Phase transitions in Sn-modified lead zirconate titanate antiferroelectric ceramics

Hui He
Iowa State University

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Phase transitions in Sn-modified lead zirconate titanate antiferroelectric ceramics

by

Hui He

A dissertation submitted to the graduate faculty
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Xiaoli Tan, Major Professor
Ashraf F. Bastawros
Matthew J. Kramer
R. William McCallum
Joerg Schmalian

Iowa State University

Ames, Iowa

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Dedicated to my parents and Hang Yan

for their love and support during my education
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Abstract

Electric field-induced antiferroelectric-to-ferroelectric phase transformation forms the physics basis for the applications of the PbZrO$_3$-based antiferroelectric ceramics. The primary objective was to gain a better understanding of the phase transitions in between ferroelectric and antiferroelectric states. A secondary goal was to verify certain feasible applications by taking advantage of the phase transitions. In-situ techniques were extensively used including in-situ TEM and in-situ Raman microscopy.

Electric field in situ TEM technique was used in the study of the electric field induced antiferroelectric to ferroelectric phase transformation in PbZrO$_3$-PbTiO$_3$-PbSnO$_3$ (PZST) ceramics. Our TEM study indicates that the incommensurate modulation in the modified perovskite antiferroelectrics we studied exists in the form of a transverse Pb-cation displacement wave. The observed incommensurate modulation at large scale is suggested to be a mixture of commensurate modulations at local scale. The modulations were found to disappear at a field level close to the critical field for the antiferroelectric-to-ferroelectric transformation.

Raman peaks that represent ferroelectric and antiferroelectric in PZST 43/y/2 ceramics were identified in order for subsequent monitoring of the phase transitions. Temperature and thermal history dependence of the phase transitions was directly observed with an in situ Raman microscopy technique. Field induced ferroelectric phase stability was analyzed with Raman microscopy. Electric field-induced AFE-FE phase transition was directly observed with an in situ Raman microscopy technique.

With the structural information and the knowledge of the phase transitions in these materials, the electric field-induced fracture behavior was compared in an
antiferroelectric and a ferroelectric ceramic with close chemical compositions. The volume expansion during the electric field-induced phase transition leads to the superior fracture resistance in the antiferroelectric ceramic. This volume strain may also toughen the antiferroelectric ceramic under applied mechanical loadings.
1. Introduction

This dissertation is composed of a number of journal articles published or submitted for publication. The introductory chapter contains background information and a comprehensive literature review of the topics addressed in subsequent chapters. Chapters 2 and 3 contain journal articles which have been published in *Applied Physics Letters* and *Physical Review B*. Chapter 4 and 5 contain journal articles which have been submitted to *Journal of the American Ceramic Society* and *Journal of Physics: Condensed Matter*. Chapter 6 contains general conclusions and recommendations for further study. Works cited are listed at the end of each chapter in which they appear.

The main focus of the research work presented in this thesis is antiferroelectric to ferroelectric (AFE-FE) phase transformations in lead-zirconate titanate stannate (PZST) system. In this chapter, concepts and definitions for the phases and structures will be explained followed by the introduction to phase transitions and the selected materials system.

1.1 Perovskite Structure

Perovskite\(^1\text{-}^4\) was used to name a group of ferroelectrics from the mineral perovskite (calcium titanium oxide, CaTiO\(_3\)). The perovskite structure with hard sphere and reduced sphere model are shown in Figure 1-1. The perfect structure of perovskite is cubic with a general formula ABO\(_3\) where A and B are cations of different sizes. For example, in PbTiO\(_3\), Pb atoms occupy A sites, Ti atoms occupy B sites. Different A and B cations can lead to distortions\(^2\text{-}^4\), as CaTiO\(_3\) itself has a distorted perovskite structure. The B cation is the cation in the middle of the cube and A is at the corners. The oxygen ions are at the
Figure 1-1 The perovskite structure
centers of the unit cell faces. An alternative expression puts the A-cation at the center of the cube, the B-cation at the corners and the anion (usually oxygen) at the center of the edges\(^4\). This expression regards the perovskite structure as a set of BO\(_6\) octahedra linked together by sharing oxygen atoms\(^5\).

There are complex perovskites which contain two different B-site cations which results in ordered and disordered variants\(^4,5\). The ordered structure can usually be indexed by a trigonal unit cell with the B-site ions at the center of the oxygen octahedra\(^2,4\). Many ferroelectric, piezoelectric, ferroelectric and superconducting materials have perovskite-like structures\(^5,6\).

1.2 Ferroelectricity (FE) and Antiferroelectricity (AFE)

The ferroelectric effect\(^5\) is an electrical phenomenon whereby certain ionic crystals and piezoelectric polymers may exhibit a spontaneous dipole moment, which can be reversed by the application of an electric field. The term ferroelectricity is used in analogy to ferromagnetism\(^5,7\), in which a material exhibits a permanent magnetic moment. Older publications used the term electret for ferroelectric materials\(^8-12\).

There are two main types of ferroelectrics: displacive and order-disorder\(^5,7,13-18\). The effect in PbTiO\(_3\) and BaTiO\(_3\), typical ferroelectrics of the displacive type, is due to a polarization catastrophe\(^7\), in which, if an ion is displaced from equilibrium slightly, the force from the local electric fields due to the ions in the crystal increase faster than the elastic-restoring forces. This leads to an asymmetrical shift in the equilibrium ion positions and hence to a permanent dipole moment. The most important displacive type ferroelectric materials are PbTiO\(_3\)-PbZrO\(_3\) solid solutions\(^19-22\). In an order-disorder
ferroelectric, there is a dipole moment in each unit cell, but at high temperatures they are pointing in random directions\textsuperscript{17,23}. Upon lowering the temperature and going through the phase transition, the dipoles order, all pointing in the same direction within a domain.

A closely related concept is antiferroelectricity\textsuperscript{5}. In an antiferroelectric crystal, the net spontaneous polarization is zero at ground state. However, each unit cell has a net dipole moment, individual dipoles are arranged antiparallel to adjacent dipoles\textsuperscript{5}. Antiferroelectricity arises when an anti-parallel alignment of dipole moments occurs. From the phenomenological point of view\textsuperscript{5}, the antiferroelectricity occurs when the state with antiparallel dipole moments in neighboring unit cells has a lower free energy than the state with parallel moments in a ferroelectric form. It results in a doubling of the unit cell through the $\uparrow\downarrow$ ordering. When an antiferroelectric crystal is subjected to a sufficient external electric field, the dipoles tend to shift and align with the field so that the net polarization will be parallel to the field, ferroelectricity is therefore induced. Upon the release of the external electric field, the dipoles will recover back to their original state thus the net polarization of the crystal will be back to zero. A typical example for the antiferroelectricity is lead zirconate (PbZrO$_3$) perovskite.

Ferroelectric crystals often show Curie points and electric polarization hysteresis\textsuperscript{5,5,7}, as in ferromagnetic crystals. By analogy to magnetic core memory, this hysteresis can be used to store information in ferroelectric random access memory\textsuperscript{24} (FeRAM), which has ferroelectric capacitors as memory cells. Ferroelectrics often have very high dielectric constants, and thus are often used as the dielectric material in capacitors. They also often have unusually large nonlinear optical coefficients.
Lead titanate (PbTiO$_3$) is a prototype ferroelectric crystal$^2$. Its Curie point at 495°C marks a paraelectric cubic to ferroelectric tetragonal phase transition. At room temperature, the tetragonal $c$ axis is about 6% longer than its $a$ axis. Lead zirconate (PbZrO$_3$) is a prototype antiferroelectric crystal with a Curie point of 234°C. It transforms from the high temperature paraelectric cubic phase to an antiferroelectric orthorhombic phase with space group $Pbam$. The dipoles moments due to cation displacements in adjacent primitive cell are alternatively directed in opposite senses so that the spontaneous polarization is zero.

1.3 The Antiferroelectric to Ferroelectric Phase Transitions

Figure 1-2 illustrates typical polarization reversal for ferroelectric (FE), antiferroelectric (AFE) and field forced AFE to FE phase transition. Parameters of interest for ferroelectric material include coercive field ($E_c$), spontaneous polarization ($P_s$) and remanent polarization ($P_r$). Spontaneous polarization ($P_s$) is the polarization at maximum saturation field minus the induced contribution, remanent polarization ($P_r$) is the polarization that exists at zero field, coercive field ($E_c$) is the field required to reverse the remanent polarization back to zero. Figure 1-2(b) shows the P-E response for an AFE material when the applied electric field strength is less than the critical field required to induce the FE state. The field induced polarization in the AFE state shows a linear response similar to a linear dielectric. Figure 1-2(c) shows a field forced AFE to FE phase transition where $E_F$ and $E_A$ are the electric fields needed to induce the FE phase and to revert back to the AFE phase respectively. $P_F$ is the field induced polarization at the AFE to FE phase transition. The AFE to FE phase transition is not only the process of aligning
Figure 1-2  Polarization versus electric field characteristics for a (a) ferroelectric hysteresis loop, (b) antiferroelectric phase and (c) field forced antiferroelectric to ferroelectric phase transition.
antiparallel dipole moments along the field direction, but also a first order structural transition which involves expansion of the molar volume.

However, the electric field-induced AFE to FE phase transition in pure PbZrO$_3$ crystal can be hardly observed at room temperature because the $E_F$ is in the range of dielectric breakdown strength. As a result, dielectric breakdown occurs often. The substitution of Zr with Ti to form solid solution Pb(Zr$_x$Ti$_{1-x}$)O$_3$ can reduce $E_F$ effectively, which will be discussed in the following section.

1.4 PZT (Lead Zirconate Titanate) System

The prototype ferroelectric PbTiO$_3$ and the prototype antiferroelectric PbZrO$_3$ form complete solid solutions Pb(Zr$_x$Ti$_{1-x}$)O$_3$ (abbreviated as PZT in literature)$^{25-27}$. PZT ceramics display a perovskite ABO$_3$ structure with random B-site occupation by Zr or Ti at all phases and compositions$^{28}$. PZT material shows a marked piezoelectric effect. Since their discovery in 1950s, they have been the most widely used piezoelectric ceramics. With increasing Ti content, the solid solution changes from antiferroelectric to ferroelectric at roughly $x=0.94$.

The six structural phases in the solid solution Pb(Zr$_x$Ti$_{1-x}$)O$_3$ that have been observed at ambient pressure$^{26,27,29,30}$ are an antiferroelectric (A) phase for compositions near PbZrO$_3$, ferroelectric low-temperature (R$_{II}$) and high-temperature (R$_I$) rhombohedral phases for most Zr-rich alloys, a newly discovered monoclinic$^{31}$ (M) ferroelectric phase near 50% Zr/50% Ti composition, a tetragonal (T) ferroelectric phase for Ti-rich alloys, and a cubic (C) paraelectric phase for all compositions at sufficiently high temperature. The overall structure of PZT changes with the ratio of Ti:Zr atoms is shown in Figure 1-3, a current version of the sub-solidus pseudo-binary phase diagram$^{28,29}$. It should be noted
that in this pseudo-binary phase diagram, the continuous solid solution of PbZrO$_3$-PbTiO$_3$ maintains a perovskite structure throughout the pseudo-binary phase diagram. Furthermore, the proportion of PbO is fixed and all the A sites are occupied by Pb in the perovskite structure, while Zr and Ti only share B sites. In this system, by distorting the same high-symmetry cubic parent structure, all the phases are generated and are distinguished only by slightly lattice parameters and by the directions of the structural distortions.\textsuperscript{26,27,29,30} Grinberg \textit{et al.}\textsuperscript{32} showed that the complex phase behavior of different Zr/Ti compositions can be explained by averaging the changing distribution of Pb displacements, which depend on their local environment. One should notice that for the antiferroelectric phase, increase in Ti content decreases the E$_F$ dramatically. With only 6
at% Ti substituting the Zr on the B-site, the $E_F$ diminishes to zero and the solid solution becomes ferroelectric at room temperature.

For piezoelectric applications, the most commonly studied chemical composition is $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$. It features an extremely large dielectric constant. The increased dielectric constant, piezoelectric response and poling efficiency near $x = 0.52$ is due to the increased number of allowable domain states at the morphotropic phase boundary (MPB). At this boundary, the 6 possible domain states with $<001>$ polar vectors from the tetragonal phase and the 8 possible domain states with $<111>$ vectors from the rhombohedral phase are equally favorable energetically, thereby allows a maximum 14 possible domain states. These properties make PZT-based compounds one of the most prominent and useful electroceramics. Commercially, it is usually not used in its pure form, rather it is doped with either acceptor dopants, which create oxygen (anion) vacancies, or donor dopants, which create cation vacancies and facilitate domain wall motion in the material. In general, acceptor doping creates hard PZT while donor doping creates soft PZT\textsuperscript{33-35}. Soft PZT has a higher piezoelectric constant, but has larger losses in the material due to internal friction. In hard PZT\textsuperscript{33,34}, domain wall motion is pinned by the impurities thereby lowering the losses in the material, but at the expense of a reduced piezoelectric constant.

PZT is used to make ultrasound transducers and other sensors and actuators, as well as high-value ceramic capacitors and FRAM chips. PZT is also used in the manufacturing of ceramic resonators for reference timing in electronic circuitry.
1.5 Sn-Modified Antiferroelectric PZT System

As discussed in the previous section, antiferroelectricity is only preserved in compositions very close to PbZrO$_3$ in the PZT solid solution. For the purpose of optimizing the properties and promote the processability, most antiferroelectric ceramics are further chemically modified from PbZr$_x$Ti$_{1-x}$O$_3$ by adding Sn, and minor amount of Nb or La (usually 2 at%) $^{36-42}$. It has been widely observed that optimized properties in these ceramics are resulted from their hierarchical microstructures: the subgrain level antiferroelectric 90° domains (the checkerboard pattern) and the nanoscale incommensurate modulations within the domains $^{37,42-44}$. Increase in Ti content eventually destroys these microstructures and leads to a normal ferroelectric behavior.

The Sn modified PbZrO$_3$-PbTiO$_3$ system was first reported for piezoelectric applications $^{28,45}$ by Jaffe et al. A ternary phase diagram for PbZrO$_3$-PbTiO$_3$-PbSnO$_3$ (PZST) $^{30}$ is shown in Figure 1-4. The morphotropic phase boundary traverses the field between the morphotropic boundaries of the binary end members. There is a dissociation boundary at 70mol% PbSnO$_3$. Beyond this limit, complete solid solution occurs in the PZST system. The tetragonal antiferroelectric structures actually consist of a small number of extremely similar phases only discernible by slender differences in x-ray lines which show the multiplicity. The number of these phases is not yet accurately known. These phases were grouped as a single phase since no polymorphic inversions or dielectric discontinuities between them were detected $^{30}$.

The chemical formulae Pb$_{1-0.5x}$Nb$_x$ [(Zr$_{1-x}$Sn$_x$)$_{1-y}$Ti$_y$]$_{1-z}$O$_3$, abbreviated as PZST 100x/100y/100z, is generally used to denote different compositions in this system $^{30}$. This notation will also be used for this thesis. In Figure 1-4, the following phases were
reported: tetragonal antiferroelectric (AFE$^r_T$), orthorhombic antiferroelectric (AFE$^o_T$),
tetragonal ferroelectric (FE$^r_T$), high temperature rhombohedral ferroelectric (FE$^r_{R(HT)}$)
and low temperature rhombohedral ferroelectric (FE$^r_{R(LT)}$). By increasing Ti content, the
ferroelectric phases become stable over a wide range of compositions. As Sn content
increases, the antiferroelectric phase becomes more stable. Evidence has shown that the
substitution of Nb into perovskite structure can occur on B site and create A site
vacancies$^{46}$ and is associated with a decrease in coercive field and enhancement of the
squareness of the hysteresis loop$^{47}$. These properties are highly desirable for applications
including display and ferroelectric memory. Also, the addition of Nb tends to stabilize the
ferroelectric phases in the PZST system$^{47}$.

