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In situ transmission electron microscopy study of the microstructural origins for the electric field-induced phenomena in ferroelectric perovskites

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In situ transmission electron microscopy study of the microstructural origins for the electric field-induced phenomena in ferroelectric perovskites

by

Hanzheng Guo

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Materials Science & Engineering

Program of Study Committee:
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Matthew J. Kramer

Iowa State University
Ames, Iowa
2014

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DEDICATION

Dedicated to my parents for their continuous love and support in my life.
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ABSTRACT

Ferroelectrics are important materials due to their extensive technological applications, such as non-volatile memories, field-effect transistors, ferroelectric tunneling junctions, dielectric capacitors, piezoelectric transducers, sensors and actuators. As is well known, the outstanding dielectric, piezoelectric, and ferroelectric properties of these functional oxides originate from their ferroelectric domain arrangements and the corresponding evolution under external stimuli (e.g. electric field, stress, and temperature). Electric field has been known as the most efficient stimulus to manipulate the ferroelectric domains through polarization switching and alignment. Therefore, direct observation of the dynamic process of electric field-induced domain evolution and crystal structure transformation is of significant importance to understand the microstructural mechanisms for the functional properties of ferroelectrics.

In this dissertation, electric field in situ transmission electron microscopy (TEM) technique was employed to monitor the real-time evolution of the domain morphology and crystal structure during various electrical processes: (1) the initial poling process, (2) the electric field reversal process, and (3) the electrical cycling process. Two types of perovskite-structured ceramics, normal ferroelectrics and relaxor ferroelectrics, were used for this investigation. In addition to providing the microscopic insight for some well-accepted phase transformation rules, discoveries of some new or even unexpected physical phenomena were also demonstrated.

For the initial poling process, microstructural origins for the piezoelectricity development in the three most promising lead-free piezoceramic systems were
investigated. For the non-ergodic relaxor ferroelectric compositions ($x = 6\% - 9\%$) in the 
$(1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3-x\text{BaTiO}_3$ system, well-developed piezoelectricity was realized at 
poling fields far below the coercive field and phase transition field. Such an unusual 
behavior is attributed to the electric field-induced irreversible $P4bm$ nanodomains 
coalescence into thin lamellar domains prior to the phase transition. In the 
$(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$-based ceramics, as demonstrated by an archetypical polymorphic phase 
boundary (PPB) composition of $0.948(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3-0.052\text{LiSbO}_3$, the origin of 
the excellent piezoelectric performance is due to a tilted monoclinic phase that emerges from 
the tetragonal and orthorhombic PPB at the poling fields beyond 14 kV/cm. This 
monoclinic phase, as manifested by the appearance of blotchy domains and $1/2\{oeo\}$ 
superlattice diffraction spots, was determined to possess a $Pm$ symmetry with $a^0b^+c^0$ 
oxygen octahedra tilting and antiparallel cation displacements. For the PPB composition 
of $x = 0.5$ in the $(1-x)\text{Ba(}Zr_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ solid solution system, the original 
multi-domain state was found to transform into a unique single-domain state with 
orthorhombic symmetry at very moderate poling fields of 3~6 kV/cm. This single-
domain state is suggested to be primarily responsible for the observed large 
piezoelectricity due to its significant elastic softening.

In the electrical reversal process, a highly unusual phenomenon of electric field-
induced ferroelectric-to-relaxor phase transition was directly observed in a lead-free 
composition of $[(\text{Bi}_{1/2}\text{Na}_{1/2})_{0.95}\text{Ba}_{0.05}]_{0.98}\text{La}_{0.02}\text{TiO}_3$. It is manifested by the disruption of 
large ferroelectric domains with long range polar order into polar nanodomains with short 
range orders when the polarity of electric field is reversed. This observation was further
rationalized by a phenomenological model that takes the large difference in kinetics between the phase transition and the polarization reversal processes into account.

During the electrical cycling process, the microstructural mechanisms for electric fatigue behaviors of two ceramics were investigated. In 0.7Pb(Mg_{1/3}Nb_{2/3})O_3-0.3PbTiO_3, the frozen domain configuration after $10^3$ cycles is responsible for the pronounced functionality degradation. Both seed inhibition and domain wall pinning mechanisms were suggested to be the reasons for the observed fatigue behavior. In the polycrystalline ceramic of [(Bi_{1/2}Na_{1/2})_{0.95}Ba_{0.05}]_{0.98}La_{0.02}TiO_3, a novel phenomenological mechanism of domain fragmentation was found in addition to the domain wall pinning mechanism. Domain fragmentation contributes to the switchable polarization reduction by breaking the long-range polar orders, as visualized by the decomposition of large domains into domain fragments upon bipolar electrical cycling.
CHAPTER 1. Introduction

1.1 Motivation: understanding the functionalities of ferroelectrics from microscopic insight

As is well known, ferroelectrics are polar materials. The functionalities of ferroelectrics, for example, the dielectric, piezoelectric, ferroelectric, pyroelectric, and electrocaloric properties, can be traced to the polarization states and their responses to external stimuli. Generally, these polarization states are manifested in the form of ferroelectric domain, within which the polarization is uniform. When a ferroelectric crystal is exposed to an external electric field, polarization switching will take place and can be visualized through domain morphology alteration. On the other hand, the polarization state in a ferroelectric crystal is directly determined from its structural symmetry. The polarization variance is highly electrical-process-dependent, and often times yields to phase transitions. Therefore, direct observation of the ferroelectric domain and crystal structure evolution under various electrical processes are the key to clarifying the microstructural origin for functionalities of ferroelectrics. The in situ transmission electron microscopy (TEM) investigation presented in this dissertation is to serve this purpose.

As illustrated in Fig.1-1, three electrical processes are mainly focused in this thesis research. The initial poling process, where the electric field is applied for the first quarter cycle to a ceramic at its virgin state, is crucial to the piezoelectricity development in polycrystalline ceramics. Piezoelectricity is forbidden in the virgin state of ceramics because of the centrosymmetric m symmetry resulted from the randomly oriented
grains. Upon initial poling, polarization switching and alignment take place, leading to a domain morphology change and also possible phase transitions. For the three most promising lead-free ceramic systems studied in this dissertation, namely \((K_{0.5}Na_{0.5})NbO_3\) (KNN)-based, \(((Bi_{1/2}Na_{1/2})TiO_3-BaTiO_3\) (BNT-BT), and \(Ba(Zr_{0.2}Ti_{0.8})O_3-(Ba_{0.7}Ca_{0.3})TiO_3\) (BZT-BCT) solid solutions, the optimized piezoelectricity is always found at the morphotropic phase boundary (MPB) or polymorphic phase boundary (PPB) with coexisting phases in the virgin state. However, how these energetically comparable states evolve (both phenomenologically and crystallographically) under poling fields still puzzles researchers in the piezoelectrics community. In this dissertation, this question has been clearly addressed from a microscopic point of view by using the in situ TEM technique.
Fig. 1-1 Polarization evolution during various electrical processes: (1) the initial poling process, (2) the electrical reversal process, and (3) the electrical cycling process. Schematic illustrations of the polarization switching and alignment in processes (1) and (2) are respectively shown on the upper right and left. The polarization evolution as a function of the number of electrical cycles during fatigue is schematically depicted at the lower right corner.

After initial poling, the switched domains yield remnant polarization and impart piezoelectricity to the ceramic. Microscopically, micron-sized domains with long range polar orders are developed as a consequence. Additionally, the electric field (with \( \infty m \) symmetry) triggers a symmetry change from \( \infty \infty m \) to \( \infty m \) in this process according to Curie’s principle. This is the case for normal ferroelectrics, as well as for relaxor ferroelectrics. Following Curie’s principle and Coulomb’s law, electric fields would only favor the poled ferroelectric phase with an \( \infty m \) macroscopic symmetry. Therefore, upon electrical reversal, it is generally observed that the \( \infty m \) symmetry is still preserved through nucleation and growth of new domains with aligned polar vector [see the schematic illustration on the upper left part in Fig. 1-1 for process (2)]. This process is shown here unexpectedly that phase transitions that form transient phases take place, competing with polarization reversal. A relaxor ferroelectric with finely tuned composition of \([(Bi_{1/2}Na_{1/2})_{0.95}Ba_{0.05}]_{0.98}La_{0.02}TiO_3\) (BNT-5BT-2La) was first designed and then demonstrated as a model system to investigate the transient state due to its extremely slow kinetics of phase transition during electrical reversal. A highly unusual phenomenon of electric field-induced isotropization was revealed through a ferroelectric-to-relaxor transition and visualized under TEM.

As illustrated in the third process with repetitive applications of electrical reversals, the electric fatigue phenomenon occurs. It is generally manifested by the reduction in
switchable polarizations as well as the increase in coercive field as the electrical cycle proceeds. Electric fatigue in ferroelectric oxides has been a long-lasting research topic due to its importance to the fundamental science and relevance to extensive technological applications. During the past several decades, extensive studies have been carried out to uncover the underlying mechanisms for electric fatigue. However, the vast majority of these efforts have focused on the macroscopic behavior instead of microscopic events. As emphasized in the beginning, the domain dynamics is fundamental to elucidating the functionality evolution in ferroelectrics. The microscopic observations on the domain morphology and crystal structure evolution during fatigue process provide direct evidences to clarify the microstructural mechanisms for electric fatigue. In this dissertation, the electric field in situ TEM, for the first time, was employed for the electric fatigue studies. Two representative ceramics, [(Bi$_{1/2}$Na$_{1/2}$)$_{0.95}$Ba$_{0.05}$]$_{0.98}$La$_{0.02}$TiO$_3$ (BNT-5BT-2La) and 0.7Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-0.3PbTiO$_3$ (0.7PMN-0.3PT), were used for the demonstration. In addition to confirming some well-known fatigue mechanisms, a novel mechanism of domain nanofragmentation was discovered in [(Bi$_{1/2}$Na$_{1/2}$)$_{0.95}$Ba$_{0.05}$]$_{0.98}$La$_{0.02}$TiO$_3$.

Through the studies included in this dissertation, the electric field in situ TEM technique is demonstrated as an efficient and powerful probing tool to provide deep insight into the functionality evolution of ferroelectrics.

1.2 The key experimental technique: electric field in situ TEM

The electric field in situ TEM experimental setup is illustrated in Fig. 1-2. Disk specimens (3 mm in diameter) were prepared from as-processed pellets through standard
procedures including grinding, cutting, dimpling, and ion milling. The dimpled disks were thermally annealed above the Curie temperature to minimize residual stresses before Ar-ion milling to the point of electron transparency. Gold electrodes separated by \( \sim 120 \ \mu m \) were evaporated onto the flat side of the specimen as illustrated in Fig. 1-2a. One droplet of insulating varnish was used to fix the specimen to the sample cup (right side in Fig. 1-2c). The electrodes of the specimen were connected to the two electrical contacts, respectively, by using platinum wires and conductive epoxy in the way shown in Fig. 1-2a.

*In situ* TEM experiments were carried out on specimens that were crack-free at the edge of the central perforation on a Phillips CM30 microscope operated at 200 kV. The presence of a central perforation intensified the electric field in the TEM specimen.\(^{16,17}\) This intensification ratio is 2 for an ideal circular perforation.\(^{16,17}\)
Fig. 1-2 The electric field *in situ* TEM technique. (a) Schematic illustration of the sample configuration for the electric field *in situ* TEM experiment. The examined regions at the perforation are marked in red. (b) Schematic illustration of the connection of the high-voltage power supply to the TEM specimen. (c) Photograph of the tip of the electric field *in situ* TEM specimen holder used in the present study. The Pt thin wires in (a) are connected to the electrical contacts.
1.3 Dissertation organization

This dissertation is composed of a number of journal articles published or submitted for publication and organized as follows:

Chapter 1 is the introduction to the research motivation and the setup of the in situ TEM experiment.

Chapter 2 provides the important technical background information with several basic concepts that are frequently referred to in this dissertation. Then, a comprehensive literature review relevant to the topics in subsequent chapters follows.

Chapter 3 focuses on the microstructural origins for the piezoelectricity development in lead-free piezoelectric ceramics during the initial poling process. Four journal papers on three ceramic systems are assembled: a published paper in Applied Physics Letters on (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-BaTiO$_3$ ceramics; a published paper in Journal of Applied Physics on (K$_{0.5}$Na$_{0.5}$)NbO$_3$-based ceramics; and two papers in Physical Review B (one published and one in press) on Ba(Zr$_{0.2}$Ti$_{0.8}$)O$_3$-(Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$ ceramics.

Chapter 4 contains a journal paper submitted to Nature Materials concerning the electric field-induced ferroelectric-to-relaxor phase transition in the [(Bi$_{1/2}$Na$_{1/2}$)$_{0.95}$Ba$_{0.05}$]$_{0.98}$La$_{0.02}$TiO$_3$ ceramic during the electrical reversal process.

Chapter 5 focuses on the microstructural evolution during bipolar fatigue in two ceramics. It contains a journal paper submitted to Nature Communications on the [(Bi$_{1/2}$Na$_{1/2}$)$_{0.95}$Ba$_{0.05}$]$_{0.98}$La$_{0.02}$TiO$_3$ ceramic, and the other one submitted to Journal of Materials Research (focused issue on In situ and Operando Characterization of Materials) on 0.7Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-0.3PbTiO$_3$. 
Chapter 6 summarizes the main conclusions of this dissertation and also presents perspectives for further investigations.

References


CHAPTER 2. Literature Review

This chapter provides the necessary technical background for the dissertation. It starts with a general introduction to concepts and characteristics of piezoelectrics, ferroelectrics, relaxor ferroelectrics, perovskite structure, ferroelectric domain and phase boundaries. Then, a comprehensive literature review on the current research progress on (1) microscopic understanding of electric fatigue, and (2) lead-free solid solutions, are presented. For the lead-free ceramics, three most promising systems, the \((K_{0.5}Na_{0.5})NbO_3\)-based, \(Ba(Zr,Ti)O_3-(Ba,Ca)TiO_3\), and \((Bi_{1/2}Na_{1/2})TiO_3-BaTiO_3\) solid solutions, are included.

2.1 Piezoelectrics and ferroelectrics

2.1.1 Concepts and characteristics

Piezoelectricity is understood as the linear electromechanical coupling between mechanical stress and electric polarization (the direct piezoelectric effect) or between mechanical strain and applied electric field (the converse piezoelectric effect) in crystalline materials without inversion symmetry.\(^1\) Mathematically, the tensor form expression of the direct and converse piezoelectric effect can be written as:

\[
P_i = d_{ijk}X_{jk} \text{ (direct piezoelectric effect)}
\]

\[
x_{ij} = d_{ijk}E_k \text{ (converse piezoelectric effect)}
\]

where \(P\) is the electric polarization, \(X\) is the mechanical stress, \(x\) is the mechanical strain, \(E\) is the electric field, and \(d\) is the piezoelectric coefficient, which is a third rank tensor to characterize the degree of this coupling effect. The subscripts indicate the direction of
these physical quantities. The thermodynamic theory has proved the equivalence of the direct and converse piezoelectric effect.  

Because of the symmetric nature of the stress tensor \(X_{jk} = X_{kj}\), the original 27 (=\(3^3\)) tensor components in \(d_{ijk}\) can be reduced to 18 independent ones. Furthermore, a \(6 \times 3\) (or \(3 \times 6\)) matrix \(d_{ij}\) can be used for the matrix form of the piezoelectric effect:

\[
P_i = d_{ij}X_j \text{ (direct piezoelectric effect)}
\]

\[
x_j = d_{ij}E_i \text{ (converse piezoelectric effect)}
\]

where \(i = 1-3, j = 1-6\).

---

**Fig. 2-1** Classification of piezoelectrics, pyroelectrics and ferroelectrics in terms of the crystallographic symmetry.

As illustrated in Fig. 2-1, among the 32 point groups, there are 11 centrosymmetric point groups do not exhibit piezoelectricity. This is due to the fact that: the nature of \(d\) is a third rank tensor, the existence of the inversion center makes \(d_{ijk} = 0\) after applying the Neumann’s principle, which states: “The symmetry of any physical properties of a crystal must include the symmetry elements of the point group of the crystal.” In other words,
the tensor form of the physical properties keeps unchanged before and after applying the crystal structure symmetry operation. For point group 432, although it is a noncentrosymmetric group, the high symmetry nature yields zero value to all of the tensor components in $d$ after applying Newmann’s principle. Therefore, only 20 point groups are allowed for the piezoelectricity: 1, 2, 3, 4, 6, m, 3m, mm2, 4 mm, 6 mm, 222, 4, 422, 42m, 32, 6, 622, 62m, 23, 43m.

The above summarized rules can be also applied to the polycrystalline ceramics. For the as-sintered polycrystalline ceramics, the grains are randomly oriented. The macroscopic symmetry is isotropic, and hence is designated as the centrosymmetric Curie group $\infty\infty m$. As a result, piezoelectricity is not allowed. In order to achieve piezoelectricity in polycrystalline ceramics, macroscopic net spontaneous polarization should be introduced, which requires the material to be ferroelectric.

Ferroelectricity refers to a property of certain crystals that have the spontaneous electric polarization, and also the spontaneous polarization can be reoriented by the applied external electric field. Thus ferroelectrics can only be found in pyroelectric point groups, which is a subgroup of piezoelectric point groups. The unique polar axis in the pyroelectrics dictates the spontaneous polarization $P_s$. In addition, only the pyroelectrics with electric field-reversible polarizations can be ferroelectrics. The pyroelectric point groups are the first 10 listed in the aforementioned piezoelectric point groups.

As mentioned above, the macroscopic isotropy of polycrystalline ceramics (with $\infty\infty m$ symmetry) should be broken in order to exhibit piezoelectricity. Thus the electrical poling process, where a direct current electric field (with $\infty m$ symmetry) is applied to align the polarization in the ceramics, can be applied for this purpose.
Curie’s principle, a crystal under an external force will exhibit only those symmetry elements that are common to the crystal and the force.\textsuperscript{1} Therefore, the original Curie group $\infty\infty m$ is transformed to $\infty m$ for all piezoelectric ceramics after electrical poling.\textsuperscript{1} For the piezoelectric coefficient matrix, it can be further reduced to three independent coefficients ($d_{15}$, $d_{31}$ and $d_{33}$). Among them, $d_{33}$ is often used to characterize the piezoelectric activity of the polycrystalline ceramics, because it reveals the polarization (or strain) introduced along the direction of applied stress (or electric field).

2.1.2 Ferroelectric domains and domain walls

Ferroelectric domain is the fundamental microstructural unit to the study of the piezoelectric ceramic. It dictates the dielectric, ferroelectric, and piezoelectric properties of these polycrystalline ceramics.\textsuperscript{4} The spontaneous polarization in the perovskite structure is originated from the separation between the positive and negative charge centers. It can point to different directions in the polycrystalline ceramics, or even within one grain. The region in a grain that exhibits a uniform polarization is called a ferroelectric domain (Fig. 2-2).\textsuperscript{5} A grain is always occupied by many different ferroelectric domains. The plane separating two adjacent domains is a domain wall (Fig. 2-2).\textsuperscript{5} Generally, the polarizations in different domains are arranged in the “head-to-tail” configuration to satisfy the charge neutral condition at the domain wall.\textsuperscript{5, 6} The spontaneous polarizations in ferroelectric domains are not randomly oriented, but limited to certain crystallographic directions based on the crystal structure.\textsuperscript{5, 6} It thus yields certain crystallographic planes for the domain wall.\textsuperscript{5, 6}
Fig. 2-2 Schematic diagram of ferroelectric domains and domain walls within one grain of tetragonal BaTiO$_3$. The polarizations $P_S$ within each domain are marked by blue arrows. The crystallographic directions are based on the pseudocubic (pc) system.

If taking BaTiO$_3$ as an example, the polarizations can only be along the six equivalent $<$001$>_{pc}$ directions for the tetragonal structure, because the lattice elongates along the $c$-axis of the cubic BaTiO$_3$, which leads to the positive/negative charge center separation along the same direction. The subtending angle between the two neighboring polarizations across a domain wall can only be either 90° or 180°. For the resulted domain walls, only $\{110\}_{pc}$ planes are permissible for the 90° configuration. Similarly, the polarization within a domain can only adopt one of the eight $<$111$>_{pc}$ directions for a rhombohedrally structured crystal. The domain walls are limited to $\{100\}_{pc}$ and $\{110\}_{pc}$ planes for 71° and 109° configurations, respectively. For the orthorhombic structure, twelve $<$110$>_{pc}$ directions are available for the polarization. The $\{100\}_{pc}$ and $\{110\}_{pc}$ planes are found for the 90° and 120° domain walls. The orientation of the 60° domain walls depends on the piezoelectric coefficient of the materials. For the 180° domain wall in all these structures, it is required only to be parallel to the respective polarizations and do not have to be on a specific crystallographic plane. The orientation of domain walls is
a helpful tool to analyze the crystal structure, especially in cases that no superlattice diffraction can be used for differentiation.

Fig. 2-3 Multi-domain morphology of a poled BaTiO$_3$ ceramic.\textsuperscript{7}

In essence, the ferroelectric domain is a result of twinning process, which is commonly observed in ceramics and metals below the temperature of the ferroelastic or ferroelectric structural phase transition as a consequence of energy minimization.\textsuperscript{4,8-10} In ferroelectrics, electrical and mechanical boundary conditions may arise due to the crystal lattice distortions when the crystal is cooled through the paraelectric-to-ferroelectric phase transition temperature.\textsuperscript{4} The sum of electrostatic energy and the elastic energy associated with the electrical (spontaneous polarization) and mechanical (spontaneous strain) constraints may be minimized by the formation of ferroelectric or ferroelastic domains, when the energy of domain walls is counter balanced.\textsuperscript{10} Generally, two types of domain walls of the 180$^\circ$ and non-180$^\circ$ configurations are observed in ferroelectrics. The electrostatic energy is minimized when the polarization vectors in adjacent domains adopt a configuration such that div $\mathbf{P} = 0$ at the domain wall.\textsuperscript{8} This is satisfied for both non-180$^\circ$ and 180$^\circ$ walls, where neighboring polarization vectors take the “head-to-tail”
arrangement across the domain boundary in non-180° configurations, or opposite orientations in the 180° case. Therefore, both types of domain walls are ferroelectric domain walls because of the orientation difference between the adjacent polarization vectors. Additionally, the non-180° walls are created to release internal stresses in the crystal during the paraelectric-to-ferroelectric phase transition. They are also ferroelastic domain walls due to the orientation difference of the spontaneous strains. For the 180° wall, there is no elastic energy associated. In a word, the formation of domain walls is an inevitable process during the paraelectric-to-ferroelectric phase transition in ferroelectrics for energy minimization. Non-180° domain walls are created to minimize both electrostatic and elastic energies, while for 180° walls, electrostatic energy reduction is predominant.

In polycrystalline ceramics, a crystallite (grain) is clamped by its neighboring grains in all three dimensions, which usually leads to a complex multi-domain structure (Fig. 2-3). In ferroelectric single crystals, which are mechanically free and therefore, in principle, do not need the presence of domains, the formation of domain walls is also inevitable due to minimization of electrostatic energy and possible inhomogeneous internal stresses or inhomogeneous compositions. A single-domain state without any domain walls may be achieved in a single crystal by electrical poling though domain switching. For polycrystalline ceramics, however, the single-domain state is extremely difficult to be reached by poling because many domains cannot be completely re-oriented and aligned along the external field direction due to a complex set of internal stresses.
2.1.3 Normal ferroelectrics

The functionalities of ferroelectric crystals are significantly influenced by the difference in domain structures, leading to different types of ferroelectric materials. In this dissertation, two types of ferroelectrics, the normal ferroelectric and relaxor ferroelectrics, are investigated. This section and the following one will introduce the concepts and characteristics of each type.

To a microscopic point of view, normal ferroelectric crystals are usually manifested with micrometer-sized large domains. As for this domain structure, an example is shown in Fig. 2-4a for a set of 90° domains in tetragonally structured BaTiO$_3$. As can be seen, well-aligned domains with different contrast are arranged in an alternative way, yielding to a micrometer-sized lamellar domain patterns with well-defined domain walls along the [101]$_{pc}$ direction. The size of these lamellar domains indicates a long range polar order at the length scale of micrometer.

![Fig. 2-4 Bright-field TEM micrographs of the ferroelectric domain switching in tetragonal BaTiO$_3$ single crystal along the [010]$_{pc}$ zone axis.](image)

(a) Initial morphology in the virgin state; and (b) 3.76 kV/cm for 120 min. The direction of the external field is along [001]$_{pc}$ and marked by the bright arrow in (a).
As illustrated in Section 2.1.2, the polarization of the tetragonal phase can only point to \(<001>_{pc}\) directions. In Fig. 2-4a, the two polarizations of adjacent domains are aligned along \(<001>_{pc}\), but are \(90^\circ\) apart across the domain wall. When a sufficiently strong electric field (e.g. along the \([001]_{pc}\) direction) is applied to the crystal, the polarizations will be aligned along the field direction through Coulomb force. As a result, the domains with polarizations close to the electric field direction grow at the expense of other domains with unfavored polarizations (Fig. 2-4b). Macroscopically, the polarization switching process under applied electric field can be reflected in the polarization \((P)\) vs. electric field \((E)\) hysteresis loop, which has been known as the most important characteristic of ferroelectric materials.\(^1\) As shown in Fig. 2-5, after sufficient domain switching under the maximum electric field \((E_m)\), the polarization reaches a saturated value. Upon removal of the field, the domain morphology is mostly preserved, leading to a remnant polarization \((P_r)\). When the polarity of the driving electric field is reversed, the polarization also follows the reversal as a response. During this process, the coercive
field $E_C$ is usually used to characterize the critical field that brings the polarization to zero.\(^1\) If electric fields with both polarities are applied for a full cycle, a closed $P$-$E$ hysteresis loop is thus observed.

![Dielectric permittivity vs. temperature](image)

**Fig. 2-6** Typical temperature dependence of dielectric permittivity for normal ferroelectrics.

When a normal ferroelectric crystal is heated up, it undergoes a first-order phase transition from a low-temperature ferroelectric polar state to a high-temperature paraelectric non-polar state.\(^4\) The temperature of this phase transition is the Curie temperature ($T_C$).\(^4\) Above $T_C$, the dielectric permittivity decreases with temperature following the Curie-Weiss law: $\varepsilon' = \varepsilon_0 + C/(T - T_C)$, where $C$ is the Curie constant, and $\varepsilon_0$ is the vacuum permittivity.\(^4\) For normal ferroelectrics, the dielectric permittivity changes dramatically when the ferroelectric-to-paraelectric phase transition is approached, leading
to a sharp dielectric anomaly at $T_C$ (Fig. 2-6). In addition, another feature of normal ferroelectrics is the absence of frequency dispersion of the permittivity below $T_C$. This is an important characteristic to distinguish the normal ferroelectrics from the relaxor ferroelectrics.

2.1.4 Relaxor ferroelectrics

Fig. 2-7 (a) Schematic illustration of the polar nanoregions; (b) and (c) Bright field TEM micrographs of relaxor ferroelectrics under lower and higher magnifications.

Relaxor ferroelectrics or relaxors are characterized by the polar nanoregions (PNRs), as illustrated in Fig. 2-7. Instead of the well-defined micrometer-sized domains in normal ferroelectrics, relaxors exhibit nanodomains without clearly contrasted domain walls under TEM (Figs. 2-7b,c). Also, a different dielectric behavior is noted (Fig. 2-8). In contrast to the sharp transition at $T_C$ in normal ferroelectrics, relaxors display a diffuse phase transition with a broadened dielectric maximum. In addition, a strong frequency dispersion in the dielectric permittivity is observed below the temperature at the maximum permittivity ($T_m$).
Fig. 2-8 Temperature dependent dielectric permittivity of relaxor ferroelectrics.\textsuperscript{13} PE, ER, NR, and CW law refer to paraelectric, ergodic relaxor, non-ergodic relaxor, and Curie-Weiss law, respectively.

Similar to normal ferroelectrics, relaxors possess a cubic paraelectric phase at high temperatures. The dielectric permittivity still follows the Curie-Weiss law without frequency dispersion.\textsuperscript{13} Upon cooling, PNRs are formed inside the cubic matrix, accompanied with a slight frequency dispersion in the permittivity. At this stage, the system is called “ergodic relaxor” because the polarizations in the PNRs can experience all the possible equivalent polar states under the influence of thermal fluctuation.\textsuperscript{13} The temperature that marks the paraelectric-to-ergodic state is denoted as Burns temperature ($T_B$).\textsuperscript{13} When the temperature is decreased below $T_B$, the dynamics of the PNRs gradually slows down, leading to a broad permittivity and pronounced frequency dispersion due to the elongated dipole relaxation time.\textsuperscript{13} Also, the temperature of the maximum permittivity ($T_m$) becomes significantly frequency dependent. With further decrease in the temperature to below the so-called “freezing temperature ($T_f$)”, the ergodic PNRs are completely frozen into the non-ergodic state.\textsuperscript{13} For the non-ergodic relaxors, an important characteristic is that the frozen PNRs can be irreversibly switched and aligned under
externally applied electric field, and thus leading to a development of large ferroelectric domains with long range polar orders through a relaxor-to-ferroelectric transformation, as demonstrated in Fig. 2-9. If the non-ergodic relaxor is subject to an electric cycle, a \( P-E \) hysteresis loop similar to the normal ferroelectrics will be observed.

