, and 3.87 Å, respectively[34]. The compressive misfit strain brings BZT’s tetragonal and rhombohedral equilibrium phases closer together at room temperatures, thus satisfying the requirement for the formation of mixed tetragonal and rhombohedral domains, i.e. heterophase polydomain structure.

Thickness of the film also plays a significant role in influencing the elastic domain architecture. 20% Zr-doped BTO exhibits rhombohedral bulk symmetry at room temperature, however, the film is compressively strained near the tetragonal substrate. This results in the BZT
lattice favoring tetragonal domain formation near the interface. The strain-fields generated by inter-locking, tetragonal domains formed at the substrate interface propagate along the films thickness, dominating in thin films. In thicker films (350 nm or more), strain-field relaxation takes place away from the substrate and results in a lowering of crystalline symmetry so that tetragonal phases can transition into rhombohedral ones. The mixture of rhombohedral and tetragonal domains in a mechanically constrained ferroelectric film can thus be modulated using thickness and substrate strain effects. Superior dielectric properties are accomplished through the formation of such heterophase polydomain structures[80]. These complex elastic domain structures are able to undergo versatile structural evolutions under the influence of an external electric field, thus leading to favorable results such as lower remnant polarization and delayed saturation. This ultimately helps lower energy density loss during charge-discharge cycles and increase storable energy densities.

2.5 Optical Second Harmonic Generation

When light strikes a material, the electric field of the optical wave drives charge oscillations along chemical bonds. Within the dipole approximation, these charge oscillations lead to an oscillating electric polarization which then re-radiates its own electric field as governed by Maxwell’s wave equation:

\[-\nabla \times (\nabla \times \mathbf{E}) + \frac{n^2}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} = \mu_0 \frac{\partial^2 \mathbf{P}}{\partial t^2}\]

(2.20)

In Eq. 2.20, \(n\) is the refractive index of the material, \(c\) is the speed of light in free space, \(\mu_0\) is the permeability of free space, and the optically induced polarization field, \(\mathbf{P}(r, t)\), acts as a source of
new radiation \((\mathbf{E}(\mathbf{r}, t))\). In general, this optically induced polarization must be expanded as a power series with respect to the electric field of the incident light to account for nonlinear sources of radiation.

\[
P(t) = \varepsilon_0 \left( \chi^{(1)} E(t) + \chi^{(2)} E(t)^2 + \chi^{(3)} E(t)^3 + \cdots + \chi^{(n)} E(t)^n \right)
\] (2.21)

Higher power terms \((n > 1)\) give rise to nonlinear optical effects, however, the second-order polarization is the most important term to consider since this term gives rise to the optical process known as second harmonic generation (SHG).

In the nonlinear optical process of SHG, two photons of frequency \(\omega\) are absorbed and a photon of frequency \(2\omega\) is emitted, as shown in Fig. 2.8.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2_8.png}
\caption{Energy diagram for optical second harmonic generation. Two photons of energy \(E = \hbar\omega\) are absorbed, exciting the system to a virtual state. Then, one photon of energy \(E = 2\hbar\omega\) is emitted as the system returns to its ground state.}
\end{figure}
This process is forbidden in crystal point groups exhibiting a center of inversion symmetry, i.e. crystal symmetry that remains indistinguishable under the translational operation \( \mathbf{r} \rightarrow -\mathbf{r} \) [57, 81-83]. This crucial property elevates optical SHG as an effective tool for investigating the formation of non-centrosymmetric defects and strain at the unit cell scale in degraded perovskite-based dielectrics as well as polar domains in perovskite-based ferroelectrics [84-87].

2.5.1 Nonlinear Electron Spring Model

To understand the origin of optical nonlinearity, we may look at the interaction between light and matter from a classical standpoint. When electromagnetic radiation interacts with an atom, the oscillating electric field of the light wave polarizes the negatively charged electron cloud with respect to the positively charged nucleus. This interaction leads to an oscillating electric dipole moment at the same frequency as the light wave. Utilizing a classical framework, we are allowed to express the Coulomb attraction between the electron cloud and nucleus as the restoring force of a spring (Lorentz Oscillator Model)[40, 74, 85], as illustrated in Fig. 2.9.
**Figure 2.9:** Illustration of an electric field polarizing the electron cloud around an atom. The interaction can be modeled as an effective charge attached to a spring where $F_R$ and $F_L$ are the restoring force of the spring and Lorentz force, respectively.

For small charge displacements resulting from weak optical fields, the induced electric dipole moment is linearly proportional to the optical field, *i.e.* a linear response. Thus, we can express the linear restoring force according to Hooke’s Law:

$$F_R(x) = -kx \hat{x}$$  \hspace{1cm} (2.22)

Here, $k$ is a proportionality constant describing the electronic spring’s stiffness and $x$ is the displacement from equilibrium along the $x$-axis. However, with strong optical fields, such as those from intense laser light, nonlinearities within the electronic spring are no longer negligible and Hooke’s Law is no longer valid. Instead, we can rewrite Eq. 2.22 to include higher order terms by expanding the restoring force as a power series with respect to $x$. However, we need only focus on the first and second-order terms of the series to elucidate nonlinear effects:

$$F_R(x) = -kx - ax^2 \hat{x}$$  \hspace{1cm} (2.23)

We can see that as a consequence, inversion symmetry has been broken by the second-order term. Looking at the elastic potential energy functions, $U(x) = -\int F(x) \cdot dx$, of the linear and nonlinear springs, we obtain the following formulae:

$$U_{\text{linear}}(x) = \frac{1}{2}kx^2$$  \hspace{1cm} (2.24a)
\[ U_{\text{nonlinear}}(x) = \frac{1}{2} kx^2 + \frac{1}{3} ax^3 \]  

(2.24b)

It can easily be verified that \( U_{\text{linear}}(-x) = U_{\text{linear}}(x) \) from Eq. 2.24a, which means that the linear spring is centrosymmetric. However, \( U_{\text{nonlinear}}(-x) \neq U_{\text{nonlinear}}(x) \) from Eq. 2.24b, which shows that the nonlinear spring is non-centrosymmetric. In order to describe the nonlinear response of the system, we may solve Newton’s Second Law \( F_{\text{net}} = m \frac{d^2x}{dt^2} \) along the \( x \)-axis. This dynamical problem becomes that of a driven, nonlinear oscillator where the optical field acts as the driver:

\[ F_R + F_d + F_L = m \frac{d^2x}{dt^2} \]  

(2.25)

Here, \( F_R \) is the spring’s restoring force, \( F_d \) is a damping force, and \( F_L \) is the Lorentz force due to optical field acting on the effective charge of the spring. The mass in this case is the mass of the effective charge. After substitution into Eq. 2.25 we obtain the following equation:

\[ \frac{d^2x}{dt^2} + 2\gamma \frac{dx}{dt} + \omega_0^2 x + \frac{a}{m} x^2 = - \frac{q}{m} E(t) \]  

(2.26)

Here, \( 2\gamma \) is a scaling factor for the damping force, \( a \) is the proportionality constant of the nonlinear term, and \( \omega_0 \) is the natural frequency of the electronic spring. In this problem, we are neglecting the motion of the nucleus by only considering relative displacements of the effective charge, \( q \).

The external electric field can be described by a monochromatic optical wave of frequency \( \omega \) using complex notation:
The solution of Eq. 2.23 can be found using perturbation theory. We want a solution in the form of a series expansion of the displacement along the $x$-axis, $x(t) = \sum \lambda^i x^{(i)}(t)$. Thus, we first solve for the first-order solution by dropping the higher-order terms of $x (n > 1)$:

$$\frac{d^2 x^{(1)}}{dt^2} + 2\gamma \frac{dx^{(1)}}{dt} + \omega_0^2 x^{(1)} = -\frac{q}{m} E(t)$$

Eq. 2.28 can be easily solved by taking the general form of the solution to match that of the driving function, $E(t)$. Thus, we may input $x^{(1)}(t) = A e^{-\lambda_0 t} + B e^{i\lambda_0 t}$ into Eq. 2.28 and solve for the coefficients. The first-order solution can then be written out as:

$$x^{(1)}(t) = -\frac{q E_0 e^{-i\lambda_0 t}}{2m(\omega_0^2 - \omega^2 - i2\gamma\omega)} - \frac{q E_0^* e^{i\lambda_0 t}}{2m(\omega_0^2 - \omega^2 + i2\gamma\omega)}$$

In this simplistic model, the net polarization per unit volume in the material can be expressed by taking into account $N$ independent electronic springs per unit volume. Thus, we have:

$$P^{(1)}(t) = -N q x^{(1)}(t)$$

$$P^{(1)}(t) = \frac{N q^2 E_0 e^{-i\lambda_0 t}}{2m(\omega_0^2 - \omega^2 - i2\gamma\omega)} + \frac{N q^2 E_0^* e^{i\lambda_0 t}}{2m(\omega_0^2 - \omega^2 + i2\gamma\omega)}$$

The resulting harmonic polarization has the form, $P^{(1)}(t) = \frac{1}{2} (P^{(1)}(\omega) e^{-i\lambda_0 t} + P^{(1)}(\omega)^* e^{i\lambda_0 t})$, where the linear susceptibility can be pulled out from the first polarization amplitude using the form of Eq. 2.30b:
\[ P^{(1)}(\omega) = \epsilon_0 \chi^{(1)}(\omega; \omega) E^\omega \] (2.31a)

\[ \chi^{(1)}(\omega) = \frac{Nq^2}{\epsilon_0 m (\omega_0^2 - \omega^2 - i2\gamma \omega)} \] (2.31b)

The first-order susceptibility describes the linear optical response of the collective dipoles in the material. A plot of the linear optical susceptibility as a function of frequency using the real and imaginary parts of Eq. 2.31b is shown in Fig. 2.10. The real part represents the dispersion function while the imaginary part corresponds to the resonance condition centered at the natural, or resonant, frequency of the oscillating dipoles in the medium.

**Figure 2.10:** Linear optical susceptibility as a function of frequency. The dispersion function is represented by the real part (solid red line) and the resonance function is represented by the imaginary part (dashed black line). Curves are rescaled for convenience.
The linear response is only valid for optical fields which are too weak to generate higher-order effects arising from nonlinearity in the electronic spring’s restoring force. In order to solve for the second-order equation of motion, we may take the first-order solution from Eq. 2.29 and plug into the second-order term of Eq. 2.28, dropping the $E(t)$ term, so that we have:

$$\frac{d^2 x^{(2)}}{dt^2} + 2\gamma \frac{dx^{(2)}}{dt} + \omega_0^2 x^{(2)} + \frac{a}{m} \left(x^{(1)}\right)^2 = 0 \quad (2.32)$$

In Eq. 2.32, $\frac{a}{m} \left(x^{(1)}\right)^2$ serves as the excitation term and we are left to solve for the second-order equation of motion from the following differential equation:

$$\frac{d^2 x^{(2)}}{dt^2} + 2\gamma \frac{dx^{(2)}}{dt} + \omega_0^2 x^{(2)} = -\frac{a}{m} \left(x^{(1)}\right)^2 \quad (2.33a)$$

$$-\frac{a}{m} \left(x^{(1)}\right)^2 = -\frac{aq^2}{4m^2} \left(\frac{E^\omega E^{\omega^*} + E^{\omega^*} E^\omega}{((\omega_0^2 - \omega^2)^2 + (2\gamma\omega)^2)} - \frac{aq^2}{4m^2} (E^\omega)^2 e^{-i2\omega t}
- \frac{aq^2}{4m^2} \left(\frac{(E^{\omega^*})^2 e^{i2\omega t}}{E^\omega} \right) \right) \omega = \omega_0 - m \gamma \quad (2.33b)$$

The first term in Eq. 2.33b is an optical rectification term representing the establishment of an optically induced electrostatic field in the medium. We may drop this term since it does not give rise to a radiating dipole source. The second and third terms of Eq. 2.33b represent an electric field oscillating at twice the frequency of the incident electric field. In order to obtain the time-dependent second-order equation of motion, we input $x^{(2)}(t) = Ce^{-i2\omega t} + De^{i2\omega t}$ into Eq. 2.33a to solve for the coefficients to find the second-order equation of motion as follows:
\[
x^{(2)}(t) = -\frac{aq^2 (E^\omega)^2 e^{-i2\omega t}}{4m^2 (\omega_0^2 - 4\omega^2 - i4\gamma\omega)(\omega_0^2 - \omega^2 - i2\gamma\omega)^2} - \frac{aq^2 (E^{\omega*})^2 e^{i2\omega t}}{4m^2 (\omega_0^2 - 4\omega^2 + i4\gamma\omega)(\omega_0^2 - \omega^2 + i2\gamma\omega)^2}
\]

(2.34)

Thus, we find the second-order polarization:

\[
P^{(2)}(t) = -Nq x^{(2)}(t)
\]

(2.35a)

\[
P^{(2)}(t) = \frac{Naq^3 (E^\omega)^2 e^{-i2\omega t}}{4m^2 (\omega_0^2 - 4\omega^2 - i4\gamma\omega)(\omega_0^2 - \omega^2 - i2\gamma\omega)^2} + \frac{Naq^3 (E^{\omega*})^2 e^{i2\omega t}}{4m^2 (\omega_0^2 - 4\omega^2 + i4\gamma\omega)(\omega_0^2 - \omega^2 + i2\gamma\omega)^2}
\]

(2.35b)

The resulting second-order polarization has the form, \( P^{(2)}(t) = \frac{1}{2} (P^{(2)}(2\omega) e^{-i2\omega t} + P^{(2)}(2\omega)^* e^{i2\omega t}) \), where the second-order susceptibility can be pulled out from the second-order polarization amplitude just like the first-order case:

\[
P^{(2)}(2\omega) = \epsilon_o \chi^{(2)}(2\omega; \omega, \omega) E^\omega E^\omega
\]

(2.36a)

\[
\chi^{(2)}(2\omega; \omega, \omega) = -\frac{Naq^3}{4\epsilon_o m^2 (\omega_0^2 - 4\omega^2 - i4\gamma\omega)(\omega_0^2 - \omega^2 - i2\gamma\omega)^2}
\]

(2.36b)

The second-order susceptibility describes the nonlinear optical response of the collective dipoles in the material. A plot of the nonlinear optical susceptibility as a function of frequency using the real and imaginary parts of Eq. 2.36b is shown in Fig. 2.11.
Figure 2.11: Nonlinear optical susceptibility as a function of frequency. The dispersion function is represented by the real part (solid red line) and the resonance function is represented by the imaginary part (dashed black line). Curves and axes are rescaled for convenience.

The nonlinear susceptibility has two resonance frequencies, one when the fundamental frequency of the incident light ($\omega$) is equal to the natural dipole frequency ($\omega_0$) and one when the doubled-frequency of the incident light ($2\omega$) is equal to the natural dipole frequency. It is important to note that the second-order response is expected to be at least $10^{10-12}$ times weaker than the first-order one [39]. Thus, we have illustrated the origin of optical nonlinearity using a simple classical depiction of coulombic interactions in an atom.
2.5.2 Tensor Representation of the Second-Order Susceptibility

The nonlinear, second-order polarization can be formally described in full detail by writing the second-order susceptibility as a third-rank tensor:

\[ P_{2\omega} = \sum_{j,k} \chi_{ijk}^{(2)} (2\omega; \omega, \omega) E_j^\omega E_k^\omega \]  

(2.37)

Here, \( \chi_{ijk}^{(2)} (2\omega; \omega, \omega) \) represents the second-order susceptibility tensor components and we’ve dropped the \( \epsilon_{\sigma} \) factor in front of the sum for simplicity. Eq. 2.37 can be expanded explicitly as[39]:

\[
\begin{pmatrix}
P_{x}^{2\omega} \\
P_{y}^{2\omega} \\
P_{z}^{2\omega}
\end{pmatrix} =
\begin{pmatrix}
\chi_{xxx}^{(2)} & \chi_{xxy}^{(2)} & \chi_{xxz}^{(2)} \\
\chi_{yxx}^{(2)} & \chi_{yyx}^{(2)} & \chi_{yxz}^{(2)} \\
\chi_{zxx}^{(2)} & \chi_{zyx}^{(2)} & \chi_{zzx}^{(2)}
\end{pmatrix}
\begin{pmatrix}
E_{x}^{\omega^2} \\
E_{y}^{\omega^2} \\
E_{z}^{\omega^2}
\end{pmatrix}
\]

(2.38)

For the special case of second harmonic generation (SHG), we are able to respect permutation symmetries between the two optical fields since \( E_j^\omega E_k^\omega = E_k^\omega E_j^\omega \). This equivalency allows us to reduce the second-order susceptibility from a tensor with 27 components to one with 18 components. Using the convention \( i, j, k = 1, 2, 3 \) to denote the \( x, y, \) and \( z \) axes, the second-order polarization in Eq. 2.38 becomes:
\[
\begin{pmatrix}
    p_{\omega}^2 \\
    p_{2\omega} \\
    p_{3\omega} \\
\end{pmatrix} = 
\begin{pmatrix}
    d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\
    d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\
    d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \\
\end{pmatrix}
\begin{pmatrix}
    E_{x}^2 \\
    E_{y}^2 \\
    E_{z}^2 \\
    2E_{y}^\omega E_{y}^\omega \\
    2E_{x}^\omega E_{z}^\omega \\
    2E_{x}^\omega E_{y}^\omega \\
\end{pmatrix}
\]  

(2.39)

For the above tensor equation, \(xx = 11 = 1\), \(yy = 22 = 2\), \(zz = 33 = 3\), \(yz = 23 = 32 = 4\), \(xz = 13 = 31 = 5\), and \(xy = 12 = 21 = 6\) [39, 40]. The non-vanishing components of the second-order susceptibility hold all the significant structural information of the material being probed and are determined according to the lattice symmetry, \textit{i.e.} crystal point group symmetry. In order to obtain any useful information about the material’s structure, or polar ordering, the SHG intensity must be measured.