![Figure 1-4](image)

**Figure 1-4**  Ternary phase diagram for PbZrO$_3$- PbTiO$_3$- PbSnO$_3$ (PZST)$^{30}$
1.6 Incommensurate Modulations in Perovskite

In many solid, a local property such as electric polarization, magnetization, charge density, mass density and atomic position is modulated with a periodicity which is incommensurate to the periodicity of the underlying lattice. Such incommensurate modulations are often associated with antiferroelectric order and observed in the AFE phase. When an incommensurately modulated AFE phase transforms to FE phase, this incommensurate modulation is expected to disappear. However, there is no direct evidence to support this speculation yet.

Incommensurate modulations have been observed experimentally by transmission electron microscopy (TEM) in many perovskite ferroelectric ceramics, such as PbZrO$_3$, Pb(Zr$_{1-x}$Ti$_x$)O$_3$, Sn-modified Pb(Zr$_{1-x}$Ti$_x$)O$_3$ (PZST), La-modified Pb(Zr$_{1-x}$Ti$_x$)O$_3$ (PLZT), Pb(Co$_{1/2}$W$_{1/2}$)O$_3$, and Pb(Sc$_{1/2}$Ta$_{1/2}$)O$_3$. The incommensurate modulations are often associated with antiferroelectric order. These modulations are characterized by the satellite reflections in electron diffraction patterns and the regular fringes in image contrast. The modulation wave vector represented by the satellites is along the normal direction of those fringes, and the distance of the satellites to the fundamental reflections in reciprocal space corresponds to the spacing of the fringes in real space. The wave vector is parallel to the $<110>$ direction in most cases and the wavelength lies in the range of 5 to 20 $a$, where $a$ is the lattice parameter of the parent paraelectric structure.

Transformation of the intermediate incommensurate phase to other phases can be triggered by external stimuli, such as chemical composition and temperature. Sn- or Ti-content in PZST system and La-content in PLZT system were utilized before as
controlling variables for the phase transformation\textsuperscript{37,52,54}. In PZST system, it has been shown that decrease in Sn-content or increase in Ti-content leads to the incommensurate antiferroelectric-to-ferroelectric phase transformation. In the PLZT system, the modulation wavelength was observed to increase with Ti molar fraction\textsuperscript{37}. Utilizing temperature as the controlling variable in the study of such transformations allows \textit{in situ} TEM studies, where the evolution of the satellite reflections can be directly observed\textsuperscript{42,44,51,52}. The hot-stage \textit{in situ} TEM observations revealed that the modulation wavelength increases continuously with increasing temperature. Based on these studies, Viehland et al.\textsuperscript{37} suggested that the competing ferroelectric and antiferroelectric ordering in these perovskites are responsible for the presence of incommensurate modulations. However, unambiguous evidence has yet to be found.

The modulation wave vector is parallel to the $<110>$ direction in PbZrO$_3$, PZST, and PLZT, and the wavelength lies in the range of 5~20$\text{a}$, where $a$ is the lattice parameter for the parent paraelectric structure. In general, the satellites can be expressed as $h\hat{a}^* + k\hat{b}^* + l\hat{c}^* \pm \frac{1}{n} \{h\hat{a}^* + k\hat{b}^*\}$, where $n$ is a non-integer number. In literature, they are also expressed as $\frac{1}{n} \{110\}$ for the sake of simplicity. However, this wave vector seems to be different in un-doped PZT\textsuperscript{50,59}.

One well accepted phenomenon in PZT-based oxides is that the incommensurate phase would not be observed to develop until the oxide is cooled below the Curie temperature, strongly suggesting that the incommensurate structure resides in the polar order. Currently, there is no general agreement on the modulation mechanism. It could result from either octahedral tilts or antiparallel cation displacements, or both. It is also
suggested that the incommensurate modulation may be due to elastic strain\textsuperscript{37,52}. The modulation is believed to consist of regular arrays of antiphase boundaries separating the octahedral tilts or cation displacements.

1.6.1 Effect of Chemical Compositions

In PbZrO\textsubscript{3}, the incommensurate phase manifests itself as \( \frac{1}{n} \{110\} \) satellite spots and modulation fringes with a periodicity of 1.8nm within a narrow temperature range of \( \sim 225 - 230^\circ C \textsuperscript{48} \). When doped with Ti to form Pb(Zr\textsubscript{1-x}Ti\textsubscript{x})O\textsubscript{3} solid solution, the temperature range for the presence of the incommensurate phase expands to the whole high-temperature ferroelectric rhombohedral phase (F\textsubscript{R} HT) up to x = 0.10. The wavelength of the modulation increases with x and the satellites move closer to the fundamental reflections\textsuperscript{37}. The modulation can be stabilized to room temperature by a field-on cooling of Pb(Zr\textsubscript{0.95}Ti\textsubscript{0.05})O\textsubscript{3} composition. A long wavelength (about 8 nm) is measured in this field-stabilized incommensurate phase. At the same time, the wave vector seems to deviate from the \(<110>\) direction\textsuperscript{50,59}.

PZT oxides are often doped with Sn, Nb, or La to broaden the paraelectric to ferroelectric phase transition and reduce the free energy difference between ferroelectric and antiferroelectric states\textsuperscript{36,60,61}. The most widely used formula for Sn-doping is Pb\textsubscript{0.99}Nb\textsubscript{0.02}[Zr\textsubscript{1-x}Sn\textsubscript{x}]\textsubscript{1-y}Ti\textsubscript{y}O\textsubscript{3}, denoted in literature as PZST 100x/100y/2. In these oxides, satellites appear along the \(<110>\) direction\textsuperscript{51}. In a PZST 45/100y/2 system, as Ti increases, the room temperature phase sequence is commensurate (antiferroelectric) \( \rightarrow \) incommensurate \( \rightarrow \) commensurate (ferroelectric)\textsuperscript{42}. 
The incommensurate phase appears at room temperature for $0.03<y<0.08$, as seen in the phase diagram in Figure 1-5. As Ti content increases, satellites get closer to fundamental reflections, indicating an increase in modulation wavelength.

La-doping typically follows the formula of $\text{Pb}_{1-x}\text{La}_x(\text{Zr}^{1-y}\text{Ti}_y)_{1-x/4}\text{O}_3$ with B-site vacancies and denoted as PLZT 100x/100(1-y)/100y $^{62}$. Incommensurate modulations with $\frac{1}{n}\{110\}$ satellite spots were observed in oxides with high Zr-content base-PZT compositions. Increasing La-content decreases modulation wavelength while increasing the Ti-content in the base composition increases the modulation wavelength, as depicted in Figure 1-6.
These observations tend to support the theory that the strong coupling between ferroelectric and antiferroelectric ordering is responsible for the presence of the incommensurate phase. The antiferroelectric state can be considered as a modulated ferroelectric structure with a wave vector of $\frac{1}{4}\{110\}$ while the ferroelectric state can be thought of as modulated with an infinitively long wavelength. The modulation wavelength of the incommensurate phase would lie in between these two limits. PbZrO$_3$, the prototypical antiferroelectric perovskite, hence sets the lower limit of the modulation wavelength in PZT system, which is about 1.1nm. The effect of compositions on the modulation wavelength in both PZST and PLZT oxides consistently show that increasing the content in a manner that favors the ferroelectric state leads to the increase in modulation wavelength, which favors antiferroelectric order leads to the decrease in modulation wavelength.
1.6.2 Effect of Temperature

The general pattern for the phase transformation in a system that contains an intermediate incommensurate phase is illustrated in Figure 1-7. At temperature $T_{ic}$, a lock-in transition occurs and the incommensurate structure turns into a commensurate structure$^{7,63}$. However, limited experimental observations have shown that this pattern may not apply to perovskite ferroelectrics. In PZT-based oxides, there is an additional commensurately modulated phase above temperature $T_i$. In addition, the lock-in transition, which occurs over a wide temperature range, is not an abrupt transition$^{51,52}$. In the complex perovskite $\text{Pb(Mg}_{1/2}\text{Te}_{1/2})\text{O}_3$, the incommensurate phase was observed to persist down at least to 6K$^{64}$. Therefore, the low temperature commensurate phase appears to be missing in this compound.

![Figure 1-7](image)

**Figure 1-7** General pattern for incommensurate phase transition.

The sequence of thermally induced phase transition in the PZST 42/4/2 was investigated by Xu et al.$^{51,52}$ with TEM temperature varying stages. Their observations indicate that the incommensurate to commensurate phase transition occurs over a wide temperature range between –60°C and –150°C.
The temperature dependence of the modulation wavelength in PZT oxides displays an opposite trend to theoretical predictions. As shown in Figure 1-8, the wavelength increases with increasing temperature. The model of competing ferroelectric and antiferroelectric ordering can lend itself to the interpretation of the abnormal temperature dependence when a strong assumption is made. This assumption is that the ferroelectric state is enhanced at high temperatures in all PZT oxides. However, the only experimental evidence for such enhancement is the appearance of $\frac{1}{2}\{110\}$ superlattice reflections. Stronger direct evidence is needed to justify this assumption.

### 1.6.3 Effect of Electric Fields

The variables used in previous studies for the incommensurate phase transition are chemical composition and temperature. Changing the chemical composition introduces
complications such as compositional heterogeneities, while increasing temperature may favor either ferroelectric or antiferroelectric ordering. It is reasonable to ascertain that for these electrically active solids, the electric field is a much “cleaner,” more direct driving force for the incommensurate phase transition. Electric fields are known to enhance ferroelectric ordering and can transform the antiferroelectric phase into the ferroelectric phase\textsuperscript{60-62}. The effect of electric fields on the incommensurate phase in perovskite ferroelectrics has been utilized in Watanabe and Koyama’s work in the Pb(Zr\textsubscript{0.95}Ti\textsubscript{0.05})O\textsubscript{3} composition, where an electric field of 500V/cm was observed to stabilize the incommensurate phase down to room temperature\textsuperscript{59}. However, an electric field-driven incommensurate phase transition study has never been conducted.

1.7 Materials System for This Thesis

Electric field-induced antiferroelectric-to-ferroelectric phase transformation forms the physics basis for the applications of the PbZrO\textsubscript{3}-based antiferroelectric ceramics. The most intensively studied antiferroelectric ceramics are chemically modified PbZrO\textsubscript{3} with Sn, Ti, and Nb or La\textsuperscript{36-42}.

The material system studied in this thesis is marked in the ternary phase diagram for PbZrO\textsubscript{3}-PbTiO\textsubscript{3}-PbSnO\textsubscript{3} shown in Figure 1-9. Within this composition field there are three ferroelectric and two antiferroelectric phases. Since our focus is on the antiferroelectric to ferroelectric phase transition, our materials are selected close to the AFE and FE phase boundaries with the formula Pb\textsubscript{0.99}Nb\textsubscript{0.02}[(Zr\textsubscript{0.57}Sn\textsubscript{0.43})\textsubscript{1-y}Ti\textsubscript{y}]\textsubscript{0.98}O\textsubscript{3} (abbreviated as PZST 43/100y/2). They lie on the line crossing the tetragonal antiferroelectric (AFE\textsubscript{T}), orthorhombic antiferroelectric (AFE\textsubscript{o}) and low temperature rhombohedral ferroelectric (FE\textsubscript{R}(LT)) phases. For example, PZST 43/3/2 sits in the AFE\textsubscript{o}. 
region, PZST 43/12/2 sits in the $\text{FE}_R(\text{LT})$ region and PZST 43/7/2 sits in the $\text{AFE}_T$ field. The serials of $y=0.03\sim0.12$ for PZST 43/100y/2 are prepared in order to study the AFE to FE phase transition.

### 1.8 Key Experimental Approach

In order to understand the antiferroelectric to ferroelectric phase transition under grain size level, structural information must be acquired together with the instrumental capability of keeping track of certain grains. Based on these criteria, transmission electron microscopy (TEM) and micro-Raman microscopy are ideal approaches.

![Ternary phase diagram for PbZrO$_3$-PbTiO$_3$-PbSnO$_3$ (PZST)]
1.8.1 Transmission Electron Microscopy

The transformation of the incommensurate modulation in PbZrO$_3$-based antiferroelectrics has been investigated by changing in chemical compositions and temperatures. It is still reasonable to argue that electric field is a much “cleaner,” more unidirectional driving force for the incommensurate phase transformation in these electrically active solids. Electric fields are known to enhance ferroelectric ordering and transform antiferroelectric phases into ferroelectric ones$^{30,38,60,65}$. On the other hand, electron diffraction, to the authors’ best knowledge, is the only technique employed so far to reveal the incommensurate modulation in these ceramics. Therefore, an in situ TEM technique capable of delivering high electric fields to TEM specimens while imaging would be ideal for the study of incommensurate modulation evolution during electric field-induced antiferroelectric to ferroelectric phase transition$^{66-68}$.

In order to interpret the information obtained by TEM, close attention are paid to the fine features in diffraction patterns such as superlattice reflections, diffuse scattering and streaks. In an ordered material which has a larger unit cell, superlattice reflections$^{30,69}$ can be observed since the unit cell in reciprocal-space in smaller. The deviations from a perfect order in a crystal can cause diffuse scattering located outside Bragg reflections. The scattered intensity of a perfect crystal would exclusively consist of discrete sets of Bragg reflections, but at least thermal motion brings a certain amount of disorder to an ideally perfect crystal. In practice, atomic displacements or atom replacements are characteristics in most crystals$^{30,69}$.

At the same time, lattice strain and the shape of crystal defects can give rise to streaks since they modify the shape of reciprocal lattice points$^{30,70}$. As the electric field
applied to a specimen increases, streaking is expected since the electric field will induce lattice strain.

1.8.2 Raman Spectroscopy

Raman scattering is a form of molecular spectroscopy, it is used to obtain information on molecular structures and compositions of organic and inorganic materials from vibrational transitions\(^\text{15,71-78}\).

When an intense beam of monochromatic light impinges upon a material, it can be scattered in all directions with the frequency same as that of the original light \(\nu_0\) which is known as Rayleigh scattering. Scattering also occurs with significantly lower intensities with frequencies higher or lower than \(\nu_0\) which is known as Raman scattering\(^\text{79}\). The differences between incident and scattered radiation frequencies are equal to the vibrational frequencies of the materials. A Raman scattering is defined as Stokes Raman scattering\(^\text{79}\) if the molecule gains vibrational energy while an anti-Stokes Raman scattering\(^\text{79}\) is so defined when the molecule loses vibrational energy starting from an elevated vibrational level.

Raman scattering was proved a powerful tool in the study of structural phase transitions which are usually induced by changing one of the thermodynamic variables such as temperature, pressure, etc\(^\text{79}\). Usually, when a lattice contracts the phonon frequencies increase slowly, the relative changes in frequency are small. A not so small deviation often indicates a phase transition. If a Raman-active mode has the proper symmetry to induce structural phase transition, then this mode is called a soft mode\(^\text{80,81}\).

There is growing interest in solid solution systems that display structural
ferroelectric phase transitions as a function of composition\(^{80,81}\). For the sake of their device applications, Raman study on Pb(ZrxTi\(_{1-x}\))O\(_3\) system started in the seventies in the last century and much focus has been set on low-frequency vibrational modes\(^{15,71-78}\). Currently, with the help of microscope accessories, Raman spectra can be obtained on the area of interest of the order of 5 \(\mu\text{m}\) in size.