![Fig. 2-9 Bright field TEM micrographs of a non-ergodic relaxor to ferroelectric transformation under electric field. (a) the virgin state, (b) at 10 kV/cm, and (c) at 15 kV/cm. (from my own unpublished results).]

### 2.2 Perovskite structure

Perovskite structure is one of the most extensively studied structures regarding to its dielectric, piezoelectric and ferroelectric properties. All of the compositions concerned in this dissertation adopt the perovskite structure. The general formula of perovskite structure is \( \text{ABO}_3 \) with B and A cations locate at the body center and eight corners of a cube, respectively; while the oxygen anions are situated at six cubic face centers (Fig. 2-10). Thus the corner-linked \( \text{BO}_6 \) octahedra is formed in the 3-dimension space.
The prototype of the perovskite structure is a centrosymmetric cubic, where neither piezoelectricity nor ferroelectricity can be found. However, the piezoelectricity and ferroelectricity can be achieved after composition, temperature, stress, and electric field-induced lattice deviation from the prototypic cubic structure. Microscopically, the spontaneous polarization is induced via the separation between the charge centers of cations and anions. Generally, such deviations are caused by two ways: cation displacement and oxygen octahedra tilting. The relationship between charge centers displacement and spontaneous polarization can be well illustrated by the thermal-induced lattice distortions in BaTiO$_3$ (see Fig. 2-11). Above Curie temperature $T_C$, there is no spontaneous polarization because the cubic prototype is preserved. Below $T_C$, three ferroelectric phases of tetragonal, orthorhombic and rhombohedral are found stable upon cooling. The displacement between the charge centers of cations and anions are along
<001>pc, <110>pc, and <111>pc directions respectively for these three phases, and so as the spontaneous polarizations.²

Fig. 2-11 Crystal structure evolution of BaTiO₃ as a function of temperature.²
2.3 Morphotropic phase boundary and polymorphic phase boundary

Fig. 2-12 Phase diagram of Pb(Zr$_{1-x}$Ti$_x$)O$_3$ reported by Jaffe et al. $^2$

The morphotropic phase boundary (MPB) refers to a composition range across which the composition-induced phase transition occurs.$^2$ It is a phase region where multiple phases may coexist. As illustrated by the phase diagram of Pb(Zr$_{1-x}$Ti$_x$)O$_3$ (Fig. 2-12), a nearly temperature-independent MPB is observed to separate the rhombohedral and tetragonal phases at $x = 0.48$. Not like the vertical MPB in Pb(Zr$_{1-x}$Ti$_x$)O$_3$ ceramics, tilted MPBs are often found in other systems, such as (K$_{0.5}$Na$_{0.5}$)NbO$_3$-based,$^{17}$ Ba(Zr,Ti)O$_3$-(Ba,Ca)TiO$_3,$$^{18}$ and (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-BaTiO$_3$ solid solutions. As exemplified by the phase diagram of Ba(Zr,Ti)O$_3$-(Ba,Ca)TiO$_3$ (see Fig. 2-23 in Section 2.5.3.), a temperature-sensitive MPB is present to separate the rhombohedral and tetragonal phases. Thus the name of polymorphic phase boundary (PPB) instead of MPB is more often used to describe the temperature-dependent nature. MPB (or PPB) is of significant importance for the piezoelectric ceramics, because the superior piezoelectric performance is always
found in MPB (or PPB) compositions.\textsuperscript{20} This is true for the Pb(Zr,Ti)O$_3$ ceramics, as well as the three most promising lead-free candidates discussed in this dissertation.

The phase coexistence at the MPB or PPB is an indication of the small free energy barrier between different phases. The enhanced piezoelectric performance achieved at MPB or PPB is a result of the low polarization anisotropy caused by the phase instability. The response to the external electric field may either stabilize a certain phase, or induce phase transformations. Therefore the evolution of the MPB or PPB under electrical poling fields is the key to understanding the excellent piezoelectric activity in the MPB or PPB compositions.

2.4 Electric fatigue

2.4.1 Concepts and characteristics

Electric fatigue in ferroelectrics refers to a continuous reduction of the switchable polarization under repetitive bipolar cycling.\textsuperscript{21,22} As illustrated in Fig. 2-13, the $P$-$E$ hysteresis loop of the fatigued state becomes depressed with a reduced $P_r$, but an increased $E_c$. For normal ferroelectrics, such as Pb(Zr,Ti)O$_3$ and BiFeO$_3$, the fatigue behavior usually exhibits a nonlinear decay with a typical three-stage configuration, including a plateau of slow stage (~$10^4$ cycles), a logarithmic stage (~$10^6$ cycles), and a saturated stage (up to $10^8$ cycles), by plotting the switchable polarization with respect to logarithm of electrical reversals (Fig. 2-14).\textsuperscript{24} The obtained fatigue profiles are generally fitted by functions like $P_r \propto N^{1/4}$, $P_r \propto (aN+1)^{-m}$, or $P_r \propto A+\exp(-aN)$.\textsuperscript{22,23}
Fig. 2-13 Polarization ($P$) vs. electric field ($E$) hysteresis loops before and after bipolar fatigue.

Fig. 2-14 Evolution of the switchable polarization as a function of bipolar fatigue cycles: (a) slow fatigue stage, (b) logarithmic stage, and (c) saturated stage.
2.4.2 Mechanisms and models

It is commonly accepted that electric fatigue is a defect-chemistry related phenomenon in ferroelectrics of both thin film and bulk forms. Complicated processes are involved during applied electrical cycling, primarily including (1) the creation and/or redistribution of charged defects, and (2) correspondingly their influences on the ferroelectric domain switching process. The possible scenarios of electrical fatigue has been summarized and schematically depicted in Fig. 2-15. For the extrinsically induced new defects, it can be electrons and holes injected from the electrodes; while for
the intrinsic point defects, it can be oxygen vacancies, aliovalent substituting cations, or vacancies resulted from element evaporation loss during high temperature sintering.\textsuperscript{21}

Electric fatigue in ferroelectric oxides is a complicated process, and both intrinsic and extrinsic contributions devote to the reduction of switchable polarization.\textsuperscript{21-23} During the past several decades, numerous fatigue models have been proposed, including electrode degradation, passive layer formation, nucleation inhibition, local phase decomposition, near-by-electrode injection, defects redistribution, and domain wall pinning.\textsuperscript{21-23} However, a consensus has not been reached. Among these models, the domain wall pinning and seed inhibition mechanisms are widely accepted.\textsuperscript{22} For the domain wall pinning mechanism, it is believed that during the continuous electrical reversals the charge-neutral domain walls in the un-fatigued state most likely become charged.\textsuperscript{21,25} The interactions between the polarized domain walls and charged defects form a self-stabilizing configuration through charge compensation, and finally the domain wall motion is significantly suppressed.\textsuperscript{21,22,25} For the nucleation inhibition scenario, a similar microscopic description is provided, but the nucleation seeds for the reversed domains are blocked in their embryonic state before they can create a macroscopic domain.\textsuperscript{22} Both cases show the frozen domain configuration after fatigue.\textsuperscript{22}
2.4.3 Techniques for microscopic investigation

Fig. 2-16 PFM micrographs of the domain evolution during fatigue in an epitaxial BiFeO$_3$ thin film.\textsuperscript{26}

Fig. 2-17 X-ray microdiffraction images of the domain evolution during fatigue in a polycrystalline Pb(Zr,Ti) thin film.\textsuperscript{27}

As is well known, the polarization state and polarization switching in ferroelectric crystals are intrinsically linked to ferroelectric domain arrangements and their transformations.\textsuperscript{4} Thus, direct imaging of domain evolution during electrical cycling is critical to elucidate the underlying mechanisms for electric fatigue. However, only very limited techniques have been developed and applied for such purpose up to date. Most of these studies mostly focused on thin films of normal ferroelectrics, such as BiFeO$_3$ and
Pb(Zr,Ti)O$_3$ (PZT), by mainly employing piezoresponse force microscopy (PFM)\textsuperscript{26,28-33} and synchrotron X-ray microdiffraction.\textsuperscript{27} Although these probing tools can provide microscopic pictures (see Figs. 2-16 and 2-17), they are still challenged by technical restrictions. For example, PFM only monitors the domain morphology change without providing any crystallographic information about the structural phase transitions. Electric field has been demonstrated to induce structural phase transitions, and thus have significant influences on macroscopic properties and microscopic morphologies of functional ferroelectrics.\textsuperscript{34,35} However, domain morphology only is not able to distinguish the subtle difference between the phase variants in perovskite ferroelectrics. For the X-ray microdiffractions, the spatial resolution is around micrometers.\textsuperscript{27} Even with the recent development of submicron X-ray diffraction, higher resolution is still quite challenging, especially when the length scale is down to individual grain level and multi-domains are present within.

Compared with PFM and X-ray microdiffraction, the \textit{in situ} TEM technique is suggested to be a promising probing tool to investigate the microstructural mechanisms for electrical fatigue due to its nanometer-scaled resolution, and also the capability of monitoring the crystal structure evolution by selected area electron diffraction. However, no such experiments have been reported in the literature.

\section*{2.5 Lead-free piezoelectric ceramics}

Concerned about the environmental and human health issues, materials scientists recently carried out a large body of research work on the development of lead-free piezoelectric ceramics to replace the Pb(Zr,Ti)O$_3$-based compositions, which have been
the workhorse in the piezoelectric market for over half a century. The research has been focused on three most promising lead-free solid solution systems, the (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-BaTiO$_3$, (K$_{0.5}$Na$_{0.5}$)NbO$_3$-based, and Ba(Zr,Ti)O$_3$-(Ba,Ca)TiO$_3$ ceramics. Here, in this section and the followed two, a comprehensive literature review of the recent research progress on these three ceramic systems is provided.

2.5.1 (1-x) (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-xBaTiO$_3$

The (1-x)(Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-xBaTiO$_3$ (referred as to BNT-BT) solid solution was first reported by Takenaka et al. in 1991. The proposed phase diagram (Fig. 2-18) was constructed using data from dielectric properties measurements and room temperature XRD measurement on the poled bulk ceramics. Similar to the aforementioned lead-containing and lead-free piezoceramic systems, enhanced piezoelectric performance was observed at the MPB (MPB instead of PPB is used in BNT-BT system just in order to keep consistent with the literatures) composition of $x = 6$ mol.%. The MPB in BNT-BT, which separates the ferroelectric (F) rhombohedral and tetragonal phases, is highly temperature dependent, and thus is tilted instead of a vertical-type in PZT. In contrast to the phase diagrams of PZT and BZT-BCT, an intermediate antiferroelectric (AF) phase occurs during the ferroelectric-to-paraelectric phase transformation.
Twenty years later, a new phase diagram (Fig. 2-19) based on the unpoled BNT-BT ceramics was constructed by combining the dielectric characterization and TEM analysis on domain morphology and crystal structures. Significant difference can be noticed when compared with the previous phase diagram on poled samples. By using TEM, the domain morphologies and associated crystal structure are analyzed. The two ferroelectric (FE) phases, rhombohedral $R3c$ and tetragonal $P4mm$ phases, possess complex and lamellar domains, respectively. Between them, a relaxor antiferroelectric (AFE) phase is found in a certain compositional range with $P4bm$ nanodomains. Therefore, two MPB are produced when the two ferroelectric phases overlap with the relaxor antiferroelectric phase at $x = 7$ mol.% and $x = 10$ mol.%, respectively. The most important indication provided by the new phase diagram on the unpoled ceramics is that two types of electric field-induced phase transformations, the relaxor-to-ferroelectric and the antiferroelectric-to-ferroelectric transitions, occur during the poling process. Apparently, the originally
existent PPBs in the virgin ceramics experience an evolution process under poling electric field accompanying with the piezoelectricity development.

![Phase diagram of BNT-BT reported by Ma et al. based on unpoled ceramics.](image)

Fig. 2-19 Phase diagram of BNT-BT reported by Ma et al. based on unpoled ceramics.³⁶

Fig. 2-20 displays the poling field $E_{pol}$ versus composition $x$ phase diagram for polycrystalline BNT-BT ceramics by combining the piezoelectric measurements with the electric field in situ TEM analysis on the evolution of domain morphologies and crystal structures.³⁵ The results clearly demonstrate that the MPBs can be irreversibly destroyed or created by the poling field, so as the associated piezoelectricity enhancement. For $x = 6$ mol.%, the original $P4bm/R3c$ MPB evolves into $P4mm/R3c$ MPB with an enhanced piezoelectricity first, but then transforms into a single $R3c$ phase with a reduction of $d_{33}$ at higher poling field. For $x = 7$ mol.%, a new $P4mm/P4bm$ MPB can be induced out of the $P4bm$ single phase, and then evolves into another $R3c/P4mm$ MPB with an enhancement of piezoelectric performance. It should be pointed out that in addition to the relaxor-to-ferroelectric and antiferroelectric-to-ferroelectric transitions, the ferroelectric-to-ferroelectric phase transformations must be considered to fully understand the microstructural evolution of the piezoelectricity in this system.
The poling field $E_{pol}$ vs. $x$ phase diagram for BNT-BT reported by Ma et al.\textsuperscript{35} The corresponding piezoelectric property $d_{33}$ as a function of $E_{pol}$ is displayed for (a) $x = 5.5$ mol.\%, (b) $x = 6$ mol.\%, and (c) $x = 7$ mol.\%.

The parent phase (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$ (BNT) in BNT-BT system has been assigned as rhombohedral $R3c$ structure at room temperature for a long time.\textsuperscript{37} However, recent reports suggested a monoclinic $Cc$ phase instead of $R3c$ for pure BNT.\textsuperscript{38-40} A novel method of electron diffraction analysis on the oxygen octahedra tilting in multiple domains was performed by Ma et al. to confirm the proposed $Cc$ symmetry for BNT.\textsuperscript{41} More importantly, it was found that the $Cc$ phase evolved into $R3c$ phase with the addition of BaTiO$_3$, and finally formed a $Cc/R3c$ phase boundary at $x = 3-4$ mol.\%.\textsuperscript{41} Combining with the results from previous electric field-strain measurements, a new $E_{pol}$-$x$ phase diagram for BNT-BT with this new phase boundary at the low-BaTiO$_3$ side is updated (Fig. 2-21).
Fig. 2-21 The poling field $E_{pol}$ vs. $x$ phase diagram for BNT-BT ceramics. The $Cc/R3c$ phase boundary (grey area) is revealed by Ma et al., with critical fields (crosses) obtained from the strain curves. Other phase boundaries are determined from the previous study.

2.5.2 (K$_{0.5}$Na$_{0.5}$)NbO$_3$-based solid solution

K$_x$Na$_{1-x}$NbO$_3$ is a solid solution of KNbO$_3$ and NaNbO$_3$. It was found to be ferroelectric by Shirane et al., and the follow-up investigations by Egerton and Dillon suggested an enhanced ferroelectric properties at $x \approx 0.5$. The latest phase diagram of K$_x$Na$_{1-x}$NbO$_3$ updated by Glazer et al. is shown as Fig. 2-22. The first-order and second-order phase transitions are indicated by the solid and dotted lines, respectively. As can be seen, a nearly vertical MPB, similar to that in PZT, is observed to separate the Amm2 and Pm phases at $x \approx 0.5$. 
Fig. 2-22 Phase diagram of $K_xNa_{1-x}NbO_3$ reported by Glazer et al.45

For the compositions in the K-rich side, they are iso-structural with $BaTiO_3$ but with different phase transition temperatures. All of the temperature dependent phase transitions are first-order transitions. There is no oxygen octahedra tilting for the whole temperature range. For the Na-rich side, the $Pm$ phase is divided into three sub-phases with distinct octahedra tilting. The transitions between the sub-phases are of second-order nature. For the temperature-induced phase transitions, the $Pm$ phase transforms into $R3c$ phase during cooling. When heated up, the $Pm$ phase with relatively lower Na content follows the same transitions of the K-rich side; for the $Pm$ phase with relatively higher Na content, it transforms into the F phase with the $Amm2$ symmetry around 200 °C, and then becomes $T_2$ phase with $P4bm$ symmetry around 400 °C prior to transforming to the cubic $Pm\bar{3}m$ phase. It should be pointed out that the polymorphic phase transition from orthorhombic $Amm2$ to tetragonal $P4mm$ phase around 200 °C is important for the piezoelectric performance in the KNN-based ceramics. This temperature can be effectively reduced down to room temperature after chemical modification, and directly contributes to the enhanced piezoelectric activity.46
(K_{0.5}Na_{0.5})NbO_3-based solid solution is one of the most extensively studied systems because of their superior piezoelectric performance and high working temperature. The unmodified K_{x}Na_{1-x}NbO_3 ceramic shows a best but still low piezoelectric $d_{33}$ value of ~100 pC/N at the MPB. Also, it is difficult to obtain good quality samples via conventional solid state reaction due to several factors: the volatility of alkali oxides, limited sintering temperature range, compositional inhomogeneity, and poor density. To facilitate processing and optimize the piezoelectric property, chemical modification has been employed. KNN-based ceramics received tremendous attentions after Satio et al. reported a comparable electromechanical performance to Pb(Zr,Ti)O_3 family in the Li, Sb and Ta modified compositions in 2004. Such enhancement in piezoelectric properties of these compositionally modified KNN ceramics has been shown to be a result of shifting the orthorhombic-to-tetragonal phase transition temperature $T_{O-T}$, from ~210 °C for unmodified KNN, to near room temperature.

After Satio’s work, various chemical modifiers have been employed to explore the $T_{O-T}$ effect on the piezoelectricity enhancement in KNN-based ceramics. For the base compositions K_{x}Na_{1-x}NbO_3, the most frequently used K/Na ratio is 1:1, although other ratios around the MPB have been investigated. It was found that the transition temperatures and the shifting of the transition temperatures significantly depend on the types of cations. Generally, the parent compound KNN has limited solubility with doping cations lower than 10 mol.%. These KNN-based solid solutions generally adopt orthorhombic structure initially, but transform to the tetragonal phase with increasing doping content. As a result, an orthorhombic-tetragonal PPB can be established at room temperature. For example, Li$^+$ substitution for the A-site has been extensively studied in
the \((1-x)(K_{0.5Na_{0.5}})NbO_3-xLiNbO_3\) system.\(^{49-51}\) The crystal structure transforms from orthorhombic to tetragonal with Li\(^+\) content increasing from \(x = 0\) to \(x = 8\) mol.\%. The orthorhombic-tetragonal phase coexistence region is found at \(x = 6\) mol.% with shifting the transition temperature \(T_{O-T}\) from \(\sim 210^\circ\)C down to room temperature. The corresponding piezoelectric activity shows an excellent \(d_{33}\) value of \(\sim 250\) pC/N in this system.\(^{49-51}\) With further substitution of Sb\(^5+\) on the B-site, a similar trend is observed in the \((1-x)\,(K_{0.5Na_{0.5}})NbO_3-xLiSbO_3\) system.\(^{52,53}\) The \(T_{O-T}\) is more effectively reduced to room temperature at \(x = 5.2\) mol.\%, and the \(d_{33}\) is further improved to be \(\sim 265\) pC/N.\(^{52,53}\) The cations that have been widely investigated are Li\(^+\), Ag\(^+\), and Bi\(^3+\) for the A-site, and Sb\(^5+\), Ta\(^5+\), and Ti\(^4+\) for the B-site.\(^{48-57}\) Despite the variety of the chemical modifiers, all of the KNN-based ceramics display a significant piezoelectricity enhancement when \(T_{O-T}\) is shifted down to room temperature.\(^{46}\)

Various techniques, such as TEM,\(^{61}\) piezoresponse force microscope (PFM),\(^{62}\) and scanning electron microscope (SEM),\(^{63}\) have been employed to explore the domain morphology of the KNN or KNN-based virgin samples. A common feature of herringbone domains is widely observed in the pure KNN and KNN-based solid solutions at the PPB. More specifically, the domain morphology is with a hierarchal structure: the \(\mu\)m-sized lamellar domains intersect each other to form a V-shaped herringbone, and the coexistent orthorhombic and tetragonal nanodomains are observed within.\(^{61}\) Therefore, the presence of the nanometer-sized domains was thought to be responsible for the piezoelectricity enhancement by facilitating the domain alignment process during poling. In the single phase region, complex domains with irregular-shaped domain walls are
often observed for the orthorhombic phase; and the lamellar domains are more typical in the tetragonal structured compositions.\textsuperscript{51}

Macroscopically, the average structure evolution under poling fields of the KNN-based bulk ceramics are investigated only very recently, and limited to very few reports with the X-ray diffraction (XRD) technique.\textsuperscript{64-66} For the virgin ceramics, the coexistence of orthorhombic and tetragonal phases has been verified by the XRD results when the compositions are changed from orthorhombic to tetragonal structure.\textsuperscript{51} The space groups are assigned to $Amm2$ for the orthorhombic phase, and $P4mm$ for the tetragonal one.\textsuperscript{50} The superlattice diffraction is forbidden in both space groups. After applying poling electric field, the phase transformations were observed to occur.\textsuperscript{64-66} For example, the \textit{in situ} XRD study on (Na,K)(Nb,Sb)O$_3$-LiTaO$_3$ ceramics reported by Zuo \textit{et al.} revealed that the original orthorhombic phase first irreversibly transforms into a monoclinic phase at low poling fields, and then the monoclinic phase reversibly transforms into the tetragonal phase at high poling fields.\textsuperscript{66} No electric field-induced superlattice diffraction was observed.

Although the KNN-based ceramics have been extensively studied, several critical issues still remain unknown. Phenomenologically, it has been accepted that the enhanced piezoelectricity is owing to the shifting of $T_{O-T}$ down to room temperature.\textsuperscript{46} However, the microstructural origin for this enhancement has not been addressed yet, even though the existence of nanometer-sized domains in the virgin state was observed and considered to be responsible for the enhancement. Presumably, switching of nanometer-sized domains and furthermore phase transformations may occur under poling electric fields, and hence these domains do not survive after electrical poling. Although the poling field-
induced phase transformations have been revealed by the XRD measurements, the corresponding microstructural mechanism, such as the domain evolution, has not been imaged. In addition, the monoclinic, orthorhombic and tetragonal phases in the KNN or KNN-based ceramics have comparable free energies in the virgin state. Which phase is favored by the poling field, and how does the phases transform, all remain open issues. If the monoclinic phase eventually survive poling, which sub-phase, or tilting system, does it take? And what influence does it have on the developed piezoelectricity?

2.5.3 \((1-x)\text{Ba(Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x\text{(Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3\)

The \((1-x)\text{Ba(Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x\text{(Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3\) (referred to as BZT-BCT) solid solution was recently reported by Liu and Ren to exhibit ultra-high \(d_{33}\) of up to 620 pC/N at room temperature. The proposed temperature-composition phase diagram, which is determined by X-ray diffraction and dielectric properties measurements, is shown as Fig. 2-23. It can be divided into three phase regions with rhombohedral \(R\overline{3}m\), tetragonal \(P4mm\), and cubic \(Pm\overline{3}m\) structures. The thermal-induced phase transformations between any two phases are considered as first-order nature. The paraelectric-to-ferroelectric phase transition temperature \(T_C\) varies from 0 to 100 °C with regarding to the compositional change. For the BZT-rich side with \(x \leq 30\) mol.%, only \(R\overline{3}m\) phase is observed at the temperature below 0 °C. The rhombohedral phase directly transforms into cubic phase upon heating. With increasing \(x \geq 30\) mol.%, the tetragonal phase starts to appear as an intermediate phase between rhombohedal and cubic phases during heating. As a result, a tilted PPB is found to separates single rhombohedral and tetragonal phases by a phase coexistence region. This PPB is strongly temperature dependent. It starts at ~
50 °C at \( x = 30 \text{ mol.\%} \), and then the rhombohedral-to-tetragonal phase transition temperature \( (T_{R-T}) \) monotonically decreases with the increase of BCT content. The PPB intersects with the paraelectric-to-ferroelectric phase boundary at a tricritical point of \( x = 30 \text{ mol.\%} \), at which the rhomboidal, tetragonal and cubic phases converge together. For the composition of BZT-50BCT, mixed phases of rhombohedral and tetragonal are found at room temperature. The compositional dependent \( d_{33} \) measurement shows a peak value of up to 560 - 620 pC/N depending on poling conditions.\(^{18}\) For the compositions slightly deviated from BZT-50BCT, they still exhibit a high \( d_{33} \) value of \( \sim 350 \text{ pC/N} \).\(^{6}\) The enhanced piezoelectricity is suggested to be attributed to the presence of the tricritical point, which leads to a vanishing polarization anisotropy and thus facilitates polarization rotation between rhombohedral and tetragonal phases.\(^{18}\)

![Phase diagram of BZT-xBCT](image)

**Fig. 2-23** Phase diagram of BZT-xBCT reported by Ren et al.\(^{18}\)

For the parent compound BaTiO\(_3\) in the BCT-BZT system, an intermediate orthorhombic phase is observed to separate the rhombohedral and tetragonal phases at temperatures slightly below room temperature.\(^{2}\) This fact has been motivated
investigations to explore the existence of an orthorhombic phase in the BCT-BZT solid solution. However, this issue is still under controversy. Some evidences resulted from the dielectric spectroscopy and high-resolution synchrotron X-ray diffraction measurements seem to prove the existence of the orthorhombic phase in a very narrow temperature-composition range.\(^67,68\) as shown in Fig. 2-24 the updated phase diagram.

![Revised phase diagram of BZT-BCT reported by Keeble et al.\(^68\)](image)

Fig. 2-24 Revised phase diagram of BZT-BCT reported by Keeble et al.\(^68\)

The phase transition sequence and space group symmetry of BCT-BZT ceramics are now identical with the parent BaTiO\(_3\) in a narrow composition range.\(^68\) The previously reported rhombohedral-to-tetragonal transition is re-assigned as orthorhombic-to-tetragonal transition.\(^68\) Contrary to this report, Haugen et al. ruled out the orthorhombic phase by a high-resolution XRD measurement at temperatures from -100 °C to 150 °C for \(x = 50\) mol.\%.\(^69\) The inconsistence in the literature may come from the fact that the structure of the BZT-BCT ceramics is sensitive to the processing conditions. It has been
shown that the crystal structure and piezoelectric properties may vary depending on calcination and sintering conditions.\textsuperscript{70-72}

TEM study has been carried out to investigate the ferroelectric domain morphology of BZT-BCT ceramics in compositions across the piezoelectricity-optimal PPB.\textsuperscript{73}

![TEM observation of composition-induced R-PPB-T transition in BZT-xBCT reported by Gao et al.\textsuperscript{73} The corresponding CBED patterns are displayed below the BF images. R and T stands for rhombohedral and tetragonal, respectively.](image)

As shown in Fig. 2-25, the BZT-rich composition ($x = 40$ mol.%$)$ with a single rhombohedral structure adopts the wedge-shaped domains, while BCT-rich composition ($x = 60$ mol.%$)$ with a single tetragonal structure exhibits typical lamellar domains. Both types of domains are in micron size. The local crystal symmetries of rhombohedral and tetragonal structures are confirmed respectively by the convergent beam electron diffraction (CBED). For the PPB composition of $x = 50$ mol.\%, it is interesting to notice that the coarse nanodomains are developed within the micron-sized domains to form a hierarchical domain structure. The CBED patterns suggest that the rhombohedral and tetragonal phases coexist among these nanodomains. This type of microstructure is thought to be commonly associated with high piezoelectric performance by flattening the free energy of polarization anisotropy, and in turn easy polarization rotation and
alignment during poling. However, similar to the aforementioned KNN-based ceramics, these nanodomains cannot survive electrical poling, and hence their direct contribution to the excellent piezoelectric activity is still a question. In addition, no electric field-induced phase transformations are reported until now, even though some XRD studies have been carried out on the poled BCT-BZT ceramics. However, questions concerning the microstructural evolution of BZT-BCT ceramics during poling have not been addressed in the literature.

References


CHAPTER 3. *In situ* TEM Study of the Microstructural Origins for the Piezoelectricity Development in Lead-free Ceramics

3.1 (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-BaTiO$_3$ solid solution: Electrical poling below coercive field for large piezoelectricity


Hanzheng Guo, Cheng Ma, Xiaoming Liu, and Xiaoli Tan

Abstract

Isotropic polycrystalline ferroelectric ceramics have to be electrically poled to develop a net macroscopic polarization and hence piezoelectricity. It is well accepted that a sufficient poling can only be realized under an electric field that is much higher than the coercive field. In this study, we observed in (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-BaTiO$_3$ ceramics that large piezoelectricity can develop at poling fields far below the measured coercive field. Using *in-situ* transmission electron microscopy, such an unusual behavior is interpreted with the polarization alignment of polar nanodomains in the non-ergodic relaxor phase.