To derive the general expression for the SHG intensity, we start with Eq. 2.20 with the second-order polarization acting as a source for radiation at the second-harmonic frequency:

\[
\nabla \times (\nabla \times E^{2\omega}(r, t)) + \frac{(n^{2\omega})^2}{c^2} \frac{\partial^2 E^{2\omega}(r, t)}{\partial t^2} = \mu_o \frac{\partial^2 P^{2\omega}(r, t)}{\partial t^2} 
\]

(2.40)

Let’s examine the case where the second-harmonic field is propagating along the \(z\)-axis inside a nonlinear medium. The harmonic electrical and polarization fields can then be defined as follows:

\[
E^{2\omega}(r, t) = E^{2\omega}(z)e^{-i(2\omega t)} \tag{2.41}
\]

\[
P^{2\omega}(r, t) = P^{2\omega}(z)e^{-i(2\omega t)} \tag{2.42}
\]
Plugging these fields into the wave equation and carrying out time-derivatives leaves us with a spatially-resolved wave equation in terms of the amplitude functions:

\[-\nabla \times (\nabla \times E^{2\omega}(z)) + \frac{(n^{2\omega})^2(2\omega)^2}{c^2} E^{2\omega}(z) = \mu_o (2\omega)^2 P^{2\omega}(z)\]  \hspace{1cm} (2.43)

Since we are considering a unidirectional propagation along the z-axis, the following approximation for the curl term can be made [39, 88]:

\[-\nabla \times (\nabla \times E^{2\omega}(z)) = \frac{\partial^2 E^{2\omega}(z)}{\partial z^2} + 2ik^{2\omega} \frac{\partial E^{2\omega}(z)}{\partial z} - (k^{2\omega})^2 E^{2\omega}(z)\]  \hspace{1cm} (2.44)

Since the change in amplitude of the second-harmonic field over the length of a wavelength is negligible, the slowly-varying amplitude approximation can be used to simplify Eq. 2.44 by dropping the second-order derivative with respect to z. Thus, Eq. 2.43 becomes:

\[2ik^{2\omega} \frac{\partial E^{2\omega}(z)}{\partial z} - (k^{2\omega})^2 E^{2\omega}(z) + \frac{(n^{2\omega})^2(2\omega)^2}{c^2} E^{2\omega}(z) = \mu_o (2\omega)^2 P^{2\omega}(z)\]  \hspace{1cm} (2.43)

The second and third terms on the left-hand side cancel out because \(k^{2\omega} = \frac{2\omega \cdot n^{2\omega}}{c}\). We are left with:

\[2ik^{2\omega} \frac{\partial E^{2\omega}(z)}{\partial z} = \mu_o (2\omega)^2 P^{2\omega}(z)\]  \hspace{1cm} (2.45)

We now can make the substitution for the amplitude functions of the second-harmonic electric and polarization fields:
\[ E^{2\omega}(z) = E^{2\omega}(z)e^{i(2\omega z)} \] (2.46)

\[ P^{2\omega}(z) = 2\varepsilon_0\chi^{(2)}_{\text{eff}}(E^{\omega})^2 e^{i(2k^\omega z)} \] (2.47)

In Eq. 2.47, \( \chi^{(2)}_{\text{eff}} \) is the effective second-order susceptibility which takes into account polarization directional vectors as well as Fresnel transformation factors for the single-frequency electric fields. Then Eq. 2.45 can be rearranged into the following differential equation:

\[
\frac{\partial E^{2\omega}(z)}{\partial z} = -i\omega n^2\varepsilon_0 c \chi^{(2)}_{\text{eff}}(E^{\omega})^2 e^{i(\Delta k z)}
\] (2.48)

In Eq. 2.48, \( \Delta k = 2k^\omega - k^{2\omega} \). Integrating with respect to \( z \) over the interaction length, \( L \), and solving for the second-harmonic optical intensity finally leaves us with:

\[
I^{2\omega} = \frac{2\omega^2|\chi^{(2)}_{\text{eff}}|^2 L^2}{n^2\omega(n^\omega)^2c^3\varepsilon_0}\left(\frac{\sin(\Delta kL/2)}{\Delta kL/2}\right)^2 (I^{2\omega})^2
\] (2.49)

The result in Eq. 2.49 shows that the functional form of the SHG intensity depends directly on the structural symmetry of the probed region, while the magnitude of the SHG intensity scales with the square of the incident optical intensity. In practice, the SHG intensity profile may be fitted according to the proportionality, \( I^{2\omega} \propto |\chi^{(2)}_{\text{eff}}|^2 \) or \( I^{2\omega} \propto |P^{2\omega}|^2 \) depending on the system being studied. Various factors, such as refraction, sample orientation, and optical polarization axes, must
be taken into consideration to properly analyze information about the structure and/or polar
ordering of the material, which will be discussed as needed in later chapters.

2.5.3 SHG Phase-Matching

A very significant phase-matching condition becomes apparent as a result of the sinc
functional term present in the expression. Firstly, Eq. 2.49 was derived under the assumption that
the SHG conversion efficiency is low and that the incident fundamental light does not deplete as
it travels through the nonlinear medium. Secondly, the sinc term limits the SHG intensity unless
the argument, $\Delta kL/2$, is equal to zero. This means that for very efficient SHG conversion, we want
$\Delta k = 2k_\omega - k_{2\omega} = 0$, or $n_{2\omega} = n_\omega$. This is typically not the case and many materials
demonstrate $n_{2\omega} > n_\omega$. Thus, the depth in a material from which second-harmonic light can be
generated is limited by what’s known as the SHG coherence length. This is the distance that SHG
light can travel before destructively interfering with itself. As a result, it does not pay off to use
nonlinear materials thicker than the coherence length since SHG light is limited to this depth. To
illustrate the coherence length, we may plot the sinc function, as shown in Fig. 2.12.
**Figure 2.12:** Shows the sinc functional term plotted as a function of distance from the surface of the nonlinear material. Considering light propagation in the positive direction, the SHG coherence length is given by the two vertical red lines, with the second line marking the start of destructive interference. Complete destructive interference occurs at twice the coherence length, as shown by the first minima.

The coherence length is formally defined as $L_{coh} = \frac{\pi}{\Delta k}$, marking the distance over which SHG radiation travels before it begins to destructively interfere with itself. Complete, 180° out-of-phase, destructive interference occurs at $L = 2L_{coh}$. In practice, it is most convenient to redefine the coherence length with respect to the optical properties of the material being studied. $\Delta k$ can be rewritten as $\frac{4\pi}{\lambda} (n^\omega \pm n^{2\omega})$ where we take (+) for reflected SHG and (-) for transmitted SHG. The SHG coherence length can thus be formally expressed as:

$$L_{coh} = \frac{\lambda_\omega}{4|n^\omega \pm n^{2\omega}|} \quad (2.50)$$
It becomes clear that the coherence length has a dependence on the refractive indices of the material ($n^\omega$ and $n^{2\omega}$) as well as the wavelength of the fundamental laser light ($\lambda_\omega$) used to induce a nonlinear response. Further experimental details about the SHG coherence length in STO and BTO are given in the next chapter.
Chapter 3: Experimental Details

This chapter presents details of sample preparation and experimental methods used for second harmonic generation, confocal Raman, and fluorescence measurements. In section 3.1, descriptions regarding the preparation of Fe-doped SrTiO$_3$ single crystals and ferroelectric Zr-doped BaTiO$_3$ thick films are given. Section 3.2 goes over the femtosecond laser systems used for second harmonic generation measurements. Section 3.3 discusses polarization-resolved second harmonic generation measurements. Section 3.4 and 3.5 give brief descriptions for the collection of confocal Raman and steady-state fluorescence spectra.

3.1 Samples

3.1.1 Fe:STO Single Crystals

(100) SrTiO$_3$ single crystals doped with 0.01 wt.% Fe (Fe:STO) were purchased from MTI corporation (Richmond, CA) and cut into 5 x 5 x 0.5 mm$^3$ pieces and epi-polished on both 5 x 5 mm$^2$ faces. The Fe:STO single crystals were then annealed in a tube furnace at 900°C under a partial oxygen pressures of 2x10$^{-5}$ bar and 0.2 bar for reduction and oxidation treatment, respectively. Reduced crystals were then quenched in argon and oxidized crystals were quenched in air at 25°C to freeze-in ionic defect concentrations ([Fe]$_{tot}$ $\sim$ 5.58 x 10$^{18}$/cm$^3$). Calculated defect concentrations [$V_0^-$], [Fe$^{3+}$], and [Fe$^{4+}$] based on mass action constants are given in Table 3.1[51]. Reduced crystals have larger concentrations of Fe$^{3+}$ and oxygen vacancies while oxidized crystals have larger concentrations of Fe$^{4+}$ and oxygen. Electrochemically reduced and oxidized crystals enabled comparative analyses based on oxygen vacancy concentrations.
Table 3.1: Defect concentrations for the initial, undegraded Fe:STO states at the annealing (900 °C), quenching (25 °C), and investigation (25 °C) conditions.

<table>
<thead>
<tr>
<th>pO2 (bar)</th>
<th>T (°C)</th>
<th>[Vo] (cm(^{-3}))</th>
<th>[Fe(^{3+})] (cm(^{-3}))</th>
<th>[Fe(^{4+})] (cm(^{-3}))</th>
<th>[Fe(^{4+})]/[Fe]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>900</td>
<td>1.03 × 10(^{18})</td>
<td>3.28 × 10(^{18})</td>
<td>2.30 × 10(^{18})</td>
<td>0.59</td>
</tr>
<tr>
<td>0.2</td>
<td>25</td>
<td>1.03 × 10(^{18})</td>
<td>2.06 × 10(^{18})</td>
<td>2.52 × 10(^{18})</td>
<td>0.37</td>
</tr>
<tr>
<td>2 × 10(^{-5})</td>
<td>900</td>
<td>2.43 × 10(^{18})</td>
<td>5.04 × 10(^{18})</td>
<td>5.44 × 10(^{17})</td>
<td>0.90</td>
</tr>
<tr>
<td>2 × 10(^{-5})</td>
<td>25</td>
<td>2.43 × 10(^{18})</td>
<td>4.85 × 10(^{18})</td>
<td>7.30 × 10(^{17})</td>
<td>0.87</td>
</tr>
</tbody>
</table>

To generate oxygen vacancy migrations inside the crystals, amorphous platinum (Pt) electrodes were sputter-grown on the crystals for *dc* electric field application. X-ray diffraction (XRD) spectra were collected from Fe:STO with and without electrodes to verify the amorphous structure of the platinum layers, as shown in Fig. 3.1. Both XRD spectra exhibit cubic (*Pm\(3m\)*) lattice symmetry, although the platinum layer significantly decreases the XRD intensity by attenuating the signal reflected from the Fe:STO surface. A thin, amorphous electrode layer means that optical SHG from the surface is negligible and the SHG signal will come primarily from the non-centrosymmetric Fe:STO surface.
Three pairs of reduced and oxidized Fe:STO single crystals were used for all experiments. The first pair of samples studied were undegraded reduced and oxidized Fe:STO single crystals with planar 10 nm thick electrodes. These samples were used to assess structural changes at electrode interfaces in response to $dc$ electrical stress and oxygen vacancy migration at room temperature. The second pair of samples were electrodegraded reduced (B042) and oxidized (B045) Fe:STO single crystals with planar 10 nm thick electrodes. These crystals were degraded at 210°C under a $dc$ voltage of 40V. The last pair of Fe:STO samples were electrodegraded reduced (B057) and oxidized (B056) Fe:STO single crystals with lateral 100 nm thick electrodes. These samples were degraded at 210°C under a $dc$ voltage of 100V. Electrode placements are shown in Fig. 3.2.
Figure 3.2: Planar and lateral platinum electrode placement for dc electric field application across Fe:STO single crystals.

Leakage current measurements for the electrodegraded Fe:STO single crystals, B042/B045 and B056/B057, are shown in Fig. 3.3. The increase in leakage current by around two orders of magnitude for each crystal is a direct result of insulation resistance degradation due to oxygen vacancy migrations.

Figure 3.3: (a) Current density measurements taken from the electrodegraded Fe:STO single crystals with planar electrodes, B042 and B045. (b) Current density measurements taken from the electrodegraded Fe:STO single crystals with lateral electrodes, B056 and B057.

Annealing, quenching, electrode deposition, and electrodegradation of all Fe:STO single crystals were performed by Prof. Clive Randall’s research group from Pennsylvania State University.
3.1.2 BZT Films

LaAlO$_3$ (LAO), (La,Sr)(Al,Ta)O$_3$ (LSAT), and SrTiO$_3$ (STO) substrates with dimensions of 10 x 10 x 0.5 mm$^3$ and SrRuO$_3$ (SRO) ceramic targets ($\Phi = 50$ mm, $t = 5$ mm, 3N purity) were provided by the Anhui Institute of Optics and Fine Mechanics of the Chinese Academy of Sciences. Ba(Zr$_{0.2}$Ti$_{0.8}$)O$_3$ (BZT) ceramic targets were prepared using a solid solution-based reaction by Prof. Jun Ouyang’s research group from Shandong University. Titanium oxide (TiO$_2$, 98%), zirconium oxide (ZrO$_2$, 99%), and barium carbonate (BaCO$_3$, 99%) powders were used as primary reagents. Details on the ceramic sintering process are discussed elsewhere[79]. RF-magnetron sputtering, with a base chamber pressure of $2.0 \times 10^{-9}$ bar ($2.0 \times 10^{-4}$ Pa), was used for the deposition of ~100 nm SRO electrode layers on the top of each substrate followed by the epitaxial growth of ferroelectric BZT thick films. Lastly, circular gold (Au) electrodes ($\Phi = 200$ $\mu$m) were sputtered on the BZT films at room temperature using a shadow mask. An SEM side profile of a typical Au plated surface, ferroelectric BZT film, SRO electrode, and perovskite oxide substrate structure is shown in Fig. 3.4.

Figure 3.4: Shows the typical sequential structure for the ferroelectric thick films studied in this work. Circular Au electrodes are spread across the BZT surface. Beneath the bulk layers of the BZT film lies the SRO electrode layer over the surface of the perovskite oxide substrate.
Overall, nine ferroelectric BZT thick films were prepared for optical SHG polarimetry measurements. BZT films with thicknesses of 350 nm, 700 nm, and 1800 nm were grown on LAO, LSAT, and STO substrates, as listed in Table 3.2. At room temperature, BZT exhibits rhombohedral (3m) phase symmetry with a lattice parameter of $a = 4.0 - 4.02$ Å. Compressive strain is exerted on the films due to lattice parameter mismatches between the BZT and the substrates. This compressive strain drives the formation of tetragonal domain structures along the thickness of the film.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BZT Thickness</th>
<th>Substrate</th>
<th>Substrate Lattice Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>350 nm</td>
<td>STO</td>
<td>$a = 3.905$ Å</td>
</tr>
<tr>
<td>Sample 2</td>
<td>700 nm</td>
<td>STO</td>
<td>$a = 3.905$ Å</td>
</tr>
<tr>
<td>Sample 3</td>
<td>1,800 nm</td>
<td>STO</td>
<td>$a = 3.905$ Å</td>
</tr>
<tr>
<td>Sample 4</td>
<td>350 nm</td>
<td>LAO</td>
<td>$a = 3.79$ Å</td>
</tr>
<tr>
<td>Sample 5</td>
<td>700 nm</td>
<td>LAO</td>
<td>$a = 3.79$ Å</td>
</tr>
<tr>
<td>Sample 6</td>
<td>1,800 nm</td>
<td>LAO</td>
<td>$a = 3.79$ Å</td>
</tr>
<tr>
<td>Sample 7</td>
<td>350 nm</td>
<td>LSAT</td>
<td>$a = 3.87$ Å</td>
</tr>
<tr>
<td>Sample 8</td>
<td>700 nm</td>
<td>LSAT</td>
<td>$a = 3.87$ Å</td>
</tr>
<tr>
<td>Sample 9</td>
<td>1,800 nm</td>
<td>LSAT</td>
<td>$a = 3.87$ Å</td>
</tr>
</tbody>
</table>

Table 3.2: Ferroelectric BZT film samples listed with their respective thicknesses, substrates, and substrate lattice parameters[34] at room temperature.

Crystallographic structure of the BZT films were analyzed using X-ray diffraction (XRD) using a commercial Rigaku Dmax-rec diffractometer (regular $\theta$-2$\theta$ scans), and a high power IP crystal X-ray diffractometer equipped with an R-Axis Spider ($\Phi$-scans and $\theta$-2$\theta$ scans with a rotated $\chi$ angle). Phase structures and nanostructures were also investigated using transmission electron microscopy (TEM) in a JEM-2010 microscope (JEOL, Tokyo, Japan). Ferroelectric $P-E$ hysteresis loops were measured using an RT-Precision LC ferroelectric testing system (Radiant
Technology, NM, USA), and the dielectric properties ($C_f$, $C-V$) were measured with a high precision digital bridge (LCR meter, QuadTech 7600plus) and an Agilent1505A power device analyzer (by applying a 50 mV, 5 kHz $ac$ signal and sweeping a $dc$ bias voltage from a negative to positive maximum value). Temperature-dependent measurements were taken using a temperature-controlled probe station (Linkam-HFS600E-PB2). Characterization of dielectric properties and measurement of ferroelectric hysteresis curves were performed by Dr. Jun Ouyang’s research group from Shandong University.

### 3.2 Femtosecond Laser Systems

As a nonlinear optical process, SHG requires high power light sources to take place. Although only milliwatt-range power is needed to induce a nonlinear response from a non-centrosymmetric medium, a significantly high amount of energy is required to produce high intensity laser fields using continuous wave (CW) lasers. Thus, pulsed laser systems are essential components for probing nonlinear structure in crystalline solids using SHG. Two femtosecond laser systems were used in this experimental work, a Ti:Sapphire (Ti:Al$_2$O$_3$) oscillator (Tsunami, Spectra-Physics) and a Ti:Sapphire regenerative amplifier (RegA 9000, Coherent).

#### 3.2.1 Mode-locked Ti:Sapphire Oscillator

Our primary femtosecond pulsed laser system consists of a Diode-Pumped Frequency-Doubled CW-Nd:Vanadate Laser (Millennia Pro, Spectra-Physics) and a Broadband Tunable Ti:Sapphire Oscillator (Tsunami, Spectra-Physics). A schematic for the mode-locked Ti:Sapphire oscillator is shown in Fig. 3.5.
Figure 3.5: Schematic for the mode-locked Ti:Sapphire oscillator (Tsunami, Spectra-Physics).

Incident light from the CW-Nd:Vanadate enters the oscillator and is directed by a pump steering mirror (P₁) to a pump focus mirror (P₂). Light is reflected from the pump focus mirror (P₂) and focused through a cavity focus mirror (M₃) into the Ti:Sapphire crystal. Fluorescence from the Ti:Sapphire crystal is then collimated and expanded while the residual pump beam is dumped through the second cavity focus mirror (M₄). Cavity mirrors (M₄ and M₅) then direct the beam to a prism (Pr₁). Prisms Pr₁ and Pr₄ work together with an adjustable pair of prisms, Pr₂ and Pr₃, in order to compensate for group velocity dispersion in the cavity. The tuning slit positioned between Pr₂ and Pr₃ is used for tuning the central wavelength and bandwidth of the cavity output. Mirrors M₆ through M₉ steer the beam through and prisms and into an acousto-optic (A/O) modulator used to help stabilize pulsing using radio-frequency (RF) electronics. The beam then retroreflects from the output coupler (M₁₀) back through the cavity to the high reflector (M₁). The output coupler (M₁₀) lets < 5% of the laser light from the cavity leave as the output beam. Near the output, a beam splitter reflects a small percentage of the light into a silicon photodiode which monitors whether light in the cavity is pulsing or CW. This photodiode can also be used in conjunction with an oscilloscope for monitoring voltage signals from the pulsed light when tuning the repetition rate.
The alignment of the laser beam within the resonant cavity is critical for the generation of infrared pulsed light. The pump beam entering the oscillator from the CW-Nd:Vanadate Laser (Millenia Pro, Spectra-physics) must be collinear with the cavity mode over the Ti:Sapphire rod. This is done so by overlapping beam paths of the pump light and the fluorescence light from the Ti:Sapphire crystal. To optimize mode-locking within the cavity, the prism system is used to control dispersion compensation. Micrometers on the exterior of the Ti:Sapphire oscillator body allow the user to tune the heights of prisms Pr₂ and Pr₃. These prism heights must be tuned until the laser’s output bandwidth expands to a maximum. Next, the vertical and horizontal axes of the end mirrors, M₁ and M₁₀ can be adjusted to optimize the output power. Once the system is pulsing with an optimized output power of ~780 – 800 mW, it is best to only adjust M₁ for power tuning during day-to-day operation to avoid walking the output beam path over time. It is crucial that the output power be adjusted while monitoring the output spectrum to make sure the laser is stable and pulsing.

The generation of laser pulses in the oscillator is due to a very important principle known as mode-locking. In a laser cavity, a standing wave is formed when propagating light waves constructively interfere with each other at fixed positions along the beam path. Optical wavelengths which satisfy this condition are known as the longitudinal modes of the laser cavity. As a simplification, consider light reflecting back and forth between the end mirrors, M₁ and M₁₀, of the optical cavity. By using the wave equation, we may solve for the longitudinal modes:

\[ \nabla^2 E(z, t) - \frac{1}{c^2} \frac{\partial^2 E(z, t)}{\partial t^2} = 0 \]  

(3.1)
Our boundary conditions are \( E(z = 0, t) = 0 \) and \( E(z = L, t) = 0 \) where \( L \) represents the cavity length as the distance between end mirrors along the \( z \)-axis. Using separation of variables, we may write the electric field as \( E(z, t) = Z(z)T(t) \), such that Eq. 3.1 becomes:

\[
Z''(z)T(t) - \frac{1}{c^2} Z(z)T''(t) = 0
\]  

(3.2)

Dividing through by \( Z(z)T(t) \) gives us the following equations:

\[
\frac{Z''(z)}{Z(z)} - \frac{1}{c^2} \frac{T''(t)}{T(t)} = 0
\]

(3.2)

\[-k^2 + \frac{\omega^2}{c^2} = 0\]

(3.3)

Thus, Eq. 3.1 becomes two separate ordinary differential equations which we can solve for without much difficulty:

\[
Z''(z) = -k^2 Z(z)
\]

(3.4)

\[
T''(t) = -\left(\frac{\omega}{c}\right)^2 Z(z)
\]

(3.5)

General solutions for Eq. 3.4 and Eq. 3.5 are \( Z(z) = A\sin(kz) + B\cos(kz) \) and \( T(t) = Ce^{-i\left(\frac{\omega}{c}\right)t} + De^{i\left(\frac{\omega}{c}\right)t} \), respectively. To satisfy the first boundary condition, we must have \( Z(0) = Asin(0) + Bcos(0) = 0 \), so coefficient B has to be 0. To satisfy the second condition, \( Z(L) = Asin(kL) \) can only be 0 if \( kL = n\pi \). Thus, \( k = \frac{n\pi}{L} \) and we obtain a dispersion relation for the longitudinal modes of the system using Eq. 3.3:
\[
\left(\frac{n\pi}{L}\right)^2 = \frac{\omega^2}{c^2}
\]  
(3.6)

By substituting \(\omega = 2\pi \nu\) and \(c = \nu \lambda\), allowed optical wavelengths in the cavity which gives rise to longitudinal modes are expressed as follows:

\[
\lambda_n = \frac{2L}{n}
\]  
(3.6)

Here, \(n\) is the order of the longitudinal mode and \(L\) is the distance between the end mirrors, \(i.e.\) the cavity length. Fig. 3.6 shows the first nine longitudinal modes formed in the cavity.

