Insights into performance stability of lead-free piezoelectric ceramics

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Insights into performance stability of lead-free piezoelectric ceramics

by

Zhongming Fan

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The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this dissertation. The Graduate College will ensure this dissertation is globally accessible and will not permit alterations after a degree is conferred.

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Developing materials with superior functional properties is the primary goal of materials engineering. Nonetheless, the stability of performance during practical service should be of equal importance. This is, with no doubt, also true for piezoelectric materials.

The working conditions of piezoelectric materials can lead to either gradual or abrupt degradation in their functional properties. First, fatigue. In analogy to structural materials under cyclic stresses, the piezoelectric properties deteriorate during the electric field cycling. Second, aging. While the service is paused and the piezoelectric material is sitting idle, the piezoelectric properties will decay over time. Third, thermal depolarization. Electronic devices are not necessarily working at room temperature. The piezoelectric properties may fluctuate with temperature change, or even vanish above a threshold value.

These three major forms of performance instability of piezoelectric materials have been studied for decades. Exploring the microstructural origins can help to find approaches to mitigate the degradation. The current dissertation aims to investigate the micromechanisms of electric fatigue, polarization aging, and thermal depolarization in lead-free piezoelectric ceramics. Electric field in-situ transmission electron microscopy (TEM) is utilized to directly monitor the microstructure evolution during electric cycling, aging, and temperature rise.
CHAPTER 1. INTRODUCTION

1.1 Background and Motivation

The past fifteen years witnessed a surging enthusiasm in seeking for new lead-free piezoelectric ceramics. With the expanding access to the high-end transmission electron microscopes (TEM), more and more researchers are currently eager to either verify the proposed hypotheses or identify new mechanisms underlying the piezoelectric performance, including its stability.

Among the advanced TEM techniques, in-situ TEM is one of the most powerful. It enables recording the real-time response in a specimen under an external stimulus, such as heating, cooling, stress, magnetic field and electric field, or their combination. Therefore, in-situ TEM is an ideal tool to study the performance stability in piezoelectric ceramics because it can, to the greatest extent, mimic the actual working conditions.

Fatigue is a common form of failure in materials subject to repeated cycling of forces. When the force is of mechanical nature such as stress or strain, fatigue failure manifests itself as the initiation and growth of cracks, which eventually lead to catastrophic fracture. For piezoelectric materials in use, the force is an electric field. Upon electric field cycling, piezoelectric ceramics are also susceptible to fatigue, not necessarily a crack formation, but the degradation of piezoelectric/ferroelectric properties instead. In the meantime, raising the working temperature may also risk diminishing the properties in the compositions with poor thermal stability. Even if no cycling or heating is applied, the performance could decay with the aging time.

To mimic the working conditions associated with these three types of performance instability, special specimen holders are needed for in-situ TEM experiments. For fatigue and aging experiments, an electric biasing holder should be used. To study the thermal instability,
hot stage holder has to be employed. The microstructural evolution is expected to be recorded during the cycling/heating/aging.

1.2 Dissertation Organization

This dissertation will cover the in-situ TEM results on fatigue, aging, and thermal depolarization in BaTiO$_3$- and (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-based ceramics.

Chapter 2 presents an overview of piezoelectricity, lead-free piezoceramics, and the three forms of performance instability.

Chapter 3 is an article published in Acta Materialia. An ideal amplitude window against electric fatigue in BaTiO$_3$-based lead-free piezoelectric materials is discovered.

Chapter 4 is a manuscript under review with Scripta Materialia. A comparative study on two (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-based relaxors is carried out.

Chapter 5 is an article published in Journal of the European Ceramics Society. The accumulation of point defect is directly visualized in an aged BaTiO$_3$-based piezoceramic.

Chapter 6 is an article published in Physical Review Materials. The enhanced thermal stability in a (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-based ceramic composite is investigated via comprehensive microscopy characterizations.