3.1.1 Introduction

Piezoelectric materials are key to numerous important technologies, including energy harvesting,¹ noise cancellation,² and minimally invasive surgery.³ The defining property is a third rank tensor, which requires a macroscopically broken spatial-inversion symmetry in order to exhibit non-zero values.⁴ For an originally isotropic polycrystalline ferroelectric ceramic, a polar symmetry ($\infty m$) needed for the existence of piezoelectricity
can be brought by a poling process, where a strong direct current electric field is applied to switch ferroelectric domains and align spontaneous polarizations.\textsuperscript{5,6} Therefore, it is commonly believed that poling fields have to be much greater than the coercive field $E_C$, which characterizes the difficulty of polarization reversal in ferroelectrics.\textsuperscript{6} Such an empirical rule is based on and supported by numerous experimental observations on all of the widely studied piezoelectrics so far, including Pb(Zr$_{1-x}$Ti$_x$)O$_3$-based,\textsuperscript{7} BaTiO$_3$-based,\textsuperscript{8} K$_{0.5}$Na$_{0.5}$NbO$_3$-based,\textsuperscript{9} and (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-based\textsuperscript{10} compositions; optimal piezoelectricity of these systems (represented by the $d_{33}$ coefficient) can only be achieved when poled at or above $2E_C$. Poling fields below or around $E_C$ only yield very small $d_{33}$ values that are close to zero.\textsuperscript{8,10} In this study, we report the observation of large piezoelectricity realized at poling fields significantly below experimentally measured $E_C$. This peculiar behavior occurs in a limited composition range of (1-$x$)(Bi$_{1/2}$Na$_{1/2}$)TiO$_3$–$xBaTiO_3$, the most extensively studied lead-free piezoelectric system.\textsuperscript{11-15} The observed phenomenon is rationalized using the electric-field in-situ transmission electron microscopy (TEM) technique.

### 3.1.2 Experimental procedure

The preparation of polycrystalline ceramic samples of (1-$x$)(Bi$_{1/2}$Na$_{1/2}$)TiO$_3$–$xBaTiO_3$ ($x = 6\%, 7\%, 8\%, 9\%$) was described previously.\textsuperscript{16} Hot-pressed Pb$_{0.92}$La$_{0.08}$(Zr$_{0.65}$Ti$_{0.35}$)O$_3$ (PLZT 8/65/35) ceramic was acquired from a commercial source (Boston Applied Technologies, MA, USA). The electric field-induced volume strain was calculated from the strains measured parallel and perpendicular to the field direction simultaneously at 0.62 Hz. The details about this technique can be found in the previous reports.\textsuperscript{17,18} The
polarization versus electric field hysteresis loops were measured with the standardized ferroelectric test system (RT-66A, Radiant Technologies, Albuquerque, NM, USA) at room temperature at 4 Hz. For piezoelectric characterization, the ceramic specimens were poled at various electric fields at room temperature (25 °C) for 20 minutes. The piezoelectric coefficient $d_{33}$ was measured with a piezo-$d_{33}$ meter (ZJ-4B, Institute of Acoustics, Chinese Academy of Sciences) 24 h after poling. Electric-field in-situ TEM experiments were carried out on a Phillips CM30 microscope operated at 300 kV. Experimental details were described in previous articles. \(^{19-22}\)

### 3.1.3 Results and discussion

The abnormal poling behavior is illustrated in Fig. 1, using the 93%($\text{Bi}_{1/2}\text{Na}_{1/2}$)$\text{TiO}_3$-7%$\text{BaTiO}_3$ ceramic as an example. This composition was observed to experience a transition from the $P4bm$ phase to long-range-ordered ferroelectric phases at a critical field (referred to as $E_F$ in the present work) during poling, and the induced ferroelectric phases persist after removal of fields.\(^{15,17,23,24}\) Figure 1(a) shows the evolution of volume strain and the simultaneously measured polarization during the very first cycle of electric field. The anomaly on the volume strain curve, resulted from the unit cell volume change, marks the critical phase transition field $E_F$.\(^{17}\) Accompanied with this volume strain anomaly is a slope change in the polarization curve, from which $E_F$ is determined as 2.5 kV/mm for $x = 7\%$. The comparison between the volume strain and polarization curves in Fig. 1(a) clearly suggests a significant amount of macroscopic polarization is developed in the $P4bm$ phase. Figure 1(b) presents the $E > 0$ portion of the polarization $P$ vs. electric field $E$ hysteresis loop measured in the second electric field
cycle. A coercive field $E_C$ of 2.4 kV/mm is recorded. Figure 1(c) shows the piezoelectric coefficient $d_{33}$ as a function of poling field. An abrupt increase in $d_{33}$ is observed at 1.5 kV/mm. This critical poling field is denoted as $E_P$. It is noted that $d_{33}$ only slightly increases and quickly saturates beyond $E_P$. Figure 1 unambiguously indicates that $E_P$ is significantly lower than both $E_F$ and $E_C$ in the 93%(Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-7%BaTiO$_3$ ceramic.

The highly unusual phenomenon is also observed in other compositions with the $P4bm$ phase in the virgin state ($x = 6\%$, $8\%$, and $9\%$). For all of these compositions, a remarkable jump of piezoelectric coefficient $d_{33}$ is also clearly observed in the poling field dependence of the $d_{33}$ curves shown in Fig. 2(a). Again, the $d_{33}$ value of all these compositions barely increases when the poling field beyond $E_P$ is applied. Figure 2(b) displays the values of $E_F$, $E_C$, and $E_P$ of these compositions, which are determined in the same way as in Fig. 1. Similar to $x = 7\%$, the critical poling field $E_P$ is much lower than the coercive field $E_C$ in all of them. For $x = 9\%$, $E_P$ is even smaller than one third of its $E_C$.

One possible explanation for the results shown in Figs. 1 and 2 is that $E_P$ is determined under DC field while $E_C$ is under AC field and is known to be strongly frequency dependent. However, it should be pointed out that such an unusual poling behavior is not observed in compositions in the $R3c$ and $P4mm$ ferroelectric phase regions in (1-$x$)(Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-$xBaTiO$_3$, but only in those with the $P4bm$ phase. The frequency effect is hence not the primary factor here.

Furthermore, the fact that $E_P$, where the $d_{33}$ coefficient suddenly increases and then saturates, is significantly lower than $E_F$, where phases with long-range ferroelectric order emerge, also rules out any possible contributions from phase transition to $d_{33}$ at $E_P$. As a
result, the observed phenomenon must be rooted in the $P4bm$ phase: The high $d_{33}$ developed below $E_C$ is a result of the poling of the $P4bm$ phase.

In the virgin state prior to poling, ceramics with these compositions crystallize in the $P4bm$ space group, with polar nanodomains in microstructure and strong frequency dispersion in their dielectric permittivity.$^{13,14,16}$ The polar $P4bm$ space group allows for the presence of dipole moment within the tetragonal unit cell$^{28}$ and hence these compositions are referred to as relaxor ferrielectric with a spontaneous polarization.$^{23,24}$ The $P4bm$ phase undergoes an irreversible electric-field-induced phase transition to ferroelectric phases with large domains during poling.$^{24}$ The large domains in the ferroelectric $R3c$ and $P4mm$ phases are disrupted into $P4bm$ nanodomains when heated to the thermal depolarization temperature $T_d$, which is equivalent to the freezing temperature in Pb-containing relaxor ferroelectrics.$^{18,29}$ It was reported that the $T_d$ for the compositions concerned here ($6\% \leq x \leq 9\%$) is above 100 °C.$^{30}$

Therefore, these compositions should be characterized as non-ergodic relaxor ferrielectric at room temperature with static polar nanodomains. These nanodomains, unlike the dynamically fluctuating polar nanoregions in ergodic relaxors, can be poled and aligned under applied field to develop piezoelectricity.

Using the electric-field $in-situ$ TEM technique,$^{19-22}$ the domain switching process during the poling of the $P4bm$ non-ergodic relaxor ferrielectric phase in composition $x = 7\%$ is directly imaged and displayed in Fig. 3. A representative grain along its [112] zone axis is selected for study. As shown in Fig. 3(a), at zero field it consists of polar nanodomains, which shows the $P4bm$ symmetry as indicated by the presence of $1/2\{oee\}$ and absence of $1/2\{ooo\}$ spots ($o$ and $e$ stand for odd and even Miller indices,
respectively). When a nominal field of 1.4 kV/mm is applied (Fig. 3(b)), the nanodomains coalesce into a tweed structure, and some regions near the grain boundary transform to thin lamellar domains. However, the diffraction pattern still suggests the $P4bm$ symmetry across the entire grain, indicating no phase transition has occurred. At 2.8 kV/mm, the volume with nanodomains is completely consumed by that with thin lamellar domains (Fig. 3(c)). Again, electron diffraction indicates that the symmetry is still $P4bm$. These $P4bm$ lamellar domains persist at least two hours after removal of fields in TEM.

It should be noted that the microstructural response to poling field in composition $x = 7\%$ displayed in Fig. 3 appears to be inconsistent with our previous observations where $P4bm$ nanodomains directly transform to thick lamellar $P4mm$ domains. The discrepancy is reconciled with the fact that the electric field in the TEM specimen is not uniform due to the presence of a central perforation and randomly oriented grains. Since the actual field value is not known, we report the nominal values (the applied voltage divided by the electrode spacing). As explained previously, there are areas along the rim of the central perforation with intensified as well diluted electric fields. All our previous in-situ TEM experiments were focused on the field intensified area, but the present one examined a grain out of this area in order to focus on the responses at low poling fields. The results in Fig. 3 reveal the changes in the $P4bm$ phase prior to the transition to the $P4nm$ phase and directly support the poling field $E_{pol}$ vs. composition $x$ phase diagram, which indicates that the $P4bm$ phase is stable against poling field up to $~3.0$ kV/mm.
The in-situ TEM observations (Fig. 3) reveal that the poling of the P4bm non-ergodic relaxor ferroelectric phase takes place through the irreversible coalescence of individual nanodomains into thin lamellar domains. The electric field required for such a coalescence to occur is lower than the field triggering the high-field ferroelectric phases (E_F) in the first quarter cycle. The measurement of the coercive field E_C takes place after the high-field ferroelectric phases are formed and hence E_C in these compositions represents the resistance for switching the induced large ferroelectric domains, not the P4bm nanodomains. Apparently, the critical field E_P is the onset field for the alignment of the polarizations associated with P4bm nanodomains. This provides the microstructural origin for the observed strong piezoelectricity below E_F and E_C.

This unusual poling behavior is also observed in lead-containing relaxor ferroelectric ceramics such as (Pb_{0.92}La_{0.08})(Zr_{0.65}Ti_{0.35})O_3 (PLZT8/65/35). This composition is a non-ergodic relaxor at room temperature with a freezing temperature of (36±2) °C. An exceptionally low E_P value of 0.25kV/mm is found for this composition, which is lower than both E_C (0.3kV/mm) and E_F (0.5kV/mm). The result suggests the high d_{33} coefficient in this composition is also originated from the coalescence of the polar nanodomains during poling.

3.1.4 Conclusion

In summary, well-developed piezoelectric properties are observed in polycrystalline (1-x)(Bi_{1/2}Na_{1/2})TiO_3–xBaTiO_3 ceramics with the P4bm relaxor ferroelectric phase even when they are poled at fields significantly lower than both the phase transition field and the coercive field. The microstructural origin for this behavior is attributed to the electric
field-induced irreversible nanodomains coalescence into thin lamellar domains prior to the phase transition. The discovery suggests that non-ergodic relaxors should be included in the search of lead-free piezoelectrics for replacing the industrial standard, but environmentally hazardous, lead-containing ones.

Acknowledgements

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FIG. 1. The three critical fields defined from data of the 93%(Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-7%BaTiO$_3$ ceramic. (a) $E_F$, the critical field for the electric field-induced $P4bm$-to-$P4mm$ phase transition; (b) $E_C$, the coercive field; (c) $E_P$, the critical poling field where $d_{33}$ abruptly increases.
FIG. 2. Electrical properties of \((1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3-x\text{BaTiO}_3\) \((x = 6\%, 7\%, 8\%, 9\%)\) polycrystalline ceramics. (a) Poling field dependence of the piezoelectric coefficient \(d_{33}\); (b) critical fields \(E_F\), \(E_C\), and \(E_P\).
FIG. 3. Electric field in-situ TEM results of a representative grain in the 93\%(Bi_{1/2}Na_{1/2})TiO_3-7\%BaTiO_3 ceramic studied along the [112] zone-axis. Bright-field micrographs at (a) 0 kV/mm, (b) 1.4 kV/mm, and (c) 2.8 kV/mm are displayed. The in-situ electric field direction is indicated by the dark arrow. The selected area diffraction pattern at each field is shown in the insets, with 1/2\{00e\} spots highlighted by the bright arrow.
References

3.2 (K_{0.5}Na_{0.5})NbO_3-based solid solution: Microstructural origin for the piezoelectricity evolution in (K_{0.5}Na_{0.5})NbO_3-based lead-free ceramics


Hanzheng Guo, Shujun Zhang, Scott P. Beckman, and Xiaoli Tan

**Abstract**

Chemically modified (K_{0.5}Na_{0.5})NbO_3 compositions with finely tuned polymorphic phase boundaries (PPBs) have shown excellent piezoelectric properties. The evolution of the domain morphology and crystal structure under applied electric fields of a model material, 0.948(K_{0.5}Na_{0.5})NbO_3-0.052LiSbO_3, was directly visualized using *in situ* transmission electron microscopy. The *in situ* observations correlate extremely well with measurements of the electromechanical response on bulk samples. It is found that the origin of the excellent piezoelectric performance in this lead-free composition is due to a tilted monoclinic phase that emerges from the PPB when poling fields greater than 14 kV/cm are applied.

**3.2.1 Introduction**

Piezoelectric materials are crucial in numerous important applications and are the foundation of a multibillion dollar industry. For over half a century, the principle piezoelectric materials used in engineering technologies have been based on Pb(Zr,Ti)O_3; however, the toxicity of lead is a significant problem, and recent legislations have been enacted that restrict the use of lead-based compounds. One of the
most promising alternatives is the (K$_{0.5}$Na$_{0.5}$)NbO$_3$ (KNN)-based solid solution system.$^5$ Various chemical modifiers, such as LiTaO$_3$$^{12,13}$, LiNbO$_3$$^{14-16}$ and LiSbO$_3$$^{17,18}$ have been employed to facilitate processing and optimize the piezoelectric behavior. The enhanced piezoelectricity in these compositionally modified KNN-based oxides is a result of reducing the temperature of the polymorphic phase boundary (PPB), where the tetragonal and orthorhombic phases coexist, from $\sim$210 °C, for unmodified KNN, to near room temperature.$^5$

The physical mechanism for the piezoelectric activity in these KNN-based oxides, particularly those with a PPB near room temperature, has only recently been investigated. Observations from conventional transmission electron microscopy (TEM) attribute the enhanced piezoelectricity to the existence of nanodomains of mixed tetragonal and orthorhombic phases in the virgin state.$^{19}$ However, for originally isotropic polycrystalline ferroelectrics, the piezoelectricity is imparted through a poling process, where a strong direct current electric field is applied to develop a polar symmetry ($\infty m$) by spontaneous polarization alignment in the form of ferroelectric domain switching.$^{20}$ Recent X-ray diffraction on bulk samples of KNN-based ceramics during electrical poling indicate that, in addition to domain switching, phase transitions have also been observed.$^{21-23}$ Presumably, the nanodomains do not survive the poling process, which raises questions about their relevance.

It has been known that domains and crystal structures dictate the physical properties of ferroelectric crystals. Therefore, the evolution of ferroelectric domain and phase symmetry under a poling field is key to understanding the microstructural origin of the piezoelectricity development at the PPB. Such information requires in situ TEM study
and is still missing from literature for KNN-based piezoelectrics. In a recent study on the 
\((1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3-x\text{BaTiO}_3\) (BNT–BT) system, we have directly observed, via electric 
field \textit{in situ} TEM, that the poling process can destroy morphotropic phase boundaries 
(MPBs) as well as create new MPBs from a single phase region.\textsuperscript{24} The poling-created 
MPB is responsible for the enhanced piezoelectricity.\textsuperscript{24} In contrast to BNT–BT, the best 
piezoelectric properties in KNN-based ceramics are observed in the PPB compositions. 
To uncover the microstructural mechanism responsible for the enhanced piezoelectricity, 
several critical questions need to be answered: Does the PPB survive electrical poling? 
How do the domain morphology and the crystal structure change? Do these changes 
correlate with the macroscopic piezoelectricity?

In this study, the ferroelectric domain morphology and crystal symmetry are 
simultaneously monitored in real time during poling with an electric field \textit{in situ} TEM 
technique.\textsuperscript{25 - 29} The PPB composition of 0.948(K\textsubscript{0.5}Na\textsubscript{0.5})\text{NbO}_3-0.052\text{LiSbO}_3 (KNN– 
5.2LS) is studied because its structure (mixed tetragonal and orthorhombic phases) and 
piezoelectric response \((d_{33} \sim 265 \text{ pC/N})\) are representative of KNN-based 
piezoelectrics.\textsuperscript{17,18} The \textit{in situ} observations are combined with the corresponding 
dielectric, piezoelectric, and \textit{ex situ} X-ray diffraction measurements to determine the 
microstructural origin of the piezoelectricity evolution at the PPB in KNN-based 
piezoelectrics.

\subsection{3.2.2 Experimental procedure}

The solid state reaction method was used to prepare the 0.948(K\textsubscript{0.5}Na\textsubscript{0.5})\text{NbO}_3- 
0.052\text{LiSbO}_3 ceramic, with K\textsubscript{2}CO\textsubscript{3} (99.5%), Na\textsubscript{2}CO\textsubscript{3} (99.8%), Li\textsubscript{2}CO\textsubscript{3} (99.9%), Nb\textsubscript{2}O\textsubscript{5}
(99.5%), and Sb$_2$O$_3$ (99.9%) as starting materials. All the raw powders were dried at 200 °C and subsequently weighed according to the formulation. The powders were milled in anhydrous ethanol for 24 h and then calcined at 880 °C for 2 h. The calcined powders were once again milled, and 3 wt % binder was added to the dried powder. Granulated powder was pressed into pellets 12 mm in diameter. The binder was removed at 600 °C, followed by sintering at 1100 °C for 2 h in air. After sintering, hot isostatic pressing at 21 MPa and 1000 °C for 2 h was carried out in an argon atmosphere with 2% oxygen.

For piezoelectric characterization, silver films were sputtered onto the pellet to serve as electrodes. The ceramic specimens were poled at a series of electric fields at room temperature (25 °C) for 10 minutes. The piezoelectric coefficient $d_{33}$ was measured with a piezo-$d_{33}$ meter (ZJ-4B, Institute of Acoustics, Chinese Academy of Sciences) 24 h after poling. For dielectric properties measurements, silver paste (Dupont 6160) was fired on at 750 °C for 6 min as electrodes. Dielectric properties were measured immediately after room-temperature poling during separate heating and cooling processes. The measurement upon heating was carried out using an LCR meter (HP-4284A, Hewlett-Packard) in a tube furnace at a rate of 4 °C/min. Measurements below room temperature were carried out during continuous cooling with liquid N$_2$ at the same rate with an LCZ meter (Keithley 3330) in conjunction with a temperature chamber.

For ex situ X-ray diffraction measurements, conductive epoxy was applied on the polished surfaces and then removed chemically with acetone after poling. The whole diffraction spectra were recorded with a Siemens D500 diffractometer using Cu-Kα radiation at a 0.05° step size and a 1 second per step dwell time. To monitor the development of the 1/2(103) superlattice peak, the dwell time per step was 150 seconds.
For electric field *in situ* TEM experiments, disk specimens (3 mm in diameter) were prepared from as-processed pellets through standard procedures including grinding, cutting, dimpling, and ion milling. The dimpled disks were annealed at 400 °C for 2 h to minimize the residual stresses before Ar-ion milling to the point of electron transparency. *In situ* TEM experiments were carried out on a specimen that was crack free at the edge of the central perforation on a Phillips CM30 microscope operated at 200 kV. The presence of a central perforation intensified the electric field in the TEM specimen. This intensification ratio is 2 for an ideal circular perforation.27 The electric fields quoted in the text and figure captions for the *in situ* TEM results are double of the nominal fields.

### 3.2.3 Results and discussion

**Electric field *in situ* TEM study.** Three nearby grains in one TEM specimen were focused along their [111], [110], and [001] zone axes, respectively. Fig. 1 shows the results from the [111]-aligned grain, where Fig. 1a and b are the overview of almost the entire grain in the virgin state and at 8 kV/cm, respectively. The dashed area in Fig. 1a was further focused. In the virgin state (Fig. 1a, c), most domains are found to form the typical herringbone morphology, which is a common pattern in unpoled BaTiO$_3$ ceramics,30 unmodified KNN ceramics,31 as well as KNN-based PPB compositions.19,32 The herringbone pattern contains parallel strips less than 1 μm in width, several to tens of μm in length, and a substructure of narrow V-shaped domains. Within most of the herringbone strips, parallel short lamellar domains with alternating bright and dark contrast are present. The V-shape forms a 120° angle and is bisected by the long domain wall. Both walls for the short lamellar domains and the long domains are found along the
<2\bar{1}\bar{1}> directions (Fig. 1c). With assistance from a [111] stereographic projection map, these edge-on domain walls are determined to be on the \{01\bar{1}\} planes. In addition to the herringbone pattern, another type of domain morphology with broader width (~1 \text{µm}) and inclined domain walls (referred to as broad strips) are found at the left corner of the grain (Fig. 1a). Under the poling field of 8 kV/cm, the short lamellar domains in the herringbone pattern disappear, and the long domains become much narrower (Fig. 1b). Additionally, islands of another set of lamellar domains (indicated by bright triangles in Fig. 1b), whose domain walls are inclined and parallel to that of the original broad strips in Fig. 1a, are observed. The normal \textbf{n} to the trace of these domain walls is found to be about 48.5° from [10\bar{1}] (\textbf{e}_1 in Fig. 1d) and 11.5° from [01\bar{1}] (\textbf{e}_2 in Fig. 1d). Crystallographic analysis indicates that the domain walls of the broad strips in the virgin state (left corner of the grain in Fig. 1a) and those in the isolated islands at 8 kV/cm (Fig. 1b) are most likely on the \{12\bar{1}\} planes. Increasing the poling field from 8 to 24 kV/cm leads to the disruption of the \textmu m-sized lamellar domains to sub-\textmu m-sized features (100 ~ 200 nm) and eventually to a new domain morphology with nano-sized blotches (referred to as blotchy domains). Fig. 1e shows the domain morphology at 14 kV/cm, where some hints of the original \textmu m-sized lamellar domains can still be found. The lamellar domains continue transforming to blotchy domains with increasing field (Fig. 1f) and eventually completely disappear at 24 kV/cm (Fig. 1g).

The evolution of the corresponding selected area electron diffraction pattern (EDP) is displayed in Fig. 1h-k. The EDP recorded at 8 kV/cm (Fig. 1i) stays the same as the virgin state (Fig. 1h). However, it is interesting to notice that one set of 1/2\{oeo\} (\textit{o} and \textit{e} stand for the odd and even Miller indices, respectively) superlattice diffraction spots (one
is highlighted by a bright circle) is observed at 14 kV/cm (Fig. 1j). This is the poling field where the blotchy domains start to appear (Fig. 1e). Further increasing the poling field to 24 kV/cm preserves the superlattice spots (Fig. 1k). It is known that the PPB composition in the virgin state of KNN-based ceramics is a mixture of orthorhombic (space group Amm2) and tetragonal (space group P4mm) phases,\textsuperscript{15,16} both of which do not show any superlattice diffraction spots. Therefore, the appearance of $1/2\{100\}$ superlattice diffraction spots certainly reveals an electric field-induced oxygen octahedra tilting at 14 kV/cm and beyond.

Fig. 2 shows the microstructural responses to poling fields in another grain recorded along its [110] zone axis. In the virgin state, the broad strips with inclined domain walls along the [1$\overline{1}$1] direction occupy the upper half of the grain (Fig. 2a). The typical herringbone domains are found in the lower half with two sets of short lamellar domains along two $<1\overline{1}1>$ directions. Crystallographic analysis using the [110] stereographic projection map indicates the walls of the lamellar domains in the herringbone structure are on the $\{01\overline{1}\}$ planes. The domain walls of the broad strips are verified to be along the $\{12\overline{1}\}$ planes, which is consistent with the results for the [1$\overline{1}$1] zone axis shown in Fig. 1. Again, the herringbone type domains are transformed to $\mu$m-sized long lamellar domains at 8 kV/cm (Fig. 2b) without any noticeable change in EDP (shown in the insets). Fig. 2a and b seem to suggest that the domains with $\{12\overline{1}\}$ walls change to those with $\{01\overline{1}\}$ walls under low poling fields. Similar changes are also observed in Fig. 1a and b along the [111] zone axis. Therefore, the walls of the lamellar domains observed at 8 kV/cm may be on either the $\{01\overline{1}\}$ planes, the $\{12\overline{1}\}$ planes, or a mixture of the two. Further increase in the poling field to 14 kV/cm leads to the appearance of the $1/2\{100\}$
superlattice diffraction spots and blotchy domains (Fig. 2c), and these features remain at 24 kV/cm (Fig. 2d). It should be noted that the formation of a microcrack was observed very close to this grain at 24 kV/cm. This may have diluted the electric field in this grain, and hence only slight changes in domain morphology are observed from 14 to 24 kV/cm. However, most of the grain is transformed to blotchy domains, which is accompanied by the presence of 1/2(oeo) superlattice diffraction spots.

Fig. 3 shows another scenario along the [001] zone axis. Similar responses to the poling field are observed again. In the virgin state, herringbones are found with the intersecting line along the [010] direction (Fig. 3a). Within the herringbone bands, parallel and perpendicular lamellar domains are observed. At 8 kV/cm, the whole grain is occupied by two sets of thin, long lamellar domains along two <110> directions (Fig. 3b). Slightly increasing the poling field to 10 kV/cm results in one set of the lamellar domains disappearing. Nearly half of the grain is transformed to μm-sized rectangular blocks that have slightly curved boundaries roughly along two <100> directions (Fig. 3c). Crystallographic analysis indicates that these inclined boundaries are most likely on the (011) and (101) planes. The lamellar domains completely disappear at 14 kV/cm, and the entire grain adopts the rectangular structure (Fig. 3d). It should be pointed out that this occurs at the same poling field where the blotchy domains and the 1/2(oeo) superlattice spots appear in the other two grains. When the field is further increased to 18 kV/cm, one set of the inclined boundaries disappears and the blotchy domains become apparent and uniform (Fig. 3e). At 24 kV/cm, the second set of inclined boundaries also disappears, and small blotchy domains as well as large dark patches with diffused contrast are seen (Fig. 3f). However, the EDP always stays unchanged from the virgin
state with no 1/2{010} superlattice spots. This might be due to the fact that the oxygen octahedra tilting axis is perpendicular to the [001] zone axis and is invisible under this configuration.\textsuperscript{33}

The domain configuration in the left part of the grain shown in Fig. 3b was further analyzed. This area contains two sets of edge-on lamellar domains with an intersecting line along the [010] direction, see Fig. 4a for an enlarged view. One plausible interpretation is that they are two sets of 120° domains of the orthorhombic phase, and the [010] intersecting line is constructed of alternating 90° and 180° domain wall segments (Fig. 4b). Since 180° domain walls usually display extremely weak contrast under TEM, the intersecting line appears discontinuous in the bright field images.

To analyze the domain configurations, charge neutral domain walls are assumed to simplify the process.\textsuperscript{34,35} Four essentially different domain walls with spontaneous polarization ($P_s$) subtending angles of 60°, 90°, 120° and 180° can be adopted in the orthorhombic phase, while only 90° and 180° types exist in the tetragonal phase. These ferroelectric domain walls are limited to {100} planes for orthorhombic 90° domains and {110} for both orthorhombic 120° and tetragonal 90° domains. The 180° domain walls for both structures are required only to be parallel to the respective $P_s$ and do not have to be on a specific crystallographic plane. The {12\overline{1}} domain walls observed in the two grains along the [111] and [110] zone axes are most likely the orthorhombic 60° domain walls. The curved and inclined boundaries roughly along (011) and (101) planes observed in Fig. 3c-e could be domain walls of the monoclinic phase, which will be discussed in more detail later.
In summary, the *in situ* TEM results confirm the existence of the characteristic herringbone domains in the virgin state. These domains transform to thin and long lamellar domains around 8 kV/cm, and then are disrupted and replaced by the blotchy domains at 14 kV/cm and beyond. The blotchy domains are accompanied by the 1/2(oeo) superlattice diffraction spots, which are related to electric field-induced oxygen octahedral tilting. All of these microstructural changes under poling fields were found to remain unchanged in TEM at least 30 minutes after the applied field was removed; the domain morphology alteration and crystal structure transition under poling is an irreversible process in KNN–5.2LS.

*Ex situ* X-ray diffraction measurements. The appearance of 1/2(oeo) superlattice diffraction during poling was not reported in previous X-ray diffraction experiments on bulk KNN-based PPB compositions.\textsuperscript{21-23} *Ex situ* X-ray diffraction is employed on the bulk specimen to verify the appearance of 1/2(oeo) superlattice spots observed in the *in situ* TEM experiments. The whole spectra before and after poling are first shown in Fig. 5a. In the virgin state, the coexistence of the orthorhombic and tetragonal phases is demonstrated by the similar intensities of the (002) and (200) peaks.\textsuperscript{15} The peak intensity ratio ($I_{002}/I_{200}$) is expected to be 2:1 for the pure orthorhombic phase and 1:2 for the pure tetragonal phase.\textsuperscript{15} After poling at 30 kV/cm, the relative peak intensities have been obviously changed, especially for the Bragg peaks between 40° and 60° in 2θ. The changes can be attributed to electric field-induced phase transitions as well as the development of a texture due to domain switching.
The development of the 1/2(103) superlattice peak at ~35.3° in the bulk specimen was monitored to verify the appearance of the 1/2{oeo} superlattice spots observed in the in situ TEM experiments. Fig. 5b shows the ex situ X-ray diffraction results after poling at a series of electric fields. As can be seen, no superlattice diffraction peak is observed in the virgin state or after poling at 8 kV/cm. The 1/2(103) peak appears at 14 kV/cm and gets slightly stronger at 30 kV/cm. Therefore, the ex situ X-ray diffraction measurements on a bulk specimen match exactly with the in situ TEM results from a thin foil specimen. In addition, the X-ray diffraction measurements also confirm the irreversibility of the microstructural evolution demonstrated by the in situ TEM study.