Figure 3.6: The first nine longitudinal modes inside the optical cavity.

Although these modes oscillate along the length of the cavity they do so with different temporal phases. Therefore, the laser’s output can contain a randomized distribution of modal phases. Assuming low energy loss within the cavity due to the energy input from the pump beam, the total
electric field in the cavity, which is a vector sum of all longitudinal modes, can be expressed as the following Fourier series:

\[
E(z, t) = \sum_n E_n \sin \left( \frac{n \pi z}{L} \right) \cos \left( \frac{n \pi t}{L} + \phi_n(t) \right)
\] (3.7)

In Eq. 3.7, \( n \) represents the longitudinal mode order and \( L \) represents the effective cavity length. \( \phi_n(t) \) represents a phase term that can be associated with each longitudinal mode. The total electric field propagating within the cavity is shown in Fig. 3.8a. Intensities, which are given by \( I \propto |E|^2 \), are shown in Fig. 3.7b.

\[\text{Fig. 3.7a} \quad \text{Fig. 3.7b}\]

**Figure 3.7:** (a) Cumulative electric field in the cavity calculated from summing the first 30 longitudinal modes. The electric field is shown propagating left to right over time. (b) Pulse intensity traveling to the right. A pulse leaves the output coupler each cycle.

The pulse train leaving the output coupler consists of 100 fs long pulses exiting the cavity at a repetition rate of 80 MHz with an average energy of about 10 nJ/pulse. One cycle has a duration
of $T = \frac{2L}{c}$, which represents the time delay between consecutive pulses [89, 90]. Taking the inverse of the repetition rate gives us the time delay, $T = 12.5$ ns, and the effective length of the oscillator cavity, $L = 187.5$ cm, which is adjustable by tuning $M_1$ if needed. The optical wavelengths accessible to the laser are determined by the gain medium, where population inversion occurs. In this cavity, Ti:Sapphire provides a gain bandwidth, $\Delta \nu$, of about 200 THz[91] and so wavelengths can be tuned within a range $\Delta \lambda = \left( \frac{\lambda_0^2}{c} \right) \Delta \nu$, where $\lambda_0 = 800$ nm is the optimal wavelength of the gain medium. Thus, the wavelength range for the Ti:Sapphire oscillator is calculated to be around $800 \pm 215$ nm, or $\sim 685 – 1015$ nm. Our system operates most efficiently using wavelengths close to 800 nm.

For all experiments, output pulses were tuned to a central wavelength of 810 nm with a bandwidth of 10 nm. The central wavelength and bandwidth of the pulsed laser output were measured using an optical spectrum analyzer (OSA) (OSM-100-VIS/NIR, Newport). The OSA has a resolution of 0.1 nm and a sensitivity of $\sim 100$ pW over the wavelength range 600 to 1,600 nm. An optical fiber is used to direct light into the OSA and the pulse spectra can be monitored and tuned in real time. An example of the Tsunami’s pulse spectrum is shown in Fig. 3.8.
Figure 3.8: Spectral distribution of the pulsed laser output measured with an optical spectrum analyzer (Newport OSM-100-VIS/NIR). In our experiments, we tune the central wavelength to 810 nm and the bandwidth (FWHM) to 10 nm.

It is important to note that laser light is not directly steered into the optical fiber coupled to the OSA. Instead, a piece of paper is used to block the beam a foot or so away from the oscillator and the OSA fiber is turned to face the beam spot formed on the piece of paper. Shining laser pulses directly into the fiber will not only saturate the OSA, but also damage the fiber.

3.2.2 Ti:Sapphire Regenerative Amplifier

In experiments where higher peak powers are required, such as for the detection of transmitted optical SHG with normally incident light, a Ti:Sapphire regenerative amplifier system (RegA 9000, Coherent) is needed. The RegA 9000 cavity is pumped by a solid-state CW-Nd:YVO₄ laser (Verdi V10, Coherent) and seeded with pulses emitted from the mode-locked Tsunami. Fig. 3.9 shows a schematic of the RegA cavity.
The Ti:Sapphire regenerative amplifier is used to amplify the peak power of femtosecond pulses from the Ti:Sapphire oscillator. CW light (10 W) from the ND:YVO$_4$ laser enters the Ti:Sapphire RegA as the pump beam (shown in green in Fig. 3.9). The pump beam is directed through the pump optics mirrors (P$_0$-P$_4$) and passed through focused (L$_1$) on a Ti:Sapphire crystal (TS). 100 fs pulses from the Tsunami are fed into the Ti:Sapphire RegA as the seed beam, passing through a polarizer (CP) and reflecting off of a mirror (IM$_4$) into a Faraday Isolator (FI) which is used to prevent pulses from reflecting backwards into the Tsunami. Tsunami pulses are injected into the RegA cavity (cavity length between M$_1$ and M$_8$) with a tellurium dioxide (TeO$_2$) acousto-optic cavity dumper (CD). Amplification inside the RegA cavity occurs over ~25 roundtrips and allows the dispersion taking place in a TeO$_2$ Q-switch (QS) to expand the 100 fs pulses to 40 ps pulses. This so-called pulse stretching step is necessary for safe energy extraction from the laser pulses, otherwise catastrophic damage can be inflicted on the cavity optics. Once pulses are stretched, the cavity dumper (CD) extracts a pulse of several $\mu$J in energy. The accumulated chirp acquired by pulses during amplification is canceled out using a single holographic diffraction grating (DG) which compresses pulses to ~200 fs pulse widths for the RegA output. Thus, the pulse train leaving the output consists of 200 fs long pulses exiting the cavity at a repetition rate of 250 kHz with an average energy of about 5 $\mu$J/pulse.
3.3 Optical SHG Polarimetry

![Diagram of optical SHG setup](image)

**Figure 3.10:** Generalized diagram for optical SHG experiments in our lab. Laser pulses emitted from either the RegA 9000 or Tsunami are passed through a mechanical chopper and enter the detection setup configured for generating polarization-resolved SHG signals. The induced SHG signal is then directed into a photomultiplier tube (PMT) and the lock-in amplified signal is recorded through a LabVIEW program.

The schematic diagram for the experimental detection of optical SHG is shown in Fig. 3.10. A femtosecond pulse laser system, either the Ti:Sapphire oscillator (Tsunami, Spectra-physics) or Ti:Sapphire regenerative amplifier (RegA 9000, Coherent), is used as the fundamental light source with a central wavelength tuned to 810 nm and bandwidth of about 10 nm. Modulation of the fundamental light at a frequency of 3 kHz is accomplished using a mechanical chopper (SR540 Chopper, Stanford Research Systems). Physically chopping the beam up allows the signal to be measured using a lock-in amplification system (7265 DSP Lock-in Amplifier, Signal Recovery) since the chopped signal is tagged according to its modulated frequency and thus easier to differentiate from background signals, significantly improving the signal-to-noise ratio.
Chopper modulated laser light is focused onto the sample in order to elicit an SHG response. SHG from the sample is then directed to a sensitive photodetector called a photomultiplier tube (PMT) (Hamamatsu, H9305-04). The PMT works by amplifying electrons generated by a photocathode exposed to the SHG signal, resulting in a measurable photo-induced voltage (~µV). This voltage signal is read by a lock-in amplifier and interfaced to a computer using a General Purpose Interface Bus (GPIB). Finally, computer software (LabVIEW, National Instruments) is utilized for automated data collection.

Two primary configurations for optical SHG measurements were used in this thesis work, namely, the reflection and transmission geometries as shown in detail by Fig. 3.11a and Fig. 3.11b, respectively.

![Fig. 3.11a](image1)

**Fig. 3.11a**

![Fig. 3.11b](image2)

**Fig. 3.11b**

**Figure 3.11:** Schematics for far-field optical SHG polarimetry setups in the (a) transmission geometry and (b) reflection geometry.

In both geometries, a fundamental light wave of frequency $\omega$ first passes through a Glan Polarizer to ensure linear polarization before passing through a half-wave plate. The half-wave plate, which is controlled by an electronic motion controller (Universal Motion Controller / Driver ESP300,
Newport) through LabVIEW, is used to rotate the polarization angle, \( \varphi \), of the incident light on the sample. Optical fields are described according to two orthogonal orientations, \( p \)-polarized and \( s \)-polarized, such that the incident optical field amplitude on the sample can be written as:

\[
E(\omega) = E_p^\omega(\varphi)\hat{p} + E_s^\omega(\varphi)\hat{s}
\]  

(3.8)

In Eq. 3.8, \( E_p^\omega(\varphi) = E^\omega \cos \varphi \) and \( E_s^\omega(\varphi) = E^\omega \sin \varphi \), where \( E^\omega \) is the amplitude of the optical field. In all of our experiments, \( p \)-polarized optical fields are considered as travelling parallel to the optics table while \( s \)-polarized optics fields travel perpendicular to the optics table. After the half-wave plate, the fundamental light wave is then passed through a long-pass filter (LPF) which blocks optical wavelengths below 780 nm. This is to make sure that no SHG signals from the pulse lasers or optical components will enter the PMT. A converging lens (L1), with a focal length of 35 mm, is then used to focus the fundamental light onto the sample in order to achieve a high enough energy density for eliciting a measurable nonlinear response. After signal is generated from the sample’s non-centrosymmetric surface, interface, or bulk, it is passed through a second Glan Polarizer used to analyze either \( p \)-polarized or \( s \)-polarized SHG intensities as functions of the incident polarization angle, \( \varphi \), which are measured by the PMT.

To calculate the energy density at the focused beam spot, one must first find the diameter of the beam spot incident on the sample. The focused beam spot diameter can be estimated using the following equation [92, 93]:

\[
d_f = \frac{4\lambda f M^2}{\pi d_i}
\]  

(3.9)
In Eq. 3.9, \( \lambda \) is the central wavelength of the incident light, \( f \) is the focal length of the converging lens (L1), \( M \) is the quality factor of the gaussian beam (~1.0), and \( d_i \) is the beam diameter in front of converging lens (L1). For an average measured beam diameter of ~0.5 cm at the converging lens (L1), the focused beam spot diameter is calculated to be ~10 \( \mu \)m. The energy density, or fluence, is then calculated by the Energy/Area as follows:

\[
\mathcal{E} = \frac{\langle P \rangle}{R_{\text{rep}} \left( \frac{\pi}{2} \left( \frac{d_i}{2} \right)^2 \right)}
\]  

(3.9)

For the Ti:Sapphire oscillator, the average power used on the sample is 70 mW and the repetition rate is 80 MHz. Thus, the fluence on the sample when using the Tsunami, is ~1 mJ/cm\(^2\). For the RegA 9000, fluences are especially high as a result of the lower repetition rate and care was taken to ensure no materials were damaged during second harmonic generation measurements. The average power used on the samples was 40 mW with a defocused beam spot diameter of ~15 \( \mu \)m. The calculated fluence on the sample when using the RegA 9000, is ~100 mJ/cm\(^2\).

Whether or not to detect SHG in the reflection or transmission geometry depends on whether one is probing a surface, interface, or bulk region. In general, the reflection geometry is used for probing surface and interface structure, while the transmission geometry is used to probe bulk regions. In particular, one must take into account the coherence length of SHG radiation. The SHG coherence length in the reflection (+) and transmission (−) geometries can be expressed as[82, 85]:

\[
L_{\text{coh}} = \frac{\lambda_\omega}{4|n_\omega \pm n_\omega^2|}
\]

(3.10)

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The coherence length is the distance within the sample that SHG light can travel before destructively interfering with itself. This length represents an upper limit on the depth (not the actual depth) within the sample that SHG signals come from. If the length of the polar region being probed is less than the SHG coherence length, then SHG will come from the polar region only since SHG is not allowed in non-polar, or centrosymmetric, media. Eq. 3.10 also reveals that the coherence length of SHG not only depends on the fundamental wavelength, but also the wavelength-dependent refractive index of the material being studied. In our experiments, doped STO and BTO-based perovskites were studied using optical SHG and so it is necessary to know the refractive indexes of both materials for the fundamental and SHG wavelength light. An assumption can be made that the Fe and Zr doping have a negligible effect on the refractive index since these insulating materials have low free carrier concentrations at room temperature. The refractive index of both STO[94] and BTO[95] as functions of wavelength can be obtained from their Sellmeier Equations:

\[ n(\lambda)^2 - 1 = \frac{3.042143\lambda^2}{\lambda^2 - (0.1475902)^2} + \frac{1.170065\lambda^2}{\lambda^2 - (0.2953086)^2} + \frac{30.833326\lambda^2}{\lambda^2 - (33.18606)^2} \] (3.11)

\[ n(\lambda)^2 - 1 = \frac{4.187\lambda^2}{\lambda^2 - (0.223)^2} \] (3.12)

Eq.11 and Eq.12 are the dispersion formula for the refractive index of STO and BTO, respectively, at room temperature and are only valid for wavelength units in micrometers (µm). Fig. 3.12 shows a plot of both refractive index values as functions of wavelength, with the relevant values used for calculating coherence length appearing in the upper right corners.
Figure 3.12: Refractive index for STO and BTO plotted as functions of the optical wavelength in micrometers. Index of refraction values for 810 nm and 405 nm light are given in the upper right-hand corners of each subplot.

For incident light of wavelength 810 nm, the coherence length in the reflection and transmission geometries are ~40 nm and ~660 nm, respectively, for both STO and BTO due to their similar refractive index values. Thus, the reflection geometry is inherently sensitive to surface and interface layers, while the transmission geometry can be used to study bulk layers.

Sample orientation plays a significant role in the detection of polarization-resolved optical SHG. By varying the tilt angle, $\theta$, which is the angle between the sample’s surface normal and the propagation vector of the incident light, one can adjust the relative strengths of certain nonlinear susceptibility components. For our experiments, $\theta = 45^\circ$ in the reflection geometry is used when probing tetragonal symmetries in Fe:STO surfaces/interfaces. We also use normal incidence, $\theta = 0^\circ$, in the transmission geometry when probing mixed tetragonal and rhombohedral domains in the
BZT film bulks. We can adjust Eq. 3.8 so that the incident optical field inherently takes the tilt angle into account by performing a rotational transformation about the \( y \)-axis. This way the laboratory coordinate system will accurately describe the optical field with respect to the sample orientation. Thus, Eq. 3.8 can be transformed as follows:

\[
\begin{pmatrix}
E_x^0 \\
E_y^0 \\
E_z^0
\end{pmatrix} = \begin{pmatrix}
\cos \theta & 0 & -\sin \theta \\
0 & 1 & 0 \\
\sin \theta & 0 & \cos \theta
\end{pmatrix}
\begin{pmatrix}
E_p^0 \\
E_s^0
\end{pmatrix}
\] (3.13)

Eq. 3.13 gives us:

\[
E(\omega) = E^0(\cos \theta \cos \varphi \hat{x} + \sin \varphi \hat{y} + \sin \theta \cos \varphi \hat{z})
\] (3.14)

Here, \( E^0 \) is the amplitude of the incident optical field, \( \varphi \) is the angle between the optical field axis and the \( xz \)-plane, and \( \theta \) is the angle between the incident light propagation vector (traveling along the \( xz \)-plane) and the surface normal of the sample. However, one final, important detail must be taken into account. The electric field propagating through air is not the same as the electric field propagating through the medium. We can take this into account by calculating the local optical field inside the medium, \( E^{loc}(\omega) = \hat{L}(\omega) \cdot E(\omega) \) where \( \hat{L}(\omega) = L_{xx}^{0} \hat{\imath} + L_{yy}^{0} \hat{j} + L_{zz}^{0} \hat{k} \) is a diagonal tensor composed of Fresnel transformation factors. These factors act as local-field correction factors for light propagating at frequency \( \omega \) through the material[96-99]. The Fresnel transformation factors can be expressed as follows:

\[
L_{xx}^{0} = \frac{2n_1(\Omega)\cos \theta'}{n_2(\Omega)\cos \theta + n_1(\Omega)\cos \theta'} \] (3.15a)

\[
L_{yy}^{0} = \frac{2n_1(\Omega)\cos \theta}{n_1(\Omega)\cos \theta + n_2(\Omega)\cos \theta'} \] (3.15b)
\[ L_{zz}^{\Omega} = \frac{2n_2(\Omega)\cos \theta}{n_2(\Omega)\cos \theta + n_1(\Omega)\cos \theta'} \left( \frac{n_1(\Omega)}{n_{SHG}(\Omega)} \right)^2 \]  (3.15c)

The above equations give the diagonal elements of the Fresnel transformation tensor, \( \hat{L}(\Omega) \).

\( n_{SHG}(\Omega) \) represents the refractive index of the probed SHG-active region at frequency \( \Omega \), \( n_1(\Omega) \) is the refractive index of the initial medium (can be air or another material layer) at frequency \( \Omega \), and \( n_2(\Omega) \) is the refractive index of the second layer, usually the medium being studied, at frequency \( \Omega \). Typically, an approximation is made that \( n_{SHG}(\Omega) \approx n_2(\Omega) \). \( \theta \) is the incident angle of the beam path with respect to the surface normal axis of the SHG active plane and \( \theta' \) is the refracted angle of the light within the nonlinear medium, e.g. \( n_1(\Omega)\sin \theta = n_2(\Omega)\sin \theta' \). In our experiments, \( \Omega = \omega \) for fundamental light and \( 2\omega \) for second harmonic light, however, it is most practical to perform refractive index calculations using optical wavelengths as previously mentioned.

### 3.4 Confocal Raman Spectroscopy

Confocal Raman spectroscopy is a nonlinear spectroscopic technique used for probing vibrational modes in materials. Incident laser light is directed onto the material and the scattered signal is composed of both quasi-elastic (\( \omega \approx \omega_{\text{laser}} \)) and inelastic (\( \omega = \omega_{\text{laser}} \pm \omega_{\text{vibration}} \)) photon scattering known as Rayleigh and Raman scattering, respectively. Raman scattering only occurs if the laser-induced collective vibrations alter the molecular polarizability of the probed material. The resulting Raman intensity peak positions depend on mechanical parameters such as bond length, bond strength, atomic masses, and molecular symmetry while the Raman intensities depend on electronic parameters such as ionocovalence, band structure, and charge defect concentrations[100].
Figure 3.13: Experimental configuration for confocal Raman spectroscopy in the reflection geometry. Laser light is focused onto the sample and Raman scattered light is directed into a spectrograph using focusing lenses.

The experimental setup for taking confocal Raman measurements is shown in Fig. 3.13. Raman spectra were collected in the reflection geometry at room temperature from electrodegraded Fe:STO anodic and cathodic bulk regions using a confocal Raman microscope (ARC-MCRS-Upright SP2750, Princeton Instruments-Acton). An Argon ion laser (43 Series Ion Laser, Melles Griot) was used for the excitation beam (488 nm, 2.54 eV) and focused with a 10× (N.A. = 0.3) objective. Signals were recorded with a liquid nitrogen-cooled CCD detector.