Raman spectroscopy has been extensively used in the study of the phase transition in ferroelectric oxides. The subtle changes in bond distance, bond angle and crystal symmetry during phase transitions can be detected by the change in the mode frequency and the presence of different modes. In most PbZrO\(_3\)-based ceramics, the presence of many modes of low frequency (less than 200\(\text{cm}^{-1}\)) is often indicative of the antiferroelectric order. These intense low frequency modes were assigned to the bonds between Pb cation and other ions in the unit cell. Although the normal Raman modes can be predicted from crystal symmetry, the actual frequency and intensity of each mode are strongly dependent on chemical composition and processing conditions. El-Harrad et al. have studied the phase transitions in Pb(Zr\(_{0.95}\)Ti\(_{0.05}\))O\(_3\) ceramics with Raman spectroscopy and found that 1wt\% doping of La\(_2\)O\(_3\) does not lead to any change in the spectra but 1 wt\% Nb\(_2\)O\(_5\) doping changes the Raman spectra significantly.

### 1.9 Applications of Antiferroelectric to Ferroelectric Transition

High energy DC capacitors use antiferroelectric ceramics with a high switching field. This allows for greatly increased energy storage in pulsed power and transient voltage suppression applications. Antiferroelectric capacitors bring the benefit of higher volumetric efficiency than linear paraelectric and ferroelectric dielectrics. Also,
Nonlinear antiferroelectric $\leftrightarrow$ ferroelectric phase change greatly increases energy storage.

Both antiferroelectric and ferroelectric ceramics were developed based primarily on considerations of their electrical responses, and consequently, many of them display rather poor mechanical properties, such as low fracture toughness and high susceptibility to slow crack growth$^{82-85}$. Their mechanical behavior is always of major concern because their electric and mechanical responses are intimately coupled. When driven hard repeatedly under cyclic electric loading over long periods, these ceramics may accumulate enough mechanical damage to cause subcritical crack growth or catastrophic failure$^{86-90}$. On the other hand, development of crack-like flaws under mechanical loading may generate severe local field concentrations which may result in serious degradation of their electric performance$^{91}$.

During the fracture process of ferroelectric ceramics, a phenomenon called “ferroelectric toughening” has been observed in a set of experiments comparing the fracture toughness of the ferroelectric phase (below Curie temperature) and the paraelectric phase (above Curie temperature)$^{92-94}$. The ferroelectric domains in the ferroelectric phase are ferroelastic domains at the same time and they respond to both electrical and mechanical loadings. As a consequence of domain switching, the measured fracture toughness at ferroelectric state was almost doubled as that at paraelectric state$^{93}$. However, to the authors’ best knowledge, toughening effect in antiferroelectric ceramics has not yet been reported. It has been noticed previously that the electric field-induced antiferroelectric-to-ferroelectric phase transition accompanies a volume expansion on the order of 1%$^{60,95}$. Inspired by the phase transition toughening mechanism in ZrO$_2$-based
engineering ceramics\textsuperscript{96}, we suggest that antiferroelectric ceramics may display fracture resistance superior to ferroelectric ceramics due to contributions from both the volume expansion at the phase transition and the ferroelastic domain switching in the induced ferroelectric phase. We propose that the antiferroelectric to ferroelectric phase transition may be utilized to toughen electroceramics.

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2. *In situ* Transmission Electron Microscopy Study of the Electric Field-induced Transformation of Incommensurate Modulations in a Sn-modified Lead Zirconate Titanate Ceramic


Hui He, and Xiaoli Tan*

2.1 Abstract

Electric field-induced transformation of incommensurate modulations in a Sn-modified lead zirconate titanate ceramic was investigated with an electric field *in situ* transmission electron microscopy (TEM) technique. It is found that the spacing between the $\frac{1}{x}$ satellite spots and the fundamental reflections do not change with external electric field, indicating that the modulation wavelength keeps a constant under applied field. The intensity of these satellites starts to decrease when the field level reaches a critical value. Further increase in the field strength eventually leads to the complete disappearance of the satellite reflections. In addition, the $\frac{1}{2}$t-type superlattice reflections showed no response to electrical stimuli.
2.2 Introduction

Incommensurate modulations have been observed experimentally with TEM in many perovskite ferroelectric ceramics, such as PbZrO$_3$, Pb(Zr$_{1-x}$Ti$_x$)O$_3$, Sn-modified Pb(Zr$_{1-x}$Ti$_x$)O$_3$ (PZST), La-modified Pb(Zr$_{1-x}$Ti$_x$)O$_3$ (PLZT), Pb(Co$_{1/2}$W$_{1/2}$)O$_3$, and Pb(Sc$_{1/2}$Ta$_{1/2}$)O$_3$. They are characterized by the satellite reflections in electron diffraction patterns and the regular fringes in image contrast. The modulation wave vector represented by the satellites is along the normal direction of those fringes, and the distance of the satellites to the fundamental reflections in reciprocal space corresponds to the spacing of the fringes in real space. The wave vector is parallel to the <110> direction in most cases and the wavelength lies in the range of 5 ~ 20$\lambda$, where $\lambda$ is the lattice parameter for the parent paraelectric structure.

Transformation of the intermediate incommensurate phase to other phases can be triggered by external stimuli, such as chemical composition and temperature. Sn- or Ti-content in the PZST system and La-content in the PLZT system were utilized before as controlling variables for the phase transformation. In the PZST system, it has been shown that decrease in Sn-content or increase in Ti-content leads to the incommensurate antiferroelectric-to-ferroelectric phase transformation. In the PLZT system, the modulation wavelength was observed to increase with Ti molar fraction. Utilizing temperature as the controlled variable in the study of such transformations allows in situ TEM studies, where the evolution of the satellite reflections can be directly observed. The hot-stage in situ TEM observations revealed that the modulation wavelength increases continuously with increasing temperature. Based on these studies, Viehland et al. suggested that the competing ferroelectric and antiferroelectric ordering in these
perovskites are responsible for the presence of incommensurate modulations. However, unambiguous evidence has yet to be found. In this letter, we report the study of the incommensurate phase transformation triggered by controlled electric fields. The evolution of the satellite spots driven by external electrical stimuli is recorded for the first time.

2.3 Experimental Procedure

A hybrid coprecipitation method similar to that used by Yang and Payne\textsuperscript{14} was followed to prepare the ceramic powder with a chemical formula Pb_{0.99}Nb_{0.02}[(Zr_{0.55}Sn_{0.45})_{0.94}Ti_{0.06}]_{0.98}O_3 (abbreviated as PZST 45/6/2). Pressed cylinders, 15 mm in diameter by 20 mm thick, were formed by cold-isostatic pressing at 350 MPa. The preformed pellets were then hot pressed in an Al_2O_3 die at 1150°C for 2 hours in air. Thin slices from the hot pressed piece were annealed at 1300°C for 2 hours in an atmosphere containing excess PbO. The annealed slices were then ground, polished and electroded. Dielectric characterization was performed with an LCR meter (HP-4284A, Hewlett-Packard) at frequency of 1 kHz in conjunction with an environmental chamber. A heating rate of 3°C/minute was used during measurement. Electric field-induced polarizations were recorded with a standardized ferroelectric test system (RT-66A, Radiant technologies).

TEM specimens were prepared from ultrasonically cut 3-mm diameter discs. The thickness of these discs was reduced to ~150 m by grinding and polishing. The center portion was further thinned to ~10 m by dimpling. Then the dimpled specimens were annealed at 300°C for 30 minutes to minimize residual stresses. An argon ion mill was used for further thinning until final perforation occurred in the center. Gold electrodes
with spacing of 250 μm were evaporated to the TEM specimens and platinum wires were used to connect the electrodes to the electrical contacts on the TEM specimen holder. Figure 2-1 shows the schematic diagram of the TEM specimen configuration. Details of the electric field in situ TEM technique can be found elsewhere.\textsuperscript{15-18} TEM studies were carried out on a Phillips CM-30 microscopy operating at 300 kV.

2.4 Results

Temperature dependence of the dielectric permittivity of PZST 45/6/2 is shown in Figure 2-2. The dielectric constant peaks with a value of 920 at the temperature of 167°C. Electric field-induced polarization measurement showed double hysteresis loops (Figure 2-3), indicating an electric field-induced antiferroelectric-to-ferroelectric phase transformation at room temperature. These results are consistent with previous observations from other researchers.\textsuperscript{5-7}

In order to determine the field level needed for the in situ TEM study and assess the sample geometry effect on the field-induced antiferroelectric-to-ferroelectric phase transformation, a dimpled and annealed 3-mm diameter disc specimen was tested for the hysteresis measurement and the result is also plotted in Figure 2-3. Compared to the conventional circular plate sample with electric field applied along the thickness direction, the TEM-specimen-like disc shows a more gradual phase transformation with much broader loops. Furthermore, the backward switch from the induced ferroelectric phase to the antiferroelectric phase is sluggish and a non-zero remnant polarization is detected.

\textit{In situ} TEM studies were carried out on a disc specimen with a central perforation. Actual electric field in the specimen is disturbed (intensified in some areas while diluted in others) by the presence of the perforation. Electron transparent areas that are subjected
to intensified electric fields in the specimen were located in the TEM and one grain within this area was focused for the successive detailed \textit{in situ} study. For an ideal circular perforation, the intensification ratio is $2.1^9$ The local electric field strength in this grain was thus estimated by doubling the nominal field strength.

The evolution of the satellite spots in a $<112>$-zone axis selected area diffraction pattern under static electric fields is shown in Figure 2-4. Initially, this grain displays one set of incommensurate modulations. In the electron diffraction pattern, one set of the $1 \over x \{110\}$ satellite spots is evident, as shown in Figure 2-4(a). No detectable changes to these satellite spots were observed with applied static electric field up to 40 kV/cm. At the field level of 48 kV/cm, these satellites become weaker in their intensity (Figure 2-4b). This field level lies in the close vicinity of the $E_F$ (the critical field to trigger the antiferroelectric-to-ferroelectric transformation) measured from the bulk sample. However, careful measurement indicates that the modulation wavelength does not change with increasing field strength. When the field strength reached 56 kV/cm, most satellite spots disappeared. As shown in Figure 2-4(c), only very weak satellites can be barely seen surrounding the three strong fundamental reflections in the left of this micrograph. Then the field strength was reduced to 40 kV/cm. The satellites reappeared, with the strongest ones sitting in the upper-left corner of Figure 2-4(d). When the field level was raised again to 56 kV/cm (Figure 2-4e), all the satellite spots completely disappeared, indicating the complete transformation to the ferroelectric phase. After the electric field was completely removed, no satellite spots were observed to reappear, as shown in Figure 2-4(f). The observation confirms the temporal effect of the electric field-induced transformation noticed by other researchers in a similar composition.$^{20}$
2.5 Discussion

It has been suggested that in PZT-based ferroelectric perovskites, the presence of incommensurate modulations in the antiferroelectric phase is a result of the competition between the ferroelectric and antiferroelectric ordering. The continuous increase in the modulation wavelength with increasing temperature is interpreted that there exists a ferroelectric phase within a narrow temperature range just below the paraelectric transition temperature. When temperature is raised close to this temperature range the ferroelectric ordering is enhanced. The modulation wavelength is thus increased. However, our observations on the electric field-induced transformation of the incommensurate modulation show a different scenario. The intensity of the satellite reflections, rather than the modulation wavelength, changes with the applied electric field strength. The wavelength stays constant at a value of 2.3 nm. Since external electric field is known to enhance the ferroelectric ordering, we suggest that the electric field-induced antiferroelectric (incommensurate)-to-ferroelectric transformation proceeds as following. When the applied electric field reaches $E_F$, the phase transformation is initiated in some areas of the grain. The transformation is an abrupt one and no intermediate changes in the modulation wavelength takes place. With increasing electric field strength, the fraction of the transformed area increases and the intensity of the satellite diffractions gets weaker. Obviously a mechanism involving the nucleation of ferroelectric phase and the motion of the interphase interface controls the transformation process. Further studies will be focused on these issues.

In addition to the $\frac{1}{x}[110]$ satellite spots, $\frac{1}{2}[111]$-type superlattice reflections were also present in the $<112>$-axis diffraction pattern, as labeled in Figure 2-4(e). The
structural origin for these superlattice reflections is still under debate.\textsuperscript{2,5-7,9,21} However, the present \textit{in situ} TEM study provides valuable insight into the physics mechanism for the presence of these superreflections. It is clear in Figure 2-4 that the intensity of the $\frac{1}{2}\{111\}$ spots does not change with the applied electric field, implying a mechanism that is quite rigid to external disturbance. This seems to favor the oxygen octohedra tilting model.\textsuperscript{21}

2.6 Conclusion

To summarize, \textit{in situ} TEM technique was successfully applied to the study of the electric field-induced antiferroelectric-to-ferroelectric phase transformation in a PZT-based ceramic. Upon application of external electric fields, the wavelength of the incommensurate modulation in the antiferroelectric phase showed no change but the intensity of the satellite reflections decreased when the field exceeds a critical value. This critical strength matches closely to the $E_F$ measured in the bulk sample.

2.7 Acknowledgements

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2.8 Figure List

Figure 2-1  Schematic diagram of specimens for the electric field in situ TEM study.

Figure 2-2  Temperature dependence of dielectric constant in the PZST 45/6/2 ceramic.

Figure 2-3  Electric field-induced polarization measurement in a bulk circular plate sample and an unperforated TEM specimen.

Figure 2-4  Evolution of the <112> selected area diffraction pattern under applied electric fields in PZST 45/6/2. (a) Original state, (b) 48 kV/cm, (c) 56 kV/cm, (d) 40 kV/cm, (e) 56 kV/cm, (f) field removed.
Figure 2-1: Schematic diagram of specimens for the electric field *in situ* TEM study.

Figure 2-2: Temperature dependence of dielectric constant in the PZST 45/6/2 ceramic.
Figure 2-3: Electric field-induced polarization measurement in a bulk circular plate sample and an unperforated TEM specimen.
Figure 2-4: Evolution of the <112> selected area diffraction pattern under applied electric fields in PZST 45/6/2. (a) Original state, (b) 48 kV/cm, (c) 56 kV/cm, (d) 40 kV/cm, (e) 56 kV/cm, (f) field removed.
2.9 Reference


3. Electric Field-induced Transformation of Incommensurate Modulations in Antiferroelectric Pb$_{0.99}$Nb$_{0.02}$[(Zr$_{1-x}$Sn$_x$)$_{1-y}$Ti$_y$]O$_3$


H. He, and X. Tan*

3.1 Abstract

Most antiferroelectric ceramics are modified from the prototype PbZrO$_3$ by adding Sn and Ti in conjunction with small amount of Nb or La to optimize their properties. These modifiers introduce unique nanoscale structural feature to the ceramics in the format of incommensurate modulations. It was shown previously that the modulation is strongly responsive to a change in chemical composition or temperature. However, its response to an electric field, the driving force in real applications, has not been explored before. In the present work the dynamic evolution of the incommensurate modulation during the electric field-induced antiferroelectric-to-ferroelectric transformation was observed with an in situ transmission electron microscopy (TEM) technique. The results indicate that the incommensurate modulation exists as a transverse Pb-cation displacement wave. The wavelength was found to be quite stable against external electrical stimuli, in sharp contrast to the dramatic change under thermal stimuli reported previously. It is suggested that the appeared incommensurate modulation is an average effect of a mixture of two commensurate modulations. The electric field-induced antiferroelectric-to-ferroelectric transformation proceeds with aligning the Pb-cation displacements, which resembles the process of 90° reorientation and 180° reversal in normal ferroelectrics.
3.2 Introduction

In many solids a local property, such as electric polarization, magnetization, charge density, mass density, and atomic position, is modulated with a periodicity $q_I$ which is incommensurate to the periodicity $q_p$ of the underlying lattice.\textsuperscript{1,2} Such incommensurate modulations have been observed in PbZrO$_3$ and PbZrO$_3$-based ferroelectric and antiferroelectric perovskite, using the selected area electron diffraction (SAED) technique in transmission electron microscopy (TEM).\textsuperscript{3-17} Based on the prominent effects of chemical composition and temperature on the modulation wavelength, it has been suggested that frustration from the competing ferroelectric ordering and antiferroelectric ordering is responsible for the presence of the incommensurate structure.\textsuperscript{9} However, the exact cause of the incommensurate phase in these oxides is still under debate. Several mechanisms have been offered so far for the structural mechanism, including Pb-cation displacement, O-octahedron tilting, lattice strain, and vacancy ordering.\textsuperscript{3-17} One well accepted phenomenon in these polar oxides is that the incommensurate phase would not be observed to develop until the solid is cooled below the Curie temperature, strongly suggesting that the incommensurate structure resides in the polar order. The presence of incommensurate modulations in ferroelectric perovskite is highly unique because cation displacement is coupled with electric polarization in these ceramics.
The PbZrO\textsubscript{3}-based antiferroelectrics are also of technological importance due to their wide applications in microelectromechanical systems and energy storage devices\textsuperscript{18-21}. The electric fielded-induced antiferroelectric-to-ferroelectric phase transformation forms the physics basis for these applications. However, the transformation requires a so strong electric field in the prototype antiferroelectric PbZrO\textsubscript{3} that dielectric breakdown occurs instead\textsuperscript{22,23}. Therefore, most antiferroelectric ceramics are chemically modified by adding Sn, Ti, and Nb or La to reduce the critical field and optimize the properties\textsuperscript{3-21}. It is widely believed that the reduction in the critical field traces its origins to the hierarchical microstructures: the subgrain level antiferroelectric 90° domains (the checkerboard pattern) and the nanoscale incommensurate modulations within the domains\textsuperscript{4}. Presumably the modulation transforms into a commensurate one during the field-induced antiferroelectric-to-ferroelectric phase transformation. However, this has yet to be confirmed experimentally. Furthermore, a structure model for the incommensurate modulation in these oxides is still lacking and the details of the structure of the 90° domain wall in modulated antiferroelectrics have not been revealed so far\textsuperscript{24}.