Chapter 7 summarizes the main conclusions of this dissertation and suggests some future studies.
CHAPTER 2. LITERATURE REVIEW

2.1 Piezoelectricity and Piezoelectric Materials

Piezoelectricity refers to the linear coupling between applied mechanical stress and electric displacement. Piezoelectric materials, which possess the ability to convert electrical energy to mechanical and vice versa, are widely used in commercial applications such as sensors and actuators, etc [1,2]. Piezoelectricity is only allowed in crystals with absence of centrosymmetry [3]. A special sub-group of piezoelectric is ferroelectric. The cation displacements in the crystal lattice give rise to the spontaneous polarization in ferroelectric crystals. The polarization can be switched by an external electric field when it exceeds the coercivity $E_C$, manifested by the polarization - electric field hysteresis loop ($P$-$E$ loop) (Fig. 1) [4]. In order to minimize electrostatic and elastic distortion energy, grains in ferroelectric polycrystals are divided into many domains, which are separated by domain walls, [5]. To develop piezoelectricity, a strong DC field needs to be applied to ferroelectric polycrystals to switch the domains and align the polarization in individual grains, that is called an electric poling process (Fig. 2) [6]. Although a single crystal can exhibit much better piezoelectric performance, polycrystalline ceramics production costs much less. Most importantly, the best performing Pb(Zr$_{1-x}$Ti$_x$)O$_3$ piezoceramics are almost impossible to be grown into large crystals [3].
2.2 Lead-Free Piezoelectric Ceramics

Piezoelectric materials play the core roles in numerous applications, including energy harvesting [1,8], medical imaging [1,9], and minimally invasive surgery [10]. In the past six decades, ferroelectric Pb(Zr\(_\text{1-x} Ti\text{x}\))O\(_3\) ceramics, which contain >60 wt.% of lead, have been dominating the market for high-performance actuators and transducers because of their excellent performance and the ease of fabrication. [1]. The outstanding and reliable piezoelectric properties in Pb(Zr\(_\text{1-x} Ti\text{x}\))O\(_3\) is attributed to the temperature-independent morphotropic phase boundary (MPB), which separates the tetragonal and rhombohedral perovskite phases [1]. Due to the severe environmental concerns of lead, the worldwide search for lead-free piezoelectric materials has been extremely active in the past fifteen years [11,12]. These intense efforts have led to the identification of three major lead-free ferroelectric solid solution systems with piezoelectric properties comparable to those of Pb(Zr\(_\text{1-x} Ti\text{x}\))O\(_3\): the (K\(_{0.5} Na_{0.5}\))NbO\(_3\)-based [13,14], the (Bi\(_{1/2} Na_{1/2}\))TiO\(_3\)-based [12,15], and the BaTiO\(_3\)-based [16,17] compositions. The distinctions in the properties of the three lead-free solid solutions are schematically illustrated in a \(d_{33}\) vs. \(T_c\) map, as shown in Fig. 3. The piezoelectric coefficient \(d_{33}\) evaluates the piezoelectric performance at room temperature, and the Curie point \(T_c\) implies the performance stability over an extended temperature range. Generally speaking, BaTiO\(_3\)-based ceramics exhibit outstanding small signal piezoelectric properties (e.g. \(d_{33} > 600 \text{ pC/N}\)), while...
their working temperature is quite limited due to their low Curie point ($T_c \sim 100 \, ^\circ C$). Modified $(K_{1-x}Na_x)NbO_3$ compositions can achieve values of $d_{33}$ comparable to Pb(Zr$_{1-x}$Ti$_x$)O$_3$ and have a moderate Curie point ($> 200 \, ^\circ C$), but suffer from the low reproducibility. $(Bi_{1/2}Na_{1/2})TiO_3$-based, in spite of the mediocre $d_{33}$ values and the low depolarization temperature, can develop giant electro-strains, but the concerns are considerable hysteresis and the requirement of intense applied field.