3.5 Photoluminescence Spectroscopy

Photoluminescence emissions measured via fluorescence spectroscopy can provide useful information about existing electronic energy levels within a crystalline solid. In the bulk of the crystal, translational symmetry allows electronic energy bands to form[101]. Impurities existing
in the crystal lattice, such as ionic or structural defects, can break symmetries and alter local electronic band structure by creating electronic defect states [64, 102, 103]. These defect states result in the stabilization of electronic energy levels within the bandgap and, depending on the nature of the defect, may act as electron donors or acceptors. At low temperatures, electronic carriers can become trapped at these defect states. If these trapped carriers undergo radiative recombination by absorbing light, then the energy of the emitted light during relaxation can be analyzed to determine the energy of the defect state.

**Figure 3.14:** Experimental configuration for photoluminescence spectroscopy in the front-face detection geometry. Light from the Xenon lamp is filtered by an excitation monochromator which allows single wavelengths of light to reach the sample. The sample emits fluorescence in response to the incoming radiation which is filtered by an emission monochromator that feeds the signal into a PMT coupled to a photon counter.
The experimental setup for photoluminescence measurements is shown in Fig. 3.14. Steady-state fluorescence spectra were obtained from the anode and cathode interfaces of Fe:STO single crystals using a fluorescence spectrometer (HORIBA Scientific, FluoroLog-3)[104]. A Xenon lamp (450 W) and monochromator were used for photoexcitation (325 nm, 3.8 eV) and a photon counter measured the fluorescence intensity as counts per second, *i.e.* photons/second. It is important to use an excitation energy larger than the band gap energy of the material (in this case $E_g \sim 3.0$ eV for Fe:STO) so that radiative recombination can take place over the entirety of the gap. Photoemissions were collected from 335 nm to 640 nm with monochromator bandwidths set to 2 nm. In order to investigate fluorescence spectra from the anode and cathode interfaces of undegraded Fe:STO samples, a voltage of 1.5 kV ($E_{dc} = 30$ kV/cm) was applied at least 1 hour before measurements at room temperature.
Chapter 4: Local Structural Changes due to the Electric Field-Induced Migration of Oxygen Vacancies at Fe-doped SrTiO$_3$ Interfaces

This chapter presents the investigation of $dc$ electric field-induced structural changes resulting from short-range oxygen vacancy migration at undegraded, reduced and oxidized Fe:STO interfaces. Section 4.1 presents and discusses electric field-induced second harmonic generation (EFISHG) measurements obtained from the Fe:STO interfaces. Section 4.2 presents and discusses photoluminescence spectra collected from the Fe:STO interfaces. Section 4.3 provides a discussion of charged defect accumulation and transport at the electrode interfaces in relation to the Schottky barrier heights and depletion region widths at each interface. Section 4.4 summarizes the results presented in this chapter.

4.1 $dc$ Electric Field-induced SHG from Fe:STO Interfaces

4.1.1 Experimental and Theoretical Description

A mode-locked Ti:Sapphire pulse laser (80 MHz, 10 nJ/pulse, 100 fs) was used as the fundamental light source with a central wavelength of 810 nm and a focused energy density of $\sim$1 mJ/cm$^2$. Fig. 4.1a shows the experimental set-up where fundamental and double-frequency (SHG) light propagation and polarization vectors are resolved into Cartesian coordinate axes with respect to the crystal’s surface plane. Fe:STO crystals were aligned with surface normal axes at $\theta = 45^\circ$ with respect to the incident light traveling along the $xz$-plane. A Glan polarizer and band pass filter (Thorlabs, FB400-40) were placed in front of a photomultiplier tube module (PMT) (Hamamatsu,
H9305-04) for the detection of \( p \)-polarized (parallel to \( xz \)-plane) and \( s \)-polarized (perpendicular to \( xz \)-axis) SHG intensities. \( P \)-polarized and \( s \)-polarized SHG intensities were measured as functions of the incident light polarization angle, \( \varphi \), under an imposed \( dc \) voltage. A high voltage generator (PS300, Stanford Research Systems) was used to pole the electrodes. The external electric field is directed along the \( z \)-axis according to the laboratory coordinate axes used which are shown in Fig. 4.1b.

![Image of experimental setup](image_url)

Fig. 4.1a
**Figure 4.1:** (a) Schematic for optical SHG in the reflection geometry. Focusing lenses are marked by L1, L2, and L3. A band-pass filter (BPF) is used to block fundamental light from entering the PMT. A long-pass filter (LPF) is placed before the sample to filter out residual SHG light from the laser system. A half-wave plate (\(\lambda/2\)) is used to rotate the polarization axis of the incident fundamental light. The insert shows the configuration with a dc-bias; (b) Schematic of the incident and outgoing light path and polarization for SHG measurements in the reflection geometry. (x, y, z) define the laboratory coordinates and [100], [010], and [001] define crystal axes. Incident and outgoing pulses travel along the xz-plane at an angle \(\theta_i\) with respect to the surface normal. \(\hat{\mathbf{e}}(\omega)\) and \(\hat{\mathbf{e}}(2\omega)\) are polarization unit vectors for incident and outgoing light. Here, p- and s-polarized optical fields travel parallel and perpendicular to the xz-plane, respectively.
The coherence length for SHG radiation propagating through Fe:STO in the reflection (+) and transmission (-) geometries is given by Eq. 3.10[82, 85]. As previously mentioned in chapter 3, this length represents the maximum distance SHG light can travel through the crystal before its intensity decreases due to destructive interference with itself. For incident light of wavelength 810 nm, the coherence length in the reflection geometry is about 40 nm. As a result, SHG intensities reflected from the Pt-Fe:STO interface arise primarily from electric-dipole contributions in the interfacial region, i.e. the Fe:STO surface[82].

The leading order contributions to the second-order polarization of the interfacial region can be expressed as[37, 85, 105]:

$$\mathbf{P}^{2\omega} \propto \chi^{(2)} E^\omega E^\omega + \chi^{(3)} E^\omega E^\omega E^0$$  

(4.1)

The first and second terms account for crystallographic and electrostatic field-induced dipole contributions, respectively. At room temperature, pristine Fe:STO exhibits cubic (Pm3m) symmetry in the bulk. Although the cubic bulk is largely centrosymmetric, inversion symmetry is inherently broken at the surface due to atomic displacements that lead to tetragonal (4mm) symmetry[106]. We can expand the \(i\)-th Cartesian coordinate of the second-order polarization in Eq. 4.1 as follows:

$$P_i(2\omega) = \epsilon_o \sum_{jk} \chi^{(2)}_{ijk}(2\omega; \omega, \omega) E_{j}^{loc}(\omega)E_{k}^{loc}(\omega)$$

$$+ \epsilon_o \sum_{jkl} \chi^{(3)}_{ijkl}(2\omega; \omega, \omega, 0)E_{j}^{loc}(\omega)E_{k}^{loc}(\omega)E_{l}^{loc}(0)$$  

(4.2)
The first term in the expression accounts for the electric-dipole contribution from the interfacial region, e.g. Fe:STO surface polarity[56, 57]. The second term accounts for the electrostatic field-induced dipole contribution which gives rise to the electric field-induced SHG (EFISHG) response [107-110]. Here, $E_{i}^{loc}(\omega) = \vec{L}(\omega) \cdot \vec{E}(\omega)$, where $\vec{L}(\omega) = L_{xx}^{\omega} \hat{t} \hat{t} + L_{yy}^{\omega} \hat{f} \hat{f} + L_{zz}^{\omega} \hat{k} \hat{k}$ is as discussed in Section 3.3. The $E_{i}^{loc}(0)$ term in Eq. 4.2 represents the $l$-th Cartesian coordinate of the $dc$-field within the interfacial region. We take $l = z$ for all calculations since the $dc$-field is applied along the $z$-axis, parallel to the surface normal axis of the crystal. The non-vanishing components of the second-order and third-order susceptibility tensors in Eq. 4.2 depend on the structural symmetry of the probed region, which is tetragonal (4mm) symmetry [39]. The third-order EFISHG terms can be reduced to an effective second-order term when taking $l = z$ and integrating over the interfacial region such that we obtain:

$$
\sum_{jk} \left( \int \chi_{ijkz}^{(3)}(2\omega; \omega, \omega, 0) E_{i}^{loc}(0) dz \right) E_{j}^{loc}(\omega) E_{k}^{loc}(\omega) = \sum_{jk} \chi_{ijk}^{(2)}(2\omega; \omega, \omega) (E_{i}^{loc}) E_{j}^{loc}(\omega) E_{k}^{loc}(\omega)
$$

The transformed second-order EFISHG susceptibility $\chi_{ijk}^{(2)}(2\omega; \omega, \omega)(E_{i}^{loc})$, has the same symmetry properties as $\chi_{ijk}^{(2)}(2\omega; \omega, \omega)$ for an imposed $dc$-field along the $z$-axis. For tetragonal (4mm) symmetry, the non-vanishing second-order susceptibility components are $\chi_{zzz}, \chi_{xxx} = \chi_{yzy}, \chi_{xxz} = \chi_{yyz}$, and $\chi_{xxx} = \chi_{zyy}$. Using Eq. 4.2 and Eq. 4.3 we can explicitly solve for the components of $P(2\omega)$:
\[ P_x(2\omega) = 2\varepsilon_0 \left( 2\chi^{(2)}_{xxz} E_x^{loc}(\omega) E_z^{loc}(\omega) \right) + 2\varepsilon_0 \left( 2\chi^{(2)}_{xxz}(E_z^{loc}E_x^{loc}\omega) E_z^{loc}(\omega) \right) \] (4.4a)

\[ P_y(2\omega) = 2\varepsilon_0 \left( 2\chi^{(2)}_{xzz}(E_x^{loc}(\omega) E_z^{loc}(\omega)) \right) + 2\varepsilon_0 \left( 2\chi^{(2)}_{xzz}(E_x^{loc}(\omega) E_z^{loc}(\omega)) \right) \] (4.4b)

\[ P_z(2\omega) = 2\varepsilon_0 \left( \chi^{(2)}_{zzz}(E_z^{loc}(\omega))^2 + \chi^{(2)}_{xzx}(E_x^{loc}(\omega))^2 + \chi^{(2)}_{zxx}(E_x^{loc}(\omega))^2 \right) \] (4.4c)

\[ + 2\varepsilon_0 \left( \chi^{(2)}_{xzx}(E_x^{loc}(\omega))^2 + \chi^{(2)}_{xzx}(E_y^{loc}(\omega))^2 + \chi^{(2)}_{zxx}(E_x^{loc}(\omega))^2 \right) \]

\[ + \chi^{(2)}_{zxx}(E_z^{loc}(\omega)^2) \]

From the second-order nonlinear polarization, an effective second-order susceptibility for the 4mm interfacial region can be extracted using the following expression [39, 57, 98, 99, 111]:

\[ \chi_{eff}^{(2)} = \langle \tilde{L}(2\omega) \cdot \hat{\varepsilon}(2\omega) \rangle \cdot \frac{P(2\omega)}{2\varepsilon_0 (E^2)} \] (4.5)

Here, \( \tilde{L}(2\omega) = L_{xx}^{2\omega} \hat{n} + L_{yy}^{2\omega} \hat{j} + L_{zz}^{2\omega} \hat{k} \) is a diagonal tensor consisting of Fresnel transformation factors for double-frequency, or SHG, light propagating through the interfacial region and \( \hat{\varepsilon}(2\omega) \) is the polarization directional vector for the SHG electric fields reflected from the interface as shown in Fig. 4.1b. The effective nonlinear susceptibility takes the following form:
\[
\chi_{\text{eff}}^{(2)} = -L_{xx}^{2} \cos \theta \cos \varphi' \left[ 2 \chi_{\text{eff}}^{2} L_{xx}^{2} L_{zz}^{2} \sin \theta \cos \theta \cos^{2} \varphi \right] + \\
L_{yy}^{2} \sin \theta \sin \varphi' \left[ \chi_{\text{eff}}^{2} L_{yy}^{2} L_{zz}^{2} \sin \theta \sin \varphi \right] + \\
L_{zz}^{2} \sin \theta \cos \varphi' \left[ \chi_{\text{eff}}^{2} (L_{zz}^{2})^{2} \cos^{2} \theta \cos^{2} \varphi + \chi_{\text{eff}}^{2} (L_{yy}^{2})^{2} \sin^{2} \varphi \right] + \\
\chi_{\text{eff}}^{2} (L_{zz}^{2})^{2} \sin^{2} \theta \cos^{2} \varphi \right]
\]

(4.6)

Where

\[
\chi_{\text{eff}}^{\text{xx}} = \chi_{\text{xx}} + \delta \chi_{\text{xx}}(E_{z}^{\text{loc}}) \\
\chi_{\text{eff}}^{\text{zz}} = \chi_{\text{zz}} + \delta \chi_{\text{zz}}(E_{z}^{\text{loc}}) \\
\chi_{\text{eff}}^{\text{zz}} = \chi_{\text{zz}} + \delta \chi_{\text{zz}}(E_{z}^{\text{loc}})
\]

The above three equations represent the effective second-order susceptibility components expressed as functions of the local electric-field in the interfacial region. The terms \(\delta \chi_{\text{xx}}(E_{z}^{\text{loc}})\), \(\delta \chi_{\text{zz}}(E_{z}^{\text{loc}})\), and \(\delta \chi_{\text{zz}}(E_{z}^{\text{loc}})\) are field-induced susceptibility changes within the probed interfacial region and describe electrostrictive distortions resulting from the applied dc electric field. For a typical ABO\(_{3}\) perovskite structure, these perturbative terms have been previously expressed as\([112-114]\):

\[
\delta \chi_{\text{zz}}(E_{z}^{\text{loc}}) \propto (\delta_{B} + \delta_{O(1)}) \tag{4.7a}
\]

\[
\delta \chi_{\text{zz}}(E_{z}^{\text{loc}}) \propto (\delta_{B} + \delta_{O(1)}) \tag{4.7b}
\]

In Eq. 4.7, \(\delta_{B}\) and \(\delta_{O}\) are dc-field induced displacements for the B-site Fe:Ti cations and O-site oxygen anions as discussed by Levine et al.\([112, 113]\). In this polarizable bond-charge model, \(\delta \chi_{\text{zz}}(E_{z}^{\text{loc}})\) is qualitatively interpreted as a stretching of the Fe:Ti-O bonds along the dc electric
field axis ($z$-axis), while $\delta \chi_{xxx}(E_z^{loc})$ corresponds to a bending of the crystallographic $a$- and $b$-axis Fe:Ti-O bonds out of the $xy$-plane as in-plane oxygen ions displace towards the anode. Under Kleinman’s symmetry considerations for a $4mm$ structure, $\delta \chi_{xxx}(E_z^{loc})$ and $\delta \chi_{xxz}(E_z^{loc})$, are expected to be approximately equal in the low voltage regime [114, 115].

The $p$-polarized and $s$-polarized SHG intensity functions, $I_p^{2\omega}(\varphi)$ and $I_s^{2\omega}(\varphi)$ are found using the relation, $I^{2\omega} \propto |\chi^{(2)}_{\text{eff}}|^2$, and selecting outgoing SHG electric field polarizations either parallel to the $xz$-plane ($p$-polarized, $\varphi' = 0^\circ$) or $y$-axis (s-polarized, $\varphi' = 90^\circ$) from Eq. 10:

$$I_p^{2\omega}(\varphi) = |\chi_{pp} \cos^2 \varphi + \chi_{sp} \sin^2 \varphi|^2$$

(4.8)

$$I_s^{2\omega}(\varphi) = |\chi_{ds} \sin(2\varphi)|^2$$

(4.9)

where

$$\chi_{sp} = \chi^{\text{eff}}_{xxx} L_{zz}^{2\omega} (L_{yy}^{\omega})^2 \sin \theta$$

$$\chi_{pp} = \chi^{\text{eff}}_{zzz} L_{zz}^{2\omega} (L_{zz}^{\omega})^2 \sin^3 \theta - 2 \chi^{\text{eff}}_{xxx} L_{xx}^{2\omega} L_{xx}^{\omega} L_{zz}^{\omega} \sin \theta \cos^2 \theta + \chi^{\text{eff}}_{xxx} L_{zz}^{2\omega} (L_{xx}^{\omega})^2 \sin \theta \cos^2 \theta$$

$$\chi_{ds} = \chi^{\text{eff}}_{xxx} L_{yy} L_{yy}^{\omega} L_{zz}^{\omega} \sin \theta$$

These effective susceptibility components correspond to polarization combinations between the incident and outgoing light. The effective component, $\chi_{sp}$, corresponds to $s$-polarized input and $p$-polarized output, $\chi_{pp}$ corresponds to $p$-polarized input and $p$-polarized output, and $\chi_{ds}$ corresponds to $d$-polarized ($\varphi = 45^\circ$) input and $s$-polarized output [81, 82].
4.1.2 EFISHG from Anode and Cathode Interfaces

*Figure 4.2:* Optical SHG measurements taken from the reduced Fe:STO crystal. (a) p-polarized and (b) s-polarized EFISHG intensities plotted as functions of the incident light polarization angle for positive dc voltages (anode interface). (c) p-polarized and (d) s-polarized EFISHG intensities plotted as functions of the incident light polarization angle for negative dc voltages (cathode interface).
Fig. 4.2 shows $p$-polarized and $s$-polarized SHG intensities measured from the reduced Fe:STO crystal under an imposed $dc$-bias. Solid lines show fits obtained using Eq. 4.8 and Eq. 4.9. Magnitudes have been normalized in Fig. 2 with respect to the 0 V signals. The $p$-polarized and $s$-polarized SHG intensities increase by factors of ~5.0 under forward $dc$-bias (0V to 600V). Under reverse $dc$-bias (0V to -600V), $p$-polarized and $s$-polarized SHG intensities increase by factors of ~29.0 and ~11.5, respectively. Both out-of-plane and in-plane field-induced symmetry breaking at the reduced Fe:STO interface are greater under reverse $dc$-bias. The fits for Fig. 4.2d are improved by including a $\varphi$-independent susceptibility term, i.e. $I_s^{2\omega}(\varphi) \sim |\chi_{ds} \sin(2\varphi) + \chi_o|^2$. The apparent difference in magnitude between $I_s(45^\circ)$ and $I_s(135^\circ)$ for Fig. 4.2d spectra grows as the imposed $dc$ voltage increases, making fits worse. This can be explained by a field-induced breaking of in-plane tetragonal ($4mm$) isotropy.

![Fig. 4.3a](image1)

![Fig. 4.3b](image2)
Figure 4.3: Optical SHG measurements taken from the oxidized Fe:STO crystal. (a) p-polarized and (b) s-polarized EFISHG intensities plotted as functions of the incident light polarization angle for positive dc voltages (anode interface). (c) p-polarized and (d) s-polarized EFISHG intensities plotted as functions of the incident light polarization angle for negative dc voltages (cathode interface).

In comparison, p-polarized and s-polarized SHG intensities were also measured from the oxidized Fe:STO crystal under an imposed dc-bias, as shown in Fig. 4.3. Solid lines indicate fits using Eq. 4.8 and Eq. 4.9. The p-polarized and s-polarized SHG intensities increase by factors of ~19.5 and ~14.5, respectively, under forward dc-bias (0V to 1200V). Under reverse dc-bias (0V to -1800V), p-polarized and s-polarized SHG intensities increase by factors of ~2.5. This shows both out-of-plane and in-plane field-induced symmetry breaking under forward dc-bias at the oxidized Fe:STO interface.
**Figure 4.4:** EFISHG intensities and susceptibilities as functions of the imposed voltage. EFISHG intensities plotted as functions of the imposed dc voltage for the (a) reduced Fe:STO and (b) oxidized Fe:STO single crystals. Effective susceptibilities plotted as functions of the imposed dc voltage for the (c) reduced Fe:STO and (d) oxidized Fe:STO single crystals. Arrows point to parabolic minima. EFISHG intensities above 1200V in Fig. 5b were predicted from fitting.