The 1/2{oeo} superlattice diffraction peaks were recently reported in the refined (1-x)NaNbO_3–xKNbO_3 binary phase diagram.\textsuperscript{36,37} They originated from the $a^0b^+c^0$ oxygen octahedra tilting in the monoclinic space group $Pm$. At 25 °C, this monoclinic phase is stable in the composition range of 0.25 < $x$ < 0.40. However, according to Glazer\textsuperscript{38} and Reaney et al.,\textsuperscript{33,39} the $b^+$ in-phase tilting should produce 1/2{oeo} superlattice spots with $h \neq l$ ($h$ and $l$ are the two odd Miller indices). This implies that they should be absent in the $<110>$ zone-axis electron diffraction patterns. The experimentally observed 1/2{oeo} superlattice spots in $<110>$ zone-axis patterns in lead zirconate titanate ceramics were hence attributed to antiparallel cation displacements.\textsuperscript{40} They occur in the compositionally-induced low-symmetry intermediate structures as a result of the frustrated competition between displacive variants with different polarization vectors.\textsuperscript{41} In K$_{0.26}$Na$_{0.74}$NbO$_3$ at room temperature, Baker et al.\textsuperscript{37} showed a 1/2(323) superlattice peak (where $h = l$) in the X-ray diffraction data and described the $Pm$ monoclinic phase with both $a^0b^+c^0$ tilting and cation displacements order. Therefore, the appearance of the
$1/2\{oeo\}$ diffraction spots in both [111] and [110] zone axes at 14 kV/cm in KNN–5.2LS is due to an electric field-induced phase transition from the orthorhombic $Amm2$ phase, which has no oxygen octahedra tilting, to the monoclinic $Pm$ phase with $a^0b^+c^0$ tilting, combined with antiparallel cation displacements. At fields of 8 kV/cm and lower, there is domain switching and very likely a small extent of phase transition from tetragonal $P4mm$ to orthorhombic $Amm2$.

**Macroscopic properties.** In order to correlate the microstructural changes during poling to macroscopic properties, the dielectric and piezoelectric properties were measured on bulk specimens after poling at a series of fields. The temperature dependent dielectric constant of the bulk sample, poled at a series of fields, is shown in Fig. 6. The measurements were conducted for heating and cooling separately, both starting from room temperature. As reported before, the phase transition temperature between orthorhombic and tetragonal phases ($T_{O-T}$) of virgin state KNN–5.2LS is around room temperature. This is verified again in Fig. 6 as a hump on the dielectric constant curve right at room temperature. Compared with the virgin state, the sample after poling at 8 kV/cm displays a diminished dielectric constant around room temperature, and the hump marking the $T_{O-T}$ is broadened and appears to be shifted to between 40 °C and 60 °C. Both facts may find microstructural origin from the *in situ* TEM results indicating some extent of tetragonal to orthorhombic phase transition. After poling at 14 and 30 kV/cm, the sample shows a higher dielectric constant around room temperature but decreases much faster during cooling. When heated, a distinct peak with significantly increased values of dielectric constant is observed around 45 °C. This dielectric peak is
apparently associated with the poling-induced \( Pm \) monoclinic phase revealed by the \textit{in situ} TEM and the \textit{ex situ} X-ray diffraction experiments. It indicates the thermally induced monoclinic \( Pm \) to tetragonal \( P4mm \) phase transition, and hence the temperature of the transition is denoted \( T_{M-T} \).

The corresponding piezoelectric evolution is shown in Fig. 7, where the piezoelectric coefficient \( (d_{33}) \) is plotted as a function of poling field. Three stages can be identified that correlate perfectly with the \textit{in situ} TEM results. In stage I, the poling field is very low and only minimum \( d_{33} \) values are measured. Microscopically, the original herringbone type of domain morphology largely remains because almost no domain switching occurs. In stage II, moderate \( d_{33} \) values develop due to the herringbone domains being replaced by the lamellar domains via domain switching and phase transition. Stage III, which starts at 14 kV/cm, demonstrates a sudden jump in \( d_{33} \) to 237 pC/N. This is induced by the orthorhombic to monoclinic phase transition. Increasing the poling field further only results in a modest change in the \( d_{33} \) and finally saturates at 265 pC/N. Hence, the excellent piezoelectric response of KNN–5.2LS is attributed to the poling-induced monoclinic \( Pm \) phase with \( a^0b^+c^0 \) oxygen octahedra tilting and antiparallel cation displacements.

With these experimental results, we can now address the questions raised in the beginning. Firstly, the \textit{Amm2/P4mm} PPB is not stable against poling. Poling-induced phase transitions destroy the PPB and eventually form a single phase with the \( Pm \) space group. This is quite similar to (1-\( x \))BNT–\( x \)BT with \( x = 5.5\% \) and \( x = 6\% \), where the \textit{R3c/P4bm} MPB is destroyed and the single phase \textit{R3c} survives the high poling field.24 Secondly, the KNN–5.2LS ceramic is extremely responsive to the poling field;
complicated domain switching and phase transitions are observed to occur. In addition, dislocation activities seem to participate in the deformation process during electrical poling (Fig. 1f and 1g). Thirdly, the macroscopic properties correlate very well with the microstructural evolution during poling. The microstructural mechanism for the enhanced piezoelectricity is the presence of the tilted $Pm$ phase after poling. The large number of equivalent polar axis (24) in the monoclinic phase (for comparison, 6 in tetragonal and 12 in orthorhombic) makes the poling easier and more thorough. Of course, the close-to-room-temperature phase transition ($T_{M-T} \sim 45 \, ^\circ C$) provides the necessary structural instability. Apparently, this mechanism is quite different from that of (1-x)BNT–xBT. For $x = 7\%$, the composition with the best $d_{33}$ value, an $R3c/P4mm$ MPB is created from the original $P4bm$ single phase by poling and is responsible for the enhanced piezoelectricity.\footnote{24} Finally, we argue that even though the $Amm2/P4mm$ PPB in KNN–5.2LS does not exist after poling, it is still important to the enhanced piezoelectric response. The existence of the PPB at room temperature indicates that multiple ferroelectric phases with varied distortions have similar free energies at this temperature. This guarantees easy electric field-induced phase transitions, which allows the transformation to the monoclinic phase during poling.

The discovery presented here will be helpful to the development of lead-free piezoelectric ceramics. It demonstrates the importance of the structural instability associated with either PPB or MPB to the piezoelectric property. The coexistence of multiple phases is a sign of comparable free energies and guarantees the involvement of phase transitions during piezoelectric activities under electric fields or mechanical stresses. In addition, the strong competition between the coexisting ferroelectric phases
may also result in low-symmetry structures, and this process can be assisted by external stimuli. As proven here in the KNN-5.2LS ceramic, poling fields assisted the formation of the $Pm$ structure due to the competition between the orthorhombic phase with the $<110>$ polarization and the tetragonal phase with the $<001>$ polarization. It is also very interesting to notice that once a stable low-symmetry phase is resulted from the competition, excellent piezoelectric properties ensue. This is the case here, this is the case in lead zirconate titanate.\textsuperscript{40,42}

3.2.4 Conclusion

An electric field \textit{in situ} TEM study was conducted for the first time on an archetypical KNN-based lead-free piezoelectrics: the polymorphic phase boundary composition KNN–5.2LS. It is found that the original herringbone domain patterns of mixed tetragonal and orthorhombic phases change to thin lamellar domains when the poling field reaches 8 kV/cm. This process involves domain switching as well as some extent of tetragonal to orthorhombic phase transition. At 14 kV/cm, a monoclinic $Pm$ phase with $a^0b^+c^0$ oxygen octahedra tilting and antiparallel cation displacements forms, as manifested by the appearance of blotchy domains and 1/2{$oeo$} superlattice diffraction spots. These microstructural changes in response to electrical poling fields remain after the field is removed; therefore, they determine the macroscopic properties of poled ceramics. The poling-induced monoclinic phase and its low transition temperature ($T_{M-T}$) are responsible for the enhanced piezoelectric response of this ceramic. The microscopic structure and macroscopic property relationship elucidated here not only explains the
KNN–5.2LS but will hopefully allow for the identification of new compositions that will assist in the development of lead-free piezoelectrics.

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FIG. 1 *In situ* TEM observations of a grain along the [111] zone axis in a KNN-5.2LS specimen during electrical poling. Bright-field micrographs at (a) virgin state, and (b) 8 kV/cm are displayed to show almost the entire grain. The direction of poling fields is indicated by the bright arrow in (b). The area in the dashed box in (a) is focused for
further illustration at (c) virgin state, (d) 8 kV/cm, (e) 14 kV/cm, (f) 22 kV/cm and (g) 24 kV/cm. Representative selected area diffraction patterns recorded at (h) virgin state, (i) 8 kV/cm, (j) 14 kV/cm, and (k) 24 kV/cm are displayed, with $1/2\{00\}o$ superlattice diffraction spots highlighted by bright circles.

FIG. 2 In situ TEM observations of a near-by grain along the [110] zone axis in the same KNN-5.2LS specimen as examined in Fig.1 during electrical poling. Bright-field micrographs at (a) virgin state, (b) 8 kV/cm, (c) 14 kV/cm, and (d) 24 kV/cm are displayed. The direction of poling fields is indicated by the bright arrow in (b). Representative selected area diffraction patterns at each poling field are shown in the insets, with $1/2\{00\}o$ superlattice diffraction spots indicated by bright circles.
FIG. 3 *In situ* TEM observations of a near-by grain along the [001] zone axis in the same KNN-5.2LS specimen as examined in Fig. 1 during electrical poling. Bright-field micrographs at (a) virgin state, (b) 8 kV/cm, (c) 10 kV/cm, (d) 14 kV/cm, (e) 18 kV/cm, and (f) 24 kV/cm are displayed. The direction of poling fields is indicated by the bright arrow in (b). Representative selected area diffraction patterns at each poling field are shown in the insets.
FIG. 4 Interpretation of the orthorhombic structure observed in the left part of the [001]-aligned grain shown in Fig. 3b. (a) The close-up view of the domain configuration. (b) A schematic illustration of the domains patterns. The polarization vectors $\mathbf{P}_s$ of the adjacent four domains are indexed, and associated domain walls are labeled.
FIG. 5 Ex situ X-ray diffraction spectra of a bulk KNN-5.2LS disk poled at different fields. (a) The full spectra in the virgin state and after poling at 30 kV/cm. The peaks are indexed according to a tetragonal unit cell. (b) The profiles with extended data recording time on the same bulk disk reveal the development of the 1/2(103) superlattice peak under electrical poling.
FIG. 6 Temperature dependence of the dielectric constant measured at 10 kHz during heating and cooling on a bulk disk of KNN-5.2LS after poling at a series of electric fields.

FIG. 7 The development of piezoelectricity, as expressed by the coefficient $d_{33}$, under electrical poling in a bulk KNN-5.2LS disk.
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3.3 (1-x)Ba(Zr_{0.2}Ti_{0.8})O_3-x(Ba_{0.7}Ca_{0.3})TiO_3 solid solution: Unique single-domain state in a polycrystalline ferroelectric ceramic


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Abstract

Non-180° ferroelectric domains are also ferroelastic domains, their existence in polycrystalline materials is to relieve internal stresses generated during solid-solid phase transitions and minimize the elastic distortion energy. Therefore, grains with random orientations in polycrystalline ceramics are always occupied by many domains, especially in the regions close to grain boundaries. In this communication, we report the observation of a single-domain state in a BaTiO_3-based polycrystalline ceramic at intermediate poling electric fields with in situ transmission electron microscopy. The grains in the virgin ceramic and under high poling fields are found multi-domained. The unique single-domain state is believed to be responsible for the ultra-high piezoelectric property observed in this lead-free composition and is suggested to be of orthorhombic symmetry for its exceptionally low elastic modulus.

3.3.1. Introduction

Domains are formed in ferroelectric crystals to minimize the electrostatic energy associated with the spontaneous polarization and the elastic energy due to lattice distortion at the displacive solid-solid phase transitions.\textsuperscript{1-7} The electrostatic energy is minimized when the polarization vectors of adjacent domains are adopted such that $\text{div } P = 0$ at the domain walls.\textsuperscript{3} For non-180° ferroelectric domains, this condition is satisfied
with the “head-to-tail” arrangement of polarization vectors across the domain wall. For 180° domains, the electrostatic energy drives the domain wall parallel to the polarization vectors.\(^3\) Non-180° ferroelectric domains are also ferroelastic domains due to the orientation difference of the spontaneous strain tensors across the domain wall.\(^2,3\) They are created primarily during the paraelectric to ferroelectric phase transition to minimize the elastic energy through releasing the internal stresses.\(^1\) Further ferroelectric to ferroelectric phase transitions at lower temperatures also contribute to the formation of non-180° domains.

In ferroelectric single crystals, the multi-domain state is still favored for its low electrostatic energy even though no mechanical constraints are present on the crystal surfaces.\(^1-3\) A single-domain state could presumably be achieved by electrical poling through electric field-induced domain switching.\(^2,3\) However, elimination of domain walls in single crystals with electric field is not always guaranteed.\(^8,9\) In a polycrystalline ceramic, each grain is mechanically confined by its neighboring grains, which usually leads to a complex multi-domain structure as the favored states of low energy.\(^1\) A single-domain state of the grains is hence extremely difficult, if not impossible, to be reached by poling because of high internal stresses from the incompatible transformation strain at grain boundaries and non-uniform electric fields from the anisotropy in dielectric permittivity.\(^2\) With either \textit{ex situ} or \textit{in situ} observations, previous experimental studies invariably indicate the existence of multiple domains in grains of polycrystalline ceramics, including poled \(\text{BaTiO}_3\) with large grain sizes,\(^10\) poled \((\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3\) ceramics,\(^11\) poled \(\text{Pb(Zr,Ti)}_3\) ceramics,\(^12\) as well as \((\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\)-Ba\(\text{TiO}_3\) ceramics under applied fields during electrical poling.\(^13\) Here we report, for the first time, the
observation of poling-induced single-domained grains in the polycrystalline ceramic of 0.5Ba(Zr0.2Ti0.8)O3-0.5(Ba0.7Ca0.3)TiO3, a lead-free composition showing ultrahigh piezoelectric coefficients.14

3.3.2. Experimental procedure

The ceramic was prepared using the solid-state reaction method with details reported previously.15 The average grain size was determined to be 13.1 μm. For the electric field \textit{in situ} transmission electron microscopy (TEM) experiments,13,16-19 disk specimens (3 mm in diameter) were prepared from as-sintered pellets through standard procedures including grinding, cutting, dimpling, and ion milling. Prior to ion milling, the dimpled disks were annealed at 200 °C for 2 hours. \textit{In situ} TEM experiments were carried out on a Phillips CM-30 microscope operated at 200 kV.

3.3.3. Results and discussion

The evolution of the ferroelectric domains in the ceramic during electrical poling is exemplified with a grain imaged along its [112] zone axis, as shown in Fig. 1. In the virgin state [Fig. 1(a)], two sets of long lamellar domains are observed. In the upper left part of Fig. 1(a), the previously reported hierarchical domain structure20 is also seen with nanodomains being developed within the wedge-shaped domains. At the nominal poling field of 1.00 kV/cm, significant changes in the domain morphology are observed, indicating extensive domain switching activities at this low level of electric field [Fig. 1(b)]. It should be noted that the multi-domain state is still preserved. When the electric field reaches a nominal value of 1.33 kV/cm, all of the domain walls disappear; the whole
grain unexpectedly becomes a large single domain, as shown in Fig. 1(c). This single-domain state is found not stable against higher poling electric fields. At the field of 4.50 kV/cm, one set of long lamellar domains are formed [Fig. 1(d)]. The corresponding electron diffraction patterns during the poling process are also displayed in Fig. 1. Neither detectable changes in the diffraction pattern nor the appearance of superlattice spots are observed.

It should be emphasized that the grain shown in Fig. 1 is surrounded by neighboring grains. The observation of a grain with no domain walls in a dense polycrystalline ceramic is highly unusual because of the mechanical confinement imposed by neighboring grains. To the authors’ knowledge, the electric field-induced transition from a multi-domain to a single-domain state has only been experimentally observed in single crystals.9,21,22

To make sure this single-domain state can be reproduced in different grains in the ceramic, a number of grains (> 30) in several TEM specimens were analyzed. The presence of the single-domain state at low poling fields was repeatedly observed in all the examined grains with varied grain sizes. Figure 2 shows the results on three representative grains in the same TEM specimen with their zone axis along [100], [101] and [111], respectively. In the virgin state of the ceramic [Fig. 2(a), 2(c), and 2(e)], multiple domains with complicated hierarchical structures are observed for all three grains. This hierarchy feature is more apparent in the upper middle part of the [101]-aligned grain [Fig.2(c)], where very fine domains with sizes of 100 ~ 300 nm are observed within the [010]-oriented wedge-shaped large domains. The domain walls in the virgin state are most likely on the {001} and {110} crystallographic planes. During poling at very moderate field values, the multi-domain to single-domain transition is
clearly observed to occur at different nominal applied fields: 1.33 kV/cm for the [100]-, 2.50 kV/cm for the [101]-, and 3.20 kV/cm for the [111]-aligned grain, respectively. Again, there is no apparent change in the corresponding electron diffraction patterns. It is noticed that the single-domain state starts to appear at different poling fields in different grains. This could be a result of the following facts: (1) The electric field in the TEM specimen is not uniform due to the presence of a central perforation. The actual field may be distorted, intensified, or diluted by the perforation. Since the exact value of the actual field is not known, the values reported here are the nominal ones (the applied voltage divided by the electrode spacing). (2) The grains in the ceramic are typically in a size above ten microns. An orientation dependence of the poling response is expected, as in single crystals of other ferroelectric perovskites.

It is noticed that two other states, a nanodomains state and an isotropization state, have similar appearances in TEM bright field imaging as those shown in Fig. 1(c), and Figs. 2(b), 2(d), 2(f). However, electric field is known to favor large ferroelectric domains with long range polar ordering over nanodomains with short range ordering, as demonstrated previously in (Bi_{1/2}Na_{1/2})TiO_{3}–BaTiO_{3} solid solutions and Pb(Mg_{1/3}Nb_{2/3})O_{3}-based ceramics. The possibility of a non-polar isotropic phase can also be ruled out as it usually appears as a transient phase during temperature induced transitions. An electric field, as a driving force for phase transition with a polar cylindrical symmetry of \( \infty m \), is not expected to favor the isotropization state. Most importantly, our piezoelectric coefficient \( d_{33} \) measurements on bulk samples indicate a fast increase to \( \sim 200 \) pC/N at poling fields around 3.50 kV/cm. The formation of a non-polar isotropic phase will diminish the piezoelectricity. Therefore, we argue that the
$0.5\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-0.5\text{(Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ceramic is in a unique single-domain state with long range ferroelectric ordering formed under very moderate poling fields.

Non-$180^\circ$ domains are needed in grains in a polycrystalline ferroelectric ceramic to accommodate internal stresses and are known to persist in regions adjacent to grain boundaries even at very high poling fields.\textsuperscript{33} Therefore, the single-domain state observed in this study seems to indicate low internal stresses in the ceramic, which we suggest could be achieved through an electric field-induced transition to a pure orthorhombic phase. Previous symmetry analysis reveals that the $0.5\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-0.5\text{(Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ceramic can exist in rhombohedral, orthorhombic, tetragonal or any combination of these phases at room temperature.\textsuperscript{34} Detailed dynamic mechanical analysis indicates that the intermediate orthorhombic phase displays an elastic storage modulus below 50 GPa,\textsuperscript{35} which is not only the lowest among all phases in this particular composition but also much lower than that of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$-based and PbZrO$_3$-based ceramics.\textsuperscript{36,37} A very recent TEM study with convergent beam electron diffraction analysis shows that the $0.5\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-0.5\text{(Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ceramic is a mixture of rhombohedral and tetragonal phases in its virgin state at room temperature.\textsuperscript{38} We suggest this two-phase mixture transforms to the orthorhombic phase at moderate fields during poling, which would correspond to a significant elastic softening and the internal stresses would hence be small.

It should be pointed out that the single-domain state is not quite stable. When the poling field is removed, domain walls reappear in small portions of the grain. Even when the poling field at which the single-domain state is initially observed is maintained, domain walls start to form in regions adjacent to grain boundaries after several minutes.
Figure 3 shows an example which follows the [101]-aligned grain shown in Fig. 2(d). This grain becomes a single-domain immediately at the application of a poling field of 2.50 kV/cm [Fig. 2(d)]. After this field is maintained for 3 minutes, lamellar domains with their traces roughly along the [11$ar{1}$] direction start to nucleate from the grain boundary, as highlighted by the bright box in Fig. 3(a). Further growth of existing domains and nucleation of new domains continues as time elapses [Fig. 3(b)]. However, these domains are confined in the region close to grain boundaries and most part the grain remains free of domain walls. This seems to support our elastic softening mechanism for the single-domain state. The exceptionally low elastic modulus in the poling-induced orthorhombic phase leads to low internal stresses in the polycrystalline ceramic. The weak driving force leads to delayed and slow formation of non-180° domains in small regions close to grain boundaries.

The discovery of the unique single-domain state in the 0.5Ba(Zr$_{0.2}$Ti$_{0.8}$)O$_3$–0.5(Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$ ceramic during poling has technological implications. This composition was reported to display an ultrahigh piezoelectric coefficient $d_{33}$ over 600 pC/N (ref.14) and its property is highly sensitive to poling conditions.$^{39,40}$ As for a polycrystalline ferroelectric ceramic, the ultimate goal of electrical poling for piezoelectricity is to make all individual grains single-domain with aligned polarizations. The observed single-domain state here is very likely the primary reason for the excellent piezoelectric property in this BaTiO$_3$-based lead-free ceramic and its delicate nature well explains the strong dependence of $d_{33}$ on poling conditions.

In addition to the possible well aligned polarization, the exceptionally low elastic modulus of the single-dominated orthorhombic phase may also contribute to the ultrahigh
piezoelectric property of this ceramic. Generally speaking, lattice softening and low polarization anisotropy go hand in hand, both enhance the piezoelectric response.\textsuperscript{14} Elastic softening is believed to effectively relax the crystal lattice and facilitate the structural instability when electric fields are applied. Correspondingly, high piezoelectric properties are always observed in elastically compliant phases.\textsuperscript{15,41-43}

In conclusion, the microstructural evolution during electrical poling in the $0.5\text{Ba(Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-0.5\text{(Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ polycrystalline ceramic is investigated with in situ TEM. The grains of the original multi-domain state transform to a unique single-domain state at very moderate poling fields. It is suggested that this transition corresponds to the formation of a pure orthorhombic phase with a significant elastic softening. The single-domain state is suggested to be primarily responsible for the excellent piezoelectric property in this lead-free composition and its delicate nature can explain the high sensitivity of the property to poling conditions.

3.3.4. Conclusion

In conclusion, the microstructural evolution during electrical poling in the $0.5\text{Ba(Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-0.5\text{(Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ polycrystalline ceramic is investigated with in situ TEM. The grains of the original multi-domain state transform to a unique single-domain state at very moderate poling fields. It is suggested that this transition corresponds to the formation of a pure orthorhombic phase with a significant elastic softening. The single-domain state is suggested to be primarily responsible for the excellent piezoelectric property in this lead-free composition and its delicate nature can explain the high sensitivity of the property to poling conditions.
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FIGURES

FIG. 1 In situ TEM observations of a grain along the [112] zone axis in the 0.5Ba(Zr0.2Ti0.8)O3-0.5(Ba0.7Ca0.3)TiO3 ceramic under electric fields. Bright-field micrographs at (a) virgin state, (b) 1.00 kV/cm, (c) 1.33 kV/cm, and (d) 4.50 kV/cm are
displayed. The direction of poling field is indicated by the dark arrow in (b). Representative selected area diffraction patterns are recorded at (e) virgin state, (f) 1.33 kV/cm, and (g) 4.50 kV/cm.

FIG. 2 In situ TEM observations of a series of grains in the same specimen of the 0.5Ba(Zr$_{0.2}$Ti$_{0.8}$)O$_3$–0.5(Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$ ceramic. Bright-field micrographs are displayed for a grain along (a) the [100] zone axis in the virgin state, (b) the [100] zone axis at 1.33 kV/cm, (c) the [101] zone axis in the virgin state, (d) the [101] zone axis at 2.50 kV/cm, (e) the [111] zone axis in the virgin state, and (f) the [111] zone axis at 3.20 kV/cm. The micrographs in (b), (d), (f) were recorded within one minute after the applied field
reached the specified values. Two essential crystallographic directions in each zone axis are shown by bright arrows in (a), (c), and (e). The direction of the poling field is indicated by the dark arrow in (b), (d), and (f).

FIG. 3 The nucleation and growth of lamellar domains in the grain shown in Fig. 2(d) at 2.50 kV/cm recorded after (a) 3 minutes, and (b) 5 minutes. No further domain formation was noticed in this grain beyond 5 minutes.
References


3.4 Polarization alignment, phase transition and piezoelectricity development in polycrystalline $0.5\text{Ba(Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3\text{-0.5(Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$


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**Abstract**

The microstructural origin of the exceptionally high piezoelectric response of polycrystalline $0.5\text{Ba(Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3\text{-0.5(Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ is investigated using *in situ* transmission electron microscopy, in addition to a wide variety of bulk measurements and first-principles calculations. A direct correlation is established relating a domain wall-free state to the ultrahigh piezoelectric $d_{33}$ coefficient in this BaTiO$_3$-based composition. The results suggest that the unique single-domain state formed during electrical poling is a result of a structural transition from coexistent rhombohedral and tetragonal phases to an orthorhombic phase that has an anomalously low elastic modulus. First-principles calculations indicate that incorporating Ca$^{2+}$ and Zr$^{4+}$ into BaTiO$_3$ reduces the differences in structure and energy of the variant perovskite phases, and $0.5\text{Ba(Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3\text{-0.5(Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ is identified as unique because the variant phases become almost indistinguishable. The structural instability and elastic softening observed here are responsible for the excellent piezoelectric properties of this lead-free ceramic.
3.4.1 Introduction

Lead-free piezoelectric ceramics have received tremendous attention worldwide in the past decade due to environmental concerns over the toxicity of lead in Pb(Zr,Ti)O$_3$-based compositions, which have been the mainstay for high performance actuators and transducers for over half a century owing to their superior electromechanical properties.$^{1,2}$ Among the most studied lead-free solid solutions, Ba(Zr$_{0.2}$Ti$_{0.8}$)O$_3$–(Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$ (BZT–BCT) stands out for its exceptionally high piezoelectric properties. Specifically, a piezoelectric coefficient $d_{33}$ as high as 620 pC/N has been observed in polycrystalline 0.5Ba(Zr$_{0.2}$Ti$_{0.8}$)O$_3$–0.5(Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$ (50BZT–50BCT).$^3$ Similar to Pb(Zr,Ti)O$_3$, the BZT–BCT solid solution crystallizes in three perovskite phases: paraelectric cubic ($P m\bar{3}m$), ferroelectric rhombohedral ($R3m$), and ferroelectric tetragonal ($P4mm$).$^3$ Recent reports suggest the presence of an intermediate orthorhombic phase ($Amm2$) within a narrow temperature and composition range.$^4$–$^6$ For 50BZT–50BCT, this orthorhombic phase exists around room temperature within a temperature window narrower than 30 °C (Ref. 6). Most interestingly, it displays an anomalously low storage modulus as revealed by dynamic mechanical analysis.$^5$

Phenomenologically, the ultrahigh piezoelectric effect in 50BZT–50BCT is explained as due to the existence of a triple point close to room temperature.$^3$ From a microstructural perspective, this composition in its virgin state contains nanoscale ferroelectric domains that are believed to facilitate polarization rotation during electrical poling and to enhance piezoelectricity.$^7$ Even though ferroelectric domains are known to dictate the dielectric, piezoelectric and ferroelectric properties of polar oxides, their original morphologies and even crystal symmetries often times cannot survive the
electrical poling process, as recently demonstrated in \((K_{0.5}Na_{0.5})NbO_3\)-based\(^8\) and \((Bi_{1/2}Na_{1/2})TiO_3\)-based\(^9\) solid solutions. The effective polarization alignment and extensive phase transition during poling are cited as primary factors contributing to their excellent piezoelectric performances.\(^8,9\) Presumably the hierarchical domain structure observed in unpoled 50BZT–50BCT ceramic s does not survive electrical poling either, as both 180° and non-180° domain switching have been observed in poled BZT–BCT solid solutions.\(^10\)–\(^13\) It should be noted that these X-ray diffraction investigations only focus on the ferroelastic/ferroelectric domain switching under high poling fields (> 6.5 kV/cm), and most of the time are under *ex situ* conditions. Furthermore, no indication of any phase transition under electric field has been reported in this solid solution system. However, the coercive field of 50BZT-50BCT is extremely low [< 2 kV/cm (Ref. 3)] and several thermally induced phase transitions occur at temperatures close to room temperature.\(^6\) To formulate a physics-based interpretation of the piezoelectricity in BZT–BCT, a detailed investigation of the domain polarization alignment at electric fields near the coercive field and possible phase transitions that occur during electrical poling is needed. For this, *in situ* transmission electron microscopy (TEM) under applied electric fields becomes critical.