### 2.2.1 BaTiO$_3$-based ceramics

BaTiO$_3$ is the first simple oxide displaying ferroelectricity, and its excellent dielectric properties have put it in the dominant position for ceramic capacitors [18]. However, pure BaTiO$_3$ does not display satisfactory piezoelectric properties due to the absence of phase boundaries at room temperature [19]. In 2009, the development of Ca- and Zr-doped compositions, the Ba(Ti$_{0.8}$Zr$_{0.2}$)O$_3$–(Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$ pseudo-binary system rejuvenated the exploration for BaTiO$_3$-based compositions as piezoelectric materials [16]. The ultrahigh piezoelectric coefficient, $d_{33} > 600 \, \mu C/N$, was originally credited to the existence of a tricritical triple point [16]. Later on, people realized that Ba(Ti$_{0.8}$Zr$_{0.2}$)O$_3$–(Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$ solid solution system might have an even more complicated phase diagram (Fig. 4) [20]. Based on this, recent atomistic modeling reveals that the intermediate orthorhombic phase is the origin of the high piezoelectric property [21]. TEM analysis also shows that the orthorhombic phase exists in a unique single domain state in polycrystalline grains, which effectively promotes the piezoelectric performance [17,22].
2.2.2 (K$_{1-x}$Na$_x$)NbO$_3$-based ceramics

The MPB composition of (K$_{1-x}$Na$_x$)NbO$_3$ solid solution system is (K$_{0.5}$Na$_{0.5}$)NbO$_3$. However, pure (K$_{0.5}$Na$_{0.5}$)NbO$_3$ does not show satisfactory piezoelectric properties. In 2004, Saito et al. [13] reported a $d_{33}$ value of 416 pC/N with a high Curie temperature of 253 °C in a textured Li, Ta, and Sb co-doped polycrystalline ceramic. A new era of lead-free piezoelectric ceramics was initiated by this breakthrough discovery. After that, the world record of the best lead-free piezoceramic has been continuously broken by (K$_{0.5}$Na$_{0.5}$)NbO$_3$-based compositions, such as $d_{33} = 570$ pC/N in a non-textured polycrystalline ceramic [23] and $d_{33} > 700$ pC/N in a textured ceramic [24].

Different from the traditional Pb(Zr,Ti)O$_3$, the enhanced $d_{33}$ in chemically modified (K$_{0.5}$Na$_{0.5}$)NbO$_3$ is a result of the orthorhombic-tetragonal polymorphic phase transition temperature, $T_{O-T}$, being compositionally shifted downward to the vicinity of room temperature [25]. At much lower temperature, another polymorphic phase transition between the orthorhombic and the rhombohedral phases ($T_{R-O}$) is present [26]. Considering that the phases’ coexistence benefits the piezoelectricity, a straightforward idea to maximize $d_{33}$ is to bring these two polymorphic phase transition temperatures closer, in order to create a narrow temperature window within which all three different phases can coexist (Fig. 5). This idea has been proved viable in some very complex compositions with many dopants, which include not only Li$^+$, Sb$^{5+}$, and Ta$^{5+}$ but also other species like Bi$^{3+}$ and Zr$^{4+}$ [27]. Unfortunately, involving such a variety of minor elements will naturally impose difficulties regarding the reproducibility.

Fig. 5. Phase transition behavior of K$_{0.48}$Na$_{0.52}$Nb$_{0.98}$Sb$_{0.02}$O$_3$ ceramics. Ref. [27]
2.2.3 (Bi\textsubscript{1/2}Na\textsubscript{1/2})TiO\textsubscript{3}-based ceramics