Fig. 4.4a and Fig. 4.4b show EFISHG intensities as functions of the imposed *dc* voltage for the reduced and oxidized Fe:STO crystals. We extract the effective susceptibility components for
tetragonal ($4mm$) symmetry and plot them as functions of the imposed dc voltage, as shown in Fig. 5c and Fig. 5d. Changes to the effective susceptibility components are attributed to electric field-induced ionic displacements within local Fe:Ti-O$_6$ octahedra[66]. In response to the dc-bias applied along the $z$-axis (perpendicular to the electrode plane), O$^{2-}$ anions displace toward the anode while Sr$^{2+}$ cations, (Fe$^{3+}$/Fe$^{4+}$)/Ti$^{4+}$ cations, and oxygen vacancies displace away. The perovskite lattice becomes polarized from these relative displacements[116] and electrostrictive distortions form, as shown in Fig. 4.5.

![Fig. 4.5a](image-url)
Fig. 4.5: Illustration of electric field-induced ionic displacements in Fe:STO at the (a) anode interface (positive terminal) and (b) cathode interface (negative terminal).

Fig. 4.4a and Fig. 4.5b support that out-of-plane pp-EFISHG intensities are dominative as a result of electric field-induced ionic displacements along the applied field axis. Fits were obtained separately for reverse and forward dc-bias measurements to accommodate asymmetric voltage-dependencies. The general form of the fitting equation used is $I_j^{2\alpha} \sim a_0 + a_1V + a_2V^2 + a_4V^4$. The fourth-order term becomes negligible in some cases, such as for pp-EFISHG intensities from the reduced anode. The appearance of a fourth-order term for pp-EFISHG intensities is a strong indicator that electrostrictive distortions are taking place at the metal-dielectric interface since electrostriction is a quadratic effect [38, 67-69]. Thus, explaining quadratic effective susceptibility fits observed in response to the applied field.

Fig. 4.4c shows the effective susceptibility components from the reduced Fe:STO interface as functions of imposed dc voltage. Much smaller changes for $\chi_{xxz}^{\text{eff}}$ and $\chi_{xxx}^{\text{eff}}$ are observed since ionic
displacements occur along the applied field axis, i.e. tetragonal c-axis. A quadratic dependence on
the imposed dc voltage is revealed under reverse dc-bias for $\chi_{zzz}^{\text{eff}}$. The magnitude of $\chi_{zzz}^{\text{eff}}$ first
decreases to a minimum near -77V, before increasing. Large enhancements to $\chi_{zzz}^{\text{eff}}$ demonstrate
significant Fe:Ti-O bond stretching along the dc-field axis. In contrast, a linear dependence on the
imposed dc voltage is observed under forward dc-bias for $\chi_{zzz}^{\text{eff}}$, signifying steady Fe:Ti-O bond
stretching along the dc-field axis.

For comparison, effective susceptibility components as functions of the imposed dc voltage
for the oxidized Fe:STO interface are shown in Fig. 4.4d. A quadratic dependence on the dc voltage
is revealed under reverse dc-bias for $\chi_{zzz}^{\text{eff}}$, with a minimum point taking place near -454V. Small
changes to the effective susceptibility components correspond to weak structural changes
occurring under reverse dc-bias. Under forward dc-bias, a quadratic dependence on the dc voltage
is observed for $\chi_{zzz}^{\text{eff}}$ (0V to 800V) with a minimum appearing near 331V. The EFISHG intensities
and effective susceptibilities increase sharply above 800V, still following a quadratic trend. The
strong enhancements to $\chi_{zzz}^{\text{eff}}$ show significant Fe:Ti-O bond stretching along the dc-field axis.

### 4.2 Photoluminescence from Fe:STO Interfaces

For the case of undoped STO, most optical transitions across the conduction and valence bands
occur by occupied electronic orbitals within the Ti-O$_6$ octahedron, e.g. Ti(3d) – O(2p)
transitions[99]. The accepted value for this bandgap is around 3.2 – 3.4 eV [117-119]. Fe-doping
of STO leads to a narrowing of the bandgap due to the acceptor behavior of Fe and a higher
occupation of d-orbitals, i.e. Fe(3d) occupancy [117]. Three primary photoemission peaks are
expected to arise during radiative recombination from the Fe:STO crystal surface for emission
wavelengths between 335 nm to 640 nm. The first is the bandgap energy (~2.9 – 3.0 eV), the second is an oxygen vacancy donor state (~2.8 – 2.9 eV), and the third is a shallow acceptor state (~2.8 – 2.9 eV), as shown in Fig. 2[102, 120]. Due to their very similar emission energies, the oxygen vacancy donor and shallow acceptor state emissions cannot be fully separated within fluorescence spectra and must be carefully analyzed according to the characteristics of the interface being probed.

**Figure 4.6:** Observed bandgap and in-gap optical transitions from undoped and Fe-doped STO crystals. Bandgap transitions result in photoemission as electrons relax from the conduction band to the valence band. In-gap donor transitions result in photoemission as electrons transition from in-gap oxygen vacancy defect states to the valance band. In-gap acceptor transitions result in photoemission as electrons relax from the conduction band to shallow, in-gap defect states.

To further understand differences between the reduced and oxidized Fe:STO interfaces under forward and reverse dc-bias, steady-state fluorescence spectra were collected at room temperature. Fig. 4.7 shows the broad fluorescence spectra from the Fe:STO single crystals.
**Figure 4.7:** Fluorescence emission spectra for the (a) reduced and (b) oxidized Fe:STO interfaces. Black curves show fits for the 0 V spectra while red and blue curves show fits for the cathode and anode spectra, respectively. Photoemission energies for the two Gaussian peaks contributing to each spectrum appear on the right side of each plot.

The black curves in Fig. 4.7a and Fig. 4.7b represent emission spectra for the reduced and oxidized Fe:STO crystals without dc-field. Bandgap energies for the reduced and oxidized Fe:STO interfaces were measured to be roughly 2.94 eV at room temperature. Despite their similar emission energies, oxygen vacancy donor states are expected to dominate in the reduced crystal while shallow acceptor states are expected to dominate in the oxidized crystal.

For the reduced and oxidized Fe:STO emission spectra, both anode interfaces show enhanced fluorescence intensities. This is attributed to two causes: (1) Increased radiative recombination between the conduction and valence bands, i.e. Ti(3d) – O(2p) transitions, due to the filling of O(2p) orbital sites as a result of local oxygen accumulation, and (2) Increased density of excited holes which increases radiative recombination between conduction electrons and
shallow in-gap acceptor levels[101, 120]. In contrast, changes for the cathode emissions differ significantly between the oxidized and reduced Fe:STO crystals. Fluorescence intensities decrease for the reduced Fe:STO cathode, while intensities increase for the oxidized Fe:STO cathode. The decrease in fluorescence for the reduced Fe:STO cathode can be attributed to the depopulation of O(2p) sites due to the increased local oxygen vacancy concentration. The increase of oxygen vacancies is accompanied by an increase in conduction electrons to conserve charge neutrality. For the oxidized Fe:STO cathode, the increase in fluorescence is attributed to an increase in emissions from oxygen vacancy donor levels.

Both EFISHG and photoluminescence measurements reveal that the reduced and oxidized Fe:STO cathode interfaces behave differently due to their respective oxygen vacancy concentrations. An excess of oxygen vacancies at the reduced cathode leads to significant structural distortions as oxygen vacancy clustering leads to a depletion of O(2p) sites across the valence band, driving the local lattice away from tetragonal (4mm) symmetry. In contrast, moderate increases in the oxygen vacancy concentration at the oxidized cathode don’t cause any structural symmetry changes due to higher oxygen concentrations. Instead, the fluorescence intensity enhances simply due to increased oxygen vacancy donor states.

4.3 Schottky Junctions at Pt-Fe:STO Interfaces

In order to fully understand the EFISHG responses from the reduced and oxidized Fe:STO interfaces, we look at the charged defect properties of each interface. Due to differing work functions between the Pt electrode ($\Phi_{Pt} \sim 5.65 – 6.35 \text{ eV}$)[121, 122] and Fe:STO ($\Phi_{Ti} \sim 4.3 \text{ eV}$, $\Phi_{Fe} \sim 4.5 \text{ eV}$)[121, 122], these interfaces form Schottky junctions, as shown in Fig. 4.8[75, 123].
Schottky energy barriers are generated at the interfaces which govern electronic carrier exchange across the interface during *dc* voltage application. In addition, depletion regions form between the electrode and Fe:STO bulk due to charge defect accumulation at the junction. As a result, built-in electric fields form within the depletion regions and oppose electronic and ionic carrier migrations until the external field becomes strong enough to quench them. These built-in fields can be observed in Fig. 4.4c and Fig. 4.4d, when the external field cancels out the internal field and $\chi_{zzz}^{eff}$ reaches a minimum. For reduced Fe:STO, the built-in field at the cathode is quenched by an external field of $\sim 1.5$ kV/cm, although no built-in field is observed at the anode. For oxidized Fe:STO, the built-in fields at the cathode and anode are quenched at $\sim 9.1$ kV/cm and $\sim 6.6$ kV/cm, respectively. Weaker built-in fields in reduced Fe:STO allow stronger structural changes to occur at lower *dc* voltages compared to the oxidized Fe:STO crystal since they are easier to quench.

![Fig. 4.8a](image1)

![Fig. 4.8b](image2)

**Figure 4.8:** Energy band profiles at the (a) oxidized anode ($V_{app} > 0$) interface and the (b) reduced anode ($V_{app} > 0$) interface. Here, $E_F$ is the Fermi energy, $\Phi_B$ is the Schottky energy barrier, $E_g$ is the band gap energy, and $E_{BI}$ is the built-in electric field generated inside the...
interfacial region. The height of Schottky energy barrier is smaller in reduced Fe:STO compared to oxidized Fe:STO, resulting in a thinner depletion region.

Under forward $dc$-bias, oxygen ions migrate towards the anode interface since the electrode is positively poled. For reduced Fe:STO, no built-in electric field was observed at the anode interface and may be explained by a very thin depletion region[123, 124]. Reduction annealing of Fe:STO results in higher oxygen vacancy concentrations. Since oxygen vacancies behave as donors, a decrease of the Schottky barrier height and depletion region width is expected in the reduced crystal compared to the oxidized one[123, 125, 126]. This promotes charge migration across the depletion region at lower $dc$ voltages. In comparison, the built-in electric field at the oxidized Fe:STO anode is stronger. Oxidation annealing of Fe:STO results in lower oxygen vacancy and free carrier concentrations, thus increasing the Schottky barrier height and width of the depletion region [123, 127]. Trapped charges within the depletion region result in the formation of a much stronger built-in electric field at the oxidized Fe:STO interface compared to the reduced Fe:STO interface. Below 800V, no significant electrostrictive distortions are observed since the built-in field acts as a barrier, opposing oxygen vacancy migration. Above 800V, the external electric field quenches the built-in field, resulting in a migration of trapped oxygen vacancies that leads to strong, electrostrictive distortions[66, 72]. In particular, Fig. 5b and Fig. 5d exhibit strong Schottky-like behavior, i.e. low straining under reverse $dc$-bias and strong straining under forward $dc$-bias.

Under reverse $dc$-bias, oxygen vacancies migrate towards the cathode interface due to the electrode being negatively poled. In contrast with the reduced Fe:STO anode, a weak built-in field is seen at the cathode. This built-in field is easily quenched under low $dc$ voltage which allows for
significant charge migration to occur. However, structural changes at the reduced Fe:STO cathode differ from those occurring at the anode interface since the cathode interface acts as a sink for local oxygen vacancies. Strong structural distortions are thus explained by a $dc$ electrical stress-induced straining of oxygen vacancy defect complexes (see Fig. 4.9) that become trapped at the Fe:STO surface due to the electrode’s blocking effect[15, 16].

Figure 4.9: Illustration of electric field-induced strain on an oxygen vacancy defect complex. Oxygen ions displace towards the anode while oxygen vacancies displace towards the cathode. This effect is strongest at the reduced Fe:STO cathode interface where local oxygen vacancy concentrations are highest.

The straining of oxygen vacancies at the reduced Fe:STO cathode leads to strong EFISHG intensity and effective susceptibility enhancements. The accumulation of oxygen vacancies at the reduced Fe:STO cathode also leads to an observable breaking of in-plane tetragonal (4mm) isotropy as shown in Fig. 4.2d. Deviations from tetragonal (4mm) symmetry resulting from oxygen vacancy clustering in electrodegraded Fe:STO were also recently observed [128]. For oxidized Fe:STO, a strong built-in field can be observed in the depletion region of the cathode. However, very weak structural changes are observed at the oxidized Fe:STO cathode compared to the
reduced one. Since oxidation leads to lower oxygen vacancy concentrations, vacancy accumulation at this interface is considerably small and no straining of oxygen vacancies is observed.

4.4 Summary

In summary, electrostrictive distortions were detected at the reduced and oxidized Fe:STO interfaces by measuring electric field-induced SHG intensity changes. The asymmetric voltage-dependence of EFISHG intensities and effective susceptibilities is explained by the Schottky behavior of the Pt-Fe:STO interfaces. Evidence shows that high oxygen vacancy concentrations decrease Schottky barrier heights and depletion region widths, facilitating ionic and electronic carrier transport near the interface. For reduced Fe:STO, structural changes at the anode are explained by steady electrostrictive distortions of Fe:Ti-O$_6$ octahedra as oxygen vacancies migrate towards the cathode. Changes at the reduced Fe:STO cathode are explained by a dc electric field-induced straining of oxygen vacancies trapped at the cathode surface due to the electrode’s blocking effect. For oxidized Fe:STO, structural changes are due to strong electrostrictive distortions as vacancies migrate to the cathode after the large built-in field in the depletion region is quenched. In contrast to reduced Fe:STO, structural changes at the oxidized Fe:STO cathode are very weak due to low oxygen vacancy concentrations.

Both EFISHG and photoluminescence measurements revealed different behaviors for the cathodes of the reduced and oxidized Fe:STO single crystals. The clustering of oxygen vacancies at the reduced cathode leads to a depopulation of O(2p) orbitals and a breaking of in-plane tetragonal (4mm) isotropies. In contrast, no significant structural deviations from tetragonal (4mm) symmetry are observed at the oxidized Fe:STO cathode due to its lower oxygen vacancy
concentration. Overall, the results show that optical SHG and photoluminescence are excellent techniques for studying $dc$ electric field-induced structural changes at electrode interfaces. We show that oxygen vacancy concentration and diffusion play a critical role in the formation of structural distortions at interfacial depletion regions.
Chapter 5: Formation of Structural Defects and Strain in Electrodegraded Fe-doped SrTiO$_3$ Single Crystals due to Oxygen Vacancy Migration

This chapter presents the investigation of structural defect and strain formation resulting from long-range oxygen vacancy migration in electrodegraded, reduced and oxidized Fe:STO single crystals. Section 5.1 presents and discusses optical second harmonic generation (SHG) measurements taken from the electrodegraded Fe:STO interfaces and bulk regions. Section 5.2 presents and discusses confocal Raman spectra collected from the electrodegraded Fe:STO bulk regions. Section 5.3 provides a contextualized discussion of the oxygen vacancy migration-induced structural changes presented in Sections 5.1 and 5.2. Section 5.4 summarizes the results presented in this chapter.

5.1 Optical SHG from Electrodegraded Fe:STO Single Crystals

5.1.1 Experimental and Theoretical Description

Verneuil-grown, 10 x 10 x 0.5 mm$^3$, (100) SrTiO$_3$ single crystals doped with 0.01 wt% Fe were cut into four, 5 x 5 x 0.5 mm$^3$, pieces and epi-polished on both sides (MTI, Richmond, CA). Crystals were annealed in a tube furnace at a temperature of 900 °C under a $p$O$_2 = 2 	imes 10^{-5}$ bar and a $p$O$_2 = 0.2$ bar, respectively. Afterwards, reduced crystals (B042, B057) were quenched in argon ($p$O$_2 = 2 	imes 10^{-5}$ bar) whereas oxidized crystals (B045, B056) were quenched in air ($p$O$_2 = 0.2$ bar) at 25 °C to freeze-in defect concentrations. As a result of these annealing and quenching procedures,
B042 and B057 have larger Fe$^{3+}$ and $V_0^-$ concentrations while B045 and B056 have larger Fe$^{4+}$ concentrations, as shown in Table 3.1 [10, 51].

For B042 and B045, 10 nm planar, amorphous platinum electrodes were deposited on the polished sample surfaces for longitudinal $dc$ field application. These samples were placed in a temperature bath of 210 °C under an applied $dc$ voltage of 40V ($E_{dc} = 0.8$ kV/cm for ~2.8 hours) to induce oxygen ion and vacancy migrations towards the anode and cathode interfaces, respectively[48]. For B056 and B057, 100 nm lateral, amorphous platinum electrodes were deposited on the sample edges for transverse $dc$ field application. These samples were placed in a temperature bath of 210°C under an applied $dc$ voltage of 100V ($E_{dc} = 0.2$ kV/cm for ~27.8 hours) to induce oxygen ion and vacancy migration. Fig. 5.1 shows the Fe:STO single crystals after the electrodegradation process.

**Figure 5.1:** The top row of images shows the (a) schematic for $dc$ voltage application across the Fe:STO samples with planar electrodes and photographs of the electrodegraded (b) oxidized and (c) reduced Fe:STO crystals with planar electrodes. Probed areas are labeled as the central, inner, and outer regions (roughly 1 mm apart). The bottom row of images shows a (d) schematic for $dc$
voltage application across the Fe:STO samples with lateral electrodes and photographs of the
electrodegraded (e) oxidized and (f) reduced Fe:STO crystals with lateral electrodes. The anodic,
mixed, and cathodic regions are labeled under each sample. The red dashed lines in (e) and (f)
mark probed paths between electrodes.

Fig. 5.1a shows the setup for dc voltage application on Fe:STO crystals with planar electrodes
deposited on their 5 x 5 mm² faces. Fig. 5.1b and Fig. 5.1c show B042 and B045 after the
electrodegradation process, i.e. after the onset of voltage-induced resistance degradation and
oxygen vacancy demixing. Inhomogeneous electrocoloration is clearly observable in the
B042/B045 crystals where darker regions absorb more visible light due to higher Fe⁴⁺ and oxygen
concentrations[20, 48]. Three regions of the electrodegraded interfaces in Fig. 5.1b and Fig. 5.1c
were probed, namely, the central, inner, and outer regions. These regions are named by their
relative distances from the center of the square interfacial plane. A distance of approximately 1
mm lies between the central and inner regions and the inner and outer regions. For comparison,
Fig. 1d shows the setup for dc voltage application on Fe:STO crystals with lateral electrodes grown
on their 5 x 0.5 mm² sides. Fig. 5.1e and Fig. 5.1f show B056 and B057 after the electrodegradation
process. A more homogenized electrocoloration is observable across the B056/B057 crystals as
well as the formation of an electrocoloration boundary, or color front, between the anodic and
cathodic bulk regions. As shown in Fig. 3.3, an increase in current density by roughly two orders
of magnitude is observed in all crystals as a result of resistance degradation[4, 7].

For samples B042 and B045, optical SHG measurements were taken in the reflection
geometry in order to probe the nonlinear response of the degraded electrode interfaces. For samples
B056 and B057, optical SHG measurements were collected in the transmission geometry in order
to probe the nonlinear response of the degraded crystal bulks. A mode-locked Ti:Sapphire pulse laser (80 MHz, 10 nJ/pulse, 100 fs) was used as the fundamental light source (810 nm, ~1 mJ/cm²) in both detection geometries, with an estimated beam spot diameter of ~10 µm.

\[ \hat{e}_r(\omega) = (\cos \varphi \cos \theta, \sin \varphi, \cos \varphi \sin \theta) \]

\[ \hat{e}_r(2\omega) = (-\cos \varphi' \cos \theta, \sin \varphi', \cos \varphi' \sin \theta) \]

**Figure 5.2:** Schematic for the incident (red), reflected (top blue), and transmitted (bottom blue) light paths and polarization vectors for SHG measurements. (x, y, z) define the laboratory coordinates whereas [100], [010], and [001] represent crystal orientation. Optical pulses travel along the xz-plane and \( \mathcal{E}_r(\omega) \) and \( \mathcal{E}_r(2\omega) \) are the polarization directional unit vectors of the incident fundamental light and the outgoing SHG light in the reflection geometry, while \( \mathcal{E}_t(\omega) \) and \( \mathcal{E}_t(2\omega) \) are for the transmission geometry. The p-polarized optical fields oscillate parallel to the xz-plane and s-polarized optical fields oscillate parallel to the y-axis.