The transformation of the incommensurate modulation in PbZrO\textsubscript{3}-based antiferroelectrics has been investigated by changing in chemical compositions and temperatures. It is still reasonable to argue that electric field is a much “cleaner,” more unidirectional driving force for the incommensurate phase transformation in these electrically active solids. Electric fields are known to enhance ferroelectric ordering and transform antiferroelectric phases into ferroelectric ones\textsuperscript{18-21}. On the other hand, electron diffraction, to the authors’ best knowledge, is the only technique employed so far to reveal the incommensurate modulation in these ceramics. Therefore, an in situ TEM
technique capable of delivering high electric fields to TEM specimens while imaging would be ideal for the study of such transformation.\textsuperscript{25-27} In the present work, we report detailed information obtained from such \textit{in situ} TEM experiments on the evolution of incommensurate modulations. We then propose a structure model for the incommensurate modulation and the associated antiferroelectric 90° domain wall.

### 3.3 Experimental Procedure

Hot pressing after calcination was used to prepare the antiferroelectric ceramic. Raw powders with purity better than 99.9\% of PbO, Nb$_2$O$_5$, ZrO$_2$, SnO$_2$, and TiO$_2$ were batched according to the chemical formula Pb$_{0.99}$Nb$_{0.02}$[(Zr$_{0.58}$Sn$_{0.42}$)$_{0.955}$Ti$_{0.045}$]$^{0.98}$O$_3$ (abbreviated as PZST 42/4.5/2). Isopropyl alcohol was added to the mixed powders and the slurry was then milled in a plastic bottle with zirconia media on a vibratory mill for 6 hours. The slurry was dried in an oven at 150°C for 24 hours. After drying, the powders were calcined at 860°C for 4 hours in a covered alumina crucible. The calcined powder was then milled again for 6 hours. After drying, pressed cylinders, 15 mm in diameter by 20 mm high, were formed by cold-isostatic pressing at 350 MPa. The preformed pellets were then hot pressed in an Al$_2$O$_3$ die at 1100°C for 2 hours in air. Thin slices from the hot pressed piece were annealed at 1300°C for 6 hours in an atmosphere containing excess PbO. After removal of surface layers by grinding, the annealed slices were polished and electroded. Dielectric characterization was performed with an LCR meter (HP-4284A, Hewlett-Packard) at frequency of 1 kHz in conjunction with an environmental chamber. A heating rate of 3°C/minute was used during measurement. Electric field-induced polarization was recorded with a standardized ferroelectric test
After electrical measurements, disks of 3-mm in diameter were ultrasonically cut from the specimens. The thickness of the disks was reduced to about 150 μm by mechanical grinding and polishing. The center portion was further thinned to around 10 μm by mechanical dimpling. Then the specimens were annealed at 250°C for 30 minutes to minimize residual stresses. An argon ion mill was used for the final thinning until perforation occurred in the center. Gold electrodes with spacing of 250 μm were evaporated to the TEM specimens and platinum wires were used to connect the electrodes to the electrical contacts on a special double-tilt TEM holder (Gatan, Inc.). Fig.1 shows the schematic diagram of the TEM specimen geometry. Details of the electric field in situ TEM technique can be found elsewhere.25-27 TEM studies were carried out on a Phillips CM-30 microscope operating at 300 kV.

It should be noted that the presence of the central perforation disturbs the electric field between the two half-circle-shaped electrodes. In this study, observations were made on grains located within the two dark areas shown in Figure 3-1. For an ideal circular perforation, it was shown that the actual field at these two sites preserves the direction of the nominal field and its magnitude is intensified by a factor of two.28 The nominal field equals to the applied voltage divided by the gap spacing. In this article, the value of the electric field strength refers to the actual field at these two sites.
3.4 Results

3.4.1 Average Structure and Electrical Properties

X-ray diffraction was used to determine the average crystal structure of the annealed slices and the spectrum is show in Figure 3-2. The ceramic takes a pseudo-tetragonal structure with lattice parameters of $a=b=4.116\text{ Å}$ and $c=4.090\text{ Å}$. In this study, we adopt this pseudo-tetragonal structure for our discussion, even though there is dispute about the fine structure of these ceramics.\textsuperscript{13-15,23,24}

Temperature dependence of the dielectric permittivity of PZST 42/4.5/2 is shown in Figure 3-3. One distinct feature in the dielectric response is the existence of a dielectric plateau region between $134^\circ \text{C}$ and $180^\circ \text{C}$. The dielectric constant peaks with a value of 1394 at the temperature of $180^\circ \text{C}$. Two secondary dielectric anomalies are also noticed in this composition. One is at $134^\circ \text{C}$ and the other is around $-34^\circ \text{C}$. Based on previous studies on ceramics with similar compositions,\textsuperscript{13} the PZST 42/4.5/2 ceramic is paraelectric with cubic structure at temperatures above $180^\circ \text{C}$, antiferroelectric with incommensurate modulations between $-34^\circ \text{C}$ and $134^\circ \text{C}$, antiferroelectric with commensurate modulations below $-34^\circ \text{C}$. The ceramic is in a multicell cubic state in the plateau region from $134^\circ \text{C}$ to $180^\circ \text{C}$. The multicell cubic region was previously attributed to the disruption of the paraelectric-antiferroelectric transformation by Sn doping.\textsuperscript{30}

Electric field-induced antiferroelectric-to-ferroelectric phase transformation is revealed by the polarization measurement. A circular disk specimen with a diameter about 12 mm and a thickness about 300 μm was used. The electric field was applied along the thickness direction at about 4 Hz. The characteristic double hysteresis loops are
shown in Figure 3-4 with the dashed curve labeled as “Bulk”. It is evident that the antiferroelectric phase transforms to a ferroelectric phase at a critical electric field about 50 kV/cm (it is referred to as $E_F$ in literature), and the reverse transformation occurs when the field is lowered down to 38 kV/cm (it is referred to as $E_A$ in literature). Both transformations are abrupt and take place within a narrow field strength range.

In order to determine the voltage needed for the \textit{in situ} TEM study and assess the sample geometry effect on the field-induced antiferroelectric-to-ferroelectric phase transformation, a dimpled and annealed 3-mm diameter disc TEM specimen (not perforated) was also tested. This was a TEM specimen prior to the argon ion mill and was electroded in the configuration shown in Figure 3-1. Such electrode configuration produces an in-plane electric field between the two half-circle electrodes. The result is plotted in Figure 3-4 with the solid line labeled as “TEM”. The voltage applied was normalized by the gap spacing, 250 μm. Compared to the bulk circular plate sample with electric field along the thickness direction, the TEM-specimen-like disk shows a more gradual phase transformation starting at a higher $E_F$ about 70 kV/cm. The difference in the phase transformation behavior of the two types of specimen may arise from the different geometries, including the electrode geometry and the thickness difference. For the TEM-specimen-like disk, the field was applied to a thickness-varying portion, with the thinnest part around 10 μm, comparable to the grain diameter in the material.

\subsection*{3.4.2 The Incommensurate Modulation}

Conventional TEM examination reveals that the antiferroelectric PZST 42/4.5/2 ceramic displays hierarchical microstructural features, as shown in Figure 3-5. The characteristic checkerboard patterns of antiferroelectric 90° domains were found in the
majority of the grains, as shown in Figure 3-5(a) where the electron beam was along the [001] direction. The 90° domain walls roughly follow the (100) or (010) plane. Small segments were also found to be parallel to the 60° plane.

Close up examination of individual 90° domains along [001] zone axis reveals the incommensurate modulation stripes along 60 planes and selected area diffraction shows the corresponding satellite spots surrounding fundamental reflections (Figure 3-5b). In general, the satellite reflections in these modified antiferroelectric ceramics can be expressed as \( ha^* + kb^* + lc^* \pm \frac{1}{n} \{a^* + b^* \} \), where \( h, k, l \) are integers and \( n \) can be directly measured from the diffraction pattern. The measured \( n \) can be used to derive the modulation wavelength if lattice parameters are known. From the inset of Figure 3-5(b), \( n \) is measured to be 6.02, which gives a wavelength of 1.75 nm. This value matches exactly to the direct measurement from the image. Close examination of the electron diffraction pattern shows that all the satellite spots around the \( hh0 \)-type fundamental spots (these fundamentals are sitting on the row including the transmitted spot) are much weaker than the others. According to Zuo and Tao’s analysis on a different perovskite oxide\(^{30} \), this suggests that the incommensurate modulation exists in the form of a transverse atomic displacement wave. Therefore, our study supports the Pb-cation displacement structural mechanism.

When the selected area includes a 90° domain wall, two sets of satellite spots are obtained, as depicted in Figure 3-5(c). Careful measurements from the inset diffraction pattern indicate that \( n = 6.97 \) for the vertical set of satellite spots (the corresponding modulation stripes in the image are in the horizontal direction with a wavelength of 2.03 nm) while \( n = 7.33 \) for the horizontal set of satellite spots (the corresponding modulation
stripes in the image are in the vertical direction with a wavelength of 2.13 nm). It is evident, therefore, that the modulation wavelength varies even across a 90° domain wall within a single grain. It should be noted that the material was annealed at 1300°C for 6 hours after hot pressing. Therefore, the difference was likely to be caused by residual stresses, not by heterogeneity in chemical composition. It is also interesting to note that the 90° domain wall in Figure 3-5(c) deviated from the (100) plane. This will be addressed in detail in the discussion section in the following. Again, the weaker satellite spots in the vertical set in the column passing through the transmitted beam and those in the horizontal set in the row passing through the transmitted beam than the others suggest a primary contribution from the Pb-cation displacements.

3.4.3 In situ TEM Study

In situ TEM studies were carried out on a specimen that was crack-free at the edge of the central perforation. For an ideal circular-shaped perforation, the actual electric field at the two sites that are highlighted in Figure 3-1 is intensified by a factor of 2 (Ref. 28). The direction of the actual field at these two sites preserves the direction of the undisturbed field which is perpendicular to the electrode edges. When this specimen was loaded to the special TEM holder, the gap between the two half-circle electrodes was aligned with the long axis of the whole holder, in other words, the primary tilting axis. In such a configuration, the undisturbed electric field (the nominal electric field) is along the secondary tilting axis, perpendicular to the primary tilting axis. Based on this relation, the direction of the actual electric field is determined.

Electron transparent grains within the two highlighted areas outlined in Figure 3-1 in the specimen were examined in the TEM. One of the grains was found to have its [001]
axis parallel to the electron beam without secondary tilting. This grain was about 5 μm in size. The [001] zone-axis SAED pattern was recorded at different field levels to monitor the evolution of the incommensurate modulation. The electric field strength was estimated by doubling the nominal field strength.

The change of the satellite spots in the [001] zone-axis SAED pattern under static electric field is depicted in Figure 3-6. Initially, this grain displays two sets of satellite reflections. As evident in Figure 3-6(a), the satellite spots are strong in intensity and slightly elongated in shape. Similar to the diffraction pattern shown in the inset of Figure 3-5(c), the difference in the intensity of satellite spots was again observed, indicating a transverse Pb-cation displacement wave. Next, static electric fields were applied and increased stepwise. The applied field direction was determined to be along the gray line in Figure 3-6(b). At an actual electric field of 60 kV/cm, the horizontal set of satellite spots almost completely disappeared. For the vertical set, many satellite spots disappeared as well and the remaining spots exhibited severe streaking (Figure 3-6b).

The bright rectangular boxes in Figs. 6(a) and 6(b) enclose two fundamental reflections of 120 and 210. The appearance of the satellite spots of these two fundamental reflections at a series of field levels of 0, 8, 20, 30, 40, and 60 kV/cm is shown in Figure 3-7. It is evident that satellite reflections in both sets started to become weaker at an electric field of 8kV/cm, which is far below the macroscopic critical field for the antiferroelectric-to-ferroelectric phase transformation. The satellite spots in the horizontal set almost completely disappeared at 40 kV/cm and became slightly diffused before their final disappearance. On the other hand, the satellite reflections in the vertical set started to show severe streaking at 20 kV/cm and their presence persists up to 60
kV/cm. This shows an orientation dependence of their response to the external field. Details will be discussed in the next section.

The value of \( n \) in \( h \mathbf{a}^* + k \mathbf{b}^* + l \mathbf{c}^* \pm \frac{1}{n} \{ \mathbf{a}^* + \mathbf{b}^* \} \) was measured from electron diffraction patterns at different field levels and is plotted in Figure 3-8. At each field level, at least 10 pairs of satellites were measured. For diffused satellite spots, the measurement was performed at the point with the highest intensity. Again, a significant difference in \( x \) occurred across a 90° domain wall within a single grain. At zero field, \( n = 6.78 \) for the horizontal set of satellite spots, corresponding to a wavelength of 1.97 nm, and \( n = 7.67 \) for the vertical, corresponding to 2.23 nm. It is should be noted that the grain was about 5 \( \mu \)m in size and the material was annealed at 1300°C for 6 hours after hot pressing. Therefore, residual stresses are likely to be responsible for the significant difference in wavelength.

Another evident feature in Figure 3-8 is the negligible change in the incommensurate modulation wavelength under strong applied electric fields. A linear fit to the mean value of \( n \) gives a slope of -0.0061Å per kV/cm for the horizontal set and -0.0035Å per kV/cm for the vertical set, respectively. The higher rate of change for the horizontal set is in accordance with the evolution of the satellite spots of that set under electric fields. It was shown in Figure 3-7 that these spots disappeared at a lower field level. The wavelength in real space decreases slightly with increasing electric fields for both sets. At 40 kV/cm, it was recorded as 1.95nm (a 1.2% decrease from the initial wavelength) for the horizontal set and 2.22nm (a 0.7% decrease from the initial wavelength) for the vertical set, respectively.
3.5 Discussion

Although incommensurate modulations in perovskite antiferroelectrics modified from PbZrO$_3$ were first observed twenty years ago, there have been very limited publications on this issue. A structural model for the modulation wave is still missing. Based on previous studies the results obtained in this study, we propose a model for the observed incommensurate modulation in these perovskite antiferroelectrics. The model sheds light on the detailed structure of the antiferroelectric 90° domain wall and explains the orientation dependence of the response to applied electric field.