The (Bi\textsubscript{1/2}Na\textsubscript{1/2})TiO\textsubscript{3}-based ceramics, as shown in Fig. 4, does not have advantages over BaTiO\textsubscript{3}- or (K\textsubscript{1-x}Na\textsubscript{x})NbO\textsubscript{3}-based compositions, with respect to either piezoelectric coefficient or the Curie point. Actually, (Bi\textsubscript{1/2}Na\textsubscript{1/2})TiO\textsubscript{3}-based ceramics are relaxor ferrielectric in the unpoled state and transform to the ferroelectric state and develop piezoelectricity during poling [15,28]. In the most studied (1-x)(Bi\textsubscript{1/2}Na\textsubscript{1/2})TiO\textsubscript{3}–xBaTiO\textsubscript{3} binary system, \(d_{33}\) is maximized at \(x = 0.06\sim0.07\) because of the poling-induced \(R3c/P4mm\) MPB (Fig. 6) [15,29]. Unfortunately, the relaxor nature of (Bi\textsubscript{1/2}Na\textsubscript{1/2})TiO\textsubscript{3}-based compositions further narrows the working temperature window by pulling the upper limit from Curie point (\(T_c\)) down to a much lower depolarization temperature (\(T_d\)).

Even though the low \(T_d\) gives (Bi\textsubscript{1/2}Na\textsubscript{1/2})TiO\textsubscript{3}-based ceramics poor piezoelectric performance, but further lowering \(T_d\) close to room temperature leads to their outstanding feature of developing giant electro-strains, e.g. 0.45% at 80 kV/cm [30]. Since the giant electro-strain is owing to the fact that the relaxor-ferroelectric transformation becomes reversible at room temperature, the pre-existing ferroelectric seeds in the relaxor matrix should be capable of facilitating the phase transition. This has been proved to be helpful through either artificially constructing a ferroelectric/relaxor composite [31] or to take advantage of the core/shell
microstructure that is common in (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-based ceramics [32,33]. A fine adjustment to the Nb-doping concentration in 0.96[Bi$_{1/2}$(Na$_{0.84}$K$_{0.16}$)$_{1/2}$](Ti$_{1-x}$Nb$_x$)O$_3$–0.04SrTiO$_3$ solid solution system leads to a giant strain of 0.70% at 50 kV/cm [34], as shown in Fig. 7. Such a strain value is remarkable for non-textured polycrystalline ceramics, although the thermal stability and the cycling reliability are still needing improvements.

2.3 Cyclic Stability --- Fatigue

Electric fatigue in ferroelectric and piezoelectric ceramics is reflected by the reduction of switchable polarization and achievable strain upon repeated electric field cycling [35-38], as shown in Fig. 8. The remanent polarization, $P_r$, is significantly reduced while the coercive field, $E_c$, is found to increase. The strain vs. electric field curves become asymmetric and the maximum achievable strain is greatly suppressed [38]. Such performance degradation has been the principal concern for their device applications in non-volatile random access memories [39-41] and piezoelectric actuators [36,39]. The decayed electrical properties can be largely recovered by thermal annealing at a temperature above the Curie point [36]. The electric field-induced strain, a manifestation of
electromechanical coupling in piezoelectric materials, implies that electric fatigue also has a mechanical component. The incompatible piezoelectric strains at domain walls and grain boundaries can potentially initiate and grow microcracks at these sites [42,43]. Apparently, once microcracks are formed, the damage is permanent and non-recoverable. This thesis research is to focus on the polarization degradation prior to microcrack nucleation.

As is well known, the polarization state and polarization reversal in ferroelectric crystals are manifested by ferroelectric domain arrangements and their transformations [1,3]. Consequently, ferroelectric domains dictate the dielectric, piezoelectric, and ferroelectric properties of the crystal. It is logical to reach the conclusion that direct imaging of domains and their evolution during electric cycling is essential to uncovering the underlying mechanisms of electric fatigue. Piezoresponse force microscopy (PFM), owing to its capability of visualizing the ferroelectric domains, is so far the most widely employed tool to provide the microscopic information on electric fatigue [44-49]. However, PFM has its apparent drawbacks. First, PFM is most suitable for ferroelectric thin films since it only records the morphology change on the top surface during fatigue. Second, PFM is not capable of revealing the crystal structure and its transition. It has been known that lead-free piezoceramics experience complicated crystal structure changes under electric fields [15,17] and phase transitions profoundly influence their fatigue behavior [50,51]. Third, PFM is not capable of imaging the defects. It is commonly accepted that electric fatigue is a defect-chemistry induced phenomenon in ferroelectrics [52], so that the defect-domain interaction should be the most essential information accounting for the electric fatigue. In addition, the scanning nature of the technique limits its time resolution [53].