As shown in Fig. 5.2, Fe:STO crystals were aligned with their surface normal axes at \( \theta = 45^\circ \) with respect to the incident pump pulses traveling along the xz-plane. A Glan Polarizer and band
pass filter (Thorlabs, FB400-40) were placed in front of a photomultiplier tube module (Hamamatsu, H9305-04) connected to a lock-in amplifier for collecting \( p \)-polarized or \( s \)-polarized SHG intensities as functions of the incident light polarization angle. The incident polarization angle was rotated using a half-wavelength plate. For B042/B045, reflected SHG signals were collected from three spots across the outer, inner, and central regions[128, 129]. For B056/B057, transmitted SHG signals were measured across a \(~4.5\) mm path between the platinum electrodes, covering the anodic, mixed, and cathodic bulk regions[130]. All SHG signals were detected at room temperature, after completion of the electrodegradation process.

The SHG intensities, \( I_{p-out}^{2\omega}(\varphi) \) and \( I_{s-out}^{2\omega}(\varphi) \), can be expressed as functions of the polarization angle \( \varphi \) of the incident pump pulses. Following the relation that \( I^{2\omega} \propto |\chi_{eff}^{(2)}|^2 \) and selecting for outgoing SHG electric field polarizations parallel to the \( y \)-axis (\( s \)-polarized, \( \varphi = 90^\circ \)) or \( xz \)-plane (\( p \)-polarized, \( \varphi = 0^\circ \)), the \( p \)-polarized and \( s \)-polarized SHG intensities are as follows [97, 98, 110]:

\[
I_{p-out}^{2\omega}(\varphi) = |\chi_{pp} \cos^2 \varphi + \chi_{sp} \sin^2 \varphi|^2 \tag{5.1}
\]

\[
I_{s-out}^{2\omega}(\varphi) = |\chi_{ds} \sin(2\varphi)|^2 \tag{5.2}
\]

where,

\[
\chi_{sp} = \chi_{zzz} I_{zzz}^{2\omega} (L_{yy}^{\omega})^2 \sin \theta
\]

\[
\chi_{pp} = \chi_{zzz} I_{zzz}^{2\omega} (L_{zz}^{\omega})^2 \sin^3 \theta + 2 \chi_{xxz} I_{xx}^{2\omega} I_{zz}^{\omega} \cos^2 \theta + \chi_{xxz} I_{zz}^{2\omega} (L_{xx}^{\omega})^2 \sin \theta \cos^2 \theta
\]

\[
\chi_{ds} = \chi_{xxz} L_{yy}^{\omega} L_{zzz}^{\omega} \sin \theta.
\]
The effective susceptibility component $\chi_{sp}$ corresponds to $s$-polarized input and $p$-polarized output, $\chi_{pp}$ corresponds to $p$-polarized input and $p$-polarized output, and $\chi_{ds}$ corresponds to $d$-polarized input ($\phi = 45^\circ$) and $s$-polarized output. $L^\omega$ and $L^{2\omega}$ represent the Fresnel transformation factors for the fundamental and SHG light at frequencies $\omega$ and $2\omega$, respectively [97, 98]. In the expression for $\chi_{pp}$, we take (-) in the reflection geometry and (+) in the transmission geometry for the second term. Utilizing a polarizable bond-charge model for a 4$mm$ ABO$_3$ structure, susceptibility components $\chi_{zzz}$, $\chi_{xxx}$, and $\chi_{xxx}$ can be interpreted physically as Fe:Ti-O bond “stretching” and “bending” contributions to the SHG response [112-114, 131]. Out-of-plane stretching and compressing of Fe:Ti-O bonds along the crystallographic $c$-axis influences the magnitude of $\chi_{zzz}$ while in-plane stretching and compressing of Fe:Ti-O bonds in the crystallographic $ab$-plane influences the magnitude of $\chi_{xxz}$. Out-of-plane bending of crystallographic $a$- and $b$-axis Fe:Ti-O bonds contributes to the magnitude of $\chi_{zzx}$. 
5.1.2 SHG from Electrodegraded Interfaces

Fig. 5.3a

Fig. 5.3b
**Figure 5.3:** (a) Shows p- and s-polarized SHG intensity profiles as functions of the incident polarization angle from the degraded anodes of B042 and B045. (b) Shows p- and s-polarized SHG intensity profiles as functions of the incident polarization angle from the degraded cathodes of B042 and B045. Solid lines show fits from Eq. 5.1, 5.2, and 5.3.

<table>
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<tr>
<th>Sample / Region</th>
<th>Outer Region (a.u.)</th>
<th>Inner Region (a.u.)</th>
<th>Central Region (a.u.)</th>
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<td></td>
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<td>( \chi_{zxx} = 0.066 )</td>
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<td>( \chi_{yyy} = 0.038 )</td>
<td>( \chi_{yyy} = 0.035 )</td>
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**Table 5.1:** Extrapolated nonlinear susceptibility components from SHG intensity fittings for the electrodegraded Fe:STO anode and cathode interfaces.

**Anode Interfaces:**

Fig. 5.3a[128] shows SHG spectra collected from the electrically degraded anodes of B042 and B045. Extrapolated values for the tetragonal susceptibility components, \( \chi_{zzz} \), \( \chi_{xxz} \), and \( \chi_{zxx} \),
are also shown in Table 5.1[128, 129]. The first row of polar plots in Fig. 5.3 shows the $p$-polarized and $s$-polarized SHG intensity profiles from the degraded anode of B042 where solid lines represent the fits obtained from Eq. 5.1 and Eq. 5.2. Total SHG intensities are shown to decrease as the beam spot is moved from the outer region to the central region, indicating more broken symmetry in the outer regions of the interface where more Fe$^{3+}$:Ti$^{4+}$-O$_6$ octahedra have formed due to lower local oxygen concentrations. The susceptibility components, $\chi_{zzz}$ and $\chi_{xxx}$ are ~ 2.8 and ~1.4 times greater in the outer region than in the central region (Table 5.1), revealing stronger $c$-axis stretching and $ab$-bond bending in the outer region. Structural distortions decrease towards the oxygen-sufficient central region where more oxygen vacancy sites have been filled to form Fe$^{4+}$:Ti$^{4+}$-O$_6$ octahedra. For comparison, SHG spectra measured from the degraded anode of B045 are shown in the second row of polar plots in Fig. 5.3. In comparison to anode of B042, the opposite trend is observed for B045 where total SHG intensities increase from the outer region towards the central region[128, 129]. The susceptibility components, $\chi_{zzz}$ and $\chi_{xxx}$ are ~5.1, and ~7.4 times greater in the central region than in the outer region (Table 5.1), revealing greater $c$-axis stretching and $ab$-bond bending in the central region. Since B045 has a lower oxygen vacancy concentration than B042, a greater concentration of fully coordinated oxygen octahedra can be expected, i.e. Fe$^{4+}$:Ti$^{4+}$-O$_6$. We attribute the enhanced SHG intensities of B045’s oxygen-rich central region to a strong structural symmetry reduction of Fe$^{4+}$:Ti$^{4+}$-O$_6$ octahedra, in the form of Jahn-Teller distortions. Oxygen aggregation at the anode oxidizes the local lattice and leads to an increase in Fe$^{4+}$ sites. In order to prevent, or lift, $d$-orbital degeneracies, local Fe$^{4+}$ centers must undergo a geometric deformation in which $c$-axis oxygen bonds elongate while $ab$-planar oxygen bonds constrict, as shown in Fig. 2.4c[59]. These distortions can also occur at the anode of B042, but are less energetically favorable due to the larger concentration of Fe$^{3+}$ centers.
Cathode Interfaces:

Fig. 5.3b[128] shows SHG spectra taken from the electrically degraded cathodes of B042 and B045. The first row in Fig. 5.3b shows the $p$-polarized and $s$-polarized SHG intensity profiles from the degraded cathode of B042 where solid lines for the outer region spectra represent fits obtained from Eq. 5.1 and Eq. 5.2. The $p$-polarized SHG intensities are shown to decrease from the outer region to the central region, however, the $s$-polarized SHG intensity increases. A transition from four-fold to two-fold symmetry for the in-plane SHG response is also revealed, as shown in Fig. 5.3b. Similar trends can be observed in the SHG spectra from the degraded cathode of B045, as shown in the second row of Fig. 5.3b. SHG intensity maxima, $I_p(0^\circ)$ and $I_s(45^\circ)$, decrease from the outer region towards the central region, while $I_s(90^\circ)$ increases. The nonlinear response ultimately deviates from 4mm symmetry, similar to the cathode of B042. SHG intensity fits for the inner and central cathode regions in Fig. 5.3b are obtained by including an incoherent SHG radiation contribution from the susceptibility component, $\chi_{yyy}$, as follows:

$$I_{s-out}^{2\omega}(\phi) = |\chi_{ds} \sin(2\phi)|^2 + |\chi_{ss} \sin^2 \phi|^2$$

(5.3)

In Eq. 5.3, $\chi_{ss} = \chi_{yyy} I_{yy}^{2\omega} (I_{yy}^\omega)^2$. This term can be attributed to a surface reconstruction from the formation of oxygen vacancy clusters near the oxygen-deficient central region. Strong contributions from the $\chi_{yyy}$ symmetry component may arise from oxygen vacancy-induced monoclinic distortions in oxygen-deficient areas across the cathode surface. Structural symmetry transitions aren’t detected in the outer regions of the cathode since oxygen vacancy clustering is not as prominent there[20, 128].
5.1.3 SHG from Electrocolored Bulks

Figure 5.4: (a) pp-, sp-, and ds-SHG intensities as functions of distance from the anode interface of the oxidized (B056) crystal. The dashed black line marks the coloration front. The solid lines are trend lines, not fits. (b) pp-, sp-, and ds-SHG intensities as functions of distance from the anode interface of the reduced (B057) crystal. The dashed black lines mark the color front positions. Error bars are represented by the black markers over each data point.

Figure 5.5: (a) Ratios between the nonlinear susceptibility components, $|\chi_{xxx}/\chi_{zzz}|$, $|\chi_{xxz}/\chi_{xxx}|$, and $|\chi_{xxx}/\chi_{zzz}|$ as functions of position between the anode and cathode of the oxidized (B056)
crystal. The solid lines are trend lines, not fits. (b) Ratios between the nonlinear susceptibility components, $|\chi_{xxx}/\chi_{zzz}|$, $|\chi_{xxz}/\chi_{zzz}|$, and $|\chi_{xxz}/\chi_{zzz}|$ as functions of position between the anode and cathode of the reduced (B057) crystal.

To further understand structural changes resulting from voltage-induced oxygen vacancy migration in Fe:STO, optical SHG was also collected from electrocolored bulk phases of the B056 and B057 Fe:STO single crystals[130], as shown in Fig. 5.4. Fig. 5.4a shows the $pp$-, $sp$-, and $ds$-SHG intensities plotted as functions of distance from the anode interface for B056, where the vertical dashed line marks the coloration front position. In the anodic region, all three SHG intensities increase gradually as the detection site moves towards the mixed region. The $pp$-SHG intensity is larger than both $sp$- and $ds$-SHG intensities, with $sp$-SHG being greater than $ds$-SHG in the anodic region. In the mixed region, the highest SHG intensities are observed with maxima positioned on the coloration front. Past the coloration front, the SHG intensities decrease into the cathodic region. For the cathodic region, $ds$-SHG increases over $sp$-SHG, opposite of what is observed for the anodic region. The spatial distribution of SHG intensity provides a good estimate for the structural strain distribution across the electrocolored crystal. Strain increases from the anode towards the mixed region, and then decreases towards the cathode. The coloration front in the mixed region marks an electrochemical interface between the anodic ($p$-type, dark brown) and cathodic ($n$-type, light brown) bulk regions of the crystal. At this coloration front, a strain field has formed due to dipole moments aligned between Fe$^{4+}$·Ti$^{4+}$·O$_6$ and Fe$^{3+}$·Ti$^{4+}$·O$_6$ octahedra packed along the front [85, 97].

Fig. 5.4b shows the $pp$-, $sp$-, and $ds$-SHG intensities plotted as functions of distance from the anode interface for B056, where the vertical dashed line marks the coloration front position. In the
anodic region, SHG intensities decrease slightly into the anodic region before increasing towards the mixed region. Similar to the SHG measurements from B056, the pp-SHG intensity is larger than both sp- and ds-SHG intensities, with sp-SHG being greater than ds-SHG in the anodic region. In the mixed region, strong SHG intensities are observed on the coloration front before decreasing into the cathodic region. Again, we observe that ds-SHG increases over sp-SHG in the cathodic region. Relating SHG intensity to the degree of structural strain across the electrocolored crystal, strain is seen to be largest near the anode interface, coloration front, and cathode interface.

In order to understand the structural changes across the oxidized (B056) and reduced (B057) crystals, ratios between the nonlinear susceptibility components, $|\chi_{zzz}/\chi_{xxx}|$, $|\chi_{xxz}/\chi_{xxx}|$, and $|\chi_{xxz}/\chi_{zzz}|$ were calculated from the SHG intensity measurements as shown in Fig. 6a and Fig. 6b. For the perovskite (ABO$_3$) structure, the susceptibility components can be interpreted as Fe:Ti-O bond “stretching” and “bending” contributions to the SHG response which occur in the Fe:Ti-O$_6$ octahedra [112-114]. Out-of-plane and in-plane Fe:Ti-O bond stretching contributions are linked to $\chi_{zzz}$ and $\chi_{xxz}$, respectively, while Fe:Ti-O bond bending contributions are linked to $\chi_{xxx}$. Ratios between these components allow us to observe the relative strength of bond stretching and bending effects in each region. From $|\chi_{zzz}/\chi_{xxx}|$ and $|\chi_{xxz}/\chi_{xxx}|$ we identify that the anodic bulk has larger Fe:Ti-O bond bending contributions around Fe$^{4+}$ defect centers, while the cathodic bulk shows larger Fe:Ti-O bond stretching around Fe$^{3+}$ defect centers [48, 59]. Greater bond bending in the anodic region is explained by the presence of Jahn-Teller type distortions around Fe$^{4+}$ defect centers. This attribution is supported by previous structural and optical spectroscopic studies which have shown strong evidence of Jahn-Teller distortions as well as modified Fe:Ti-O bond lengths and B-O-B (Fe:Ti cations at the B-sites, oxygen anions at the O-sites) bond bending angles around Fe$^{4+}$ centers in Fe-doped SrTiO$_3$ perovskites.[59] Greater bond stretching in the cathodic region
can be attributed to the presence of tetragonal Fe$^{3+}$ defect centers such as (Fe$^{3+}$ - $V_O^{-}$) defects [4]. This attribution is supported by past EXAFS and XANES measurements performed on electrocolored Fe:STO. Longer Fe-O bond lengths were revealed in cathodic regions (compared to anodic regions) [48]. The Fe:Ti-O bond stretching in the cathodic bulks is also relevant to the formation of tetragonal (Fe$^{3+}$ - $V_O^{-}$) defects.

The mixed region in B056 appears between 1.95 mm – 2.25 mm, as seen in Fig. 5.5a, with an effective thickness of ~ 0.3 mm. For B057, the mixed region is marked between 1.5 mm – 1.95 mm with an effective thickness of ~ 0.45 mm, as shown in Fig. 5.5b. The thinner anodic region of B057 compared to B056 can be explained by the oxygen vacancy concentration differences between the two samples (Table 1). In both crystals, the susceptibility ratios, $|\chi_{zzz}/\chi_{zzz}|$ and $|\chi_{xxxx}/\chi_{xxx}|$, undergo a clear transition across the coloration front, exhibiting more bond bending and stretching on the anodic and cathodic sides of samples, respectively. As a result, the coloration front is not only an electrochemical interface between two dominating Fe oxidation states, but also a structural interface between two different kinds of crystal distortion. Structural strain is the highest in this region, with non-centrosymmetric Fe$^{4+}$ and Fe$^{3+}$ defect centers packed along the anodic and cathodic sides of the coloration front, respectively. Strong strain fields have formed due to dipole moments aligned between Fe$^{4+}$:Ti$^{4+}$-O$_6$ and Fe$^{3+}$:Ti$^{4+}$-O$_6$ octahedra packed along the color fronts [85, 97]. Even though both crystals show evidence of existing strain fields at their color fronts, larger SHG intensities in B056 show greater strain compared to B057. This suggests that oxygen vacancy migration plays an important role in strain relaxation near the color fronts. We expect the oxidized crystal to have fewer oxygen vacancy diffusion pathways, leading to a less efficient demixing process during degradation [20]. As a result, more charge trap centers formed near the color front of the oxidized crystal compared to the reduced sample. Lastly, the $|\chi_{zzz}/\chi_{zzz}|$
ratio shows that in-plane and out-of-plane Fe:Ti-O bond stretching contributions to the SHG responses are approximately constant with respect to one another.

5.2 Confocal Raman from Electrocolored Fe:STO Bulks

Figure 5.6: Raman spectra collected from B056. (a) Raman spectra from the anodic region. (b) B1- and LV-mode Raman shifts as functions of the distance from the anode interface. Dashed lines mark the mixed bulk region where significant changes are observed. Black arrows point to the corresponding axes of respective data points (red squares on right, green triangles on left).
**Figure. 5.7:** Raman spectra collected from B057. (a) Raman spectra from the anodic region. (b) B1- and LV-mode Raman shifts as functions of the distance from the anode interface. Dashed lines mark the mixed bulk region where significant changes are observed. Black arrows point to the corresponding axes of respective data points (red squares on right, green triangles on left).

For comparison, confocal Raman measurements were collected from the anodic, mixed, and cathodic bulk regions of B056 as shown in Fig. 5.6. For the electrocolored B056 crystal, we look specifically at Raman peaks near 300 cm\(^{-1}\) and 690 cm\(^{-1}\)[48, 59, 132-134]. The Raman peaks near 300 cm\(^{-1}\), referred to as the B1-modes, correspond to in-plane vibrations of the oxygen sublattice, while Raman peaks near 690 cm\(^{-1}\), referred to as the LV-modes, correspond to out-of-plane local vibrations of Fe\(^{4+}\):Ti\(^{4+}\)-O\(^2-\) bonds. As concentrations of Fe\(^{4+}\) decrease, the LV-mode peak becomes less sharp and the width increases, making this mode a good indicator for the presence of Fe\(^{4+}\) cations in Fe:STO. For the B056 and B057 samples, we refer to in-plane bonds (crystallographic \(a\)- and \(b\)-axis) as parallel to the color front plane, and out-of-plane bonds (crystallographic \(c\)-axis) as perpendicular to the color front plane. The Raman shifts for the B1- and LV- modes are plotted as functions of distance from the anode interfaces in Fig. 5.6b. The B1-mode Raman shift is attributed to the in-plane oxygen sublattice expansion towards the mixed bulk region. Inside the mixed bulk region, the in-plane oxygen sublattice interestingly undergoes a compression before again expanding towards the cathode interface. For the LV-mode, the shift shows that out-of-plane Fe\(^{4+}\):Ti\(^{4+}\)-O\(^2-\) bonds undergo negligible changes in length across the anodic region. Inside the mixed region, these bonds then lengthen towards the cathodic region.
Raman measurements collected from the anodic, mixed, and cathodic bulk phases of B057 are shown in Fig. 5.7. Fig. 5.7b shows the Raman shifts for the B1- and LV-mode plotted as functions of distance from the anode interface for B057. For the B1-mode, we show that the in-plane oxygen sublattice expands towards the mixed bulk region, similar to B056. Near the mixed bulk region, the in-plane oxygen sublattice compresses before expanding slightly within the cathodic region, then compresses again near the cathode interface. For the LV-mode, out-of-plane Fe\(^{4+}\):Ti\(^{4+}\)-O\(^{2-}\) bonds undergo a lengthening from the anode interface into the cathodic region.