A relevant issue related to piezoelectricity, especially in BaTiO\(_3\)-based compositions, is aging.\(^14\) In a \((K_{0.5}Na_{0.5})NbO_3\)-based polycrystalline ceramic, the piezoelectric response decays over time, but can be recovered or even enhanced by a re-poling.\(^15\) It is therefore of fundamental importance to investigate the domain structure changes, and possible phase transitions, that occur during aging and re-poling.
In this study an electric field *in situ* TEM technique is used to monitor the polarization alignment process through domain switching and electric field-induced phase transitions due to the poling of virgin and aged polycrystalline 50BZT-50BCT. The observations in the TEM combined with electrical measurements and *in situ* X-ray diffraction experiments on bulk samples allow the elucidation of the physics origin of the piezoelectricity in 50BZT–50BCT. The experimental findings are supported by first-principles calculations on cubic, tetragonal, orthorhombic, and rhombohedral perovskite variants.

### 3.4.2 Experimental procedure

**A. Sample preparation and characterization.**

The 50BZT-50BCT polycrystalline ceramic was prepared using a solid-state reaction method with details described in our previous reports. The average grain size was determined to be 13.1 μm. A circular disk sample with sputtered silver films serving as electrodes was used for the bulk dielectric property measurements. These were carried out using a heating rate of 4 °C/min for a virgin state specimen as well as the same specimen immediately after the room-temperature poling. In the present work, the nominal electric field (the applied voltage divided by the electrode spacing) is cited for the *in situ* TEM results.

Electrodes were sputtered on to another pellet for *in situ* X-ray diffraction experiment. Cu-Kα radiation was used at a 0.02° step size for the 2θ scan. The pseudocubic (002)_C, (220)_C, and (222)_C peaks were recorded at a series of poling fields.
applied and maintained. The LHPM Rietica software package was used for Rietveld refinement of the diffraction spectra.

The piezoelectric coefficient $d_{33}$ and elastic compliance $s_{33}^{E}$ under DC bias fields were determined with an impedance method that used bar-shaped specimens ($1 \times 1 \times 3$ mm$^3$). The dwell time for the measurement at each bias field was ~20 s. In order to avoid clamping effects of the resonance bars, thin silver leads were attached to the end faces with silver epoxy. The resonance and antiresonance frequencies of the virgin specimen were measured as a function of applied DC bias, which was increased from 0 to 8 kV/cm at 0.5 kV/cm increments. Also, the capacitance of a virgin disk sample was measured at 1 kHz under the same DC bias conditions. The piezoelectric coefficient $d_{33}$ and elastic compliance constants $s_{33}^{D}$ and $s_{33}^{E}$ were then calculated. Another bar-shaped specimen was poled at room temperature with a DC field of 20 kV/cm from its virgin state. It was then allowed to age at room temperature for 5 days and the $d_{33}$ and $s_{33}^{E}$ were measured during the re-poling process following the same procedure described above.

For electric field in situ TEM experiments, disk specimens (3 mm in diameter) were prepared from as-sintered pellets through standard procedures including grinding, cutting, dimpling, and ion milling. The dimpled disks were annealed at 200 °C for 2 h to minimize the residual stresses before Ar-ion milling to the point of electron transparency. In situ TEM experiments were carried out on a Phillips CM-30 microscope operated at 200 kV. After the first poling process from its virgin state, the same specimen was kept in the TEM for 4 days for the aging process, and was then used for the re-poling study.
B. First-principles calculations

The first-principles calculations were performed using the density functional theory formalism as implemented in the ABINIT software package.\textsuperscript{20,21} Norm-conserving pseudopotentials were used in place of the all-electron ion potentials and the exchange correlation energy was approximated using the Wu-Cohen formulation for the generalized gradient approximation.\textsuperscript{22} The Brillouin zone was sampled using a Monkhorst-Pack 6×6×6 \textit{k}-point mesh\textsuperscript{23} and the wave function was represented as a plane wave expansion that was truncated at an energy of 80 Ry. Using these approximations the atomic structures were optimized until the residual forces on the atoms were less than 5 meV/Å.

The composition of interest, with the formula \(0.5\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3\), can be rewritten as \((\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Ti}_{0.90}\text{Zr}_{0.10})\text{O}_3\), which demonstrates that the compound can be imagined as a base compound BaTiO\(_3\) co-doped with Ca\(^{2+}\) and Zr\(^{4+}\) at a ratio of 3:2. The virtual crystal approximation\textsuperscript{24} was used to examine the compositions of \((\text{Ba}_{1-3x}\text{Ca}_{3x})(\text{Ti}_{1-2x}\text{Zr}_{2x})\text{O}_3\) for the range of \(0.00 \leq x \leq 0.06\). When \(x = 0.00\), the compound is pure BaTiO\(_3\) and when \(x = 0.05\) the composition is 50BZT–50BCT. For each composition, four phases were investigated: a paraelectric cubic phase and three ferroelectric phases; tetragonal, orthorhombic and rhombohedral. The orthorhombic phase was modeled using a so-called \(\sqrt{2}\) cell that is comprised of 10 atoms, but the other phases used the simple 5-atom primitive cell. Each of the atomic structures and lattices were optimized under the constraint that they maintain their crystallographic symmetries.
3.4.3 Results and discussion

A. Structure-property evolution during initial poling

A.1 In situ TEM observations

The microstructural evolution under initial poling from the virgin state of polycrystalline 50BZT–50BCT is monitored in real-time on a representative grain along its [101] zone axis, as shown in Fig.1. In the unpoled state [Fig. 1(a)], multiple domains are observed with the domain walls tracing along the <001>, <110>, and <111> directions, suggesting that they are very likely on {001} and {110} crystallographic planes. Most importantly, the hierarchical domain structure, which was reported as the distinct feature of this composition, is clearly observed in the upper middle part in Fig.1(a). When the electric field reaches 2 kV/cm during initial poling [Fig. 1(b)], the hierarchical domain feature is disrupted, and also the domain wall density decreases. Multiple domains are still present with walls along two sets of {110} planes. A slight increase in the poling electric field to 2.5 kV/cm leads to a unique domain wall-free state [Fig.1(c)], where the whole grain becomes a large single domain. However, such a single-domain state is not stable against higher poling fields. As exemplified in Fig. 1(d) at 4.25 kV/cm, two sets of {110} domain walls reappear even though the majority of the grain is still occupied by the large domain. The newly formed multi-domain configuration becomes more apparent with the increase of domain wall density when the electric field further increases. As shown in Fig. 1(e) through 1(g) at 5.75 ~ 10 kV/cm, new sets of domains are observed, and the domain wall density reaches its maximum at 8 ~ 10 kV/cm. Further increase in the poling field to 18 kV/cm leads to merging of lamellar domains into larger domains, but many domain walls still persist. The
corresponding selected area electron diffraction patterns during this initial poling process are also recorded. No noticeable changes to the fundamental diffraction spots and no appearances of any superlattice spots are observed [Fig. 1(i)].

Figure 2 shows another representative grain imaged along its [111] zone axis, where consistent results on the microstructure’s response to initial poling are observed. In the virgin state prior to poling, the multi-domain state with typical hierarchical domain structure is seen [Fig. 2(a)]. During the initial poling at 1 kV/cm [Fig. 2(b)], the domain morphology changes slightly. However, dramatic changes are observed when the electric field reaches 3.2 kV/cm; all of the domains disappear and the whole grain transforms into a single-domain state [Fig. 2(c)]. Many lamellar domains with walls along two sets of {110} planes are developed upon further increasing the electric field [Fig. 2(d)]. In contrast to (K_{0.5}Na_{0.5})NbO_3-based\(^8\) and (Bi_{1/2}Na_{1/2})TiO_3-based\(^6\) ceramics, where poling-induced microstructure is largely preserved after the removal of the electric field, the multi-domain configuration developed under high poling fields observed here in 50BZT–50BCT changes dramatically at zero field. As shown in Fig. 2(e), the long lamellar domains are disrupted by some short sets but the multi-domain state is preserved in this grain. Again, there is no observable change in the electron diffraction patterns during the poling process [Fig. 2(f)].

Our in situ TEM observations on 30+ grains reveal two scenarios for the domain configuration when the applied electric field is removed. When the grain is at the single-domain state, the removal of the poling electric field leads to the appearance of a few domains; but a good portion of the grain remains domain wall-free. The single-domain state can be reproduced during an immediate re-poling. When the applied field is high
during the initial poling and the grain is in a multi-domain state beyond the single-domain state, many domains are present in the grain after the removal of the field. The single-domain state is not observed upon an immediate re-poling.

As noticed in Figs. 1 and 2, most of the domain walls in the multi-domain state are found parallel to the \{001\} or \{110\} crystallographic planes. This information alone is not sufficient to reveal the crystal symmetry of these domains. For example, the \{110\} plane can be the 71° rhombohedral, 120° orthorhombic, and 90° tetragonal domain walls. Also, the \{100\} plane is permissible for 109° rhombohedral and 90° orthorhombic domain walls.\(^8,25\) In our previous \textit{in situ} TEM work,\(^8,9\) the crystal structure is inferred primarily from superlattice diffraction spots. Unfortunately, superlattice diffraction is not present in the current BaTiO\(_3\)-based composition, neither in its virgin state nor during poling under electric field. A separate detailed convergent beam electron diffraction analysis indicates that polycrystalline 50BZT–50BCT, at room temperature in its virgin state, is a two-phase mixture (\textit{P}4\textit{mm} + \textit{R}3\textit{m}) rather than a single \textit{Amm}2 phase.\(^26\)

The presence of the single-domain state [Figs. 1(c) and 2(c)] at very low poling fields in a polycrystalline ceramic is quite unusual. This is repeatedly observed in all of the grains (> 30) examined in several TEM specimens.\(^27\) We speculate that the unique single-domain state in polycrystalline 50BZT–50BCT is in an orthorhombic phase based on the following facts. First, the virgin state of this composition at room temperature is a mixture of rhombohedral and tetragonal phases.\(^26\) Second, the orthorhombic phase of this composition has an exceptionally low elastic modulus,\(^5\) much lower than those of (Bi\(_{1/2}\)Na\(_{1/2}\))TiO\(_3\)-based and Pb(Zr,Ti)O\(_3\)-based ceramics.\(^28,29\) During electrical poling of polycrystalline ferroelectrics for piezoelectricity, the domain polarization alignment
cannot be complete and many domains persist at grain boundary regions even at very high poling fields in order to accommodate the incompatible piezoelectric strain across the grain boundary.\textsuperscript{30} The ultrasoft nature of the orthorhombic phase makes a single-domain state possible in polycrystalline 50BZT-50BCT for much reduced internal stresses.

\textbf{A.2 In situ X-ray diffraction analysis}

To experimentally verify the speculated phase transition from the mixed rhombohedral and tetragonal phases to the orthorhombic phase during poling, \textit{in situ} X-ray diffraction experiments were carried out on a bulk sample and the pseudocubic (002)\textsubscript{C}, (220)\textsubscript{C}, and (222)\textsubscript{C} peaks were monitored. The results are displayed in Fig. 3. In the virgin state, these convoluted peaks are not well resolved due to phase coexistence. The peak profiles start to change at 4 kV/cm during initial poling, as seen for both the (002)\textsubscript{C} and (222)\textsubscript{C} reflections. When the poling field reaches 5 kV/cm, peak splitting and intensity ratio change are observed on the (002)\textsubscript{C} and (220)\textsubscript{C} peaks. Additional changes are observed upon further increase in the poling electric field to 6 kV/cm.

A partial profile Rietveld refinement is performed on X-ray diffraction peaks from the virgin state and at 6 kV/cm. In the virgin state, the fractions for the \textit{R3m} and \textit{P4mm} phases are determined to be 75\% and 25\%, respectively, with Rp = 3.48\% and Rwp = 4.81\%. At the poling field of 6 kV/cm, the best fit is found to be a mixture of \textit{Amm2} (66\%) and \textit{P4mm} (34\%), with Rp = 2.96\% and Rwp = 4.32\%. Therefore, the \textit{in situ} X-ray diffraction results support the proposed orthorhombic phase transition, even though a minor amount of the tetragonal phase is found to coexist. It is noted that the single-
domain state is observed in the *in situ* TEM experiments under nominal fields mostly of 2 ~ 3 kV/cm while the *in situ* X-ray diffraction tests recorded the orthorhombic phase between 4 and 6 kV/cm. The discrepancy in the field strength is due to several effects. First, the TEM specimen has a central perforation which intensifies the actual field in the area of interest. The intensification ratio depends on the geometry of the perforation and the dielectric permittivity. For a circular-shaped hole penetrating through the thickness of the 50BZT–50BCT ceramic, the actual field in the TEM observation area is roughly two times the nominal field. Second, the grain size in the 50BZT-50BCT ceramic is greater than ten microns. The response of individual grains to poling fields is likely to have an orientation dependence. Further, *in situ* TEM experiments examine individual grains while *in situ* X-ray tests collect information from many grains simultaneously. And at 6 kV/cm, two-thirds of the grains are in the Amm2 structure (most likely domain wall-free according to *in situ* TEM observations). It should be pointed out that the refinement analysis here is rudimentary and qualitative, at best semi-quantitative. More conclusive results are possible by refining whole diffraction patterns recorded from multiple specimens using high precision X-ray sources.

**A.3 Impact on properties**

Microstructural changes inevitably lead to alterations of properties. Figure 4 shows the temperature-dependent dielectric constant measured on a bulk sample in its virgin state, as well as after poling at 4 and 6 kV/cm, where the single-domain state in the orthorhombic phase is expected to develop. *In situ* TEM experiments reveal that large portions of the grains remain domain wall-free after the poling field is removed from the
single-domain state. Such changes in microstructure are reflected in the dielectric behavior, especially around room temperature. As highlighted in the inset, the slope change on the curve from virgin state is barely seen. After poling, the change in slope at around 35 °C becomes abundantly apparent. This appears to be consistent with the fact that polycrystalline 50BZT–50BCT is a mixture of rhombohedral and tetragonal phases in the virgin state; the transition to the tetragonal phase during heating is hence gradual and hardly detected by the change in dielectric constant. After poling to the single-domain state at 4 or 6 kV/cm, the orthorhombic phase is largely preserved when the field is removed; a sharper transition ensues during the subsequent heating.

It is also interesting to notice that the Curie temperature, $T_C$, changes with the poling field. In its virgin state, $T_C$ is 93 °C. After being poled at 4 kV/cm, it shifts to a higher temperature of 101 °C. $T_C$ drops to 87 °C after poling at 6 kV/cm. A striking shift of 14 °C is observed here. The impact of electrical poling on Curie temperature has been reported previously in various perovskite compounds and is attributed to the poling-induced domain configuration.\textsuperscript{34-36}

In order to directly correlate electromechanical properties from bulk samples with \textit{in situ} TEM and X-ray diffraction structural studies, measurements of the piezoelectric coefficient, $d_{33}$, and the elastic compliance constant, $s_{33}^E$, are carried out on a virgin sample under a series of DC bias fields, which serve as the poling fields. The results are shown in Fig. 5. The piezoelectric coefficient is observed to increase slowly before 2 kV/cm, and then displays a fast increase at 3 ~ 6 kV/cm, followed by a slow increase again at 6 ~ 8 kV/cm. The elastic compliance constant displays a discontinuous jump around 3 kV/cm, then keeps increasing and reaches its maximum value at 6 kV/cm. A
decreasing trend appears at 6 ~ 8 kV/cm. The macroscopic properties $d_{33}$ and $s_{33}^E$ measured in situ with DC bias fields correlate well with the in situ TEM results. At very low poling fields, the initial domain configuration changes slightly and the polycrystalline 50BZT–50BCT is still largely unpoled. Under the poling field of ~3 kV/cm, the unique single-domain state in the orthorhombic phase starts to form. The exceptional softness of the orthorhombic phase contributes to the abrupt increase in $s_{33}^E$. The fast increase in $d_{33}$ appears to suggest a major contribution from this elastic softening. At higher poling fields (> 6 kV/cm), another phase transition occurs and multi-domains in a different phase are formed. Correspondingly, $s_{33}^E$ decreases and the increase in $d_{33}$ slows down.

B. Structure-property evolution during re-poling

B.1 In situ TEM observations

The same grain shown in Fig. 2 is examined again under electric field after the specimen is left in the TEM column for 4 days. The microstructural evolution during the re-poling process is displayed in Fig. 6. Figure 6(a) shows the aged state prior to re-poling; the multi-domain state is still present with almost all domain walls aligned along three $<1\bar{1}0>$ directions. However, by comparing to the domain morphology in Fig. 2(e), we see that many new domains are formed during aging. At the re-poling field of 2.5 kV/cm, the grain is almost completely occupied by a major set of (01\bar{1}) domain walls [Fig. 6(b)]. These lamellar domains entirely disappear at 3.75 kV/cm, where a single-domain state is reached again, shown in Fig. 6(c). Further increasing the re-poling field to 5.5 kV/cm triggers the formation of many lamellar domains with walls along (01\bar{1})
and (1\(\bar{1}\)0) planes [Fig. 6(d)]. Also, some [10\(\bar{1}\)]-aligned domain traces emerge. These [10\(\bar{1}\)]-aligned domain walls become more apparent with the development of a cluster of thin and long lamellar domains in the upper left part of Fig. 6(e). In addition, a new feature in a lenticular shape with long axis roughly along the [\(\bar{1}\)2\(\bar{1}\)] direction is also noticed at 6.25 kV/cm. The complicated domain morphology keeps evolving as the re-poling field increases. At 8 kV/cm, many domain walls disappear with the remaining ones primarily on two sets of {110}, as shown in Fig. 6(f).

It is interesting that the single-domain state reappears during the re-poling process only after the specimen is aged. As noted in Section A.1, the single-domain state cannot be reached by re-poling immediately after the multi-domain configuration is formed during the initial poling at high fields (> 6 kV/cm). Therefore, to some extent, aging seems to resume the original rhombohedral and tetragonal phases in polycrystalline 50BZT–50BCT. This makes it possible for an electric field-induced single-domained orthorhombic phase to appear during re-poling.

B.2 Impact on properties

The \(d_{33}\) and \(s_{33}^{E}\) were also measured during the re-poling process on a bulk sample that was poled with a DC field of 20 kV/cm and then aged for 5 days. As can be seen in Fig. 7, similar trends are observed for \(d_{33}\) and \(s_{33}^{E}\); they both increase first and then decrease. An enhancement of ~20% in \(d_{33}\) to a value of 385 pC/N is achieved at the re-poling field of 4 kV/cm. At the same time, \(s_{33}^{E}\) reaches a peak value of 15.5 pm\(^2\)/N at 4.5 kV/cm, corresponding to a 10% increase from the aged state. It is believed that
elastic softening associated with the formation of the single-domain orthorhombic phase contributes to the piezoelectricity enhancement during the re-poling process.

C. Structure and energy from first-principles calculations

To better understand the relationship between the phases, first-principles calculations are performed on \((Ba_{1.3x}Ca_{3x})(Ti_{1.2x}Zr_{2x})O_3\), where \(x\) ranges from 0.00 to 0.06. The lattice parameters of the four phases for each composition are shown in Fig. 8. The base compound \(BaTiO_3\) \((x = 0.00)\) has lattice parameters that are consistent with the experimental and theoretical values reported in the literature. As \(Ca^{2+}\) and \(Zr^{4+}\) concentrations are increased, on A- and B-sites respectively, the lattice parameters begin to approach a common value and when \(x = 0.05\), which is the 50BZT–50BCT composition studied here, a uniform cubic structure is predicted. Moreover, the relative energies for this unique composition were also calculated and are compared in Fig. 9, using the energy for the relaxed cubic structure as the reference energy. It is evident that all phases in 50BZT-50BCT are equienergetic.

It is not anticipated that these results predicted in small unit cells (5-10 atoms) will mimic the observations from large multi-domain or multi-grain experiments. However, they validate the uniqueness of the 50BZT-50BCT composition. It represents a point where these four phases are energetically and structurally similar and therefore co-exist, which allows for the enhanced electromechanical properties observed in the experiment. In this capacity the first-principles calculations provide validation of the observed structural instability and the ease for the system to undergo phase transitions at low
electric fields in this composition. In particular it explains why room temperature aging can be used to modify the domain structures.

**D. Discussion**

Many factors contribute to a material having a large piezoelectric response, such as the structural instability, domain wall motion, a low-symmetry phase, and elastic softening.\(^3\)\(^4\)\(^5\)\(^6\)\(^7\)\(^8\)\(^9\)\(^38\)\(^39\) We believe the structural instability, as manifested by the easy and close-to-room-temperature phase transition, and the elastic softening associated with the field-induced domain-free orthorhombic phase are the two primary factors in polycrystalline 50BZT–50BCT.

Structural instabilities exist at polymorphic phase boundary (PPB) or morphotropic phase boundary (MPB) compositions,\(^3\)\(^9\)\(^39\) and as a result there is a significant enhancement of the piezoelectricity.\(^8\)\(^9\) Multiple perovskite variants must have comparable free energies at these PPB or MPB compositions, implying that the microstructure will be highly responsive to poling fields. The polycrystalline 50BZT–50BCT in this study displays close-to-room-temperature transitions, two are ferroelectric-ferroelectric transitions\(^5\)\(^6\) and another is the ferroelectric-paraelectric transition at 93 °C (Fig. 4). Consequently the microstructure of the ceramic responds to the poling field by domain switching starting at a very low field, then the disappearance of all domain walls and a phase transition to the orthorhombic phase, then reappearance of multiple domains and another phase transition. Evidence for the structural instabilities in 50BZT-50BCT is further provided by the first-principles calculations where the four phases are found
energetically and structurally similar and hence can easily transform to/from each other (Figs. 8 and 9).

Generally speaking, low polarization anisotropy and lattice softening go hand in hand, both contributing to the high piezoelectric response.\textsuperscript{3} Theoretical studies have shown that elastic softening can significantly enhance the piezoelectric response in perovskite-type oxides and also wurtzite structured alloys.\textsuperscript{40,41} In its virgin state, polycrystalline 50BZT–50BCT has an elastic compliance constant ($s_{33}^E$) with a peak around room temperature, which corresponds to the anomalously high piezoelectric property.\textsuperscript{16} In the present study, measurements of $s_{33}^E$ under DC bias fields, which simulate the initial poling and the re-poling process, elastic softening is also observed, as shown in Figs. 5 and 7. Correspondingly, the microstructure adopts the single-domain state with an orthorhombic structure. The correlation of enhanced piezoelectricity with high elastic compliance constant has been widely observed in perovskite-structured piezoelectrics.\textsuperscript{16,38,40,42-44} Elastic softening is believed to effectively relax the lattice of the crystal and facilitate the structural instability when external stimuli (temperature, stress, and electric field) are applied. As a consequence, optimized piezoelectric properties are always accompanied with the peak value of elastic compliance constant (or the minimum value of elastic modulus). This is the case here for 50BZT-50BCT; this is the case for lead-based\textsuperscript{38,43,44} and lead-free solid solutions,\textsuperscript{16,42} and this is the case even for the simple compound BaTiO$_3$.\textsuperscript{1,45}
3.4.4 Conclusion

In conclusion, the development of piezoelectricity in polycrystalline 50BZT–50BCT due to initial poling and re-poling is investigated and the microstructural origins are identified. First-principles calculations indicate that this composition is unique as its rhombohedral, orthorhombic, tetragonal, and cubic variant phases are almost indistinguishable in terms of lattice parameters and energetics. As a consequence, this ceramic is extremely responsive to the poling fields. In addition to extensive domain polarization alignment activities, a unique single-domain state is observed with poling fields in the range of 3 ~ 6 kV/cm. The single-domain state is believed to be in the orthorhombic phase which has an exceptionally low elastic modulus. The structural instability and the elastic softening during initial poling and re-poling are suggested to be the primary contributing factors to the excellent piezoelectricity in this newly developed BaTiO$_3$-based lead-free ceramic.

Acknowledgements

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FIGURES

FIG. 1 In situ TEM observations of a grain along its [101] zone-axis in a polycrystalline 50BZT-50BCT specimen under electric fields during initial poling. Bright-field micrographs at (a) virgin state, (b) 2 kV/cm, (c) 2.5 kV/cm, (d) 4.25 kV/cm, (e) 5.75 kV/cm, (f) 8 kV/cm, (g) 10 kV/cm, and (h) 18 kV/cm are displayed. The direction of the poling field is indicated by the bright arrow in (b). The selected area diffraction pattern recorded at the virgin state is shown in (i). No apparent changes in the electron diffraction pattern are noticed during the initial poling process.
FIG. 2 In situ TEM observations of a grain along its [111] zone-axis in a polycrystalline 50BZT–50BCT specimen under electric fields during initial poling. Bright-field micrographs at (a) virgin state, (b) 1 kV/cm, (c) 3.2 kV/cm, (d) 4.5 kV/cm, and (e) 0 kV/cm (the poling field is removed) are displayed. The direction of the poling field is indicated by the bright arrow in (d). The selected area diffraction pattern recorded at the virgin state is shown in (f). Again, no apparent changes in the electron diffraction pattern are noticed during the initial poling process.
FIG. 3 *In situ* X-ray diffraction analysis of a 50BZT–50BCT bulk sample during initial poling. The pseudocubic (002)$_C$, (220)$_C$, and (222)$_C$ reflections are recorded at the virgin state, as well as when poling fields of 4, 5, and 6 kV/cm are applied.

FIG. 4 Temperature dependence of the dielectric constant measured at 10 kHz during heating on a bulk sample of 50BZT–50BCT in its virgin state as well as after poling. The measurements were made with no DC bias.
FIG. 5 *In situ* measurements of the piezoelectric coefficient, $d_{33}$, and the elastic compliance constant, $s_{33}^E$, as a function of DC bias field on a bulk sample of 50BZT–50BCT. Error bars are less than the symbol size and are not shown. The DC bias field serves as the poling field to develop piezoelectricity.
FIG. 6 *In situ* TEM observations on the same grain shown in Fig. 2 after the specimen is aged in the TEM column for 4 days. Bright-field micrographs at (a) 0 kV/cm, (b) 2.5 kV/cm, (c) 3.75 kV/cm, (d) 5.5 kV/cm, (e) 6.25 kV/cm, and (f) 8 kV/cm are displayed to reveal the microstructural change during the re-poling process. The direction of the re-poling field is indicated by the bright arrow in (b).
FIG. 7 *In situ* measurements of the piezoelectric coefficient, $d_{33}$, and elastic compliance constant, $s_{33}^{E}$, as a function of DC bias field after the specimen is aged at room temperature for 5 days. Error bars are less than the symbol size and are not shown. The DC bias field serves as the re-poling field.

FIG. 8 Lattice parameters of the cubic, tetragonal, orthorhombic, and rhombohedral phases in (Ba$_{1-3x}$Ca$_{3x}$)(Ti$_{1-2x}$Zr$_{2x}$)O$_3$ from first-principles calculations. The composition $x = 0.05$ corresponds to the experimentally investigated 50BZT–50BCT.
FIG. 9 Relative energies for the four phases of 50BZT–50BCT. The energy of the cubic phase is arbitrarily defined as the energy zero.

References


CHAPTER 4. Microscopic Insight for the Electric Field-induced Isotropization: “Response-Stimulus Symmetry Quandary: Case of Polarization-Electric Field Dichotomy”


Hanzheng Guo, Xiaoming Liu, Wei Hong, and Xiaoli Tan

Abstract

According to Curie’s principle, a crystal under an external force will exhibit only those symmetry elements that are common to the crystal and the force. In this article, [(Bi$_{1/2}$Na$_{1/2}$)$_{0.95}$Ba$_{0.05}$]$_{0.98}$La$_{0.02}$TiO$_3$ ceramic samples are analyzed using in situ transmission electron microscopy, electrical property measurements, and X-ray diffraction to demonstrate a direct violation of Curie’s principle. The polycrystalline ceramic is exposed to a DC electric field (with symmetry $\infty m$), which induces a phase transition from a poled ferroelectric phase ($\infty m$) to a relaxor phase ($\infty\infty m$). We attribute this unusual phase transition to the extremely slow kinetics and treat this composition as an ideal model system for the investigation of the transient process in a first-order phase transition, for which ultrafast characterization tools are not required.

4.1 Introduction

Materials respond to physical forces (mechanical stress, electric field, magnetic field, temperature, etc.) by adjusting their symmetries, and given the right conditions, phase transitions will occur\(^{1-7}\). Many key engineering applications are based on these phase transitions, and the study of the transient state during the transition can provide
invaluable information for condensed matter physics. However, these studies require advanced, ultrafast characterization tools\textsuperscript{8,9}. According to Curie, the change of symmetry in materials in response to external forces is dictated by the symmetry of the free-state material and the symmetry of the external force\textsuperscript{10,11}.