Transmission electron microscopy (TEM) effectively circumvents all the mentioned technical hindrances of PFM [54-57]. For electric fatigue study, electric field in-situ TEM
technique possesses unique advantage due to its ability to monitor the microstructural evolution in one particular grain during both the initial $E$ field poling and the subsequent cycling [15,43,44]. However, only ex-situ TEM fatigue in piezoelectric ceramic has so far been reported [58]. In this dissertation, electric field in-situ TEM technique will be employed to investigate the mechanisms of electric fatigue in two lead-free bulk ceramics (Chapter 3 & 4).

2.3.1 Macroscopic electric fatigue behaviors

During service of piezoelectric devices, the ferroelectric polycrystalline ceramics are subject to repeated electric fields, and their functional properties will deteriorate. Electric fatigue has been a long-lasting research topic in ferroelectrics community for several decades due to technological relevance. A fingerprint of electric fatigue in ferroelectric oxides is the reduction of switchable polarization and the increase of the coercive field during repetitive polarization reversal (Fig. 9). To readers’ convenience, a couple of important parameters out of a $P$-$E$ loop are marked in Fig. 10. Remanent polarization, $P_r$, is the polarization under zero field. In spite of the existence of the non-switchable polarization $P_{ns}$, switchable polarization is always defined as

![Fig. 9. Hysteresis loops before and after bipolar fatigue. Ref. [37]](image)

![Fig. 10. Notation for switching characteristics extracted from the polarization hysteresis loop. Ref. [36]](image)
Coercive field, $E_C$, is the magnitude of electric field when the macroscopic polarization is zero. It represents the field needed to reverse the polarity in the ferroelectric materials. After the ferroelectric material is fatigued, the ferroelectric domains will not be as mobile as the pre-fatigue state. So, the domains can no longer be aligned as complete as that shown in Fig. 3. In addition, the original $E_C$ will become insufficient to switch the domains to the opposite direction. As a consequence, the switchable polarization is decreasing while the coercive field tends to increase along with the electric cycling (Fig. 11) [59].

It should be noted that sometimes the reduction in maximum polarization ($P_{\text{max}}$) is also recorded in electric fatigue tests (Fig. 11), but actually rarer than $2P_r$. The reason is that the most critical figure of merit for piezoelectric materials is the piezoelectric coefficient $d_{33}$, which is theoretically proportional to the spontaneous polarization ($P_s \approx P_r$). So, the reduction of the switchable polarization should be able to reflect the deterioration in piezoelectric properties, while the decrease in maximum polarization cannot. Another reason is that ferroelectric materials can be used as ferroelectric random access memories (FeRAM), in which the magnitude and the long-term reliability of the switchable polarization are the only two considered

$$P_{SW} = 2P_r$$  \tag{1}
qualities [60]. Thus, the change in switchable polarization is the most commonly collected data in electric fatigue studies.

As discussed above, the decrease in switchable polarization and the increase in coercive field always come in pair. So, in many publications, people do not incorporate data for $E_C$ after they’ve already had the $2P_r$. However, the coercive field is still of meaningfulness for the fatigue study, not the absolute value, but the difference between the positive and negative $E_C$ (Fig. 12) [58]. The internal bias is defined as,

$$E_{bias} = -\frac{E_{c,-} + E_{c,+}}{2}$$ (2)

The built of $E_{bias}$, manifested by the shift of $P$-$E$ loop along the horizontal $E$ axis, indicates that one of the two opposite polarities is being stabilized. This will be discussed in more details later.