The Raman shift changes to the B1- and LV-modes between the anode and cathode show significant structural changes due to oxygen vacancy electromigration, consistent with SHG results[130]. For the anodic bulk regions of B056 and B057, as shown in Fig. 5.6b and Fig. 5.6b, the strong presence of Fe\(^{4+}\), shorter in-plane oxygen bonds, and longer out-of-plane oxygen bonds support the formation of Jahn-Teller distortions. Increases for B1-mode shifts and decreases for LV-mode shifts are identified across both mixed regions are observed. This result confirms the compression of in-plane oxygen bonds, and the expansion of out-of-plane bonds across the color front (towards the cathode). Evidently, an elastic strain gradient exists across the color front where the elastic strain is stronger on the cathodic side of the front than the anodic side. This elastic strain correlates to a stretching of Fe:Ti-O\(_6\) octahedra along the imposed electric field axis and a squeezing along orthogonal axes, similar to an electrostrictive deformation.
5.3 Oxygen Vacancy Migration-induced Structural Changes

From optical SHG and confocal Raman measurements, we gain deeper insight into the structural and electrochemical changes occurring across electrodegraded Fe:STO interfaces and bulks. As discussed by Waser et al.[5], theories for explaining electrodegradation in dielectric ceramics fall into two primary classifications: the Grain-Boundary Model and the Reduction Model. In the Grain-Boundary Model, a field-induced deterioration of crystal grain boundaries within the ceramic occurs, resulting in local dielectric breakdown processes and a release of trapped charge carriers[63, 135]. In the Reduction Model, the migration of mobile oxygen vacancies towards the cathode leads to the formation of an electrochemical \( p-n \) junction across the material, giving rise to significant conductivity changes and increased leakage current. The samples studied in are all Verneuil-grown Fe:STO single crystals, where grain boundaries shouldn’t have played any role in the electrodegradation process. However, charged defect migration across the degraded crystals can be connected to the formation of a structural interface between the anodic and cathodic bulk phases, at the color fronts. As a result of oxygen vacancy demixing, the anodic region becomes electrochemically oxidized, forming Fe\(^{4+} \):Ti\(^{4+} \) cation centers, while the cathodic region becomes electrochemically reduced, forming Fe\(^{3+} \):Ti\(^{3+} \) cation centers. Our recent studies have shown enhanced optical SHG intensities as well as strong susceptibility ratio changes across the color fronts of both B056 and B057 crystals[130]. This is directly attributed to the formation of a dipolar layer along the plane of the color front between the \( p \)-type conducting anodic bulk and \( n \)-type conducting cathodic bulk. Thus, the color front marks the center of a space-charge region where negatively charged defects have accumulated on the anodic side of the color front and positively charged defects have accumulated on the cathodic side.
Furthermore, confocal Raman measurements reveal a structural strain gradient across the color fronts. The ionic radii of Fe\(^{4+}\):Ti\(^{4+}\) cations are shorter than that of Fe\(^{3+}\):Ti\(^{3+}\) cations and so the lattice parameter within the anodic bulk differs from the cathodic bulk, albeit not greatly. This is consistent with EXAFS results obtained by Lenser et al.\cite{48} from Fe:STO which show an expanded crystal lattice around Fe\(^{3+}\) centers in the cathodic region, where Fe-O bonds were found to be \(~ 0.03 – 0.04\) Å larger compared to the anodic region. This difference in average oxygen bond lengths between the anodic and cathodic bulk phases gives rise to oxygen sublattice mismatches across the mixed bulk region surrounding the color front. Thus, the formation of a structural interface in the mixed region is expected and is indeed supported by both SHG and Raman data.

The strain regions formed as a result of oxygen vacancy demixing in the B056 and B057 crystals can be visualized via numerical differentiation of the nonlinear susceptibility ratios obtained from optical SHG measurements, as shown in Fig. 5.8.

**Figure 5.8:** (a) Absolute values of susceptibility ratio derivatives measured across the electrocolored B056 crystal. (b) Absolute values of susceptibility ratio derivatives measured...
across the electrocolored B057 crystal. Black shows changes to \( \chi_{xxx}/\chi_{zzz} \), red shows changes to \( \chi_{xxz}/\chi_{zzz} \), and green shows changes to \( \chi_{xxz}/\chi_{zzz} \) with respect to distance from the anode. Susceptibility ratios were interpolated for numerical differentiation purposes.

The top panels show \( \chi_{xxx}/\chi_{zzz} \) (out-of-plane Fe:Ti-O bending/out-of-plane Fe:Ti-O stretching) derivative changes, middle panels show \( \chi_{xxz}/\chi_{zzz} \) (in-plane Fe:Ti-O stretching/out-of-plane Fe:Ti-O bending) derivative changes, and bottom panels show \( \chi_{xxz}/\chi_{zzz} \) (in-plane Fe:Ti-O stretching/out-of-plane Fe:Ti-O stretching) derivative changes across the crystals. As shown in Fig. 13, the mixed bulk regions of both crystals contain high levels of structural strain as discussed in our recent study[128]. From optical SHG measurements, the thickness of the mixed region in B056 is estimated to be \( \sim 0.3 – 0.58 \text{ mm} \), while the thickness of this region is estimated to be \( \sim 0.45 – 0.58 \text{ mm} \) in B057. The scale is on the order of the thickness of the B042 and B045 crystals, which correlates well with their apparent structural and electrochemical inhomogeneity. Electrocoloration across the interfaces of B042 and B045 was splotchy and non-uniform, arguably due to their thicknesses (\( \sim 0.5 \text{ mm} \)) being on the order of the width of the mixed bulk regions measured in the B056 and B057 crystals (\( \sim 0.3 – 0.58 \text{ mm} \)). In other words, the distance across which oxygen vacancy demixing occurs must play an important role in structural and electrochemical uniformity across the crystal. As the distance between electrodes decreases, the mixed bulk region starts to dominate and this leads to thinner anodic and cathodic bulk regions in the crystal. Such an effect would also depend on the oxygen vacancy concentration of the crystal.

Both optical SHG and confocal Raman measurements show that oxygen vacancies contribute to strain relaxation across the color fronts, revealed by the significantly weaker SHG intensities from B057 compared to B056 (Fig. 5.4), despite the mixed region being slightly larger in B057[71,
As strain builds up at the color front during the electrodegradation process, local oxygen migration barriers are lowered. Hence, strain facilitates oxygen ion and vacancy diffusion. However, if local oxygen vacancy concentrations are too low, built up strain at the color front cannot be released, as observed in B056. In order to relax strain across the color front, oxygen vacancies need to undergo an energetically favorable reordering across the cathodic bulk. This may introduce an extended network of defect complexes between the color front and cathode interface along diffusion pathways[20, 136]. Relatively strong strain regions are shown to be spread across the cathodic regions of both crystals for the $\chi_{\text{HHG}}/\chi_{\text{GHH}}$ (in-plane Fe:Ti-O stretching/out-of-plane Fe:Ti-O bending) ratios, which can be interpreted as oxygen vacancy clustering, or defect ordering, across the cathodic bulk. In particular, the $\chi_{\text{xxz}}/\chi_{\text{zxz}}$ ratio is affected significantly by the presence of oxygen vacancies since these defects contribute to oxygen bond bending out of the ab-plane as well as in-plane compression of the crystal unit cell, as shown in Fig. 2.4d.

### 5.4 Summary

Optical SHG and confocal Raman spectroscopy were employed to study the spatial distribution of structural defects and strain induced by the electric field-driven migration of oxygen vacancies across Fe-doped SrTiO$_3$ single crystals. Optical SHG and confocal Raman measurements revealed Jahn-Teller distortions of Fe$^{4+}$ centers near the anode interfaces, structural strain gradients across the color fronts, and evidence of distributed oxygen vacancy clusters across the cathodic bulks. Most interestingly, the dipolar region between the anodic and cathodic bulks contains a structural interface along the color front due to mismatches between the anodic and cathodic oxygen sublattices. Our nonlinear optical measurements also reveal the thickness of the
mixed regions surrounding the color front to be slightly larger electrodegraded reduced Fe:STO compared to electrodegraded oxidized Fe:STO. Moreover, SHG measurements reveal that the mixed region within electrodegraded oxidized Fe:STO has a higher degree of broken symmetry and strain compared to electrodegraded reduced Fe:STO. This result provides evidence for oxygen vacancies contributing to strain relaxation across the color front. Our studies show that oxygen vacancy migrations directly influence the formation of structural defects and strain across electrocoloration boundaries in electrodegraded Fe:STO single crystals.
Chapter 6: Detection of Coexisting Tetragonal and Rhombohedral Phases in Ferroelectric Zr-doped BaTiO₃ Thick Films using Second Harmonic Generation

This chapter presents the investigation of tetragonal and rhombohedral phases as elastic polydomain structures in compressively strained BaZr₀.₂Ti₀.₈O₃ (BZT) films. Section 6.1 presents and discusses optical second harmonic generation (SHG) measurements taken from the BZT films in the reflection and transmission geometry. Section 6.2 presents x-ray diffraction (XRD) and transmission electron microscopy (TEM) results as supporting evidence. Section 6.3 provides a concise discussion of how the detected heterophase polydomain structures contribute to lowering remnant polarizations and delaying polarization saturation in these films. Section 6.4 summarizes the results presented in this chapter.

6.1 Optical SHG from BZT Thick Films

6.1.1 Experimental and Theoretical Description

Ferroelectric BZT films of 350 nm, 700 nm, and 1800 nm thickness were epitaxially grown on LaAlO₃ (LAO), (La,Sr)(Al,Ta)O₃ (LSAT), and SrTiO₃ (STO) substrates. Details on sample preparation and equipment specifications can be found in chapter 3. Optical SHG measurements were collected at room temperature using both reflection and transmission detection geometries, as shown in Fig. 3.12. In the reflection geometry, a mode-locked Ti:Sapphire pulse laser (Tsunami, 80 MHz, 10 nJ/pulse, 100 fs) was used as the fundamental light source (810 nm, ~1 mJ/cm²) and
BZT films were aligned with surface normal axes at $\theta = 45^\circ$ with respect to the incident light traveling along the xz-plane (plane of the optics table). In the transmission geometry, pulses from the mode-locked Ti:Sapphire laser (Tsunami, 80 MHz, 10 nJ/pulse, 100 fs) were seeded into a regenerative amplifier (RegA 9000, 250 kHz, 5 $\mu$J/pulse, 200 fs) and used as the fundamental light source (810 nm, ~100 mJ/cm$^2$). Fig. 6.1 shows the reflection and transmission detection geometries with respect to the film and substrate axes.

![Figure 6.1: Film and substrate axes for (a) reflected and (b) transmitted SHG intensity detection.](image)

Unstrained $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ exhibits rhombohedral ($3m$) lattice symmetry at room temperature. By using an epitaxial lattice mismatch between the film and a tetragonal substrate where $a_f > a_s$ (See section 2.4.2), the resulting compressive strain induces a morphotropic phase boundary at room temperature and rhombohedral and tetragonal phases can coexist as elastic domains. These elastic domains form in order to minimize the long-range mechanical stress field generated at the film-substrate interface[31]. This stress field falls off with increasing BZT layers, i.e. strain relaxation away from the substrate.
The possible polarization orientations of each domain are determined by their respective crystal phase symmetry and can be described with respect to the tetragonal substrate axes labeled in Fig. 6.1. Rhombohedral domains have 8 possible polar variants (Shown in Fig. 2.1), represented by the corners of a pseudo-cubic unit cell: \([\overline{1}1\overline{1}], [111], [\overline{1}1\overline{1}], [11\overline{1}], [\overline{1}1\overline{1}], [\overline{1}1\overline{1}], [1\overline{1}1], [1\overline{1}1]\), and \([1\overline{1}1]\) [41, 85]. Tetragonal domains have 6 possible polar variants (Shown in Fig. 2.1), represented by the faces of a pseudo-cubic unit cell: \([\overline{1}00], [100], [0\overline{1}0], [010], [00\overline{1}], [001]\) and \([001]\)[41, 85]. However, since the formation of tetragonal phases in BaZr\(_{0.2}\)Ti\(_{0.8}\)O\(_3\) only occurs as a result of the compressive misfit strain from the substrate, tetragonal polar variants are predominantly oriented along the thickness of the film. Thus, tetragonal polarizations parallel to \([100]\) are expected to dominate over the other polar variants. As the thickness of the film increases, the long-range stress field generated at the film-substrate interface relaxes and rhombohedral phases begin to grow alongside tetragonal structures.

The SHG detection geometry and film orientation are important factors when probing these domain structures. For instance, SHG signals from the tetragonal domains become dominative when the films are oriented at \(\theta = 45^\circ\) with respect to the incident light[86, 137], while SHG signals from rhombohedral domains are dominative when the film is oriented at \(\theta = 0^\circ\) with respect to the incident light[85, 86, 137, 138]. This is due to the electric field of the incident light waves being orthogonal to tetragonal polarizations ([100]) when the film is probed at normal incidence. Pure tetragonal or rhombohedral phases were not observed in either geometry due to the films’ heterophase polydomain structure.

The SHG coherence length for BZT in the reflection and transmission geometries about \(\sim40\) nm and \(\sim660\) nm, respectively. Since BZT is a polar material, bulk contributions to the SHG signal dominate over contributions from the surface, which is on the scale of a unit cell. As a result,
surface layer contributions to the SHG response can be neglected and signals can be considered as originating from the polar bulk of the material[85]. Furthermore, due to the difference in coherence length between reflection and transmission detection, we mainly probe bulk contributions near the film’s surface in the reflection geometry, while in the transmission geometry we probe near-surface and deeper bulk regions of the films.

6.1.2 SHG in Reflection Geometry from BZT Films

Fig. 6.2 shows the $p$-polarized ($\varphi = 0^\circ$) and $s$-polarized ($\varphi = 90^\circ$) SHG intensities as functions of the incident polarization angle measured from the ferroelectric BZT thick films in the reflection geometry (at $\theta = 45^\circ$ incidence).
Figure 6.2: Reflected p-polarized (red) and s-polarized (blue) SHG intensities as functions of the incident light polarization angle for (a) BZT/LAO, (b) BZT/LSAT, and (c) BZT/STO.

The reflected SHG signals at a tilt angle of $\theta = 45^\circ$ are clearly dominated by strain-induced tetragonal phases oriented along the thickness of the film, i.e. $z$-axis [100]. In order to assess the growth of rhombohedral symmetry, SHG intensities were fitted using the following second-order susceptibility components, $\chi_{zxx}, \chi_{xxx}, \chi_{zxx}, \chi_{xyy}, \chi_{xxx},$ and $\chi_{yyy}$. We thus treat the near-surface bulk as an effective tetragonal region with nonzero rhombohedral susceptibility contributions. In
In this case, the nonlinear polarization of the probed near-surface bulk region can be expressed as follows:

\[
\begin{pmatrix}
P_x^{2\omega} \\
P_y^{2\omega} \\
P_z^{2\omega}
\end{pmatrix} = 2\varepsilon_0 \begin{pmatrix}
0 & 0 & 0 & 0 & \chi_{XXZ} & \chi_{XYX} \\
\chi_{XXZ} & \chi_{YXY} & 0 & \chi_{XXZ} & 0 & 0 \\
\chi_{XXZ} & \chi_{XXZ} & \chi_{XXZ} & 0 & 0 & 0
\end{pmatrix} \begin{pmatrix}
(L_x^{\omega})^2 E_x(\omega)^2 \\
(L_y^{\omega})^2 E_y(\omega)^2 \\
(L_z^{\omega})^2 E_z(\omega)^2 \\
2 L_{xx}^{\omega} L_{yy}^{\omega} E_y(\omega) E_z(\omega) \\
2 L_{xx}^{\omega} L_{zz}^{\omega} E_x(\omega) E_z(\omega) \\
2 L_{xx}^{\omega} L_{yy}^{\omega} E_x(\omega) E_y(\omega)
\end{pmatrix}
\]

(6.1)

The vector components of the nonlinear polarization are then written as:

\[
P_x(2\omega) = 2\varepsilon_0 \left( 2 \chi_{xxz} L_{xx}^{\omega} L_{xx}^{\omega} E_x(\omega) E_x(\omega) + 2 \chi_{xyx} L_{xx}^{\omega} L_{yy}^{\omega} E_x(\omega) E_y(\omega) \right)
\]

(6.2a)

\[
P_y(2\omega) = 2\varepsilon_0 \left( \chi_{yxx} (L_{xx}^{\omega})^2 E_x(\omega)^2 + \chi_{yxy} (L_{yy}^{\omega})^2 E_y(\omega)^2 + 2 \chi_{xxz} L_{yy}^{\omega} L_{yy}^{\omega} E_x(\omega) E_y(\omega) \right)
\]

(6.2b)

\[
P_z(2\omega) = 2\varepsilon_0 \left( \chi_{xxx} (L_{xx}^{\omega})^2 E_x(\omega)^2 + \chi_{zxx} (L_{yy}^{\omega})^2 E_y(\omega)^2 + \chi_{zzz} (L_{zz}^{\omega})^2 E_z(\omega)^2 \right)
\]

(6.2c)

Using Eq. 4.5, the effective nonlinear susceptibility of the region in the reflection geometry can be expressed as:

\[
\chi^{(2)}_{\text{eff}} = -L_{xx}^{2\omega} \cos\theta \cos\phi \left[ 2 \chi_{xxz} L_{xx}^{\omega} L_{xx}^{\omega} \sin\theta \cos\theta \cos^2\phi + 2 \chi_{xyx} L_{xx}^{\omega} L_{xx}^{\omega} \sin\theta \cos\phi \cos\theta \sin^2\phi + \chi_{yxy} (L_{yy}^{\omega})^2 \sin^2\phi + 2 \chi_{xxz} L_{yy}^{\omega} L_{yy}^{\omega} \sin\theta \sin\phi \cos\phi \right] + L_{zz}^{2\omega} \sin\theta \cos\phi \left[ \chi_{zxx} (L_{xx}^{\omega})^2 \cos^2\theta \cos^2\phi + \chi_{xxx} (L_{yy}^{\omega})^2 \sin^2\phi + \chi_{zzz} (L_{zz}^{\omega})^2 \sin^2\theta \cos^2\phi \right]
\]

(6.3)
Utilizing $I^{2\omega} \propto \left| \chi^{(2)}_{\text{eff}} \right|^2$, we obtain the $p$-polarized ($\varphi' = 0^\circ$) and $s$-polarized ($\varphi' = 90^\circ$) SHG intensities as functions of the incident polarization angle for a bulk region with rhombohedral-like symmetry:

\begin{equation}
I^{2\omega}_p(\varphi) = \left|\chi_{pp} \cos^2 \varphi + \chi_{sp} \sin^2 \varphi + \chi_{dp} \sin(2\varphi)\right|^2
\tag{6.4}
\end{equation}

\begin{equation}
I^{2\omega}_s(\varphi) = \left|\chi_{ps} \cos^2 \varphi + \chi_{ss} \sin^2 \varphi + \chi_{ds} \sin(2\varphi)\right|^2
\tag{6.5}
\end{equation}

where

\begin{align*}
\chi_{sp} &= \chi_{zxx}L_{zz}^{2\omega}(L_{yy}^{\omega})^2 \sin \theta \\
\chi_{pp} &= \chi_{zzz}L_{zz}^{2\omega}(L_{zz}^{\omega})^2 \sin^3 \theta - 2\chi_{xxz}L_{xx}^{2\omega}L_{zz}^{\omega} \sin \theta \cos^2 \theta + \chi_{xxx}L_{zz}^{2\omega}L_{xx}^{\omega} \sin \theta \cos^2 \theta \\
\chi_{dp} &= \chi_{xxy}L_{xx}^{2\omega}L_{yy}^{\omega} \cos^2 \theta \\
\chi_{ss} &= \chi_{yyy}L_{yy}^{2\omega}(L_{yy}^{\omega})^2 \\
\chi_{ps} &= -\chi_{yxx}L_{yy}^{2\omega}(L_{xx}^{\omega})^2 \cos^2 \theta \\
\chi_{ds} &= \chi_{xxz}L_{yy}^{2\omega}L_{yy}^{\omega}L_{zz}^{\omega} \sin \theta
\end{align*}

For the case of pure tetragonal (4mm) symmetry, only the $\chi_{zxx}$, $\chi_{xxz}$ and $\chi_{zzz}$ components are nonzero, thus we use contributions from the $\chi_{xxy}$, $\chi_{yxx}$, and $\chi_{yyy}$ components as indicators for symmetry reductions of tetragonal structures with increasing film thickness. We define the following ratio as a simple tool to quantify the growth of rhombohedral signatures:
The $\frac{R(\chi)}{T(\chi)}$ ratio as a function of film thickness for the BZT films is shown in Fig. 6.3.

\[
\frac{R(\chi)}{T(\chi)} = \frac{|\chi_{yxx}| + |\chi_{yyx}| + |\chi_{xyy}|}{|\chi_{zxx}| + |\chi_{xxz}| + |\chi_{zzz}|}
\] (6.6)

**Figure 6.3:** Ratio between rhombohedral and tetragonal susceptibility components as a function of film thickness for BZT grown on LAO ($a = 3.79\,\text{Å}$), LSAT ($a = 3.87\,\text{Å}$), and STO ($a = 3.905\,\text{Å}$)[34]. SHG signals in the reflection geometry at $\theta = 45^\circ$ are predominantly from tetragonal phases. Dashed lines show the increasing rhombohedral signature trend.