It has been well established that the Pb-cation in the parent PbZrO$_3$ structure is displaced with a periodicity of 4 layers of its pseudo-tetragonal plane. The SAED patterns shown in Figs. 5 and 6 indicate that the satellite reflections are also originated primarily from transverse Pb-cation displacement modulation waves in the modified antiferroelectrics. We believe that the structure of the commensurate modulation in the parent PbZrO$_3$ can be extended to the observed incommensurate modulations. The observed incommensurate modulation is an average effect over an ensemble of stripes of commensurate modulations. This is illustrated schematically in Figure 3-9. Figure 3-9(a) redraws the structural model of PbZrO$_3$ proposed by Sawaguchi et al., where stripes of the commensurate modulation of Pb-cation displacements with periodicity of 4 pseudo-tetragonal planes are evident. Figure 3-9(b) schematically depicts that an incommensurate modulation can be composed of commensurate modulations. In this illustration, the periodicity of the incommensurate modulation lies somewhere between 7 and 8 pseudo-tetragonal planes. Such an incommensurate modulation is composed of stripes of periodicities of $n = 7$ and 8, which are commensurate to the underlying lattice.
In the SAED pattern, the satellite reflections appear to be incommensurate due to an average effect.

This structure model gains support from the following evidences. The first evidence is related to the change of the incommensurate modulation when chemical composition or temperature varies. In the series of antiferroelectric Pb$_{0.99}$Nb$_{0.02}$(Zr$_{0.55}$Sn$_{0.45}$)$_{1-y}$Ti$_y$O$_{3.98}$ ($y = 0.00, 0.03, 0.06$), incommensurate satellite reflections are observed in compositions with $y = 0.06$ and 0.03. When $y$ is further reduced to zero, where the composition becomes Pb$_{0.99}$Nb$_{0.02}$(Zr$_{0.55}$Sn$_{0.45}$)$_{0.98}$O$_3$, the incommensurate satellite reflections transform into commensurate ones that are isomorphous to the parent PbZO$_3$ (Ref. 13). It was also found in this series (the Pb$_{0.99}$Nb$_{0.02}$(Zr$_{0.58}$Sn$_{0.42}$)$_{0.96}$Ti$_{0.04}$O$_{3.98}$ composition) that the room temperature antiferroelectric phase with incommensurate modulations transforms to an antiferroelectric one with a structure isomorphous to PbZrO$_3$ when cooled down below -150°C (Ref. 15). Furthermore, the parent PbZrO$_3$ itself was observed to display incommensurate satellite reflections when heated up to a narrow temperature range between 225°C and 230°C (Ref. 14). These findings from previous studies reveal strong and direct connections between the appeared incommensurate modulations and the commensurate modulations in these ceramics. Therefore, the structure of the observed incommensurate modulations should bear intrinsic similarities to the structure of the parent PbZrO$_3$.

The second evidence arises from a survey on the $n$ value reported in literature. The result is summarized in Table 3-1 with references, including both the PbZrO$_3$ and the modified antiferroelectric ceramics. Commensurate modulations do appear in these ceramics. For example, $n=7$ and $n=8$ were reported in the
$\text{Pb}_{0.99}\text{Nb}_{0.02}[(\text{Zr}_{0.80}\text{Sn}_{0.20})_{0.97}\text{Ti}_{0.03}]_{0.98}\text{O}_3$ in Ref. 3. It is interesting to notice that, for those non-integer $n$ values, simple combinations of two neighboring integers can be always found to generate the non-integer $n$ when averaged. These combinations are listed in the fourth column of Table 3-1. It is proposed that the incommensurate modulation in PbZrO$_3$ at 225°C with $n=6.67$ can be comprised of stripes of commensurate modulations with $n=6$ and $n=7$. When one stripe modulated with $n=6$ appears after every two stripes with $n=7$ appear in the mixture, an overall $n=6.67$ would be seen over a large volume. For the PZST 42/4.5/2 oxide examined in this study, five different $n$ values are measured from electron diffraction patterns recorded in different areas. For the values of 6.02 and 6.97, we believe they are modulated commensurately with $n=6$ and $n=7$, respectively. The modulation with $n=6.78$ can be considered as a mixture of commensurate modulations of $n=6$ and $n=7$ with a repeating pattern of $7/6/7/7$; the 7.33 as a mixture with a pattern of $7/8/7$; and the 7.67 as one with a pattern of $8/7/8$. Under the conditions of the selected area electron diffraction, an area within a 90° domain is used to produce the diffraction pattern. This area is typically on the order of 1 μm, therefore, containing several hundreds of modulation stripes. The observed satellite reflections then show an average wavelength over the selected area (volume).

In a recent study on the antiferroelectric Pb$_{0.97}$La$_{0.03}$(Zr$_{0.95}$Ti$_{0.05}$)O$_3$, Asada and Koyama$^{17}$ observed discrete $n$ values when the oxide was heated from room temperature. This is the third evidence supporting our model. Below 73°C, $n$ was measured to be 4.0. From 73 to 122°C, $n=6.0$ was recorded. From 122°C to 160°C, $n=6.5$; from 160°C to 180°C, $n=7.0$; while above 180°C, $n=7.5$. These authors hence claimed that the material is commensurately modulated. We suggest that the modulations at different temperatures
are not only commensurate, but also have an integer number of layers of the pseudo-tetragonal \textsuperscript{60} planes within a period. The modulation with overall $n=6.5$ is thus a mixture of modulations with local $n=6$ and $n=7$ while the one with overall $n=7.5$ is mixture of that with local $n=7$ and $n=8$.

The most direct evidence may be due to Cai et al.\textsuperscript{16} These researchers measured $n=7.24$ from the SAED pattern in antiferroelectric Pb$_{0.97}$La$_{0.02}$(Zr$_{0.66}$Sn$_{0.25}$Ti$_{0.09}$)O$_3$. According to our model, the appeared incommensurate modulation is comprised of commensurately modulated stripes with a pattern of 7/7/8/7 on statistical average. And indeed, they observed stripes with commensurate modulations. The high-resolution lattice image revealed a sequence of …7/7/7/7/8/77/7/8/7/7/7/8/7….

These evidences support the model described in Figure 3-9. The observed incommensurate modulation is actually a mixture of commensurate modulations. The modulation exists in the form of a transverse Pb-cation displacement wave. However, the magnitude of the displacement is a constant and the wave is not a sinusoidal wave. This model thus bears intrinsic similarities to the antiferroelectric structure of PbZrO$_3$. The model also sheds light on the fact that higher order satellite reflections are often observed when the satellites are commensurate while only the first order satellites are observed when the satellites are incommensurate. The incommensurate satellites are generated by a mixture of two commensurate modulations. Thus, the appeared incommensurate modulation exhibits less degree of order.

The structure model implies that the modulation within a 90° domain is a stack of 180° domains with antiparallel Pb-cation displacement. For most antiferroelectric ceramics, the component commensurate modulations for the observed incommensurate
modulations have \( n=6, 7, \) and \( 8, \) as demonstrated in Table 3-1. Therefore, the \( 180^\circ \) domains in these antiferroelectrics have a thickness of 3 or 4 layers of the pseudo-tetragonal \(^{60}\) plane. For the parent PbZrO\(_3\), the \( 180^\circ \) domains are 2 layers of \(^{60}\) plane thick. These \( 180^\circ \) domains are shaded differently in Figure 3-9 for clarity.

When the modulation wavelength is the same on both sides of a \( 90^\circ \) domain wall, the Pb-cation displacement can be easily arranged to a “head-to-tail” configuration in order to achieve charge neutrality at the \( 90^\circ \) domain wall.\(^{24}\) However, it is noticed in Figure 3-5(c) and Figure 3-8 that the modulation wavelength changes significantly across a \( 90^\circ \) domain wall. This may lead to a situation that a \( 180^\circ \) domain of 3 layers \(^{60}\) plane thick meets one of 4 layers thick at the \( 90^\circ \) domain wall. It can be shown that the charge neutrality is still preserved when an atomic step is created on the \( 90^\circ \) domain wall. Figure 3-10 schematically illustrates such a situation. The upper-right \( 90^\circ \) domain bears a modulation with \( n=8 \) (the \( 180^\circ \) domain slabs in this \( 90^\circ \) domain have a thickness of 4 layers of the \(^{60}\) plane) while the lower-left domain bears one with \( n=7 \) (the \( 180^\circ \) domain slabs in this \( 90^\circ \) domain have a thickness of 3 or 4 layers of the \(^{60}\) plane). The \( 180^\circ \) domain slabs are highlighted with different shades. It shows clearly that the atomic step on the \( 90^\circ \) domain wall mediates the difference in wavelength and preserves the “head-to-tail” configuration. Such a mechanism implies that the \( 90^\circ \) domain wall would follow the \( \{100\} \) plane if the two \( 90^\circ \) domains have identical modulation wavelength and would deviate from the \( \{100\} \) plane if the two domains have different wavelengths. This is indeed the case. In PbZrO\(_3\), all the modulations have identical wavelength and the \( 90^\circ \) domain wall was observed to be parallel to the \( \{100\} \) plane.\(^{24}\) In the PZST 42/4.5/2
investigated in this study, it is shown in Figure 3-5 that the 90° domain wall is tilted away from the {100} plane due to the difference in the modulation wavelength.

With the proposed structure models for the incommensurate modulation and the 90° domain wall, we now can picture the evolution of the modulations during the electric field-induced antiferroelectric-to-ferroelectric phase transformation. A fundamental difference in the response of the modulation wavelength to external electric fields is noticed in our study: the wavelength is quite stable against electric stimuli. In the PZST 42/4.5/2 studied here, about 1% decrease in wavelength was measured when an electric field of 40 kV/cm was applied. In contrast to this, Asada and Koyama 17 observed a 88% increase in wavelength when the antiferroelectric Pb_{0.97}La_{0.03}(Zr_{0.95}Ti_{0.05})O_3 was heated from room temperature to 180°C. Xu et al. 15 measured a 40% increase in wavelength in a composition very close to ours when temperature was increased from 25°C to 150°C. We thus speculate that the electric field-induced antiferroelectric-to-ferroelectric phase transformation starts with a process of aligning the Pb-cation displacements. The aligning process may be initiated preferentially from sites such as grain boundaries and 90° domain walls at a field as low as 8 kV/cm. The volume with aligned cation displacement no longer contributes to the satellite reflections and fraction of the volume increases with increasing electric field. Therefore, the intensity of the satellite reflections starts to decrease at 8 kV/cm, as revealed in Figure 3-7.

The aligning process of Pb-cation displacement also explains the orientation dependence of the satellites response revealed in Figs. 6 and 7. When the electric field direction shown in Figure 3-6 is translated into Figure 3-10, the applied field is seen to be 15° away from the Pb-cation displacement vectors in the lower-left 90° domain (this
domain generates the horizontal set of satellite reflections) and 75° away from the
displacement vectors in the upper-right 90° domain (this domain generates the vertical set
of satellite reflections). Along the direction of Pb-cation displacement, the lower-left 90°
domain would experience a resolved field of 0.96E while the upper-right one would
experience a resolved field of only 0.26E, where E is the amplitude of the applied field.
This can be stated in another way, the aligning process of Pb-cation displacement
involves a 180°-domain-switching-like process in the lower-left domain and a 90°-
domain-switching-like process in the upper-right one. It is well known that in perovskite
normal ferroelectrics, 90° domain switching is always more difficult than 180° domain
switching. This explains the orientation dependence of the response of the satellites to
external electric fields very well. In Figs. 6 and 7, the horizontal set of satellite spots
disappeared at a lower level of electric field and showed little streaking before their final
disappearance. In the 90° domain that contributes to this set of satellites, the aligning of
Pb-cation is more like a 180° domain switching in normal ferroelectrics. Since the 180°
domain slabs are very thin, 3 or 4 layers of the 60 plane in most cases, switching may well
take place at once for the whole thickness. This would decrease the intensity of the
corresponding satellites but preserves the wavelength. On contrast, the vertical set of
satellite reflections in Figs. 6 and 7 persists to a higher electric field. The aligning process
of Pb-cation displacement in the corresponding antiferroelectric 90° domain resembles
the 90°-domain-switching process sin normal ferroelectrics. Furthermore, such a 90°
reorientation may well disrupt the modulation, leading to a severe streaking in the
satellite reflections.
3.6 Conclusion

Our TEM study indicates that the incommensurate modulation in modified perovskite antiferroelectrics exists in the form of a transverse Pb-cation displacement wave. The observed incommensurate modulation at large scale is suggested to be a mixture of commensurate modulations at local scale. The modulations in antiferroelectric 90° domains are then 180° domain slabs with thickness of 3 or 4 layers of the pseudo-tetragonal 60° plane. The antiferroelectric 90° domain wall deviates from the pseudo-tetragonal {100} plane due to the atomic steps on the domain wall created to preserve charge neutrality.

The external electric field aligns the cation displacement prior to the field-induced antiferroelectric-to-ferroelectric phase transformation. The fraction of the volume with aligned cation displacement increases with increasing electric fields, which leads to a decrease in the intensity of the corresponding satellite reflections in the selected area electron diffraction patterns. The cation displacement aligning process resembles the 90° and 180° domain switching process in normal ferroelectrics. When the field is applied along the cation displacement direction, the aligning process is easier and the process preserves, to some extent, the wavelength. The modulation is disrupted when the field is applied perpendicular to the direction of cation displacement and severe streaking is observed in the corresponding satellite reflections.
3.7 Acknowledgements

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Figure 3-7 Evolution of the satellite reflections surrounding the 120 and 210 fundamental reflections. (a) E = 0, (b) E = 8 kV/cm, (c) E = 20 kV/cm, (d) E = 30 kV/cm, (e) E = 40 kV/cm, and (f) E = 60 kV/cm.

Figure 3-8 Change of \( n \) value with applied electric fields for the vertical set and horizontal set of satellite reflections shown in Figs. 6 and 7.

Figure 3-9 Structure models for perovskite antiferroelectrics. (a) The structure proposed by Sawaguchi et al.\(^{22}\) for PbZrO\(_3\), (b) the structure of the modulation in this study. The incommensurate modulation is suggested to be a mixture of commensurate modulations.

Figure 3-10 The structure of the 90° domain wall in PbZrO\(_3\)-based antiferroelectrics with incommensurate modulations. When the modulation wavelength is not equal on the two sides of the domain wall, atomic steps are introduced to preserve charge neutrality.

### 3.9 Table List

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Table 3-1 Reported $x$ in various antiferroelectric ceramics

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This study
3.10 Reference

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2http://www.cryst.ehu.es/icsdb/index.html


4. Raman spectroscopy study of the phase transitions in 

\( \text{Pb}_{0.99}\text{Nb}_{0.02}[(\text{Zr}_{0.57}\text{Sn}_{0.43})_{1-y}\text{Ti}_y]_{0.98}\text{O}_3 \) ceramics


Hui He, and Xiaoli Tan*

4.1 Abstract

Detailed studies of the phase transitions in \( \text{Pb}_{0.99}\text{Nb}_{0.02}[(\text{Zr}_{0.57}\text{Sn}_{0.43})_{1-y}\text{Ti}_y]_{0.98}\text{O}_3 \) (\( y=0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.10, \) and \( 0.12 \)) ceramics as a function of composition, temperature, electric field, and time were conducted using Raman spectroscopy. At room temperature, the as-sintered ceramics with \( y=0.03\sim0.08 \) show an antiferroelectric order while those with \( y=0.10 \) and \( 0.12 \) show a ferroelectric order. For the ceramic with \( y=0.08 \), however, a ferroelectric order can also be stabilized at room temperature when it is warmed up from lower temperatures. The electric field-induced ferroelectric phase in the ceramic with \( y=0.07 \) is metastable at room temperature and ages back to the stable antiferroelectric phase on a time scale of hours.