For the piezoceramics used in actuators, $S$-$E$ loops may be more indicative than $P$-$E$ loops [34]. Under such circumstances, the electro-strain must be the primary property to be looked at during the fatigue. As shown in Fig. 8, the fatigue-induced change in $S$-$E$ loops is not as straightforward as that in $P$-$E$ loops. An apparent asymmetry between the left and right wings is commonly seen in the fatigued state [61]. Therefore, the evolution of electro-strain as a function of cycle number is always displayed in a more complicated way (Fig. 13).

![Figure 13](image)
As can be seen in Figs. 11-13, the *Number of cycles, N* (horizontal axis) is always plotted in log scale. This is because that the degradation during the electric fatigue is usually found to obey the logarithmic relation [62], proposed by Brennan for the first time:

\[ P = P_0 + A \log(N) \]  

(3)

However, the real fatigue degradation does not always follow the logarithmic relation perfectly; sometimes there could be a huge deviation (Fig. 14) [63]. Generally, the log relation is only obeyed after the initial cycling stage has passed (region I). In some cases, there can even be an “anti-fatigue” stage during which the switchable polarization is recovered from the degraded value (region II). The mechanism behind this self-recovery is still under debate.

### 2.3.2 Electric fatigue of lead-containing ceramics

Since the electric fatigue has severely hindered the long-term operation and reliability of ferroelectric materials, a large body of experimental and theoretical studies, throughout the past several decades, has been conducted primarily on Pb(Zr\textsubscript{1-x}Ti\textsubscript{x})O\textsubscript{3}-based compositions to elucidate the origin of electric fatigue. The ultimate goal of these researches is to find out solutions to the electric fatigue or inspire people to come up with new compositions which perform against the fatigue degradation.

First, the impacts of several external conditions on piezoceramics’ electric fatigue behavior will be discussed:
1) **Electrode materials**

Traditional Pb(Zr$_{1-x}$Ti$_x$)O$_3$-based devices use metallic electrodes, such as Ag, Au or Pt. But it was found that conductive oxide electrodes, e.g. RuO$_2$, IrO$_2$ and SrRuO$_3$ are able to strongly improve the fatigue resistance [64]. As demonstrated in Fig. 15, the PZT with Pt electrodes starts to show fatigue degradation from $10^8$ cycles. On the other hand, the PZT with RuO$_x$ electrode displays fatigue-free till $10^{11}$ cycles.

It should be noted that the electrode materials’ effect on the fatigue behaviors is always seen in thin films only, in which the ferroelectric/electrode interface plays an important role. There are two main possible fatigue mechanisms.

i. **Seed Inhibition Mechanism:** It has been widely accepted by the ferroelectrics community that the domain reversal is realized through a process including the seed (with opposite polarity) nucleation, seed growth and the domain wall motion [65]. The “seed inhibition” model proposes that the domain mobility is already suppressed before the seed growth. A ferroelectric film is divided into regions, of which the switching is provided by a finite number of seeds belonging to it (Fig. 16). Along with the electric cycling, ionic or electronic defects will accumulate near the ferroelectric/electrode interface. These can be created by charges injected from the electrode or the charges that can arrive from the bulk of the material as a result of
electromigration during the electric stressing of the capacitor [53]. As a consequence, the growth of the nucleated seeds are blocked.

ii. Local Phase Decomposition mechanism: The poled state in ferroelectric thin film has extremely large depolarization field with the direction opposite to the applied field, but screened by the free charges in the electrodes. As the domain reversal initiates, the seed with the opposite polarity nucleates. It should be noted that the domain wall between the new seed and the non-reversed rest portion has the head-to-head-configuration, which generates extremely large unscreened depolarization field. This depolarization field is located near the ferroelectric/electrode interface, so it is able to produce an intensive injected current from the electrode (Fig. 17), which eventually causes local phase decomposition at the nucleation sites, and consequently, fatigue [66].