A polycrystalline material with randomly oriented grains exhibits spherical symmetry ($\infty\infty m$), while an electric field can be represented by a vector with polar cylindrical symmetry ($\infty m$). A polycrystalline ferroelectric ceramic responds to an applied electric field during poling by adopting an $\infty m$ symmetry, with the $\infty$-fold rotation axis parallel to the field direction\textsuperscript{10}. The macroscopic symmetry change is a result of the alignment of the ferroelectric domain polarization to the applied field. This domain switching process yields remanence and imparts piezoelectricity to the ceramic\textsuperscript{12,13}. Field reversal will nucleate and grow new domains with aligned polar vectors\textsuperscript{14,15}, preserving the $\infty m$ symmetry.

Electric fields always trigger a change from $\infty\infty m$ to $\infty m$ symmetry through a first-order phase transition in polycrystalline relaxor ferroelectric ceramics\textsuperscript{16-18}. Relaxor ferroelectrics are quite unique; they exhibit polar nanoregions with fluctuating polarizations and a lack of thermally induced structural transitions\textsuperscript{19-27}. Since there is a large number of polar nanodomains with disordered dipole moments in each individual grain, the $\infty\infty m$ symmetry of a relaxor polycrystalline ceramic is even preserved down to the individual grain level. Coulomb forces exerted by electric fields align the disordered dipoles and change the symmetry to $\infty m$ both at the grain level and at the whole specimen level. Given the right combination of composition, temperature and electric field, the
change in symmetry can lead to a poled ferroelectric polycrystalline ceramic\textsuperscript{16-20}. Following Curie’s principle and Coulomb’s law, electric fields would therefore favor only the poled ferroelectric phase with an $\infty m$ macroscopic symmetry.

Here we demonstrate, for the first time, that electric fields can induce a transition from a poled ferroelectric ceramic to a relaxor phase with disordered dipoles, \textit{i.e.}, they can trigger an apparently unlikely $\infty m$ to $\infty\infty m$ phase transition. We reveal this unusual phase transition in a lead-free relaxor composition of \((\text{Bi}_{1/2}\text{Na}_{1/2})_{0.95}\text{Ba}_{0.05}\text{La}_{0.02}\text{TiO}_3\) (BNT-5BT-2La)\textsuperscript{28} in which a ferroelectric phase can be readily formed during electric poling. The induced ferroelectric phase remains metastable after the applied field is removed. When an electric field with a reversed polarity is applied to this ferroelectric phase, the relaxor phase with nanodomains and disordered dipole moments is resumed. Our investigation suggests that the kinetics of the ferroelectric-to-relaxor phase transition is very slow and the transition competes with the ferroelectric domain polarization reversal process under fields with reversed polarity. This discovery provides critical information on the origin of excellent functional properties in perovskite oxides, such as piezoelectric\textsuperscript{29} and electrocaloric\textsuperscript{30} effects. It also identifies a model system for the study of first-order phase transition that does not require ultrafast characterization tools to reveal the transient states.

4.2 Experimental procedure

\textbf{Ceramic preparation:} The solid state reaction method was used to prepare the \([(\text{Bi}_{1/2}\text{Na}_{1/2})_{0.95}\text{Ba}_{0.05}]_{0.98}\text{La}_{0.02}\text{TiO}_3\) (BNT-5BT-2La) polycrystalline ceramic, using Bi\textsubscript{2}O\textsubscript{3} ($\geq 99.9\%$), TiO\textsubscript{2} ($\geq 99.99\%$), La\textsubscript{2}O\textsubscript{3} ($\geq 99.999\%$), Na\textsubscript{2}CO\textsubscript{3} ($\geq 99.9\%$), and BaCO\textsubscript{3} ($\geq$
99.997%) as starting materials. Na$_2$CO$_3$ and La$_2$O$_3$ powders were baked before batching. The raw powders were mixed in stoichiometric amounts and vibratory milled in ethanol with zirconia mill media for 6 hours. The mixture was dried and then calcined at 850 °C for 3 hours. With polyvinyl alcohol as binder, the calcined powder was uniaxially pressed into circular disks under 300 MPa. Buried in a protective powder of the same composition, the disks were sintered at 1150 °C for 3 hours in alumina crucibles at a heating/cooling rate of 5 °C min$^{-1}$.

**Electrical property measurements:** For dielectric, piezoelectric, and ferroelectric characterizations, silver films were sputtered to serve as electrodes. The polarization ($P$) vs. electric field ($E$) hysteresis loops were measured using a standardized ferroelectric test system (RT-66A, Radiant Technologies) at 4 Hz and room temperature. The polarization current density ($J$) vs. electric field ($E$) curve was determined by taking the derivative of polarization with respect to time, i.e., $dP(t)/dt$. The longitudinal strain ($\chi_{33}$) developed under electric field in the form of a triangular wave of 0.05 Hz was monitored with an MTI-2000 Fotonic Sensor (MTI Instruments Inc., Albany, NY). Dielectric properties were measured using an LCR meter (HP-4284A, Hewlett-Packard) in a tube furnace at a heating rate of 4 °C min$^{-1}$. For piezoelectricity measurements, the ceramic specimens were first poled at 60 kV cm$^{-1}$ for 20 min at room temperature (25 °C). Then, the poled ceramic was subject to a DC field of 12 kV cm$^{-1}$ with a reversed polarity for 1, 10, 30 and 60 min, respectively. At each time interval, the piezoelectric coefficient $d_{33}$ was measured with a piezo-$d_{33}$ meter (ZJ-4B, Institute of Acoustics, Chinese Academy of Sciences).
**Structural characterization:** For X-ray diffraction measurements, the same bulk ceramic specimen as for $d_{33}$ measurements was used. At each time interval after $d_{33}$ was measured, the silver film electrodes were removed using nitric acid dilute solution. The evolution of the ½(311) superlattice peak was immediately recorded on a Siemens D500 diffractometer using Cu-Kα radiation at a 0.02° step size and 150 s dwelling time per step. The integrated peak intensities were calculated with the baseline at $I = [I(37.80°) + I(38.65°)]/2$, where $I$ is the X-ray count. For electric field *in situ* TEM experiments, disk specimens (3 mm in diameter) were prepared from as-sintered pellets through standard procedures, including grinding, cutting, dimpling, and ion milling. The dimpled disks were annealed at 400 °C for 2 h to minimize the residual stresses before Ar-ion milling to the point of electron transparency. *In situ* TEM experiments were carried out on a specimen that was crack-free at the edge of the central perforation on a Phillips CM30 microscope operated at 200 kV. Detailed experimental setup can be found in our previous reports$^{31-34}$.

4.3 Results and discussion

**Electric field-induced relaxor to ferroelectric transition.** The electric poling-induced transition from relaxor to ferroelectric in a polycrystalline BNT-5BT-2La ceramic is illustrated in Fig. 1. The virgin state ceramic is a non-ergodic relaxor at room temperature$^{28}$, as indicated by the strong frequency dispersion in the dielectric behavior and the absence of a depolarization temperature $T_d$ (Fig. 1a). Figure 1b shows a representative grain along its [112] zone axis; here, transmission electron microscopy
TEM revealed nanometer-sized domains. Electron diffraction analysis (Fig. 1c) showed that $\frac{1}{2}\{ooo\}$- and $\frac{1}{2}\{oeo\}$-type ($o$ and $e$ stand for odd and even Miller indices, respectively) superlattice electron diffraction spots$^{18,35,36}$ were present, indicating coexisting $R3c$ and $P4bm$ phases in the form of nanodomains$^{28}$. Unlike the dynamically fluctuating polar nanoregions in ergodic relaxors$^{19,20}$, the static polar nanodomains shown in Fig. 1b can be electrically poled and aligned$^{37}$. Figure 1d shows that after poling at 60 kV cm$^{-1}$, a well-defined $T_d$ was observed in the dielectric curves. Correspondingly, the development of long lamellar ferroelectric domains with long-range polar order was observed (Fig. 1e). Crystallographic analysis indicated that the domain walls were parallel to the $\{010\}$ planes. This domain morphology transformation was accompanied by a symmetry change from $P4bm$ to $R3c$, as demonstrated by the disappearance of the $\frac{1}{2}\{oeo\}$ superlattice spots and the significantly strengthened $\frac{1}{2}\{ooo\}$ spots (Fig. 1f). Both the domain morphology and the electron diffraction pattern of the poled grain (Figs. 1e and 1f) were metastable upon removal of the applied field. The evolution from nanodomains to lamellar domains demonstrated the relaxor-to-ferroelectric phase transition in the BNT-5BT-2La ceramic; for a polycrystalline bulk specimen, it represents a transition from $\infty\infty m$ to $\infty m$ symmetry.

**Electric field-induced ferroelectric to relaxor transition.** The development and evolution of macroscopic polarization, $P$, and strain, $\varepsilon_{33}$, under the very first cycle of a bipolar electric field on a virgin BNT-5BT-2La bulk ceramic is displayed in Fig. 2a. Correspondingly, the change of domain morphology and crystal structure under electric fields is monitored *in situ* in a $[112]$-aligned grain of a TEM specimen. At zero field in
the virgin state (corresponding to \( Z_0 \) on the \( P \) and \( x_{33} \) curves), nanodomains were observed (Fig. 2b), as described earlier. Electron diffraction analysis confirmed the nature of the mixed \( R3c \) and \( P4bm \) phases (Fig. 2c). An increase in electric field to the point of \( Z_1 \) induced apparent macroscopic polarization but a negligible strain (Fig. 2a). Correspondingly, the applied field prompted the nucleation of lamellar domains along the \{010\} planes from the interior of the grain (Fig. 2d). Further increase in field to \( Z_2 \) triggered the abrupt development of large polarization and strain (Fig. 2a), which indicates that extensive relaxor-to-ferroelectric phase transition took place in the first quarter cycle of the applied field. On the microscopic scale, the nanodomains in the grain were consumed by long lamellar domains with walls along the \{010\} and \{110\} planes as well as by some large domains (Fig. 2e). The diffraction pattern shown in Fig. 2f indicates a single \( R3c \) phase, suggesting a phase transition from \( P4bm \) to \( R3c \). In the second quarter cycle, when the field was removed (\( Z_3 \)), large remanent polarization and remanent strain were recorded. At the same time, \( R3c \) ferroelectric domains were observed to persist after removal of the electric field (Fig. 2g). These results are consistent with those shown in Fig. 1, indicating that the electric field favors the long-range polar order by transforming nanodomains into micron-sized domains. The poled polycrystalline ceramic displayed \( \infty m \) symmetry, in compliance with Curie’s principle.

The well-established ferroelectrics \( \text{BaTiO}_3 \) and \( \text{PbTiO}_3 \) exhibit nucleation and growth of new domains with opposite polar vectors upon field reversal\(^{14,15}\). When they are in polycrystalline form, the \( \infty m \) macroscopic symmetry is presumably preserved during polarization reversal. However, this is not the case for the polycrystalline \( \text{BNT-5BT-2La} \) ceramic, where an unusual ferroelectric-to-relaxor phase transition occurs.
With an increase in the magnitude of the applied field with reversed polarity in the third quarter cycle (point $Z_5$), the strain reached its minimum and the macroscopic polarization vanished (Fig. 2a). *In situ* TEM observation revealed a surprising recovery of nanodomains with short-range polar order (Fig. 2h) and a diffraction pattern almost identical to that of the virgin state (Fig. 2i). The weak $\frac{1}{2}\{ooe\}$ and $\frac{1}{2}\{ooo\}$ superlattice diffraction spots confirmed a return to the coexisting of $P4bm$ and $R3c$ phases in the form of nanodomains. In a polycrystalline specimen, such a symmetry change from $\infty m$ to $\infty\infty m$ under an electric field is a direct violation of Curie’s principle.

The unexpected disruption of the long-range polar order under the influence of an electric field in BNT-5BT-2La was reproducibly observed, as shown by another grain in the same TEM specimen (Fig. 3). The nanodomains in the virgin state $Z_0$ (Fig. 3a) transformed into large lamellar domains at $Z_2$ (Fig. 3c), with the major set of domain walls along the $\{010\}$ planes. Although almost half the grain was under bend contours, the electron diffraction patterns (Figs. 3b and 3d) across the entire grain clearly suggest a phase transition from $P4bm$ to $R3c$. The $R3c$ lamellar domains remained mostly unchanged after the electric field was released ($Z_3$). When the applied electric field reversed its polarity and reached $Z_4$, most lamellar domains were disrupted into nanodomains and only a few domains with $\{010\}$ walls remained (Fig. 3e). Correlated to this morphology change was the reappearance of $\frac{1}{2}\{ooe\}$-type superlattice diffraction spots and the weakening of the $\frac{1}{2}\{ooo\}$ spots (Fig. 3f). With further increase in electric field in the reverse direction (to $Z_5$), the grain was dominated by nanodomains (Fig. 3g). The comparable intensities of the $\frac{1}{2}\{ooe\}$ and $\frac{1}{2}\{ooo\}$ superlattice spots in Fig. 3h suggested the coexistence of $P4bm$ and $R3c$ phases in similar fractions. Again, the results
underpin the conclusion that the electric field breaks the long-range polar order and leads to a phase transition from $\infty\text{m}$ to $\infty\infty\text{m}$.

Further increase in electric field from $Z_5$ to $Z_8$ reversed the macroscopic polarization and resumed the longitudinal strain (Fig. 2a). Correspondingly, the nanodomains coalesced and gradually grew into lamellar domains again (Figs. 3i-3k). The strengthened $\frac{1}{2}\{000\}$ superlattice spots and the absence of $\frac{1}{2}\{00e\}$ spots in the electron diffraction pattern (Fig. 3l) confirmed the reoccurrence of a $P4bm$-to-$R3c$ phase transition. In summary, these in situ TEM observations unambiguously demonstrated the complex phase transitions in the first and the third quarter cycle of an applied electric field. The domain polarization reversal in the investigated polycrystalline ceramic in the third quarter cycle took place through two transient phase transitions: from $\infty\text{m}$ to $\infty\infty\text{m}$ and then from $\infty\infty\text{m}$ to $\infty\text{m}$.

**Macroscopic verifications.** These phase transitions leave marks on the polarization vs. electric field hysteresis loops, which are easier identified in the curve depicting current density, $J$, vs. the electric field, $E$ (Fig. 4a). The data represent measurements of the same bulk specimen for the second full cycle of electric field application. Other than normal ferroelectrics, which show only one current peak in the first and the third quarter cycle of an applied electric field$^{38}$, BNT-5BT-2La exhibited two anomalies in each of the quarter cycles. Apparently the polarization current density peak $J_1$ corresponded to the ferroelectric-to-relaxor transition with the disruption of ferroelectric domains into nanodomains, while the peak $J_2$ indicated the relaxor-to-ferroelectric transition with the coalescence and growth of nanodomains into large lamellar domains. The same
processes were repeated at the peaks $J_3$ and $J_4$. This unique feature seems common in BNT-BT-based, non-ergodic, lead-free relaxors$^{39,40}$. Here, our \textit{in situ} TEM investigation uncovered the microstructural origin for this double peak behavior.

To further verify that the TEM observations were exposing the real processes, a bulk specimen was used to carried out \textit{ex situ} X-ray diffraction experiments to reveal the evolution of the $\frac{1}{2}(311)$ superlattice diffraction peak, and also to measure the piezoelectric coefficient $d_{33}$. In the virgin state (Fig. 4b), the $\frac{1}{2}(311)$ peak was too weak to be detected by a conventional laboratory X-ray diffractometer. However, after poling at 60 kV cm$^{-1}$ for 20 min (marked “poled” in Fig. 4b), the $\frac{1}{2}(311)$ peak appeared, supporting the TEM results of a single $R3c$ ferroelectric phase. At the same time, piezoelectricity developed with a $d_{33}$ value of 145 pC N$^{-1}$. This indicated that the polycrystalline specimen experienced a symmetry change from $\infty m$ to $\infty m$.

Subsequently, the ceramic disk was subjected to a DC field of 12 kV cm$^{-1}$ with a polarity opposite to the original poling field (corresponding to the condition “R” in Fig. 4a). The $\frac{1}{2}(311)$ superlattice peak became weaker as time elapsed, and was nearly flattened out after 60 minutes at -12 kV cm$^{-1}$. Correspondingly, the piezoelectric coefficient $d_{33}$ decreased with the reduction of the superlattice peak intensity and reached an almost-zero value (Fig. 4c). During the time period under a DC field with reversed polarity, the original relaxor phase was progressively resumed and a transition from $\infty m$ to $\infty m$ took place in the polycrystalline specimen. Therefore, the X-ray measurements on the bulk specimen not only verified the \textit{in situ} TEM observations, but also revealed the very slow kinetics of the ferroelectric-to-relaxor phase transition.
The slow relaxation under a DC field of -12 kV cm\(^{-1}\) observed in the non-ergodic relaxor BNT-5BT-2La is analogous to the piezoelectric response decay in Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-based ergodic relaxors after poling\(^{26,27}\). Both cases are attributed to flipping of polar nanoregions aligned by the applied field to the initial disordered state. The stimulus in the ergodic relaxor case was solely thermal activation, which exhibits isotropic symmetry; however, for the non-ergodic relaxor presented here, the stimulus was primarily an electric field, which exhibits polar symmetry. The decrease in \(d_{33}\) and the weakening of the integrated peak intensity can be fitted well by the Kohlrausch-Williams-Watt (KWW)-type relation\(^{26,27}\) (solid lines in Fig. 4c). The fitting curve for \(d_{33}\) is

\[
d_{33} = d_0 + d_1 \exp \left[ -\left( \frac{t}{\tau} \right)^\beta \right]
\]

with \(d_0 = -77\) pC N\(^{-1}\), \(d_1 = 222\) pC N\(^{-1}\), \(\tau = 3517\) s, and \(\beta = 0.59\). The parameter \(\tau\) is the characteristic time that describes the speed of relaxation. For Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-based ergodic relaxors, a fast relaxation with a short \(\tau \sim 20\) s was observed\(^{26}\). In the present case, \(\tau\) characterizes the time for the ferroelectric-to-relaxor phase transition, which is expected to be a function of the magnitude of the reverse electric field.

**Discussion**

Generally speaking, an electric field with a polar cylindrical symmetry of \(\propto m\) as a driving force for phase transition is known to favor large ferroelectric domains with long-range polar order over nanodomains with short-range order, as reported previously for BNT-BT\(^{18}\) and Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-based ceramics\(^{16}\). The electric field-assisted
destruction of long-range polar order observed in the present work is highly unusual and seems to be in disagreement with the general physics rules. Here, we rationalize our observations using Landau-Ginsburg-Devonshire’s phenomenological theory\textsuperscript{1}. The free-energy landscape of the polycrystalline material is sketched in Fig. 5a on the plane of polarization (while the actual space of polarization is 3D). The experimental observation suggested that the energy has local minima in both the relaxor and the ferroelectric states. Reversing the polarization in a polar ferroelectric state (\textit{e.g.}, from A to B in Fig. 5a) can take at least two different routes. The material may undergo a 180° domain reversal while remaining in the ferroelectric phase (K\textsubscript{1}), or undergo two consecutive phase transitions through the relaxor phase (K\textsubscript{2} and K\textsubscript{3}). For a polycrystalline material, the two processes take place simultaneously, but have distinct rate dependencies. It is believed that the domain switching kinetics is fast, while the phase transition kinetics is relatively slow and dependent on the loading rate.\textsuperscript{41} As a result, the intermediate relaxor phase during polarization reversal can only be seen under relatively slow or quasi-static loading conditions. The following phenomenological model was developed to better illustrate the competition between the two processes.

The free energy density \( W_{\text{FE}} \) of the ferroelectric phase near the spontaneous polarization \( P_s \) is assumed to be described in the form \( \frac{1}{2(\varepsilon - \varepsilon_0)}(P - P_s)^2 \), with \( \varepsilon \) and \( \varepsilon_0 \) the permittivity of the ferroelectric phase and vacuum, respectively. For simplicity reasons, the analysis is limited to 1D, and the spontaneous polarization is described by either a positive or a negative value. Denoting the fraction of the positively polarized
volume with respect to the entire ferroelectric phase as $f_+$, the average free-energy density of the ferroelectric phase with both polarizations reads

$$W_{FE} = \frac{1}{2(E - E_0)} \left[ f_+ (P - P_s)^2 + (1 - f_+) (P + P_s)^2 \right].$$  \hspace{1cm} (2)

To capture the resistance to domain reversal by various sources in the polycrystalline material (e.g., depolarization energy and pinning of domain walls), a random energy threshold following the normal distribution is introduced between the opposite polarized states. Consequently, the polarization fraction $f_+$ is determined by the applied electric field $E$, $f_+ = \frac{1}{2} \left[ 1 + \text{erf} \left( \frac{E + E_0}{\sqrt{2} \Delta E} \right) \right]$, with $E_c$ the mean critical field and its changing sign dependent on the direction of switching. The standard deviation $\Delta E$ characterizes the width of the transition or the energy threshold. With representative values $E_c = 16$ kV cm$^{-1}$ and $\Delta E = 5$ kV cm$^{-1}$, the resulting $P - E$ hysteresis of a pure ferroelectric phase is plotted by the red curve in Fig. 5b. It is similar to the polarization reversal in normal polycrystalline ferroelectrics.

The free-energy density of the relaxor phase, on the other hand, is described in polynomial form

$$W_{RE} = \frac{b_1}{2} P^2 + \frac{b_2}{4} P^4 + \frac{b_3}{6} P^6.$$  \hspace{1cm} (3)

Representative values for the coefficients are selected by comparing with experimental data (section Z0-Z1 in Fig. 2a): $b_1 = 10$ kV cm $\mu$C$^{-1}$, $b_2 = -0.1$ kV cm$^3$ $\mu$C$^{-2}$, and $b_3 = 1 \times 10^{-3}$ kV cm$^5$ $\mu$C$^{-3}$. The resulting hysteresis for a pure relaxor phase is represented by the blue curve in Fig. 5b.
Assuming the rule of mixture, the total free energy density of a material with coexisting ferroelectric and relaxor phases is described by

\[ W(f_{RE}, P) = f_{RE} W_{RE}(P) + (1 - f_{RE}) W_{FE}(P), \quad (4) \]

with \( f_{RE} \) the volume fraction of the relaxor phase. The change in \( f_{RE} \) is caused by the ferroelectric \( \leftrightarrow \) relaxor phase transition. It is thus assumed that the polarization is always in equilibrium with the applied electric field \( E \) through \( E = \partial W / \partial P \). In order to demonstrate the competing kinetics, a simple growth model is adopted by assuming the relation between the rate of phase transition and the dimensionless driving force \( \Delta W = \Omega (W_{FE} - W_{RE}) / kT \):

\[ \frac{df_{RE}}{dt} = \nu f_{RE} (1 - f_{RE})^2 \Delta W, \quad (5) \]

where \( \Omega \) is the volume of a unit cell, \( kT \) the temperature in the unit of energy, and \( \nu \) a rate factor dependent on various kinetic parameters such as nucleus density and interface mobility. The factor \( f_{RE} \) is introduced to account for the effect of finite size of the relaxor phase during growth, and \( (1 - f_{RE})^2 \) represents the impingement effect at high relaxor concentrations. The evolution of the relaxor factor and the competition between phase transition and polarization reversal can be calculated by integrating Eq. (5). At a slow enough loading rate, e.g., at a dimensionless rate of \( \sim 0.03 \nu E_c \Omega P_s^2 / kT \), shown by the black curve in Fig. 5b, the averaged \( P - E \) hysteresis of the two-phase mixture agrees qualitatively with the experimental observation displayed in Fig. 4a. While closer-to-experiments transient behavior predictions may be obtained by selecting more
complicated models for nucleation and growth, such approach was not of primary interest in the present work.

4.4 Conclusion

In summary, an electric field-induced disruption of long range polar order in a lead-free perovskite oxide was directly observed using in situ TEM. Dielectric, ferroelectric, electromechanical (strain and piezoelectric coefficient), as well as X-ray diffraction measurements on bulk polycrystalline specimens supported the TEM results and further suggested that this highly unusual phenomenon represents a ferroelectric-to-relaxor phase transition. Even though the experimental observations seem to violate Curie’s Principle and Coulomb’s Law, it can be rationalized by a phenomenological model that takes the large difference in kinetics between the phase transition and the polarization reversal processes into account.

Acknowledgements

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Figures

**Figure 1** | The relaxor-to-ferroelectric transition during electric poling in BNT-5BT-2La demonstrated by dielectric behavior and *in situ* TEM observations. **a**, Temperature dependent dielectric constant and loss tangent for a virgin bulk specimen.  **b**, Bright field micrograph of a grain along its [112] zone axis, and **c** the corresponding electron diffraction pattern prior to poling.  **d**, Temperature dependent dielectric properties of the same bulk specimen as in **a** after poling.  **e**, Bright field micrograph and **f**, electron diffraction pattern of the same grain as in **b** after poling. The apparent depolarization temperature $T_d$ is marked in **d**. The direction of the poling field in the *in situ* TEM experiment is indicated by the bright arrow in **e**. The $\frac{1}{2}\{ooo\}$ and $\frac{1}{2}\{ooe\}$ superlattice diffraction spots are highlighted by a bright circle and a bright arrow, respectively, in **c**.
Figure 2 | Development and breaking of long range polar order in BNT-5BT-2La during application of the very first cycle of bipolar electric fields. **a**, Polarization, \( P \), and longitudinal strain, \( x_{33} \), developed under applied field of a bulk specimen. The point pairs on the polarization and strain curves marked as \( Z_0 \) through \( Z_8 \) indicate the fields where corresponding *in situ* TEM observations are recorded. **b** through **i**, The corresponding *in situ* TEM results on a [112]-aligned grain. The positive direction of applied fields in the TEM experiment is indicated by the bright arrow in **e**. The \( \frac{1}{2}\{000\} \) and \( \frac{1}{2}\{00\} \) superlattice diffraction spots are highlighted by a bright circle and a bright arrow, respectively, in **c**.
Figure 3 | *In situ* TEM observations on another [112]-aligned grain in the same TEM specimen as in Fig. 2. The positive direction of the applied field is indicated by the bright arrow in c and \( Z_0, Z_2, Z_4, Z_5, Z_6, Z_7, Z_8 \) mark the corresponding fields indicated in Fig. 2a. The \( \frac{1}{2}\{ooo\} \) and \( \frac{1}{2}\{ooe\} \) superlattice diffraction spots are highlighted by a bright circle and a bright arrow, respectively, in b.
Figure 4 | The breaking of long range polar order by electric field demonstrated in a bulk BNT-5BT-2La ceramic disk.  

a, Polarization, P, vs. electric field, E, hysteresis loop during the second cycle of the bipolar electric field. The corresponding polarization current density, J, curve reveals two anomalies in each of the first and the third quarter cycle.  
b, Evolution of the ½(311) superlattice diffraction peak monitored by X-ray diffraction on a disk specimen first poled at 60 kV cm$^{-1}$ for 20 min (marked as “poled”), and then subjected to a DC field of -12 kV cm$^{-1}$ (corresponding to the condition marked as “R” in a) for various times.  
c, Experimentally measured $d_{33}$ after each time period and the integrated peak intensity of ½(311) are shown as discrete points, while the solid lines are fitting curves derived using the Kohlrausch-Williams-Watt (KWW) model$^{26,27}$. The fitting equation for peak intensity is $I = -185 + 479 \exp\left(-\frac{t}{4327}\right)^{0.49}$ while that for $d_{33}$ is presented in the text. Error bars for $d_{33}$ and I are of the order of the size of symbols and not shown.
Figure 5 | A phenomenological model to rationalize the unusual electric field-induced ferroelectric-to-relaxor transition in BNT-5BT-2La. **a**, Schematic plot of the free energy on the plane of two polarization components. The polycrystalline material exhibits isotropy after homogenization, and the energy barriers for domain switching is thus not shown. Two processes, $K_1$ and $K_2 + K_3$ (shown as dashed curves), are involved under reversed electric fields from A to B. **b**, The calculated hysteresis of the material with mixed phases (black curve), plotted together with the constituent ferroelectric and relaxor phases (red and blue curves).
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CHAPTER 5. *In situ* TEM Study of the Microstructural Mechanisms for Electric Fatigue in Polycrystalline Ferroelectrics

5.1 *In situ* TEM study on the microstructural evolution during electric fatigue in 0.7Pb(Mg₁/₃Nb₂/₃)O₃-0.3PbTiO₃ ceramic


Hanzheng Guo, Shujun Zhang, and Xiaoli Tan

Abstract

In this work, we report an experimental technique with nanometer resolution to reveal the microstructural mechanism for electric fatigue in ferroelectrics. The electric field *in situ* transmission electron microscopy (TEM) was employed to directly visualize the domain evolution during the fatigue process in a 0.7Pb(Mg₁/₃Nb₂/₃)O₃-0.3PbTiO₃ ceramic. The structure-property relationship was well demonstrated by combing the microscopic observations with corresponding dielectric, piezoelectric, and ferroelectric properties measured on bulk specimens. It was found that the domain switching capability was substantially suppressed after $10^3$ cycles of bipolar fields, leading to an immobilized domain configuration thereafter. Correspondingly, a pronounced degradation of the functionality of the ceramic was manifested, accompanying with a coercive field bumping and polarization current density peak broadening. The reduction of the polarization, dielectric constant, and piezoelectric coefficient were found to follow a power-law relation. Domain wall pinning and seed inhibition mechanisms were found to be responsible for the observed fatigue behaviors.
5.1.1 Introduction

Electric fatigue has been an ongoing research topic in ferroelectric communities for several decades due to the technological importance and extensive application of ferroelectric-based devices such as non-volatile memories, field-effect transistors, ferroelectric tunneling junctions, transducers and actuators.1-8 A fingerprint of electric fatigue in ferroelectric oxides is the degradation of their functionality (e.g. switchable polarization) during repetitive polarization switching.9,10 It has severely hindered the long-term operation and reliability of ferroelectric materials. Throughout the past half-century, a large body of experimental and theoretical studies has been conducted to investigate the origin of electric fatigue.1,9,10 Several phenomenological scenarios and microscopic mechanisms have been proposed such as electrode degradation,9 near-electrode passive layer formation,11 nucleation inhibition,12 domain wall pinning,13 and local phase decomposition.14 However, a consensus has not been reached due to the complex nature of the fatigue process.1,9

As is well known, the polarization state and polarization switching in ferroelectric crystals are intrinsically linked to ferroelectric domain arrangements and their transformations. Essentially, ferroelectric domains dictate the dielectric, piezoelectric, and ferroelectric properties for ferroelectric crystals. Thus, direct imaging of domain evolution during electric cycling is critical to elucidate the underlying mechanisms for electric fatigue. Unfortunately, vast majority of previous fatigue studies have mainly focused on macroscopic property measurements without microscopic pictures.9,10,15,16 Until now, very limited techniques, such as piezoresponse force microscopy (PFM)17-23
and X-ray microdiffraction,\textsuperscript{24} were developed to provide microscopic insight for electric fatigue. However, the application of these probing tools is still restricted by technical challenges. For example, PFM only recorded top morphology change during fatigue and was not able to monitor crystal structure evolutions.\textsuperscript{17-23} It is now understood that both macroscopic properties and microscopic morphologies are significantly influenced by structural phase transitions.\textsuperscript{25-30} For X-ray microdiffraction, high spatial resolution is still not approachable when the length scale is reduced to individual grain level and multi-domain structures are presented within. In order to circumvent these technical hindrances effectively and obtain a comprehensive understanding of electric fatigue from a microscopic viewpoint, electric field \textit{in situ} transmission electron microscopy (TEM)\textsuperscript{31-35} is employed and extended by applying an AC electric fields in this study.