Department of Materials Science & Engineering, Iowa State University, Ames, IA 50011

*Author to whom correspondence should be directed
4.2 Introduction

The PbZrO$_3$-based antiferroelectric ceramics are of technological importance due to their wide applications in microelectromechanical systems and energy storage devices$^{1-3}$. The electric field-induced antiferroelectric-to-ferroelectric phase transition forms the physics basis for these applications. The most intensively studied antiferroelectric materials are chemically modified PbZrO$_3$ by adding Sn, Ti, and Nb or La to adjust the critical field for the phase transition and to optimize the properties for processing and applications$^{1-7}$. It has been widely accepted that the optimized properties in these ceramics are resulted from their hierarchical microstructures: the subgrain level antiferroelectric 90° domains (the checkerboard pattern) and the nanoscale incommensurate modulations within the domains$^{6-13}$. Increase in Ti content eventually destroys these microstructures and leads to a normal ferroelectric behavior.

Raman spectroscopy has been extensively used in the study of the phase transition in ferroelectric oxides$^{14-17}$. The subtle changes in bond distance, bond angle and crystal symmetry during phase transitions can be revealed by the change in the mode frequency and the presence/absence of different modes. In most PbZrO$_3$-based ceramics, the presence of many modes at low frequencies (less than 150 cm$^{-1}$) is the characteristics of the antiferroelectric order$^{18-26}$. These intense low frequency modes were assigned to the bonds between the Pb cation and other ions in the unit cell$^{18}$. Although the normal Raman modes can be predicted from crystal symmetry, the actual frequency and intensity of each mode are strongly dependent on chemical composition and processing conditions. El-Harrad et al.$^{21}$ studied the phase transitions in Pb(Zr$_{0.95}$Ti$_{0.05}$)O$_3$ ceramics with Raman spectroscopy and found that 1wt% doping of La$_2$O$_3$ does not lead to any change in the
spectra but 1 wt% Nb$_2$O$_5$ doping changes the Raman spectra significantly. Several phases, including the incommensurate antiferroelectric one, have been observed in Sn-modified antiferroelectric Pb(Zr,Ti)O$_3$ ceramics$^{1-7}$. However, to the authors’ knowledge, Raman spectroscopy study on these antiferroelectric ceramics with incommensurate modulations has not yet been reported. In the present work, experimental studies with Raman spectroscopy on the composition-, temperature-, electric field-, and time-induced phase transitions in the Pb$_{0.99}$Nb$_{0.02}$[(Zr$_{0.57}$Sn$_{0.43}$)$_{1-y}$Ti$_y$]$_{0.98}$O$_3$ series were conducted.

### 4.3 Experimental Procedure

Pb$_{0.99}$Nb$_{0.02}$[(Zr$_{0.57}$Sn$_{0.43}$)$_{1-y}$Ti$_y$]$_{0.98}$O$_3$ (abbreviated as PNZST 43/100$y$/2) solid solutions with $y=0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.10, \text{ and } 0.12$ were prepared by the conventional solid state reaction method from high purity oxides. Raw powders with purity better than 99.9% of PbO, Nb$_2$O$_5$, ZrO$_2$, SnO$_2$, and TiO$_2$ were batched according to the chemical formula with 5% excess PbO powder to compensate for the lead evaporation loss in the subsequent thermal process. The powders were calcined at 850°C for 4 hours in a covered alumina crucible for two times to ensure the chemical homogeneity and the phase purity. Sintering was performed at 1300°C for 3 hours using PbZrO$_3$ as protective powder.

After removal of surface layers by mechanical grinding, these ceramics were checked by X-ray diffraction for phase purity and scanning electron microscopy (SEM) for grain morphology. Dielectric characterization was conducted with an LCR meter (HP-4284A, Hewlett-Packard) at frequency of 1 kHz in conjunction with an environmental chamber. A heating/cooling rate of 3°C/minute was used during
measurement. Electric field-induced polarization was recorded with a standardized ferroelectric test system (RT-66A, Radiant technologies).

For the Raman spectroscopy experiments, one specimen for each composition was polished and subsequently annealed at 200°C for 30 minutes to relieve the residual stress caused by cutting and polishing. A set of Raman scattering spectra were collected at room temperature with a Renishaw inVia spectrometer using the 488 nm line of the Ar⁺ laser at 50mW of power. The instrument was calibrated using an internal silicon reference, and the bands were reproducible within ±1 cm⁻¹. The laser beam was focused with a 50× lens, producing a beam size of ~3-5 μm on the polished specimen surface. Raman scattering experiment was also performed under controlled temperature in the range from -50 to 250°C. A heating/cooling rate of 3°C/minute was used during the test. The temperature was kept for 10 minutes at each predetermined point prior to recording the Raman spectrum. The Raman data were collected from exactly the same grain at different temperatures.

For the PNZST 43/7/2 specimen, two additional Raman experiments were conducted at room temperature. One is the in situ experiment on the electric field-induced antiferroelectric-to-ferroelectric phase transition. Two gold electrodes with spacing of 1mm were sputtered to one polished surface and copper wires were soldered to the Au electrodes using silver conductive epoxy. The high voltage side of the Au electrodes was covered by insulation varnish to prevent arcing. High static electric field was applied to the sample with a high voltage power supply (Model 610D, Trek). Acquisition of Raman spectra was completed at a series of field strength. The other is experiment on the aging of the metastable ferroelectric phase. For this experiment, a disk
sample was electroded with carbon paste on both faces and poled under an electric field of 20KV/cm along the thickness direction in silicone oil. The carbon paste electrodes were then removed and Raman spectra were collected from the same grain on the surface at different time points.

4.4 Results and Discussion

4.4.1 Structure and Electrical Properties

X-ray diffraction shows that all the as-sintered ceramics are phase pure with the perovskite structure. Full spectrum analysis indicates that the ceramics with $\gamma=0.03$ to 0.08 display an orthorhombic while those with $\gamma=0.10$ and 0.12 exhibit a rhombohedral symmetry. This can be clearly seen from the partial spectrum for the pseudocubic 200 peak with 20 in the range of 43.0° to 45° shown in Figure 4-1. From previous studies on ceramics with similar compositions $^{1-7}$, the orthorhombic phase is expected to be antiferroelectric while the rhombohedral phase is ferroelectric. However, the orthorhombic symmetry has been mistakenly believed to be tetragonal symmetry previously $^{1, 2}$. As Viehland pointed out, a tetragonal structure does not support the antiferroelectric order $^6$. Furthermore, our synchrotron x-ray diffraction experiment has determined the space group as $Bmm2$ $^{27}$. Previous studies suggest the space group $R3c$ for the rhombohedral phase for compositions $\gamma=0.10$ and 0.12 at room temperature $^{4-7}$.

The dielectric constant as a function of temperature was measured for these ceramics at 1kHz. Figure 2 shows the results obtained from cooling at a rate of 3°C/minute. Different scales along the ordinate were used in Figs. 2(a) and 2(b) for clarity. It is evident that as Ti content increases, the maximum dielectric constant
increases dramatically. From previous studies on ceramics with similar compositions, PNZST 43/3/2, PNZST 43/4/2, and PNZST 43/5/2 show two antiferroelectric phases in the measuring temperature range. For PNZST 43/3/2, the transition temperature between the two antiferroelectric phases is at 4°C, while that for PNZST 43/4/2 and PNZST 43/5/2 are at -30°C and -40°C, respectively. The antiferroelectric phase at lower temperatures is commensurate and isostructural to PbZrO₃ with the Pbam space group. The high temperature antiferroelectric phase has incommensurate modulations with the space group Bmm2. The incommensurate antiferroelectric phase persists to temperatures below -50°C (the lower limit for our dielectric characterization) as Ti increases to \( y = 0.06 \) and 0.07. However, further increase in Ti content leads to the development of a ferroelectric order at lower temperatures and at the same time, the temperature range for the incommensurate phase is suppressed. At \( y = 0.12 \), the ferroelectric phase is stable below 116°C, the antiferroelectric phase is stable between 116°C and 123°C. Another feature in Figure 4-2 is the presence of a plateau region in the dielectric response. This was assigned as the multicell cubic phase region between the incommensurate orthorhombic antiferroelectric phase and the paraelectric cubic phase. The multicell cubic region was previously attributed to the disruption of the paraelectric-antiferroelectric transformation by Sn modification.

The phase changes discussed above are summarized in a phase diagram, as shown in Figure 4-3. It should be noted that this diagram is based on dielectric constant measurements during cooling. Since all these phase transitions are first order in nature, a slight shift of the phase boundary lines toward higher temperatures is expected if the diagram is constructed based on heating measurement. It shows clearly that the Curie
temperature decreases continuously with increasing Ti content. In contrast, the lower temperature limit for the multicell cubic phase is only a weak function of Ti content. The incommensurate antiferroelectric phase spans the widest temperature range at intermediate Ti content of $y=0.06$ and $0.07$. This observation supports the argument that the incommensurate modulation is resulted from the frustration of competing interactions between antiferroelectric and ferroelectric orders. At low temperatures, the antiferroelectric phase (isostructural to PbZrO$_3$) transforms to the ferroelectric phase (isostructural to the R$_{LT}$ phase in lead zirconate titanate) as Ti content increases. At $y=0.12$, the two intermediate phases, the multicell cubic and the incommensurate antiferroelectric phases, almost disappear. Beyond this composition, the paraelectric cubic phase transforms directly to the ferroelectric rhombohedral phase during cooling.

The antiferroelectric-to-ferroelectric phase transition can also be triggered by applied electric fields. This is revealed by the polarization vs. electric field hysteresis loop measurement depicted in Figure 4-4. The measurement was conducted at room temperature with a frequency of 4Hz. The ceramics with $y=0.03$, 0.04, 0.05, and 0.06 display the characteristic double hysteresis loops, indicating the occurrence of the electric field-induced antiferroelectric-to-ferroelectric phase transition (Figure 4-4(a)). As Ti content increases, the critical field for the phase transition decreases while the polarization developed in the ferroelectric phase increases. For these four compositions, the induced ferroelectric phase is not stable and the reverse transition takes place during the release of the applied electric fields. For example, the forward antiferroelectric-to-ferroelectric transition occurs at 39kV/cm (referred to as $E_F$ in literature) and the reverse transition occurs when the field decreases to 18kV/cm (referred to as $E_A$ in literature) in
PNZST 43/6/2. Increase further in Ti content to \( y=0.07 \) leads to a more sluggish reverse phase transition and a distorted hysteresis loop (Figure 4-4(b)). At the measuring frequency of 4Hz, a remanent polarization of 10\( \mu \)C/cm\(^2\) was observed from Figure 4-4(b), indicating the persistence of the ferroelectric phase at this time scale. As shown in Figure 4-4(b), the \( E_F \) is determined to be 14kV/cm. PNZST 43/8/2 appears to have a single hysteresis loop as observed in normal ferroelectric ceramics. However, close examination of its hysteresis loop reveals that there is distortion on the loop when the applied field increases for both polarities, as indicated be the two dotted circles in Figure 4-4(b). Therefore, the hysteresis loop of PNZST 43/8/2 bears similarities with PNZST 43/7/2. The \( E_F \) is determined to be 6kV/cm. Figure 4-4(b) also reveals a high remanent polarization for PNZST 43/8/2 (18\( \mu \)C/cm\(^2\)), indicating a stable ferroelectric phase at room temperature. This will be further discussed in the following section. For compositions of \( y=0.10 \) and 0.12, regular single hysteresis loops were observed (now shown). Therefore, the hysteresis loops observed are consistent with both x-ray diffraction and dielectric measurement results. The observations on the electric field-induced phase transition are summarized in an electric field vs. composition phase diagram, as shown in Figure 4-5.

4.4.2 Raman Spectroscopy Studies

The Raman spectra for all compositions collected at room temperature are presented in Figure 4-6. The modes in low frequency range are focused because most active Raman modes for antiferroelectric PbZrO\(_3\) were previously found in this range \(^{18}\). Consistent with the results of x-ray diffraction, dielectric and ferroelectric measurement reported in the previous section, the ferroelectric PNZST 43/10/2 and PNZST 43/12/2
ceramics display different active Raman modes from other ceramics. As Ti content increases from $y=0.03$ to 0.12, the most prominent feature in the Raman spectra is the softening of the mode around 90cm$^{-1}$ and the emergence of the modes around 60cm$^{-1}$ and 125cm$^{-1}$. The exact frequency of these three modes in different compositions after deconvolution is plotted in Figure 4-7. Since x-ray diffraction, dielectric characterization, and hysteresis loop measurement indicate ferroelectric order in PNZST 43/10/2 and 43/12/2, and antiferroelectric order in others, the mode around 90cm$^{-1}$ (denoted as mode A hereafter) is the signature of the antiferroelectric phase and the modes around 60cm$^{-1}$ (denoted as mode F$_1$ hereafter) and 125cm$^{-1}$ (denoted as F$_2$ hereafter) are characteristic of the ferroelectric order. These low frequency modes are believed to be originated from the bonds between the Pb cation and other ions in the unit cell [18] and will be used in the following discussion for identifying different phases.

As discussed in the last section, both antiferroelectric and ferroelectric phases are stable in the PNZST 43/8/2 ceramic at room temperature. This is further confirmed by the dielectric constant measurement during heating from -50°C to 250°C. The result is shown in Figure 4-8, together with that measured during cooling from 250°C. As marked by the two vertical arrows, the antiferroelectric phase transforms to a ferroelectric phase at around -1°C during cooling while the ferroelectric phase transforms to an antiferroelectric phase at 45°C during heating. Therefore, either the ferroelectric or the antiferroelectric phase could be stabilized at room temperature, roughly 25°C, depending on the thermal history of the ceramic. This is also directly confirmed by Raman spectroscopy study. As shown in Figure 4-9, an obvious antiferroelectric mode A was detected in the sample cooled from 200°C while strong ferroelectric modes F$_1$ and F$_2$
were observed in the sample heated up from -50°C. Further heating to 75°C leads to the softening of modes F\textsubscript{1} and F\textsubscript{2} and the emergence of mode A. However, mode A at 75°C is shifted to a lower frequency than that at 25°C.

The phase diagram shown in Figure 4-3 indicates that PNZST 43/3/2, 43/4/2, and 43/5/2 can be stabilized into a commensurate antiferroelectric phase at low temperatures. For PNZST 43/4/2, this occurs at -30°C during cooling. The incommensurate antiferroelectric phase in this ceramic exists between -30°C and 144°C, the multicell cubic phase is stable between 144°C and 195°C, while the paraelectric phase exists above 195°C. The Raman spectra that are characteristic to these phases were recorded during cooling at different temperatures and are shown in Figure 4-10. At 250°C, the paraelectric cubic phase has the space group \textit{Pm3m}, there is no Raman active mode. As a consequence, no peaks between 40cm\textsuperscript{-1} and 360cm\textsuperscript{-1} were detected in the spectrum. When cooled down to 165°C, a multicell cubic state is expected. However, there are still no strong Raman modes detected in the spectrum. At 25°C, the antiferroelectric phase with incommensurate modulations shows the mode A, as indicated in Figure 4-10. Further cooling to -50°C develops the commensurate antiferroelectric phase and the Raman spectrum shows two strong modes, one around 40cm\textsuperscript{-1} and the other at 129cm\textsuperscript{-1} (marked by two arrows in Figure 4-10). Presumably the commensurate antiferroelectric phase is isostructural to PbZrO\textsubscript{3} with the space group \textit{Pbam}. And indeed, these two modes are consistent with previous Raman studies on PbZrO\textsubscript{3} [18]. Therefore, Raman spectroscopy is capable of discerning the two antiferroelectric phases, one with the commensurate the other with the incommensurate modulations.
The phase diagram shown in Figure 4-5 indicates that the electric field-induced antiferroelectric-to-ferroelectric phase transition occurs at $14kV/cm$ in PNZST $43/7/2$ at room temperature. This transition process was characterized with Raman spectroscopy with electric fields applied in situ. As shown in Figure 4-11, a strong mode A is detected initially. At $3.0kV/cm$, mode A starts to soften. However, the softening process is slow and the mode can still be detected at the field of $15kV/cm$. When the field level increases to $16.5kV/cm$, mode A is dramatically weakened. At the same time, modes $F_1$ and $F_2$ emerge, indicating the development of the ferroelectric phase. The minor discrepancy in $E_F$ determined by hysteresis loop measurement and Raman spectroscopy study may be resulted from a geometric effect. The Raman experiment detects only surface grains and the electric field was applied in plane, while the polarization measurement characterizes the bulk of the sample with electric field applied along the thickness direction.