The above two fatigue mechanisms show that the injected charge from the electrode to the ferroelectric ceramic is the fundamental cause of the seed inhibition/phase decomposition at the ferroelectric/electrode interface. So, it is not hard to understand that the electrode material is able to affect the fatigue behaviors. However, in bulk ceramics, the influence from the ferroelectric/electrode interface, if any, will be overwhelmed by the influence from the ferroelectrics interior due to the huge difference in the thickness of the two sections. Instead, some other factors are going to exert their influences on the fatigue behaviors, such as field polarity, field amplitude, cycling frequency, and testing temperature.
2) Field polarity

In some devices like ferroelectric memories, the field has to be switched back and forth between positive and negative polarities. This kind of field is called bipolar field. In some other devices like actuators, the field is only needed to be repetitively loaded/unloaded, which is called unipolar field. It was found that bipolar cycling generally leads to a more severe fatigue degradation than unipolar cycling (Fig. 18) [67].

It should be noted that there are actually two ways to measure the unipolar fatigue behaviors [68]. One is to apply a full cycle (bipolar) at every unipolar cycling interval (Fig. 19 b & d), another is applying a half cycle (unipolar) with the same polarity with the unipolar cyclic field (Fig. 19 a & c). The conclusion in the last paragraph, that unipolar cycling generates less fatigue degradation, is applicable when the value of $P$ or $S$ are extracted from the half cycle test. If the test field is a full cycle, the asymmetry in $P$-$E$ and $S$-$E$ loops will be noticed. Then the internal bias field ($E_{bias}$) (Fig. 12) and the ratio of the two strain wings (Fig. 13) should be taken into account. But in the bipolar fatigued sample, the $P$-$E$ and $S$-$E$ loops seldom display asymmetry. So, when quantifying the
unipolar fatigue degradation, it is the half cycle field that is presumably applied at each fatigue interval. On the other hand, the unipolar-fatigue-created asymmetry can be considered as an analogy to the “aging” effect, which is also a reliability concern in ferroelectric materials other than fatigue.

3) Field amplitude

The field amplitude effect on the electric fatigue behavior is analogous to that in mechanical fatigue. The well-known fatigue life vs. stress diagram (S-N curve, Fig. 20) shows that the fatigue degradation is always more severe under higher cycling stress in steel and other structural materials. In analogy, higher electric field will generally give rise to a more severe fatigue degradation in ferroelectric materials [69,70], as demonstrated in Fig. 21.

However, there is a violation of this rule found in thin films of BiFeO$_3$ and Bi-based layered perovskites [71,72]. It is believed that higher field is able to prevent the charges from accumulating at the ferroelectric/electrode interface. So, an opposite-field amplitude-fatigue resistance relation is possible in those ferroelectric thin films which have high conductivity.
4) Cycling frequency

It is generally believed that slower cycling could result in more severe fatigue degradation, as shown in Fig. 22 [73]. However, there are some violations of this common rule discovered, where the fatigue behaviors seem independent from the measuring frequency [74].

It should be noted that the electric cycling always has a side effect on ferroelectric ceramics, the self-heating due to the hysteretic loss [75]. Different cycling frequencies correspond to different level of self-heating so that the sample might be heated up to different temperatures. Then, the frequency effect on the fatigue behavior could be essentially a temperature effect, which will be discussed next.

5) Testing temperature

The temperature effect on the fatigue behavior is rather complicated. The previous results indicated both an improvement [76,77] (Fig. 23) and a deterioration [78,79] (Fig. 24) of the fatigue resistance with increasing temperature. When the sample is cycled at a temperature that is close to the Curie point (T_C), it is actually subject to a combined fatigue and annealing. Fatigue is degrading the ferroelectric properties, but the annealing is restoring the degradation [80], as long as no microcracks have formed. On the other hand, what
makes the temperature effect on fatigue complicated is that the ferroelectric ceramics could have different phases at different temperatures. This will be discussed in detail later.