The \textit{in situ} TEM technique has been demonstrated to be a powerful probing tool for investigating microstructural origins of functionality (\textit{e.g.} the piezoelectricity) evolution under electric field.\textsuperscript{25-30} Domain morphology transformations over a length scale from micrometers to nanometers can be effectively recorded due to its high resolution. Simultaneously, crystal structures evolution can also be monitored by electron diffraction patterns, especially when phase variants are inferred by superlattice diffractions.\textsuperscript{25,27} Our previous \textit{in situ} TEM studies have focused on the microstructural response to the DC electric field.\textsuperscript{25-30} Here, microstructures evolution during a bipolar fatigue process was directly visualized using an electric field \textit{in situ} TEM technique. Polycrystalline 0.7Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}-0.3PbTiO\textsubscript{3} (0.7PMN-0.3PT) ceramic was employed for the demonstration. \textit{In situ} observations combined with dielectric, piezoelectric, and
ferroelectric properties measurements on bulk specimens eventually allow for elucidation of the underlying mechanism for electric fatigue in 0.7PMN-0.3PT.

5.1.2 Experimental procedure

A. Ceramic preparation

The 0.7Pb(Mg_{1/3}Nb_{2/3})O_3-0.3PbTiO_3 ceramic (TRS Ceramics, State College, PA) was synthesized through the columbite precursor method. MgNb_2O_6 was prepared by the reaction MgO + Nb_2O_5 → MgNb_2O_6 at 1200 °C for 4 h. After dry-milling and passing through 100 mesh sieve, the columbite powder slurry was further milled with a high-energy attritor-mill for 6 h. Then, PbCO_3 and TiO_2 were added to the columbite powder and vibratory-milled for 18 h. The mixtures was dried and then calcined at 700 °C for 4 h. This powder was ground and passed through 80 mesh, then attritor-milled for 8h. With acrylic resin as binder, the calcined powder was biaxially pressed into 76mm × 50mm × 50mm blocks. The green bodies were sintered at 1250 °C for 3 h in alumina crucibles with PbZrO_3 source powder to maintain a PbO atmosphere. After sintering, the blocks were hot isostatically pressed at 1150 °C for 2 h in an O_2/Ar atmosphere.

B. Fatigue measurements on bulk specimen

The fatigue experiment was performed on bulk specimen by applying a bipolar triangular waveform with a frequency of 2 Hz and peak field of 20 kV/cm. Silver films were sputtered to serve as electrodes. Macroscopic properties were measured for various cycling intervals. For ferroelectric characterizations, the polarization (P) vs. electric field (E) hysteresis loops were measured using a standardized ferroelectric test system (RT-
66A, Radiant Technologies) at 4 Hz at room temperature. The polarization current density $J$ was determined by taking the derivative of polarization with respect to time, \textit{i.e.}, $dP(t)/dt$. For piezoelectric measurements, the piezoelectric coefficient $d_{33}$ was measured by a piezo-$d_{33}$ meter (Model ZJ-4B, Institute of Acoustics, Chinese Academy of Science, China) to take 10 measurements across the electrode of the sample. The room temperature dielectric constant was measured using an LCR meter (HP-4284A, Hewlett-Packard) at frequency of 1 kHz.

C. \textit{In situ} TEM study

For electric field \textit{in situ} TEM experiments, disk specimens (3 mm in diameter) were prepared from ceramic pellets through standard procedures including grinding, cutting, dimpling, and ion milling. The dimpled disks were annealed at 300 °C for 2 h to minimize the residual stresses before Ar-ion milling to the point of electron transparency. \textit{In situ} TEM experiments were carried out on a Phillips CM-30 microscope operated at 200 kV. The detailed experimental setup can be found in our previous reports. After the initial poling process (a DC field applied at the very first quarter cycle) from its virgin state, a bipolar cycling with a frequency of 10 Hz and peak field of 10 kV/cm was applied. TEM micrographs were recorded at zero field after certain cycles were made. In this study, only the nominal electric field (the applied voltage divided by the electrode spacing) is cited for the \textit{in situ} TEM results. However, it should be noted that the TEM specimen has a central perforation which intensifies the actual field in the target grains. In the present case, an intensification ratio of 2 is considered for the actual field strength due to the circular-shaped geometry of the perforation. Therefore, for
the fatigue measurements mentioned in section B on bulk specimens, an amplitude of 20 kV/cm was applied during the bipolar electric cycling.

5.1.3 Results and discussion

A. Domain morphology in the virgin state

The crystalline solution (1-x)PMN-xPT is known to have a systematic domain structure evolution when the phase variant evolves with PbTiO$_3$ content.$^{38-40}$ For tetragonal phase compositions ($x > 0.35$), normal micron-sized lamellar domains were observed;$^{38-40}$ while for rhombohedral phase compositions ($x \sim 0.25-0.3$), miniaturized polar nanodomains were found to form spindle-like domain features.$^{39,40}$ Between these two ($x \sim 0.3-0.35$), a morphotropic phase boundary (MPB) with a monoclinic phase was present to bridge the tetragonal and rhombohedral structures.$^{38,39,41,42}$ Correspondingly, a hierarchical domain pattern with the micron-sized lamellar-type consisting of cross-hatched nanodomains inside was adopted.$^{38,39,42-44}$ This typical domain configuration was commonly observed for both single crystals and polycrystalline ceramics at, or in the vicinity of the MPB.$^{38-40,42-44}$ In the present study, a consistent observation was also obtained in the 0.7PMN-0.3PT polycrystalline ceramic. As shown in Fig. 1 for a representative grain along its [113] zone axis in the virgin state 0.7PMN-0.3PT ceramic, the typical hierarchy domain feature was clearly demonstrated: the micron-sized (1\(\bar{1}0\)) lamellar domains were manifested with two traces of tweed-like nanodomains coexisting inside. These nanodomains were found roughly along two $<30\bar{1}>$ directions, and crosshatched with each other to form a sub-structure.
B. Domain morphology evolution during fatigue

Microstructure evolution under electric process in 0.7PMN-0.3PT ceramic was exemplified in Fig. 2 by a [001]-aligned grain. Prior to the cycling, the domain morphology evolution during the first quarter cycle (referred to as “initial poling” hereafter) was initially shown in Figs. 2a-2c. In the virgin state (Fig. 2a), two sets of orthogonal lamellar domains were clearly observed and found parallel to the \{110\} planes. Inside these micron-sized domains, nanodomains were also manifested. However, they became nearly invisible due to their extremely weak contrast at lower magnifications, as seen in Fig. 1a. When the electric field reached 6 kV/cm, apparent domain switching was noted. Some portions of the (\bar{1}10) domains were consumed by the other set of (110) domains. Further increasing the electric field to 10 kV/cm facilitated the consummation process, and finally the entire grain was occupied by the (110) domains. In addition, large domain mixed with thin domain striations were also formed at the far left side of the grain during this domain alignment process. Domain evolution during initial poling was found to be irreversible. The configuration of the poled state remained unchanged upon removal of the poling field.

Electric reversals were then carried out by repetitively applying bipolar cycles at a nominal amplitude of 10 kV/cm. It is interesting that after 20 cycles a sub-structure with nanometer-sized domain traces developed within the lamellar domains and formed a herringbone type of domain configuration (Fig. 2d). Those confined short domains appeared to have domain walls along (010) and (100) planes. Also, the far left part of this grain split into a cluster of [010]-aligned thin domain strings. Upon further cycling, domain switching proceeded. As shown in Fig. 2e, for the end-state after $10^3$ cycles some
portion of nanodomain traces disappeared, but still with some portion preserved and mixed with lamellar domains. Additionally, some newly formed defects were observed, as roughly aligned along the bright arrow indicated in Fig. 2e. It has been known that structural imperfections are generated in fatigued ferroelectrics. For the defects in Fig. 2e, they could be oxygen vacancy clusters or dislocations. After 10^3 cycles nearly all the domains became incapable of switching with further cycling, leading to a frozen configuration after fatigue. In addition to the pinned domain walls, some inhibited small domains seem to have appeared at the grain boundary in the lower part in Fig. 2e. On the other hand, the crystal structure was also monitored by the electron diffraction pattern during the initial poling and fatigue process. No noticeable changes were found compared with the virgin state pattern (Fig. 2f).

Fatigue-induced domain freezing under the influence of electric reversals in 0.7PMN-0.3PT was reproducibly observed, as shown by another grain along its [112] zone axis in the same TEM specimen (Fig. 3). The first three micrographs (Figs. 3a-3c) still show microstructural evolution during initial poling. In the virgin state (Fig. 3a), in addition to the tweed-like fine domain clusters, micron-sized lamellar domains lying on the (1̅10) crystallographic planes were observed. When the electric field was increased to 5 kV/cm, the large lamellar domains at the upper-right corner were transformed into thin-aligned striation-like domains with traces along the [1̅10] direction (Fig. 3b). At 10 kV/cm, the domain striations became predominant, as manifested by the disappearance of the large lamellar domains and the occurrence of another set of [3̅1̅1]-aligned fine traces (Fig. 3c). During the fatigue process an apparent alteration of domain morphology was observed before 10^3 cycles. As exemplified in Fig. 3d, a significant portion of [1̅31]-
aligned domain striations were induced after 20 cycles, leading to a condensed domain configuration for the entire grain. When the cycling numbers increased to $10^3$, most of the well-defined domain striations were gradually transformed into fine domain traces and large domain areas (Fig. 3e). With further increase of electric reversals, most of the domains were found inactive to the electric stimulus; the switching ability of the domains was substantially impeded. Only minor switching was noticed after $10^4$ cycles (Fig. 3f), and eventually the grain was dominated by an immobilized domain configuration (Fig. 3g). The frozen domain morphology remained even when a much higher DC field of -31 kV/cm was applied (Fig. 3h). Again, the electron diffraction pattern of the virgin state (Fig. 3i) stayed unchanged during the initial poling and fatigue process.

C. Impact on macroscopic properties

In order to correlate the fatigue-induced microstructural evolution to macroscopic properties, measurements on dielectric, piezoelectric and ferroelectric properties were carried out on bulk ceramic specimen; the results were shown in Figs. 4 and 5. A well-illustrated structure-property relationship was established. Figure 4 depicted the polarization hysteresis and corresponding polarization current density evolutions during fatigue. As can be seen, an apparent fatigue behavior was manifested by a reduction of remnant polarization ($P_r$) as well as an increase in coercive field ($E_C$) upon electric reversals (Fig. 4a), while corresponding polarization current density ($J$) peaks became lower and broadened (Fig. 4b). It is also interesting to notice that electric reversal from the virgin state ($N = 1$) has only one very sharp and narrow current density peak, suggesting a direct 180° reversal at the very first cycle. After that, doublets were seen on
the two peaks (see cycle 3 and $10^3$ curves). This may suggest that the polarization reversal occurred through a multi-step process. Further cycling smeared out the doublets and broadened the two peaks. This appears to indicate that the reversal process takes place within a wide field range due to severe domain wall pinning.

Generally, the degradation of remnant and maximum polarization ($P_m$) are indications of electric fatigue in ferroelectric properties. Both of them describe the amount of domains that can be effectively switched under electric field. However, the coercive field is usually used to characterize how difficult domain switching becomes when electric field direction is reversed. As summarized in Fig. 5a, both polarization and coercive field followed a plateau trend and changed slightly before $10^3$ cycles. Remarkable polarization decay was observed thereafter, accompanied by a bump up of the coercive field. Quantitatively, $P_m$ and $P_r$ showed a similar degradation to 79.8% and 80.0% of their original values after $10^4$ cycles, respectively, whereas $E_C$ increased to 167.1% of its initial value. For dielectric and piezoelectric properties, as characterized by dielectric constant ($\varepsilon_r$) and piezoelectric coefficient ($d_{33}$), the overall evolution followed the same reduction trend as the polarization: the dielectric constant and piezoelectric coefficient remained 93.8% and 92.0% of their original values after $10^3$ cycles, respectively, but significantly dropped to 55.3% and 50.0% after $10^4$ cycles.

For classic ferroelectrics, such as Pb(Zr,Ti)O$_3$ and BiFeO$_3$, the fatigue behavior usually exhibits a nonlinear decay by plotting remnant polarization with respect to logarithm of electric reversals. Obtained fatigue profiles are generally fitted by functions like $P_r \propto N^{-1/4}$, $P_r \propto (aN+1)^m$, or $P_r \propto A + \exp(-aN)$. Typically, a plateau stage of slow reduction is initially observed, followed by a sharp decay and subsequent
logarithmic stage.\(^{10}\) In this study, a similar fatigue behavior was also observed, as demonstrated by a stable stage within the initial \(10^3\) cycles and a fast decay stage thereafter. These macroscopic behaviors were well correlated to the \textit{in situ} TEM observations, where the domains remained actively switched within the initial \(10^3\) cycles and were progressively frozen thereafter. The degradation profile for the macroscopic properties can be well fitted by the power-law \(P_r \propto (aN+1)^{-m}\) relation.\(^9,55\) The fitting curves (solid lines in Fig. 5) are shown as the following, where \(P_{r0}, P_{m0}, d_0,\) and \(\varepsilon_{r0}\) are parameters of denoting the unfatigued state; \(N\) is the cycle number; \(a\) is the fitting constant; and \(m\) is the decay constant which characterizes the speed of the fatigue.

\[
\begin{align*}
P_r(N) &= P_{r0} (aN+1)^{-m}; \\
P_m(N) &= P_{m0} (aN+1)^{-m}; \\
d_{33}(N) &= d_0 (aN+1)^{-m}; \\
\varepsilon_r(N) &= \varepsilon_{r0} (aN+1)^{-m};
\end{align*}
\]

with \(P_{r0} = 30.330 \ \mu \text{C/cm}^2,\ a = 2.067 \times 10^{-4},\) and \(m = 0.188.\)

\[
\begin{align*}
P_m(N) &= P_{m0} (aN+1)^{-m}; \\
with \ P_{m0} = 37.274 \ \mu \text{C/cm}^2,\ a = 1.164 \times 10^{-4},\) and \(m = 0.286.\)

\[
\begin{align*}
d_{33}(N) &= d_0 (aN+1)^{-m}; \\
with \ d_0 = 805.928 \ \text{pC/N},\ a = 1.184 \times 10^{-5},\) and \(m = 6.517.\)

\[
\begin{align*}
\varepsilon_r(N) &= \varepsilon_{r0} (aN+1)^{-m};
\end{align*}
\]

with \(\varepsilon_{r0} = 5972.600,\ a = 8.448 \times 10^{-5},\) and \(m = 0.999.\)

\[D. \ \text{Discussion}\]

It has been shown that electric fatigue in ferroelectric oxides is a complicated process, and both intrinsic and extrinsic contributions devote to the reduction of switchable polarization.\(^{1,9,10}\) During the past several decades of intensive studies various models have been proposed, for example, electrode degradation, passive layer formation, domain
wall pinning, and seed inhibition.\textsuperscript{1,9,10} For the electrode degradation model, polarization parameters of the \( P-E \) loop (\textit{e.g.} \( P_r \) and \( P_m \)) and the small-signal dielectric constant are supposed to scale down by the same factor.\textsuperscript{9} However, this is not the case here because the notable difference of the decay constants \( m \) has been demonstrated for all parameters [see equations (1), (2) and (4)]. The cycling-driven formation of the near-electrode passive layer should be manifested by a strong tilt of the polarization hysteresis loop, whereas the coercive field is either not influenced or slightly decreased.\textsuperscript{9} This expectation is inconsistent with the remarkable bumping of the coercive field in the present study.

For domain wall pinning and seed inhibition mechanisms, both cases show the frozen domain configuration after fatigue. For the former scenario, the domain walls are pinned due to their interaction with the charged defects, while for the later one the nucleation seeds for the reversed domains are blocked in their embryonic state before they can create a macroscopic domain.\textsuperscript{9} However, these two mechanisms can still be experimentally distinguished from each other. The essential feature of the domain wall pinning is the dense domain structure.\textsuperscript{9} A clear manifestation of the fatigued state induced by this mechanism should be demonstrated by a high concentration of immobilized domain walls. As a consequence, the small-signal dielectric constant is expected to increase.\textsuperscript{9} In contrast, the fatigued state created by the seed inhibition mechanism generally contains relatively large domain regions, yielding to a decrease of the small-signal dielectric constant.\textsuperscript{9} From our \textit{in situ} TEM observations (Figs. 2 and 3), both pinned domain walls and growths of relatively large domains were observed, suggesting the possible coexistence of domain wall pinning and seed inhibition mechanisms. Since the domain density of the fatigued state did not show a notable increase, and also a substantial degradation of dielectric
constant occurred after fatigue (Fig. 5b), it seems to suggest a leading contribution from the seed inhibition mechanism.

Lastly, it should be stressed that other factors may also contribute to polarization fatigue, for example, cycling-induced microcracks, and the internal bias field from charge-accumulation at grain boundaries.\textsuperscript{9,10} Since such effects are always manifested beyond individual grains they are beyond the primary focus of the present work at the individual grain level.

5.1.4 Conclusion

In conclusion, an electric field \textit{in situ} TEM study was conducted to investigate the microstructural origin for electric fatigue in the 0.7PMN-0.3PT ceramic. The domain evolution within individual grains was directly visualized during the fatigue process. The \textit{in situ} observations correlated well with the macroscopic property measurements on bulk specimens. It was found that the fatigue behavior in this composition was due to the frozen domain configuration after $10^3$ cycles, yielding to a progressive degradation of polarization, dielectric constant and piezoelectric coefficient. Both seed inhibition and domain wall pinning mechanisms were suggested to be responsible for the observed fatigue behavior, but with a leading contribution from the former. The electric field \textit{in situ} TEM technique employed in this study was demonstrated to be a powerful and promising probing tool to reveal the underlying mechanism with microscopic insight for electric fatigue.
Acknowledgements

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Figures

FIG. 1 (a) Bright-field micrograph of a representative grain along its [113] zone axis in the virgin state of 0.7PMN-0.3PT ceramic. (b) Higher magnification image of the boxed area in (a) to show the hierarchical domain structure. (c) The corresponding selected area diffraction pattern.
FIG. 2 *In situ* TEM observations of a grain along its [001] zone axis in a 0.7PMN-0.3PT specimen during initial poling and bipolar electric reversals. Bright-field micrographs at (a) virgin state, (b) 6 kV/cm, and (c) 10 kV/cm during initial poling; (d) after 20 cycles, and (e) after $10^3$ cycles of bipolar cycling with a nominal amplitude of 10 kV/cm. The produced defects after $10^3$ cycles are marked roughly along the direction of the bright arrow shown in (e). The selected area diffraction pattern recorded at the virgin state is shown in (f). The positive direction of applied fields in the TEM experiment is indicated by the bright arrow in (b). No apparent changes in the electron diffraction pattern are noticed during initial poling and fatigue process.
FIG. 3 In situ TEM observations of another grain along its [112] zone axis in the same 0.7PMN-0.3PT specimen during initial poling and electric reversals. Bright-field micrographs at (a) virgin state, (b) 5 kV/cm, and (c) 10 kV/cm during initial poling; (d) after 20 cycles, (e) after $10^3$ cycles, (f) after $10^4$ cycles, and (g) after $10^5$ cycles during fatigue. After fatigue, the gain shown in (g) was further stressed at -31 kV/cm, as displayed in (h). The selected area diffraction pattern recorded at the virgin state is shown in (i). The positive direction of applied fields in the TEM experiment is indicated by the bright arrow in (b). No apparent changes in the electron diffraction pattern are noticed during initial poling and fatigue process.
FIG. 4 (a) Change of the polarization hysteresis loop and (b) polarization current density curves during electric fatigue in 0.7PMN-0.3PT bulk ceramic.
FIG. 5 (a) Polarization and coercive field, (b) dielectric constant, and (c) piezoelectric coefficient as a function of cycling number measured from the same bulk specimen as in Fig. 4. The experimentally measured results are shown as discrete points, while the solid fitting curves are derived using the power-law relation. The fitting equations are shown in the text.
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5.2 Nanofragmentation of ferroelectric domains during polarization fatigue


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**Abstract**

The microscopic mechanism for polarization fatigue in ferroelectric oxides has remained an open issue for several decades in the condensed matter physics community. Even though numerous models are proposed, a consensus has yet to be reached. Since polarization reversal is realized through ferroelectric domains, their behaviors during electric cycling are key to elucidating the microstructural origin for the deteriorating performance. In this study, electric field *in situ* transmission electron microscopy was employed for the first time to reveal the domain dynamics at the nanoscale through more than $10^3$ cycles of bipolar fields. A novel mechanism of domain fragmentation was directly visualized in polycrystalline $\left[(\text{Bi}_{1/2}\text{Na}_{1/2})_{0.95}\text{Ba}_{0.05}\right]_{0.98}\text{La}_{0.02}\text{TiO}_3$. Fragmented domains break the long-range polar order and, together with domain wall pinning, contribute to the reduction of switchable polarization. These direct microscopic observations correlate well with structure and properties measurements on bulk specimens.

**5.2.1 Introduction**

Fatigue degradation of ferroelectric materials has been a vexing issue for both fundamental science and technological applications. It is manifested primarily in the form of continuous reduction in switchable polarization upon repeated electric cycling, which has stood out as the primary hindrance to high reliability and long service life of
ferroelectric devices, such as non-volatile memories, field-effect transistors, ferroelectric tunneling junctions, transducers and actuators. To elucidate the underlying mechanisms for the performance deterioration, phenomenological and theoretical studies have been extensively conducted on ferroelectric thin film and bulk materials. Despite these efforts, the origin of polarization fatigue still remains controversial, and various models have been proposed, including passive layer formation, nucleation inhibition, local phase decomposition, near-by-electrode injection, defects redistribution, and domain wall pinning. Since polarization fatigue is a complicated defect-chemistry phenomenon, one single mechanism alone cannot explain all the observations. Some fatigue characteristics are always conjugated with each other. For example, the widely observed domain wall pinning mechanism is always accompanied with charge injection or nucleation inhibition features.

The majority of previous fatigue studies has focused on the evolution of macroscopic properties against electric cycling, such as permittivity, remanence, and coercivity. The microscopic dynamics is then indirectly inferred from the change of property. It should be noted that the polarization state and polarization reversal are intrinsically linked to ferroelectric domain arrangement and its transformation. Under externally applied electric field, ferroelectric domains adjust their configuration through domain wall motion and they eventually dictate the macroscopic properties. The domain activities occur at a length scale ranging from nanometers to micrometers. To better elucidate the domain dynamics and its role on polarization degradation during fatigue, direct microscopic imaging of domain evolution becomes essential. As such, a few studies have been reported in the literature, which employed piezoresponse force...
microscopy (PFM) and synchrotron X-ray microdiffraction to visualize domains mostly on thin films of classic ferroelectrics, such as BiFeO\(_3\) and Pb(Zr,Ti)O\(_3\). Although these probing tools can produce micrographs, they are still challenged by some technical limitations. For example, PFM only monitors the domain morphology change without providing any crystallographic information. As it is well known that electric field is capable of inducing structural phase transitions which can be detected by electron diffraction. However, it will be difficult for PFM to distinguish the subtle difference between the phase variants in perovskite ferroelectrics. For the X-ray microdiffraction, the spatial resolution is around several micrometers. Even with the recent development of submicron X-ray diffraction, higher resolution is still quite challenging, especially when individual grains with multiple domains are concerned. To circumvent these technical constraints and unravel the microstructural origin of the polarization fatigue, the electric field in situ transmission electron microscopy (TEM) technique is employed in the present study.

We report the first in situ TEM investigation on polarization fatigue in a lead-free piezoelectric ceramic. Polycrystalline ceramic of [(Bi\(_{1/2}\)Na\(_{1/2}\))\(_{0.95}\)Ba\(_{0.05}\)La\(_{0.02}\)TiO\(_3\) (BNT52) was chosen for its nonergodic relaxor nature and high piezoelectric property. The evolution of domains within individual grains under applied electric fields was directly observed at high resolution. The nanodomains in the virgin state transformed to large lamellar domains during the first quarter cycle of field through a phase transition; these large domains were disrupted gradually during bipolar electric cycling; and finally much less responsive domain fragments were formed. Correspondingly, such domain fragmentation process yielded a logarithmic reduction of switchable polarization. The
multistep process of 180° polarization reversal model is suggested to account for the observed domain fragmentation during bipolar fatigue.

5.2.2 Experimental procedure

The [(Bi\textsubscript{1/2}Na\textsubscript{1/2})\textsubscript{0.95}Ba\textsubscript{0.05}]\textsubscript{0.98}La\textsubscript{0.02}TiO\textsubscript{3} (BNT52) polycrystalline ceramic was prepared by the solid state reaction method and the details can be found elsewhere\textsuperscript{32}. The fatigue experiment on bulk specimens was performed with bipolar triangular waveform electric fields at 4 Hz and 45 kV cm\textsuperscript{-1}. Crystal structure and electric properties were measured at a series of cycling intervals. For ferroelectric characterizations, silver films were sputtered to serve as electrodes. The polarization (\(P\)) vs. electric field (\(E\)) hysteresis loops were measured using a standardized ferroelectric test system (RT-66A, Radiant Technologies) at 4 Hz at room temperature. The longitudinal strain (\(\chi_{33}\)) developed under electric field in the form of a triangular wave of 0.05 Hz was monitored with an MTI-2000 fotonic sensor (MTI Instruments Inc., Albany, NY). For X-ray diffraction measurements, the same bulk ceramic specimen for fatigue measurement was used. At each cycling interval, the silver film electrodes were chemically removed using dilute nitric acid solution. The evolution of the \(\frac{1}{2}(311)\) superlattice peak was immediately recorded on a Siemens D500 diffractometer using Cu-K\(\alpha\) radiation at a 0.02° step size and a 150 s dwelling time. The integrated peak intensities were calculated with the baseline at \(I = [I(37.80°) + I(38.65°)]/2\), where \(I\) is the X-ray photon count. For the electric field \textit{in situ} TEM study, disk specimens (3 mm in diameter) were prepared from as-sintered pellets through standard procedures including grinding, cutting, dimpling, and ion mill. The dimpled disks were annealed at 400 °C for 2 h to minimize the residual
stresses before Ar-ion milling to the point of electron transparency. *In situ* TEM experiments were carried out on a specimen that was crack free at the edge of the central perforation on a Phillips CM30 microscope operated at 200 kV. Detailed experimental setup can be found in our previous reports\textsuperscript{28-31}. For the fatigue test in TEM, bipolar electric fields in a triangular waveform at a frequency of 1 Hz and a nominal peak field of 30 kV cm\textsuperscript{-1} were applied.