As revealed by the hysteresis loop measurement shown in Figure 4-4(b), the recovery of the antiferroelectric phase from the field-induced ferroelectric phase in the PNZST $43/7/2$ ceramic is a slow process. This time-induced reverse phase transition process is examined with Raman spectroscopy. As shown in Figure 4-12, strong peaks of modes $F_1$ and $F_2$ were observed right after the electric poling at $20kV/cm$. These two peaks decayed continuously with time. The mode A, signature of the antiferroelectric order, could be barely detected after 1 hour. However, an obvious peak was observed for mode A after 4 hours. At the same time, modes $F_1$ and $F_2$ softened significantly. After 150 hours, a strong peak for mode A was developed. Residuals of peaks for the $F_1$ and $F_2$ modes can still be seen. Therefore, the time-induced reverse phase transition in PNZST $43/7/2$ occurs on a time scale of hours.
4.5 Conclusion

Raman spectroscopy studies have been conducted to characterize the composition-, temperature-, electric field-, and time-induced phase transitions in Pb$_{0.99}$Nb$_{0.02}$(Zr$_{0.57}$Sn$_{0.43}$)$_{1-y}$Ti$_{y}$O$_{3}$ ceramics. It is found that at room temperature, antiferroelectric order is developed in ceramics with $y=0.03$ through 0.08, while ferroelectric order is developed in ceramics with $y=0.10$ and 0.12. The incommensurate antiferroelectric phase in this composition series is characterized by the presence a Raman mode around 90cm$^{-1}$, and the ferroelectric phase displays strong modes around 60cm$^{-1}$ and 125cm$^{-1}$. Little difference is noticed between the paraelectric cubic phase and the multicell cubic phase in the Raman spectra, however, a different set of Raman modes is observed in the commensurate antiferroelectric phase from the incommensurate antiferroelectric phase. As revealed by Raman spectroscopy, the electric field-induced antiferroelectric-to-ferroelectric transition in PNZST 43/7/2 takes place gradually as field increases, and the reverse transition at zero field takes up to 4 hours.

4.6 Acknowledgements

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4.7 Figure List

Figure 4-1 X-ray diffraction spectra for the as-sintered Pb$_{0.99}$Nb$_{0.02}$[(Zr$_{0.57}$Sn$_{0.43}$)$_{1-y}$Ti$_y$]$_{0.98}$O$_3$ ceramics.

Figure 4-2 Dielectric constant of the Pb$_{0.99}$Nb$_{0.02}$[(Zr$_{0.57}$Sn$_{0.43}$)$_{1-y}$Ti$_y$]$_{0.98}$O$_3$ ceramics measured at 1kHz during cooling.

Figure 4-3 The temperature vs. composition phase diagram for the Pb$_{0.99}$Nb$_{0.02}$[(Zr$_{0.57}$Sn$_{0.43}$)$_{1-y}$Ti$_y$]$_{0.98}$O$_3$ ceramics derived from Figure 4-2.

Figure 4-4 The polarization vs. electric field hysteresis loops for the as-sintered Pb$_{0.99}$Nb$_{0.02}$[(Zr$_{0.57}$Sn$_{0.43}$)$_{1-y}$Ti$_y$]$_{0.98}$O$_3$ ceramics. $E_F$ is marked for PNZST 43/7/2 in (b). The slight distortion on the hysteresis loop of PNZST 43/8/2 is indicated by two dotted circles in (b).

Figure 4-5 The electric field vs. composition phase diagram for the Pb$_{0.99}$Nb$_{0.02}$[(Zr$_{0.57}$Sn$_{0.43}$)$_{1-y}$Ti$_y$]$_{0.98}$O$_3$ ceramics derived from Figure 4-4.

Figure 4-6 Raman spectra collected at room temperature from the as-sintered Pb$_{0.99}$Nb$_{0.02}$[(Zr$_{0.57}$Sn$_{0.43}$)$_{1-y}$Ti$_y$]$_{0.98}$O$_3$ ceramics.

Figure 4-7 The evolution of the characteristic modes A, F$_1$, and F$_2$ as a function of composition $y$ in Pb$_{0.99}$Nb$_{0.02}$[(Zr$_{0.57}$Sn$_{0.43}$)$_{1-y}$Ti$_y$]$_{0.98}$O$_3$ ceramics.

Figure 4-8 The thermal hysteresis of the antiferroelectric ↔ ferroelectric phase transition (marked by the two vertical arrows) in PNZST 43/8/2 revealed by dielectric constant measurement.

Figure 4-9 Thermal history effect in PNZST 43/8/2 revealed by Raman spectroscopy.
Figure 4-10 The commensurate antiferroelectric, the incommensurate antiferroelectric, the multicell cubic and the paraelectric cubic phases in PNZST 43/4/2 revealed by Raman spectroscopy.

Figure 4-11 The electric field-induced antiferroelectric-to-ferroelectric phase transition in PNZST 43/7/2 revealed by Raman spectroscopy.

Figure 4-12 The time-induced reverse transition at room temperature from the metastable ferroelectric phase in PNZST 43/7/2.
Figure 4-1 X-ray diffraction spectra for the as-sintered Pb$_{0.99}$Nb$_{0.02}$[(Zr$_{0.57}$Sn$_{0.43}$)$_{1-y}$Ti$_y$]$_{0.98}$O$_3$ ceramics.
Figure 4-2 Dielectric constant of the Pb$_{0.99}$Nb$_{0.02}$[(Zr$_{0.57}$Sn$_{0.43}$)$_{1-x}$Ti$_x$]$_{0.98}$O$_3$ ceramics measured at 1kHz during cooling.
Figure 4-3 The temperature vs. composition phase diagram for the $\text{Pb}_{0.99}\text{Nb}_{0.02}[(\text{Zr}_{0.57}\text{Sn}_{0.43})_{1-y}\text{Ti}_{y}]_{0.98}\text{O}_3$ ceramics derived from Figure 4-2.
Figure 4-4 The polarization vs. electric field hysteresis loops for the as sintered 
$Pb_{0.99}Nb_{0.02}[(Zr_{0.57}Sn_{0.43})_{1-y}Ti_y]_{0.98}O_3$ ceramics. $E_F$ is marked for PNZST 43/7/2 in (b). 
The slight distortion on the hysteresis loop of PNZST 43/8/2 is indicated by two dotted circles in (b).
Figure 4-5 The electric field vs. composition phase diagram for the

\[ \text{Pb}_{0.99}\text{Nb}_{0.02}[(\text{Zr}_{0.57}\text{Sn}_{0.43})_{1-y}\text{Ti}_y]_{0.98}\text{O}_3 \] ceramics derived from Figure 4-4.
Figure 4-6 Raman spectra collected at room temperature from the as-sintered 

\( \text{Pb}_{0.99}\text{Nb}_{0.02}[(\text{Zr}_{0.57}\text{Sn}_{0.43})_{1-y}\text{Ti}_y]_{0.98}\text{O}_3 \) ceramics.
Figure 4-7 The evolution of the characteristic modes A, F₁, and F₂ as a function of composition \( y \) in \( \text{Pb}_{0.99}\text{Nb}_{0.02}[\text{Zr}_{0.57}\text{Sn}_{0.43}]_{1-y}\text{Ti}_y\text{O}_3 \) ceramics.
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Figure 4-11 The electric field-induced antiferroelectric-to-ferroelectric phase transition in PNZST 43/7/2 revealed by Raman spectroscopy.
Figure 4-12 The time-induced reverse transition at room temperature from the metastable ferroelectric phase in PNZST 43/7/2.
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5. Phase Transition Toughening in Sn-Modified Lead Zirconate Titanate Antiferroelectric Ceramics


Hui He, and Xiaoli Tan*

5.1 Abstract

Comparative studies of the electric field-induced fracture behavior under bipolar cyclic fields in a ferroelectric Pb$_{0.99}$Nb$_{0.02}$[(Zr$_{0.57}$Sn$_{0.43}$)$_{0.94}$Ti$_{0.12}$]$_{0.98}$O$_3$ and an antiferroelectric Pb$_{0.99}$Nb$_{0.02}$[(Zr$_{0.57}$Sn$_{0.43}$)$_{0.94}$Ti$_{0.06}$]$_{0.98}$O$_3$ ceramic were conducted. Under identical electrical loadings, completely distinct fracture behaviors were observed in these two ceramics with very close compositions. Significant crack extension was found in the ferroelectric ceramic while no extension was detected in the antiferroelectric one. We propose that the high fracture resistance in the antiferroelectric ceramic is resulted from a phase transition toughening mechanism, similar to ZrO$_2$-based structural ceramics. Supporting evidence for localized phase transition was provided by an in situ Raman spectroscopic experiment.

Department of Materials Science & Engineering, Iowa State University, Ames, IA 50011

*Author to whom correspondence should be directed
5.2 Introduction

The PbZrO₃-based antiferroelectric ceramics are of technological importance due to their wide applications in microelectromechanical systems and energy storage devices. The PbZrO₃-based antiferroelectric ceramics are chemically modified from PbZrO₃ by adding Sn, Ti, and Nb or La to adjust the critical field for the phase transition and optimize the properties for processing and applications. It has been widely observed that optimized properties in these ceramics are resulted from their hierarchical microstructures: the subgrain level antiferroelectric 90° domains (the checkerboard pattern) and the nanoscale incommensurate modulations within the domains. Increase in Ti content eventually destroys these microstructures and leads to a normal ferroelectric behavior.

Both antiferroelectric and ferroelectric ceramics were developed based primarily on considerations of their electrical responses, and consequently, many of them display rather poor mechanical properties, such as low fracture toughness and high susceptibility to slow crack growth. Their mechanical behavior is always of major concern because their electric and mechanical responses are intimately coupled. When driven hard repeatedly under cyclic electric loading over long periods, these ceramics may accumulate enough mechanical damage to cause subcritical crack growth or catastrophic failure. On the other hand, development of crack-like flaws under mechanical loading may generate severe local field concentrations which may result in serious degradation of their electric performance.
During the fracture process of ferroelectric ceramics, a phenomenon called “ferroelectric toughening” has been observed in a set of experiments comparing the fracture toughness of the ferroelectric phase (below Curie temperature) and the paraelectric phase (above Curie temperature). The ferroelectric domains in the ferroelectric phase are ferroelastic domains at the same time and they respond to both electrical and mechanical loadings. As a consequence of domain switching, the measured fracture toughness at ferroelectric state was almost doubled as that at paraelectric state. However, to the authors’ best knowledge, toughening effect in antiferroelectric ceramics has not yet been reported. It has been noticed previously that the electric field-induced antiferroelectric-to-ferroelectric phase transition accompanies a volume expansion on the order of 1%. Inspired by the phase transition toughening mechanism in ZrO$_2$-based engineering ceramics, we suggest that antiferroelectric ceramics may display fracture resistance superior to ferroelectric ceramics due to contributions from both the volume expansion at the phase transition and the ferroelastic domain switching in the induced ferroelectric phase. In this paper, we present the first experimental evidence to verify the phase transition toughening effect in antiferroelectric ceramics.

5.3 Experimental Procedure

The materials used in this study were an antiferroelectric Pb$_{0.99}$Nb$_{0.02}$(Zr$_{0.57}$Sn$_{0.43}$)$_{0.94}$Ti$_{0.06}$O$_{3}$ (abbreviated as PNZST 43/6/2) ceramic and a ferroelectric Pb$_{0.99}$Nb$_{0.02}$(Zr$_{0.57}$Sn$_{0.43}$)$_{0.88}$Ti$_{0.12}$O$_{3}$ (abbreviated as PNZST 43/12/2) ceramic. Uniaxial hot pressing after calcination was employed to prepare high density ceramics. Raw powders with purity better than 99.9% of PbO, Nb$_2$O$_5$, ZrO$_2$, SnO$_2$, and TiO$_2$ were batched according to the chemical formula with 5% excess PbO powder to
compensate for the lead evaporation loss in the subsequent thermal process. Isopropyl alcohol was added to the mixed powders and the slurry was then milled in a plastic bottle with zirconia media on a vibratory mill for 6 hours. After drying the slurry in an oven at 150°C for 24 hours, the powders were calcined at 850°C for 4 hours in a covered alumina crucible. The calcined powder were then again milled for 6 hours, dried for 24 hours and calcined at 850°C for 4 hours to ensure the formation of pure perovskite phase.

The perovskite phase powder was then mixed with polyvinyl alcohol binder and cylindrical compacts were formed by uniaxial cold pressing. The preformed pellets were then hot-pressed in Al₂O₃ dies at 1150°C for 2 hours in air. Thin slices from the hot pressed pieces were annealed at 1300°C for 3 hours with PbZrO₃ as protective powder. After removal of surface layers by mechanical grinding, these ceramics were checked by X-ray diffraction for phase purity and scanning electron microscopy (SEM) for grain morphology. The antiferroelectric and ferroelectric domain structure in these ceramics was analyzed by transmission electron microscopy (TEM). Dielectric characterization was performed with an LCR meter (HP-4284A, Hewlett-Packard) at frequency of 1 kHz in conjunction with an environmental chamber. A heating/cooling rate of 3°C/minute was used during measurement. Electric field-induced polarization was recorded with a standardized ferroelectric test system (RT-66A, Radiant technologies).

One slice of each composition was polished and subsequently annealed at 200°C for 30 minutes to relieve the residual stress caused by cutting and polishing. Two gold electrodes with spacing of 2mm were then sputtered to one polished surface and copper wires were soldered to the electrodes using silver conductive epoxy. Next, a Knoop indentation was made at the center of the 2mm gap on the polished surface at a load of
1kg for 1 minute. The Knoop indentation was oriented with its longer axis parallel to the electrode edges so that the nominal electric field direction was perpendicular to the crack plane. The initial crack length, including the indentation impression length, was \( \sim 230 \) m for both samples. Figure 1(a) shows the schematic illustration of the specimen geometry.

Both specimens with Knoop indentations were then immersed into a 3M Fluorinert electronic liquid bath and connected to a high voltage amplifier (Model 610D, Trek) driven by a function generator. The two specimens were connected in parallel to ensure identical electrical loadings during test. The experimental set up is schematically shown in Figure 5-1(b). Bipolar electric fields with a sinusoidal waveform at a frequency of 30Hz were applied to the specimens. The peak electric field was held constant at \( \pm 20 \) kV/cm. The crack length was monitored and recorded by a digital optical microscope. The crack morphology was further examined in detail by SEM after the experiment.

5.4 Results

5.4.1 Structure and Electrical Properties

X-ray diffraction was used to check the phase purity and determine the average crystal structure of the ceramics. The results are shown in Figure 5-2. It is evident that both ceramics are phase pure with a perovskite structure. The PNZST 43/6/2 ceramic takes a pseudo-tetragonal structure with lattice parameters of \( a=b=4.108\)Å and \( c=4.086\)Å while the PNZST 43/12/2 takes a rhombohedral structure with \( a=b=c=8.202\)Å and \( \alpha=89.86^\circ \).
Temperature dependence of the dielectric permittivity for PNZST 43/6/2 and PNZST 43/12/2 is shown in Figure 5-3. The PNZST 43/6/2 ceramic shows a much weaker dielectric response in the test temperature range than PNZST 43/12/2. One distinct feature in the dielectric response of PNZST 43/6/2 is the presence of a plateau region between 142°C and 182°C. The dielectric constant peaks with a value of 1350 at the temperature of 182°C. According to previous studies, PNZST 43/6/2 is paraelectric at temperatures above 182°C. Below 142°C, down to the lower limit of the test temperature range, PNZST 43/6/2 exists in the antiferroelectric state. In contrast, PNZST 43/12/2 shows a typical ferroelectric behavior with a single sharp peak. At 127°C, the dielectric constant reaches its peak value of 8300. Below 127°C, PNZST 43/12/2 displays a ferroelectric behavior.