The data shows that the rhombohedral susceptibility components, $\chi_{xyx}$, $\chi_{yxz}$, and $\chi_{yzy}$, grow stronger with increasing film thickness. This demonstrates a lowering of structural symmetry as strain relaxations occur away from the film-substrate interface, creating more elastic rhombohedral. The relaxation of strain appears to be strongest for BZT/LAO and weakest for BZT/STO. This makes sense since the misfit strain between BZT and LAO is the largest (~5.25%), while the misfit strain between BZT and STO is the lowest (~2.37%).
6.1.3 SHG in Transmission Geometry from BZT Films

Fig. 6.4 shows the transmitted $d$-polarized ($\varphi' = +45^\circ$, $\varphi' = -45^\circ$) SHG intensities as functions of the incident polarization angle measured from the ferroelectric BZT thick films under normal incidence.

![Fig. 6.4a](image)

![Fig. 6.4b](image)
Figure 6.4: Transmitted $d$-polarized ($\varphi' = +45^\circ$ in pink, $\varphi' = -45^\circ$ in black) SHG intensities as functions of the incident light polarization angle for (a) BZT/LAO, (b) BZT/LSAT, and (c) BZT/STO. All SHG intensities were measured under normal incidence.

The transmitted SHG signals with a film tilt angle of $\theta = 0^\circ$ are dominated by elastic rhombohedral polydomains distributed along the thickness of the film. These domains have effective polarization orientations with respect to the tetragonal substrate axes, as shown in Fig. 6.5.

Figure 6.5: Rhombohedral domain variants probed in the transmission geometry at normal incidence. Analyzer orientations for SHG detection are marked above unit cell depictions, i.e. $d$-
polarized ($\varphi' = +45^\circ \text{ or } -45^\circ$). Polarization orientations of each variant are depicted beneath the unit cells. In total, we have 8 possible rhombohedral domain variants.

In order to fit $d$-polarized SHG intensities as a function of the incident light polarization angle, the contribution of each polar domain variant to the nonlinear polarization must be taken into account, as discussed in detail by Denev et al.[85]. However, in order to take into account incoherent interference between SHG signals coming from microscale 1$^{\text{st}}$ order and nanoscale 2$^{\text{nd}}$ order rhombohedral domains, the $d$-polarized SHG intensities as functions of the incident polarization angle were fitted according to the following equation [85, 86]:

$$I^{2\omega}_{(\eta\{110\})\varphi} = I^{2\omega}_{1j\varphi} + I^{2\omega}_{2j\varphi}$$  \hspace{1cm} (6.7a)

$$I^{2\omega}_{1j\varphi} = K^{(1)}_{1j} \left( \cos^2 \varphi + K^{(1)}_{2j} \sin^2 \varphi \right)^2 + K^{(1)}_{3j} \sin^2(2\varphi)$$

\hspace{2cm} + $K^{(1)}_{4j} \left( \cos^2 \varphi + K^{(1)}_{2j} \sin^2 \varphi \right) \sin(2\varphi)$  \hspace{1cm} (6.7b)

$$I^{2\omega}_{2j\varphi} = K^{(2)}_{1j} \left( \cos^2 \varphi + K^{(2)}_{2j} \sin^2 \varphi \right)^2 + K^{(2)}_{3j} \sin^2(2\varphi)$$

\hspace{2cm} + $K^{(2)}_{4j} \left( \cos^2 \varphi + K^{(2)}_{2j} \sin^2 \varphi \right) \sin(2\varphi)$  \hspace{1cm} (6.7c)

For Eq. 6.7, the subscript $j$ denotes $x = \langle \overline{1}10 \rangle$ or $y = \langle 110 \rangle$ to designate the analyzer polarization angle of $\varphi' = -45^\circ \text{ or } +45^\circ$, respectively. In Eq. 6.7a, the total $d$-polarized SHG intensity is expressed as an incoherent sum of polarization-resolved SHG intensities from rhombohedral microdomains and nanodomains throughout the film. Otherwise, most SHG intensity polar plots
could not be fitted without violating the important reciprocity condition, \( K_{2,x}^{(i)} \cdot K_{2,y}^{(i)} = 1 \) [85, 86, 139-144], as discussed by in the model of Denev et al. This condition was held for each set of fitting coefficients. In Eq. 6.7b and Eq. 6.7c, \( K_{1,x}^{(i)} \propto (\chi_{zxx})^2, K_{1,y}^{(i)} \propto (2\chi_{zxx} + \chi_{xxx} + 2\chi_{zzz})^2, \)
\[ K_{2,x}^{(i)} = (K_{2,y}^{(i)})^{-1} = \left(\frac{2\chi_{zxx} + \chi_{xxx} + 2\chi_{zzz}}{\chi_{zxx}}\right), \]
\[ K_{3,x}^{(i)} \propto K_{3,y}^{(i)} \propto (\chi_{xxz})^2, \]
\[ K_{4,x}^{(i)} \propto \chi_{xxz} \cdot \chi_{zzz}, \]
and
\[ K_{4,y}^{(i)} \propto (2\chi_{zxx} + \chi_{xxx} + 2\chi_{zzz}) \cdot \chi_{xxz}. \]

Since the \( d \)-polarized SHG signals in normal incidence are dominated by rhombohedral polydomains within a coherence length from the surface of the film, increasing \( d \)-SHG intensities can be used as an indication for the growth of rhombohedral structures due to strain relaxation. Thus, we use the sum of both \( d \)-polarized SHG maxima as a tool for showing the growth of rhombohedral domains with increasing film thickness, as shown in Fig. 6.6.

![Figure 6.6a](image1)

![Figure 6.6b](image2)

**Figure 6.6:** (a) sum of maximum \( d \)-polarized SHG intensities as a function of film thickness for BZT grown on LAO (\( a = 3.79\)Å)(left scale), LSAT (\( a = 3.87\)Å)(right scale), and STO (\( a = 3.905\)Å)(right scale)[34]. Dashed lines show the trends for \( d \)-SHG intensities to increase with film.
thickness. (b) Maximum $d$-polarized SHG intensities plotted as a function of the misfit strain percent between BZT and the three tetragonal substrates.

A significant degree of inhomogeneity was observed while probing the films in normal incidence, indicating that the domain distribution can vary depending on the probe site. The data in Fig. 6.6 is in agreement with the data shown in Fig. 6.3. Fig. 6.6 shows that $d$-SHG signals from rhombohedral domains is greatest for BZT/STO, which makes sense since the epitaxial misfit strain for this film is the lowest of the three substrates. On the other hand, BZT/LAO appears to have the lowest degree of bulk rhombohedral symmetry, which makes physical sense since the epitaxial misfit strain for this film is the highest of the three substrates and more strain-induced tetragonal domains are expected.

### 6.2 XRD and TEM Results from BZT Films

The SHG results are in good agreement with x-ray diffraction (XRD) and transmission electron microscopy (TEM) results obtained from the ferroelectric BZT thick films. Fig. 6.7 shows XRD spectra from the 1800 nm thick BZT film grown on STO. ($\langle 00 \rangle$) diffraction peaks were observed for the SRO electrode and the BZT film, as shown in Fig. 6.7a. The diffraction peaks show the presence of tetragonal and rhombohedral bulk phases. Fig. 6.7b shows the $\phi$-scan pattern for the (101) plane of rhombohedral bulk phases. Four strong diffraction peaks with angular displacements varying between 89.76° and 90.12° depict the pseudo-cubic epitaxial growth of the BZT film on the STO substrate.
Figure 6.7: Reproduced from Cheng et al. [24]. (a) XRD 2θ scans of 1800 nm thick BZT grown on (100) STO. The inset displays magnified peaks to show coexisting rhombohedral and tetragonal bulk phases; (b) φ-scan pattern for the (101) plane of the BZT rhombohedral phases. Angular displacements between the pseudo-cubic peaks are clearly labeled.
Figure 6.8: Reproduced from Cheng et al.[24]. (a) Cross-sectional bright field TEM image of an 1800 nm thick BZT film. The image shows vertical, or columnar, rhombohedral microdomains along the thickness of the film; (b) Magnified TEM images of domain morphologies in a 700 nm thick BZT film. Displays [101] domain walls between the nanodomains residing within the [100] microdomains.

Tetragonal and rhombohedral domain walls are visible in the TEM images for 1800 and 700 nm thick BZT grown on STO. Both 1st order and 2nd order domain structures are shown in Fig. 6.8a and Fig. 6.8b, respectively. The images clearly depict a growth of columnar microdomains along the thickness of the film. Nanoscale 2nd order rhombohedral domains, marked by their domain walls, were observed to be imbedded within the vertical microdomains. The presence of both rhombohedral microdomains and nanodomains in the TEM images can account for the complex transmitted SHG profiles. Eq. 6.7 would thus represent the incoherent sum of SHG intensities arising from microscale and nanoscale rhombohedral structures.
6.3 High Energy Performance due to the Formation of Heterophase Polydomain Structures

The energy storage properties of the BZT films are represented in Fig. 6.9. Charged energy densities and energy storage efficiencies were measured up to 166 J/cm³ and 96%, respectively.

![Figure 6.9: Reproduced from Cheng et al. [24]. Charged energy densities ($W_c$) are shown by the left axis while energy storage efficiencies (%) are shown by the right axis. The inset shows the slim P-E hysteresis loops measured in some of the BZT thick films.](image)

The excellent energy performance of the BZT films can be directly attributed to the formation of mixed tetragonal and rhombohedral polydomain structures. In the absence of compressive misfit strain between the film and substrate, BaZr$_{0.2}$Ti$_{0.8}$O$_3$ exhibits rhombohedral ($3m$) bulk symmetry. By implementing a compressive misfit strain between the BZT film and tetragonal substrate, the in-plane lattice of the BZT film, i.e. crystallographic $ab$-plane, compresses and induces the
formation of tetragonal polydomains. These phases form tetragonal polar domains with 90° domain walls and polarizations parallel to the [100] direction. As the film layers grow further from the film-substrate interface, the long-range stress field generated at the substrate interface falls off and strain relaxation occurs, allowing tetragonal polydomains to relax into rhombohedral polydomains. Thus, rhombohedral symmetry increases with increasing film thickness.

Both microscale and nanoscale rhombohedral and tetragonal polydomains were observed from the TEM measurements, which supports SHG results. This polydomain architecture consists of vertically grown tetragonal and rhombohedral microdomains separated by [100] domain walls throughout the thickness of the film. Within these microdomains resides 2nd order rhombohedral nanodomains with [101] domain walls which form to minimize elastic stresses between the larger microdomains. In particular, the observation of this hierarchical polydomain structure can explain the lower remnant polarizations and delayed polarization saturation in the films, as shown in Fig. 6.9. Rhombohedral nanostructures exhibit low self-strain (small shear stress) between adjacent domains due to their structural symmetry. This facilitates domain wall movement and allows the self-assembly of a “head-to-tail” polar ordering which promotes electroneutrality, i.e. zero net polarization, along the film thickness. This results in low remnant polarizations in the absence of an external field. Lower remnant polarizations ultimately increase the energy storage efficiency of the films during charge-discharge cycles. Under an applied electrical field, these rhombohedral nanostructures are able to evolve from their remnant, uncharged state to a polarized, charged state. During this evolution, the nanostructures tend towards a single domain state as individual nanodomains align their polarizations with the external field. This transition delays polarization saturation, allowing the film to absorb extra electric energy and contributes to greater dielectric strengths within the films, i.e. larger breakdown fields. Near saturation, elastic rhombohedral
nanodomains behave like tetragonal ones, however, the electrical field is unable to fully overpower the elastic interactions between domains and the film does not completely saturate. During the discharging process, these rhombohedral nanostructures are able to fully relax back to their remnant, multi-domain state as the external field approaches zero[31].

6.4 Summary

A rhombohedral BaZr$_{0.2}$Ti$_{0.8}$O$_3$ (BZT) solid solution was combined with a compressive film-substrate misfit strain to engineer heterophase polydomain structures in BZT ferroelectric films. High energy storage densities (up to 166 J/cm$^3$) and efficiencies (up to 96 %) were obtained with excellent field and frequency stabilities. Polarization-resolved SHG intensities were measured in the reflection and transmission geometries to study mixed tetragonal and rhombohedral phases in the epitaxially strained BZT thick films. Reflected SHG intensities measured at 45° incidence from near-surface domains show the growth of rhombohedral symmetry with increasing film thickness. Transmitted SHG intensities measured at normal incidence from deeper bulk domains also demonstrate the growth of rhombohedral symmetry with increasing film thickness. All observations are associated with structural symmetry reductions as strain-induced tetragonal domains transition into elastic rhombohedral polydomains. This symmetry reduction is explained by the relaxation of strain away from the film-substrate interface. The SHG results are consistent with those from XRD and TEM measurements, revealing the coexistence of tetragonal microstructures and rhombohedral nanostructures as elastic domains in the compressively strained films. The excellent energy storage performance of these films is a direct result of the formation of these heterophase polydomain structures which can be tuned using substrate strain and thickness scaling effects.
Chapter 7: Summary and Outlook

7.1 General Summary

We have studied local structural changes due to the dc electric field-induced migration of oxygen vacancies at Fe:STO single crystal interfaces, oxygen vacancy migration-induced structural defect and strain formation in electrodegraded Fe:STO single crystals, and mixed tetragonal and rhombohedral phases in ferroelectric BZT thick films.

First, we investigated local structural changes due to the dc electric field-driven migration of oxygen vacancies at Fe:STO single crystal interfaces using optical SHG and photoluminescence measurements. Field-induced ionic displacements were detected by changes in the susceptibility components of the tetragonal interfaces as a result of electrostrictive distortions. These distortions were described in detail according to Fe:Ti-O bond stretching and bending effects within the Fe:Ti-O$_6$ octahedron. Differences in the nonlinear responses between the oxidized and reduced sample interfaces studied were explained by their respective Schottky barriers and built-in electric fields. The built-in electric field at the interfacial depletion region is revealed to be greater in oxidized Fe:STO compared to reduced Fe:STO, providing strong evidence that oxygen vacancies contribute to lower Schottky energy barrier heights as well as thinner depletion regions. This facilitates stronger structural changes at low dc voltages in the reduced crystal compared to the oxidized one. Moreover, structural differences between the reduced and oxidized Fe:STO cathodes are indicated by the EFISHG and photoluminescence results, showing that a clustering and straining of oxygen
vacancy defects at the reduced cathode occurs. This effect breaks in-plane isotropies and the reduced cathode interface deviates from tetragonal (4mm) symmetry.

Next, we investigated structural defect and strain formation in electrodegraded reduced and oxidized Fe:STO single crystals using optical SHG and confocal Raman spectroscopy. SHG revealed high degrees of structural inhomogeneity across degraded anode and cathode interfaces which were explained by the formation of Fe$^{4+}$/oxygen ion and Fe$^{3+}$/oxygen vacancy aggregation sites, respectively. We have also shown that mixed Fe$^{3+}$/Fe$^{4+}$ states and strain form along the electrocoloration boundaries in both single crystals. This, as well as oxygen sublattice variations between the anodic and cathodic bulk shown by confocal Raman data, demonstrates that oxygen vacancy demixing generates a structural interface along the color front. In comparing both electrodegraded oxidized and reduced Fe:STO crystals, we reveal that strain is greater across the oxidized crystal’s color front compared to the reduced crystal, although the strained region is slightly wider in the reduced crystal. Our results indicate that structural and electrochemical inhomogeneity has a dependence on the distance between electrodes due to the finite size (~0.3–0.58 mm) of the strain field which forms across electrocoloration boundaries.

Lastly, we employed polarization-resolved SHG in the reflection and transmission geometries to investigate heterophase polydomain structures in compressively strained ferroelectric BZT thick films. These films exhibit high energy storage densities and efficiencies showcased by their slim, pseudo-linear $P-E$ hysteresis loops. In the reflection geometry, the SHG intensity is dominated by contributions from strain-induced tetragonal microdomains growing along the thickness of the film. In the transmission geometry, SHG contributions from tetragonal structures are suppressed and the signal arises from rhombohedral polydomains. SHG results demonstrated the growth of rhombohedral symmetry with increasing film thickness, explained by
strain relaxation away from the tetragonal film-substrate interface. Greater misfit strains between the BZT films and substrates were shown to lead to a higher degree of tetragonal symmetry. In addition, the presence of mixed rhombohedral and tetragonal phases was supported by transmission electron microscopy (TEM) and x-ray diffraction (XRD) measurements which verified the growth of columnar [100] tetragonal microdomains with [101] rhombohedral nanodomains imbedded within them. The high energy performance of the films is well explained by these mixed tetragonal and rhombohedral polydomain structures which serve to decrease remnant polarizations and delay polarization saturation.

7.2 Outlook and Future Experiments

Our investigation of structural defect and strain formation resulting from the dc electric field-induced migration of oxygen vacancies in pristine and electrodegraded Fe:STO single crystals yielded valuable insights into dc electric field-induced dielectric breakdown mechanisms. One significant insight is the competition between the conservation of electroneutrality and structural strain formation. Just as oxygen vacancies form in order to conserve charge neutrality within the perovskite unit cell, oxygen vacancy demixing occurs in order to conserve electroneutrality in the dielectric’s bulk with respect to the external electrical field. This migratory process, as we have shown, results in strain formation between anodic and cathodic bulk regions, i.e. across electrocoloration boundaries. Furthermore, dc electric stress-induced electrostriction also results in structural strain. Strain resulting from external dc electrical fields and ionic defect accumulation should not be ignored when modeling conductivity changes to describe voltage-induced resistance degradation, especially in ferroelectric ceramics where electrical and mechanical properties are strongly coupled. Structural strain serves to promote oxygen vacancy
migration by lowering migration enthalpies, compromising bond strengths, and generating defect states [70, 71, 145]. In the future, elasticity changes across electrodegraded dielectric ceramics may be investigated using coherent longitudinal acoustic phonon spectroscopy. In addition, the field-induced structural evolution of electrocoloration boundaries may also be probed in real-time using optical SHG as a direct continuation of this study. Furthermore, oxygen vacancy migration-induced structural changes should be examined in perovskite dielectrics with different chemical compositions to gain further understandings.

Our study of coexisting tetragonal and rhombohedral phases as elastic polydomain structures in ferroelectric BZT thick films has also helped provide significant insights into the strain engineering of heterophase polydomain structures for high energy performance. We have probed remnant polydomain structures in these films, however, electric field-induced polydomain evolutions would yield even more valuable structural insights. In the future, electric field-induced structural changes of these mixed tetragonal and rhombohedral polydomain structures can be investigated using optical SHG in the reflection and transmission geometries as well as confocal Raman spectroscopy. Near-field SHG microscopy, with or without voltage, would allow a direct imaging of polar domain morphologies within the films. Furthermore, field-dependent coherent longitudinal acoustic phonon spectroscopy can be performed to investigate structural changes in epitaxially strained films. Finally, since the stabilization of heterophase polydomain structures relies heavily on the long-range stress field generated at the substrate interface and chemical composition of the film, combinations of different compositions and substrate species may be probed using various nonlinear optical techniques, such as optical SHG and confocal Raman spectroscopy.
Bibliography


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