5.2.3 Results and discussion

**Domain and phase evolution during initial poling.** Prior to cycling, the domain morphology evolution during the very first quarter cycle of electric field (referred to as “initial poling” hereafter) was examined and is shown in Fig. 1. As demonstrated previously, BNT52 is a non-ergodic relaxor in its virgin state\textsuperscript{32}. As displayed in Fig. 1a of a representative grain along its [112] zone axis, it was consisted of nanometer-sized domains with the coexisting $R\bar{3}c$ and $P4bm$ phases, revealed by the weak $\frac{1}{2}\{ooo\}$- and $\frac{1}{2}\{ooe\}$-type ($o$ and $e$ stand for odd and even Miller indices, respectively) superlattice electron diffraction spots (Fig. 1b), respectively\textsuperscript{33-35}. Unlike the dynamically fluctuating polar nanoregions in ergodic relaxors\textsuperscript{36,37}, the static polar nanodomains shown in Fig. 1a can be irreversibly switched during initial poling\textsuperscript{21}. Fig. 1c shows the stable domain morphology at 30 kV cm\textsuperscript{-1}, the original nanodomains are consumed by long lamellar ferroelectric domains with the development of long-range polar ordering. Crystallographic analysis indicates that the major set of domain walls are parallel to the \{010\} planes. At the same time, this domain morphology transformation was accompanied with a $P4bm$ to $R\bar{3}c$ symmetry change, as indicated by the disappearance of
the \( \frac{1}{2}\{ooe\} \) superlattice spots and the significantly strengthened \( \frac{1}{2}\{ooo\} \) ones (Fig. 1d). Such microstructural change was repeatedly observed, as exemplified by another [112]-aligned grain (Figs. 1e-1h), and was found irreversible. Both the domain morphology alteration (Figs. 1c and 1g) and crystal structural transition (Figs. 1d and 1h) remained unchanged after the applied field is removed.

**Domain fragmentation during bipolar electric cycling.** The large lamellar domains formed during initial poling were found to be disrupted by subsequent bipolar electric cycling, as shown in Fig. 2 on a [112]-aligned grain. The major set walls of the induced lamellar domains (Fig. 2a) are along the \{110\} crystallographic plane while the selected area electron diffraction pattern (inset of Fig. 2c) suggests an \( R3c \) symmetry. After 20 cycles of bipolar electric fields of nominal intensity of 30 kV cm\(^{-1}\), the domain morphology of this grain was significantly altered. The well-aligned lamellar domains were replaced by other sets of large domains (Fig. 2b). It is interesting to notice that large domains were fragmented and small domains appeared in the central portion of the grain. The disruption of large domains continued and gradually spread to the most part of the grain during further bipolar cycling (Figs. 2c-2d). It was also observed that domains in some areas became stable and less responsive to the electric stimulus. After \( 2 \times 10^2 \) cycles (Fig. 2d), nearly a third of the grain was occupied by nanometer-sized domain fragments. On the other hand, after the initially poling no noticeable changes were found in the electron diffraction patterns during bipolar cycling.

The domain fragmentation during bipolar electric cycling was reproducibly observed in the same TEM specimen, as exemplified by another [112]-aligned grain shown in Fig.
3. Again, large lamellar domains with $R3c$ symmetry were developed during the initially poling (Fig. 3a). After $10^2$ cycles of electric cycling, the morphology of the large domains changed dramatically (Fig. 3b). When the cycling number reached $1.6 \times 10^2$, a large portion of lamellar domains in the central left part of the grain was perturbed by the emergence of condensed domain clusters (Fig. 3c). Upon further bipolar cycling (Figs. 3d-3f), more domain fragments were observed with an increased domain wall density; meanwhile the domain walls were gradually pinned during the cycling. After $10^3$ cycles (Fig. 3f), the switching ability of the domains was significantly suppressed, and eventually a configuration with mixed domain fragments and immobile large domains was resulted. Again, the electron diffraction pattern of the grain after initial poling stayed unchanged during the course of bipolar cycling.

The domain fragmentation during bipolar electric cycling occurs in grains with different crystallographic orientations as well. Figure 4 shows the process observed in a [111]-aligned grain in the same TEM specimen. A microstructural evolution similar to that in Figs. 2 and 3 was seen again. After initial poling, large lamellar domains with walls along $\{011\}$ planes were observed (Fig. 4a). It should be noted that the weak contrast of domain walls in the left part of the grain was due to bend contours. The [111] zone-axis diffraction pattern (Fig. 4b) from this grain after initial poling indicates the absence of $\frac{1}{2}\langle ooe \rangle$-type superlattice spots, which is consistent with the results from other grains shown in Figs. 1-3. During bipolar electric cycling, the large lamellar domains were continuously disrupted into small fragments. This can be clearly seen from Figs. 4d-4g, as well as from the corresponding higher magnification micrographs shown in Figs. 4h-4j. After $10^3$ cycles (Fig. 4g), the great majority of the grain was occupied by
small domain fragments. The fragmented domain configuration persisted to higher numbers of electric cycling. Compared with those grains shown in Figs. 2 and 3, the domain fragmentation in this grain is more thorough and extensive. This difference seems to indicate an orientation dependence of the fragmentation process during bipolar cycling. In addition, after $10^3$ cycles, the difference also gives rise to the crystallographic variance since both fragmentations and large domains contribute to the electron diffraction patterns. It is most interesting to see that the $\frac{1}{2}\{ooe\}$ superlattice diffraction spots seem to re-appear in the electron diffraction pattern after $10^3$ cycles (Fig. 4c). However, they were not found in the [112] zone-axes electron diffraction patterns shown in Figs. 2 and 3, which could be due to the incomplete fragmentation process. The results indicate that the bipolar electric cycling not only disrupts the large $R3c$ domains, but also has a tendency to recover the $P4bm$ phase. In other words, the electric cycling seems to gradually transform the microstructure after initial poling back to the original nanodomains in the virgin state. We have recently demonstrated that the polarization reversal in this composition takes place through complicated phase transitions $^{38}$, indicating close free energies of those variant phases. The accumulated and redistributed charged point defects, such as oxygen vacancies, during bipolar electric cycling may destabilize the long range ordered ferroelectric state (in the form of large $R3c$ domains) and favor the short range ordered relaxor state (in the form of $R3c$ and $P4bm$ nanodomains). However, the extremely weak $\frac{1}{2}\{ooe\}$ spots indicate that the fatigued specimen was still dominated by the $R3c$ phase.

The domain fragmentation process during electric cycling was found to be accompanied by the immobilization of domains walls in all grains displayed in Figs. 2-4.
Use the grain shown in Fig. 4 as an example, after $10^3$ cycles of bipolar electric cycling, the domain morphology shown in Fig. 4g did not change under a nominal DC field of 30 kV cm$^{-1}$ in both polarities, suggesting most domains were frozen. When a higher DC field of 40 kV cm$^{-1}$ was applied, those immobilized domain walls started to move and a different domain morphology was resulted (Fig. 5). Long and thin domains were formed in the central and upper-middle portions of the grain, as well as large domains grew in the lower part of the grain. However, compared with the domain morphology after the initial poling shown in Fig. 4a where only large lamellar domains were present, the morphology after fatigue shown in Fig. 5 contains a much higher domain wall density. Apparently the domain wall mobility is significantly suppressed by the electric cycling and the electric poling becomes much less effective even under a higher field of 40 kV cm$^{-1}$.

**Impact on macroscopic structure and properties.** To ensure the *in situ* TEM result is representative for the behavior of bulk ceramics, X-ray diffraction measurements on a bulk specimen were performed to monitor the evolution of the $\frac{1}{2}(311)$ superlattice diffraction peak during bipolar electric cycling. In the virgin state prior to exposure of any electric field, the $\frac{1}{2}(311)$ peak was too weak to be detected by the conventional laboratory X-ray diffractometer (Fig. 6a). However, an apparent and sharp $\frac{1}{2}(311)$ peak was detected after the first cycle of bipolar electric fields. The superlattice peak persisted but gradually became broad during the subsequent electric cycling. Figure 6b displays the integrated intensity and the full width of half maximum (FWHM) of the $\frac{1}{2}(311)$ peak against the cycle number. It is evident that the peak intensity remains almost a constant while the FWHM is almost doubled after $10^3$ cycles.
The broadening of X-ray diffraction peaks is often indicative of a reduction of the average domain size. For example, during the pressure-induced phase transition in bulk CdSe, nanodomain fragmentation yields an apparent broadening of the diffraction peaks\(^{39}\). Therefore, the X-ray diffraction analysis of the bulk BNT52 specimen correlates well with the \textit{in situ} TEM results shown in Figs. 2-4. The \textit{R}3\textit{c} phase, either in the form of large domains or domain fragments, was overwhelmingly predominant during bipolar electric cycling. However, the large domains decompose into fragments with increased electric reversals. An oversimplified estimate using the Debye-Scherrer equation gives an average domain size of 40 nm after the first electric cycle and 22 nm after 10\(^3\) cycles. These values seem reasonable for the width of domains from TEM observations.

Microstructural changes inevitably give rise to alterations of macroscopic properties. Figure 7 depicts the evolution of the polarization and strain hysteresis loops with increasing cycling numbers. The irreversible relaxor to ferroelectric transition revealed by the \textit{in situ} TEM (Fig. 1) is verified by the abrupt development of large polarization and strain during the first quarter cycle of electric field as well as the presence of remanence after initial poling. Upon increase in cycle numbers, the polarization loops became depressed with a continuous reduction of maximum and switchable polarizations \((P_m \text{ and } P_r)\), but an increase in coercive field \(E_C\) (Fig. 8a). Quantitatively, \(P_m\) and \(P_r\) show a similar degradation of 35\% and 32\% from their original values after 1.5 \times 10^4 cycles, respectively; while \(E_C\) jumps to 155\% of its initial value. Meanwhile, the positive strain deteriorates moderately and the negative strain shifts toward zero after the first cycle (Fig. 8b).
For classic ferroelectrics, such as Pb(Zr,Ti)O$_3$ and BiFeO$_3$, their fatigue behavior usually exhibits a nonlinear three-stage decay of remanent polarization when plotted against the logarithm of electrical reversals$^9$, an initial slow stage ($N \sim 10^4$), a logarithmic stage ($N \sim 10^6$), and a saturated stage ($N \sim 10^8$). The obtained fatigue profiles are generally fitted by functions like $P_r \propto N^{-1/4}$, $P_r \propto (aN+1)^{-m}$, or $P_r \propto A+exp(-aN)$ (Refs. 8, 40). In contrast, the BNT52 ceramic in the present study displayed a nearly linear polarization decay right from the beginning in the semi-log plot, as shown in Fig. 8a. The polarization degradation, both $P_r$ and $P_m$, can be well fitted by the logarithmic fatigue relation proposed by Brennan$^{41}$:

$$P = P_0 + A \log(N)$$ (1)

where $P_0$ is the polarization prior to the fatigue; $N$ is the cycle numbers; and $A$ is a rate factor and can be expressed as $(kT/c)$ with $k$ the Boltzmann constant, $T$ the temperature, and $c$ a proportionality constant. The fitting equations for $P_r$ and $P_m$ are

$$P_r = 21.9 - 1.8\log(N),$$ (2)

$$P_m = 31.1 - 2.8\log(N),$$ (3)

respectively. The rate factor $A$ characterizes the speed of polarization decay during fatigue. Apparently, it depends on the chemical composition, as well as fatigue conditions. In a ceramic with a similar composition of [(Bi$_{1/2}$Na$_{1/2})_{0.94}$Ba$_{0.06}]$TiO$_3$, a much greater $A \sim -9.9$ was observed within the first $10^4$ cycles of bipolar sinusoidal fields of 60 kV cm$^{-1}$ at 2 Hz (Ref. 42). La-addition in the present study has slowed down the polarization deterioration.
Discussion

It is commonly accepted that polarization fatigue is a defect-chemistry induced phenomenon in ferroelectrics of both thin film and bulk forms\textsuperscript{2,8}. Complicated processes are involved during electric cycling, primarily including the creation and/or redistribution of charged defects which subsequently influence the ferroelectric domain switching dynamics\textsuperscript{2,8}. Also, the initially charge-neutral domain walls can become polarized during electric reversal, which will enhance their interactions with defects\textsuperscript{17,22}. In a word, the resulting fatigue effect is generally due to the formation of mesoscopic structures of interacting charged defects and polarized walls\textsuperscript{41}. It has been shown that ionic defects may produce a self-trapping potential by polarizing the surrounding crystal lattice, leading to an increase in the activation energy for defects in the mesoscopic structures\textsuperscript{41}. As a system, the charged defects and polarized domain walls form a self-stabilizing configuration through charge compensation\textsuperscript{2,17,22,41}. For example, oxygen vacancies, the most mobile defects in perovskite oxides, aggregate at the tail-to-tail domain walls to compensate the negative charges; meanwhile the electrons accumulate at the head-to-head charged domain walls to neutralize the positive polarization charges\textsuperscript{17,22}. Such interactions result in the domain wall pinning and nucleation inhibition through deactivating domain switching events. All these microscopic processes contribute to the logarithmic decay of the switchable polarization upon electric cycling\textsuperscript{41}.

In the BNT52 ceramic reported here, charged defects can be oxygen vacancies, aliovalent substituting cation, or vacancies of Bi and Na cations due to evaporation loss during sintering. Also, extrinsic contribution from electrode injection cannot be ruled out when a prolonged cycling is considered\textsuperscript{17}. Since fatigue in BNT52 commenced at very
beginning (Figs. 7 and 8) and also progressively freezing domain configuration was reached before $10^3$ cycles (Figs. 2-4), we suggest the predominant role of the intrinsically produced charge defects instead of injected ones. The interactions between these charged defects and domain walls yield a stabilized and freezing domain configuration revealed by the in situ TEM observation. In addition to domain wall pinning, a novel phenomenon of domain fragmentation was discovered in this study. As noticed in Figs. 2-4, most of the domain fragments were distorted without a preferential crystallographic plane for their walls, suggesting they were not charge neutral\textsuperscript{22}. The formation of such fragments with charged domain walls can be well-understood with assistance of the multistep process of 180° polarization reversal model\textsuperscript{22}.

Various experimental evidences have verified that the 180° polarization reversal in rhombohedral ferroelectric perovskites [e.g. BiFeO$_3$, Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$, and Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$] is accomplished through consecutive non-180° ferroelastic domain switching instead of the straightforward reverse\textsuperscript{22,43-47}. BiFeO$_3$, possessing the same $R3c$ space group as the poled BNT52, was found to form charged domain walls through the multistep switching process\textsuperscript{22}. Moreover, both experimental observations and theoretical calculations revealed that the 71° polarization switching in (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$, the base compound of BNT52, was the dominant pathway for the electric field-induced polarization switching since the energy barrier for the 71° switching was much lower than those for the 109° switching and 180° reversal\textsuperscript{48}. Therefore, the 180° switching (e.g. [111] → [\overline{1}\overline{1}\overline{1}]) can be realized through three intermediate steps of 71° ferroelastic switching upon electric field reversal\textsuperscript{22}. There exist six different equivalent routes for this reversal and two of them are exemplified below:
Route 1 (R1): \([111] \rightarrow [1\bar{1}1] \rightarrow [\bar{1}11] \rightarrow [\bar{1}\bar{1}1]\)

Route 2 (R2): \([111] \rightarrow [11\bar{1}] \rightarrow [1\bar{1}1] \rightarrow [\bar{1}\bar{1}1]\)

In ideal situations, there is no energetic preference among the six routines\(^\text{22}\). Therefore, polarization switching in a rhombohedral crystal will follow any of the six routes and experience all the intermediate states with equal probability during electrical reversal. In this process, there is a large chance for the formation of charged domain walls when two different intermediate domains meet, for example, the conjunction of \([\bar{1}11]\) in R1 and \([11\bar{1}]\) in R2, or \([\bar{1}\bar{1}1]\) in R1 and \([1\bar{1}\bar{1}]\) in R2. Presumably, the charged walls are unfavorable due to their high electrostatic energy. However, they can be stabilized by trapping mobile charge carriers, leading to pinned domain walls with reduced mobility. As the reversal repeated over and over again, more and more intermediate domains with frozen domain walls will be accumulated. This explains the domain fragmentation and polarization degradation upon bipolar electric cycling. In \([\text{Bi}_{1/2}\text{Na}_{1/2}]_{0.94}\text{Ba}_{0.06}\)\text{TiO}_3\), the small domain fragments with randomized polarizations appear to be a pseudocubic phase under neutron diffraction\(^\text{49}\).

Another complication during bipolar electric cycling in the present BNT52 is phase transition. BNT52 is a non-ergodic relaxor with a thermal depolarization temperature \(T_d\) slightly above room temperature\(^\text{32}\). As shown in Fig. 1, there is an electric field-induced relaxor to ferroelectric phase transition during the first quarter cycle of electric field and the induced ferroelectric phase maintains in the second quarter cycle. We recently observed that the initial relaxor phase could be partially recovered when the field reversed polarity in the third quarter cycle\(^\text{38}\). Therefore there are four phase transitions
within a full cycle of bipolar electric fields and this is the cause for the pinched polarization hysteresis loop for cycle 1 shown in Fig. 7a. Also, the very weak \( \frac{1}{2} \{ ooe \} \) superlattice spots in the fatigued specimen (Fig. 4c) is another reminiscence of the transient relaxor phase during electric cycling. It appears that the subtle balance between the relaxor \( R3c \) and \( P4bm \) phases and the ferroelectric \( R3c \) phase is slightly changed by fatigue generated species, such as charged point defects and high-density domain walls.

Lastly, it should be pointed out that other factors may also have contributed to the polarization fatigue of BNT52, including electrode degradation, near-electrode passive layers, cycling-induced microcracks, and internal bias field from charge-accumulation at grain boundaries\(^{2,8,9,50}\). Since these phenomena occur at length scales longer than the grain size, they are beyond the primary interest of the present \textit{in situ} TEM study.

5.2.4 Conclusion

In summary, \textit{in situ} TEM was employed for the first time to investigate the domain structure evolution during electric fatigue in a non-ergodic lead-free relaxor BNT52. In complementary to the domain wall pinning effect, a novel fatigue mechanism of domain fragmentation was discovered. The fragmentation was suggested to be resulted from the frozen intermediate domains for the 180° polarization reversal. The pinned domain fragments led to the reduction of switchable polarization through destruction of long-range polar order. These direct nanoscale observations correlate very well with the performance deterioration seen on bulk specimens and hence broaden the current understanding of the polarization fatigue mechanisms.
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Figures

**Figure 1 | In situ TEM observations on domain and phase evolution during initial poling in BNT52.** a, Bright field micrograph of a grain along its [112] zone axis in virgin state, and b the corresponding electron diffraction pattern prior to initial poling. c, Bright field micrograph and d, electron diffraction pattern of the same grain as in a after initial poling. e, Bright field image of another [112]-aligned grain, and f the corresponding electron diffraction pattern in the virgin state. g, Bright field image and h, electron diffraction pattern of the same grain as in e after initial poling. The directions of the applied fields in the *in situ* TEM experiment are indicated by the bright arrows in c and g, respectively. The ½{ooo} and ½{ooe} superlattice diffraction spots are highlighted by a bright circle and a bright arrow, respectively, in b.
Figure 2 | Evolution of ferroelectric domains during bipolar electric cycling of BNT52. Bright field micrographs of a [112]-aligned grain a, the initially poled state at 30 kV cm$^{-1}$ prior to cycling; b, after 20; c, $10^2$; and d, $2 \times 10^2$ cycles of bipolar electric fields. The electron diffraction pattern of the poled state is shown as the inset in c. No apparent changes in the diffraction pattern were observed during cycling. The positive direction of applied fields in the in situ TEM experiment is indicated by the bright arrow in a.
Figure 3 | Evolution of ferroelectric domains during bipolar electric cycling in another [112]-aligned grain in the same TEM specimen as in Fig. 2. Bright field micrographs of a, the initially poled state at 30 kV cm$^{-1}$ prior to cycling; b, after $10^2$; c, $1.6 \times 10^2$; d, $2 \times 10^2$; e, $5 \times 10^2$; and f, $10^3$ cycles of bipolar electric fields. The electron diffraction pattern of the initially poled state is shown as the inset in a. No noticeable changes were observed during bipolar cycling. The positive direction of applied fields in the in situ TEM experiment is indicated by the bright arrow in a.
Figure 4 | Domain fragmentation during bipolar electric cycling revealed by *in situ* TEM observations on a [111]-aligned grain in the same TEM specimen as in Figs. 2 and 3. a, Bright field micrographs, and b, the corresponding electron diffraction pattern, of the initially poled state at 30 kV cm⁻¹ prior to cycling. c, Electron diffraction pattern from the same area after 10³ cycles of bipolar fields. The $\frac{1}{2}\{001\}$-type superlattice diffraction spots can be barely seen and are indicated by the bright arrow. The fragmentation of large lamellar domains during bipolar cycling is shown by the bright field micrographs, d, after $10^2$; e, $2 \times 10^2$; f, $4 \times 10^2$; and g, $10^3$ cycles of applied field. Higher magnification images of e, f, and g are shown in h, i, and j, respectively. The positive direction of applied fields in the TEM experiment is indicated by the bright arrow in a.
Figure 5 | The frozen domains after fatigue. Bright field micrograph of the domain morphology under a nominal DC field of 40 kV cm\(^{-1}\) after \(1.2 \times 10^3\) cycles in the same grain as in Fig. 4. The direction of the DC field is indicated by the bright arrow.

Figure 6 | Domain size reduction during bipolar electric cycling demonstrated in a bulk BNT52 ceramic specimen. a, Evolution of the \(\frac{1}{2}(311)\) superlattice diffraction peak monitored by X-ray diffraction at different cycling numbers. b, Integrated peak intensity and the full width of half maximum (FWHM) of the \(\frac{1}{2}(311)\) peak as a function of the cycling number.
Figure 7 | Fatigue effect on hysteresis loops in a bulk BNT52 specimen. Evolution of a, polarization, $P$, and b, longitudinal strain, $x_{33}$, hysteresis during fatigue.
Figure 8 | Evolution of the key macroscopic properties during fatigue. a, Evolution of the maximum polarization, $P_m$, remanent polarization, $P_r$, and coercive field, $E_C$, against cycling number $N$. b, Evolution of the longitudinal strain at the maximum (positive) and minimum (negative) points of the strain hysteresis loops. All discrete points are experimentally measured values and their error bars are of the order of the size of symbols and not shown. The straight solid lines in a for $P_m$ and $P_r$ are the fitting curves for the equations presented in the text.
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CHAPTER 6. Conclusions and Suggestions for Future Research

6.1 General conclusions

The primary motivation for the studies presented in this dissertation is to reveal the microstructural origins of the functionality evolution under various electrical processes in ferroelectric perovskites using the electric field in situ TEM technique. Overall, three topics are covered on different electrical processes.

A). Piezoelectricity development during initial poling.

In this topic, three most extensively studied lead-free piezoelectric ceramic systems are investigated. In polycrystalline BNT-BT ceramics, well-developed piezoelectric properties are observed in the P4bm relaxor phase region (x= 6%-9%) even when such compositions are poled at fields significantly lower than both phase transition field and coercive field. This observation is directly against the well-accepted rule that a sufficient poling can only be realized under an electric field that is much higher than the coercive field. Using in situ TEM, the underlying mechanism for such an unusual behavior has been revealed: the poling of the P4bm non-ergodic relaxor phase takes place through the irreversible coalescence of individual nanodomains into thin lamellar domains prior to the phase transition.

In the KNN-based system, the KNN–5.2LS ceramic is found to be extremely responsive to the poling field. Complicated domain switching and phase transitions are observed to occur. The original herringbone domain patterns of mixed tetragonal and orthorhombic phases change to thin lamellar domains when the poling field reaches 8 kV/cm. This process involves domain switching as well as some extent of tetragonal to
orthorhombic phase transition. At 14 kV/cm, a monoclinic $Pm$ phase with $a^0b^+c^0$ oxygen octahedra tilting and antiparallel cation displacements forms, as manifested by the appearance of blotchy domains and $1/2\{oeo\}$ superlattice diffraction spots. These microstructural changes in response to electrical poling fields remain after the field is removed; therefore, they determine the macroscopic properties of poled ceramics. The poling-induced monoclinic phase and its low transition temperature ($T_{M-T}$), together with the room temperature $Amm2/P4mm$ PPB, are responsible for the enhanced piezoelectricity.

For the PPB composition ($x = 0.5$) in polycrystalline $(1-x)$BZT-$x$BCT, the most intriguing finding is the electric field-induced multi-domain to single-domain transformation at very moderate poling fields in the range of 3 ~ 6 kV/cm. A direct correlation is established relating a domain wall-free state to the ultrahigh piezoelectric coefficient. The results suggest that the unique single-domain state formed during electrical poling is a result of a structural transition from coexistent rhombohedral and tetragonal phases to an orthorhombic phase that has an anomalously low elastic modulus. First-principles calculations indicate that incorporating Ca$^{2+}$ and Zr$^{4+}$ into BaTiO$_3$ reduces the differences in structure and energy of variant perovskite phases, and this composition is identified as unique because the variant phases merge into a single phase. The structural instability and elastic softening observed are responsible for the excellent piezoelectric property.
B). Isotropization transformation during electric field reversal.

In the electric field reversal process in polycrystalline BNT-5BT-2La, a highly unexpected isotropization transition was demonstrated to occur through the electric field-induced ferroelectric-to-relaxor transition, which is a direct violation of Curie’s Principle and Coulomb’s Law. This transition was manifested in both macroscopic scale on bulk ceramics and microscopic scale at the individual grain level. It was found that the virgin state of relaxor with $R3c$ and $P4bm$ nanodomain mixtures transformed into the ferroelectric $R3c$ phase with micron-sized lamellar domains during initial poling. Upon electric reversal, the nanodomain mixtures can be recovered through backward transition. This observation was rationalized by a phenomenological model that suggested an extremely slow kinetics of the phase transition compared with the polarization reversal process. The BNT-5BT-2La was identified as an ideal model composition to investigate the transient process in a first-order phase transition, for which ultrafast characterization tools are not required.

C). Fatigue behavior during bipolar electric cycling.

In this topic, two representative ceramics are investigated. For the lead-free composition of BNT-5BT-2La, in situ TEM was employed for the first time to investigate the domain structure evolution during electric fatigue. In complementary to the domain wall pinning effect, a novel fatigue mechanism of domain fragmentation was discovered. The nanodomains in the virgin state transformed to large lamellar domains during the first quarter cycle of field through a phase transition; these large domains were disrupted gradually during the subsequent bipolar electric cycling; and finally much less responsive
domain fragments were formed. The fragmentation was suggested to be resulted from the frozen intermediate domains for the 180° polarization reversal. The pinned domain fragments led to the reduction of switchable polarization through destruction of long-range polar order.

For the 0.7PMN-0.3PT ceramic, domain evolution within individual grains was directly visualized during the fatigue process. It was found that the domain switching capability was substantially suppressed after 10^3 cycles of bipolar fields, leading to an immobilized domain configuration thereafter. Correspondingly, a pronounced degradation of the functionality of the ceramic was manifested, accompanying with a coercive field bumping and polarization current density peak broadening. The reduction of the polarization, dielectric constant, and piezoelectric coefficient were found to follow a power-law relation. Both domain wall pinning and seed inhibition mechanisms were found to be responsible for the observed fatigue behaviors, but with a leading contribution from the former.

6.2 Suggestions for future studies

The electric field in situ TEM technique employed in this study has been demonstrated to be a powerful and promising probing tool to reveal the underlying mechanism for the functionality evolution with a microscopic insight. Based on the research accomplishments represented in this dissertation, the following future work is suggested:

A). For the PPB composition (x = 0.5) in the polycrystalline (1-x)BZT-xBCT system, the most important feature during initial poling is the electric field-induced single-domain
state. The crystal structure cannot be directly inferred due to the lack of superlattice diffraction spots in its electron diffraction patterns. The proposed orthorhombic symmetry shall be verified through the convergent beam electron diffraction (CBED) technique in the future. On the other hand, the orthorhombic phase in the composition of $x = 0.5$ has been known to appear within the temperature range of 0 - 30 °C. With the assistance of a recently developed new in situ TEM technique with combined capabilities of cooling/heating and applying electric field simultaneously, the microstructural evolution of the orthorhombic single-domain phase can be effectively monitored during cooling and subsequent heating while maintaining an applied electric field. When the temperature is out of the orthorhombic phase region, different phase variants are expected to appear ($T > 30$ °C for the tetragonal phase while $T < 0$ °C for the rhombohedral phase). Correspondingly, the single domain morphology is most likely switched to a multi-domain configuration.

B). In this dissertation, electric field-induced phase transitions have been widely demonstrated. To better reveal the microstructural evolution during phase transition, especially for the direct imaging of local phase nucleation event during electric reversal process, a time-dependent in situ TEM study is desired. To obtain the time-resolved micrographs, electrical pulses with a period varying from nanosecond to microsecond may be applied. This approach may have broad applications for the investigation of various phase transition behaviors, for example, ferroelectric↔ferroelectric, relaxor↔ferroelectric, and antiferroelectric↔ferroelectric phase transitions.

C). For the three most promising lead-free ceramic systems (namely BNT-BT, KNN-based, and BZT-BCT solid solutions), the current thesis research is mainly focused on
understanding the microstructural origin for piezoelectricity development during the initial poling process. For real devices, however, these materials will be subject to repetitively applied electric fields, either bipolar or unipolar. In this regard, microscopic mechanisms for the fatigue behaviors of these three systems are suggested to be investigated in the future, using the electric field *in situ* TEM technique.
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APPENDIX: Publication List


10. X. Liu, H.Z. Guo, and X. Tan: Evolution of structure and electrical properties with lanthanum content in [(Bi$_{1/2}$Na$_{1/2}$)$_{0.95}$Ba$_{0.05}$]$_{1-x}$La$_x$TiO$_3$ ceramics, *J. Eur. Ceram. Soc.* 34, 2997 (2014).


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