The polarization vs. electric field hysteresis measurement at room temperature confirmed the antiferroelectric order in PNZST 43/6/2 and the ferroelectric order in PNZST 43/12/2. As shown in Figure 5-4, characteristic double hysteresis loops were observed in PNZST 43/6/2 while a single hysteresis loop was recorded in PNZST 43/12/2. The antiferroelectric phase in PNZST 43/6/2 at room temperature transforms to a ferroelectric phase at a critical electric field about 39 kV/cm (referred to as $E_F$ in literature), and the reverse transition occurs when the field is lowered down to 18 kV/cm (referred to as $E_A$ in literature). Both transitions are abrupt and take place within a narrow range of field strength. For PNZST 43/12/2, a remanent polarization of 30μC/cm² and a coercive field of 6kV/cm were measured from the hysteresis loop.

SEM examination indicates a high relative density of both ceramics, as shown in Figure 5-5. The average grain size was estimated from SEM micrographs using a linear
intercept method. It is 3.1 m for PNZST 43/6/2 and 4.2 m for PNZST 43/12/2, respectively. TEM analysis revealed the subgrain domain structure in both ceramics. The PNZST 43/6/2 ceramic displays a domain structure with checkerboard-like patterns (Figure 5-6(a)), which are typical for antiferroelectric ceramics.\textsuperscript{6-9} The patches in the pattern are antiferroelectric 90° domains. Higher magnifications reveal a modulated fine structure with regular fringes at a periodicity around 2nm within the antiferroelectric domains. In contrast, regular ferroelectric domain stripes were found in the PNZST 43/12/2 ceramic (Figure 5-6(b)).

5.4.2 Electric field-induced fracture

The extension of indentation cracks under the application of bipolar cyclic electric fields was investigated for both PNZST 43/6/2 and PNZST 43/12/2. The crack length was continuously monitored and measured at a series of predetermined number of cycles. Under the test configuration depicted in Figure 5-1, cracks are expected to grow from both indentation tips. To minimize the disturbance to the experiment and ensure accuracy, crack growth from one indentation tip for each specimen was measured. The measurement was taken from the center of the indentation impression to the tip of the monitored crack and is referred as “half-crack length” hereafter. The results are shown in Figure 5-7. The most striking feature of the measurement is that significant crack growth was recorded for the ferroelectric PNZST 43/12/2 ceramic while absolutely no growth was detected for the antiferroelectric PNZST 43/6/2 ceramic. The half-crack length grew from 110\(\mu\)m to 580\(\mu\)m after 1.2\(\times\)10\(^6\) electrical cycles for PNZST 43/12/2 while stayed unchanged at 120\(\mu\)m for PNZST 43/6/2. The applied peak electric field, 20kV/cm, is 3.3 times of the coercive field of the PNZST 43/12/2 ceramic. The observed crack growth
driven by bipolar electric fields in the PNZST 43/12/2 ferroelectric ceramic is consistent with previous studies in Pb(Zr$_{1-x}$Ti$_x$)O$_3$ ferroelectric ceramics.$^{15,16,18}$ It is evident that under identical processing and testing conditions, the antiferroelectric PNZST 43/6/2 ceramic, with a very similar chemical composition, suppresses the electric-induced cracking completely, indicating a superior fracture resistance.

After the crack growth study, the two specimens were examined by SEM. The micrographs shown in Figure 5-8 reveal the crack morphology on the polished surfaces of both specimens. Extensive crack extension took place in the ferroelectric PNZST 43/12/2 ceramic along grain boundaries. The intergranular nature of the electric field-induced fracture in PNZST 43/12/2 is consistent to previous studies in Pb(Zr$_{1-x}$Ti$_x$)O$_3$ ceramics.$^{18}$ SEM examination also confirms that there was no electric field-induced fracture in the antiferroelectric PNZST 43/6/2 ceramic.

5.5 Discussion

We postulate that the ultrahigh fracture resistance in the antiferroelectric ceramic is resulted from localized antiferroelectric-to-ferroelectric phase transition induced by the applied electric fields. The presence of an insulating flaw in ferroelectric materials disturbs the electric field. For an infinite plane body with a through flaw in the form of an elliptical cylinder with the major and minor axes 2$a$ and 2$b$, the applied nominal electric field $E_0$ is intensified at the flaw tip by a factor of $\frac{1 + \frac{b}{a}}{\frac{b}{a} + \epsilon_f / \epsilon_m}$, where $\epsilon_f$ and $\epsilon_m$ are the dielectric constants of the flaw interior and the body, respectively.$^{19}$ For a slim ellipse where $b$ is much less than $a$, the intensification can be high but is bounded by $\epsilon_m / \epsilon_f$. For an crack-like flaw in the PNZST 43/6/2 ceramic filled with the Fluorinert liquid at
room temperature, \( \varepsilon_m = 430 \) and \( \varepsilon_f = 1.75 \). This leads to an intensification ratio of 246.

For the geometry in the current test specimens (Figure 5-1), the flaw is an indentation surface crack. Severe electric field intensification is expected at crack tips but the exact ratio may be different from 246. Nevertheless, at the applied peak field of 20kV/cm, the local electric field at the crack tip is expected to exceed the critical field \( E_F \) of 39kV/cm. As a consequence, the antiferroelectric-to-ferroelectric phase transition is expected to take place. Such phase transition is highly localized in the vicinity of the crack tip.

Attempts were then made to verify the existence of local phase transition at crack tips in PNZST 43/6/2 with micro Raman spectroscopy (inVia Raman Microscope, Renishaw). A laser with wavelength 488nm and beam size \(~2 \mu m\) was used. Unfortunately all attempts failed in PNZST 43/6/2 because arcing discharge invariably occurred before the electric field-induced phase transition. Therefore, a ceramic with a composition of \( \text{Pb}_{0.99}\text{Nb}_{0.02}[(\text{Zr}_{0.57}\text{Sn}_{0.43})_{0.93}\text{Ti}_{0.07}]_{0.98}\text{O}_3 \) (abbreviated as PNZST 43/7/2, with 1at.% higher Ti content than PNZST 43/6/2) was prepared and tested. The assintered PNZST 43/7/2 ceramic displays an antiferroelectric order with a much lower \( E_F \). The \textit{in situ} Raman experiment with applied electric field was successful with the PNZST 43/7/2 specimen and the results are shown in Figure 5-9. The Raman mode at 86cm\(^{-1}\) is a signature of the antiferroelectric order while the mode at 122cm\(^{-1}\) indicates the ferroelectric order. A strong peak at 86cm\(^{-1}\) while no peak at 122cm\(^{-1}\) was observed in the as sintered PNZST 43/7/2 ceramic. At a nominal applied electric field of 15kV/cm, the peak at 86cm\(^{-1}\) was weakened and the peak at 122cm\(^{-1}\) started to emerge for most areas between the two electrodes. However, at a spot in the close vicinity of a crack tip, the peak at 86cm\(^{-1}\) almost completely disappeared and an evident peak at 122cm\(^{-1}\) was
noticed. The results, therefore, demonstrated the occurrence of the electric field-induced antiferroelectric-to-ferroelectric phase transition at a local scale close to the crack tip.

We also performed *in situ* synchrotron x-ray diffraction experiment on a PNZST 43/6/2 sample under electric fields.\textsuperscript{27} Lattice structure Rietveld refinement indicates that the PNZST 43/6/2 ceramic at zero field actually takes an orthorhombic structure with the space group Bmm2 and the induced ferroelectric phase takes a rhombohedral structure with the space group R3c. A volume expansion of 0.5\% was measured at this electric field-induced phase transition.\textsuperscript{27} Therefore, the induced ferroelectric phase at the crack tip generates local compressive stresses, closing the crack wake and arresting the crack growth. Furthermore, the domain switching in the induced ferroelectric phase still contributes to ferroelectric toughening. Both mechanisms work in synergy, leading to superior fracture resistance in antiferroelectric ceramics.

### 5.6 Conclusion

The electric field-induced fracture behavior was compared in an antiferroelectric and a ferroelectric ceramic with close chemical compositions. Despite the ferroelectric domain switching toughening, extensive crack growth was still observed in the ferroelectric ceramic. In contrast, the electric field-induced fracture was completely suppressed in the antiferroelectric ceramic. A localized antiferroelectric-to-ferroelectric phase transition was confirmed to occur in the vicinity of crack tips in the antiferroelectric ceramic. The volume expansion during the electric field-induced phase transition leads to the superior fracture resistance in the antiferroelectric ceramic. This volume strain may also toughen the antiferroelectric ceramic under applied mechanical loadings.
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Figure 5-6 TEM micrographs of the subgrain domain structure. (a) the checkerboard pattern of the antiferroelectric 90° domains in the PNZST 43/6/2 ceramic, and (b) the regular ferroelectric domains in the PNZST 43/12/2 ceramic.

Figure 5-7 Half-crack length vs. cycles of applied bipolar electric fields at the peak level of ±20kV/cm.

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Figure 2 X-ray diffraction patterns for the PNZST 43/6/2 and the PNZST 43/12/2 ceramics.
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Figure 5-8 SEM micrographs of the crack morphology after the crack growth experiment.

(a) the PNZST 43/6/2 ceramic, and (b) the PNZST 43/12/2 ceramic.
Figure 5-9  *In situ* Raman spectroscopy with electric fields in PNZST 43/7/2 to verify the localized antiferroelectric-to-ferroelectric phase transition.
5.8 Reference

26 H. He, and X.Tan, “*In situ* Raman spectroscopic study of the phase transitions in Pb0.99Nb0.02[(Zr0.57Sn0.43)1-yTi_y]0.98O3 ceramics,” submitted to *Journal of Physics: Condensed Matter*.
27 G. Tutuncu, H. He, X. Tan, and E. Ustundag, “*In situ* synchrotron x-ray diffraction study of the electric field-induced phase transition in an antiferroelectric ceramic,” in preparation.
6 General Conclusions

The primary objective of the work presented in this dissertation was to gain a better understanding of the phase transitions in between ferroelectric and antiferroelectric states. A secondary goal was to verify certain feasible applications by taking advantage of the phase transitions. In-situ techniques were extensively used including in-situ TEM and in-situ Raman.

Electric field in-situ TEM technique is extremely powerful in revealing underlying physics mechanisms of field-induced phenomena in ferroelectric materials. With the new configuration of electroding on TEM specimens, the following observations were successfully made for the first time:

In situ TEM technique was used in the study of the electric field induced antiferroelectric to ferroelectric phase transformation in PZST 45/6/2 ceramic. Upon application of external electric fields, the wavelength of the incommensurate modulation in the antiferroelectric phase showed no change but the intensity of the satellite reflections decreased when the field exceeds a critical value. This critical strength matches closely to the $E_F$ measured in the bulk sample.

Our TEM study indicates that the incommensurate modulation in modified perovskite antiferroelectrics exists in the form of a transverse Pb-cation displacement wave. The observed incommensurate modulation at large scale is suggested to be a mixture of commensurate modulations at local scale. The modulations in antiferroelectric $90^\circ$ domains are then $180^\circ$ domain slabs with thickness of 3 or 4 layers of the pseudo-tetragonal $^{60}$ plane. The antiferroelectric $90^\circ$ domain wall deviates from the pseudo-tetragonal \{100\} plane due to the atomic steps on the domain wall created to preserve
The external electric field aligns the cation displacement prior to the field-induced antiferroelectric-to-ferroelectric phase transformation. The fraction of the volume with aligned cation displacement increases with increasing electric field, which leads to a decrease in the intensity of the corresponding satellite reflections in the selected area electron diffraction patterns. The cation displacement aligning process resembles the 90° and 180° domain switching process in normal ferroelectrics. When the field is applied along the cation displacement direction, the aligning process is easier and the process preserves. The modulation is disrupted when the field is applied perpendicular to the direction of cation displacement and severe streaking is observed in the corresponding satellite reflections.

The modulations were found to disappear at a field level close to the critical field for the antiferroelectric-to-ferroelectric transformation. In both PZST 45/6/2 and PZST 42/4.5/2 ceramics, only little increase (less than 2%) in the wavelength of the modulation was observed prior to the disappearance of the modulation.

Complementary to TEM, Raman spectroscopy also provided adequate information on the phase transitions in between ferroelectric and antiferroelectric states. Raman peaks that represent ferroelectric and antiferroelectric in PZST 43/y/2 ceramics were identified in order for subsequent monitoring of the phase transitions. As the Ti content increases from y=0.03 to 0.12, the most prominent feature in the Raman spectra is the softening of the mode around 90cm\(^{-1}\) and the appearance of the modes around 60cm\(^{-1}\) and 125cm\(^{-1}\). Temperature and thermal history dependence of the phase transitions was directly observed with an in situ Raman microscopy technique. Field induced ferroelectric phase
stability was analyzed with Raman microscopy. Electric field-induced AFE-FE phase transition was directly observed with an in situ Raman microscopy technique.

With the structural information and the knowledge of the phase transitions in these materials, the electric field-induced fracture behavior was compared in an antiferroelectric and a ferroelectric ceramic with close chemical compositions. Despite the ferroelectric domain switching toughening, extensive crack growth was still observed in the ferroelectric ceramic. In contrast, the electric field-induced fracture was completely suppressed in the antiferroelectric ceramic. A localized antiferroelectric-to-ferroelectric phase transition was confirmed to occur in the vicinity of crack tips in the antiferroelectric ceramic. The volume expansion during the electric field-induced phase transition leads to the superior fracture resistance in the antiferroelectric ceramic. This volume strain may also toughen the antiferroelectric ceramic under applied mechanical loadings.
7 Recommendations for Further Study

This work has revealed the evolution of the incommensurate modulation in antiferroelectric to ferroelectric phase transitions by means of monitoring the diffraction patterns in-situ. Future study in this field of antiferroelectric to ferroelectric is suggested to focus on the high resolution transmission electron microscopy with an in-situ technique similar to what was shown in this thesis. In this way, the change of the modulation fringes can be directly monitored at atomic resolution.

For Raman study, a well build model is needed to further explain the evolution of the monitored Raman modes associated with the AFE and FE phases. In addition, quantification of the peak position and intensity as a function of composition, temperature, electric field and time should be pursued. Thermodynamics and kinetics models are suggested to be developed to interpret the phase transitions.

For the phase transition toughening effect, detailed experiments, such as fracture toughness measurement with and without applied electric fields, are needed to further evaluate the increased resistance for crack growth.
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Appendix: Publication List


2. **H. He**, and X. Tan, Electric field-induced transformation of incommensurate modulations in antiferroelectric Pb0.99Nb0.02[(Zr1-xSnx)1-yTiy]0.98O3, *Physical Review B*, 72, 024102-1-10 (2005).

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5. N. Vittayakorn, G. Rujijanagul, X. Tan, **H. He**, M. A Marquardt, and D. P Cann, Dielectric properties and morphotropic phase boundaries in the xPbZn1/3Nb2/3O3-(1-x)PbZr0.5Ti0.5O3 pseudo-binary system, Journal of Electroceramics (2006), 16(2), 141-149


7. **H. He**, and X. Tan, Raman spectroscopy study of the phase transitions in Pb0.99Nb0.02[(Zr0.57Sn0.43)1-yTiy]0.98O3 ceramics, *Journal of Physics: Condensed Matter*, 19, 136003-1-13 (2007).