In addition to the external testing conditions discussed above, the impact of the ferroelectric ceramic compositions on fatigue has also been well studied.

6) Chemical composition

It is commonly accepted that electric fatigue is a defect-chemistry induced phenomenon in ferroelectrics of both thin film and bulk forms [53]. 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. The most common charged defect in perovskite ceramics is oxygen vacancy. Even though oxygen vacancies can always form during high temperature sintering,

\[ O_0^\times \leftrightarrow V_0^- + 2e^- + \frac{1}{2} O_2(g) \]  \hspace{1cm} (4)

their concentration cannot be very high in the absence of volatile species, such as Pb,

\[ Pb^\times_{Pb} + O_0^\times \leftrightarrow V_{Pb}^{\prime\prime} + V_0^- + PbO(g) \]  \hspace{1cm} (5)

or acceptor dopants, such as Fe occupying Ti site in PZT,

\[ 2Fe^{3+} \leftrightarrow 2Fe^{4+}_{Ti} + V_0^- \]  \hspace{1cm} (6)
Since undoped PZT intrinsically contains a certain amount of oxygen vacancies due to the Pb and O evaporation, fatigue degradation always occurs. More severe fatigue degradation should be expected in acceptor-doped PZT because of the increased amount of oxygen vacancies. On the other hand, donor dopants should mitigate the fatigue degradation in PZT, ascribing to their ability to reduce the amount of oxygen vacancies.

However, the real situation is much more controversial. La-doping (donor doping) in PZT indeed has a positive effect on the fatigue resistance (Fig. 25) [81], but Fe-doping (acceptor doping) has been found to positively affect the fatigue resistance as well (Fig. 26) [82]. Moreover, Sr-doping (isovalent doping) can result in better fatigue resistance (Fig. 27) [83]. Actually, many articles dealing with the effect of doping on fatigue behavior have reported inconsistent, even contradictory results.

The interaction between charged defects and ferroelectric domain switching dynamics can be described with the “domain wall pinning” model. The initially charge-neutral domain walls can
become polarized during electric reversal, which will enhance their interactions with defects [47]. In a word, the resulting fatigue effect is generally due to the formation of mesoscopic structures of interacting charged defects and polarized domain walls [63]. 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 [63]. As a system, the charged defects and polarized domain walls form a self-stabilizing configuration through charge compensation [63]. For example, ferroelectric materials contain only “head-to-tail” domain configurations in the virgin state, guaranteeing the neutralization of the domain walls (Fig. 28) [84]. Under the initial loading of electric field, the original domain configuration transforms into a nearly single domain (Fig. 1). During the subsequent electric cycling, the domain is continuously switching from the poled single domain state to another single domain state with opposite polarity (Fig. 2). This 180° domain switching will not be completed through one single step, for example from to [111] to [111̅] directly in rhombohedral phase. Instead, the process always contains multiple steps, which are two intermediate 71° switchings. Two exemplified routes are shown in Fig. 29. The charged domain walls are possibly created through these intermediate switching events. Imagine that two adjacent unit cells are
about to start the $180^\circ$ switching at the same time (Fig. 30). If they go through different routes, like those shown in Fig. 29. Then head-to-head or tail-to-tail configuration are created at intermediate steps, which makes the domain wall no longer neutral. On the other hand, 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 (Fig. 31). Such interactions result in the domain wall pinning and nucleation inhibition through deactivating domain switching events. All these microscopic processes contribute to the decay of switchable polarization upon electric cycling.

The “domain wall pinning” model is so far the most accepted electric fatigue mechanism. Several experimental results have successfully supported the validity of this model. Clusters of charged point defects are directly observed adjacent to domain walls in a fatigued Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$–PbTiO$_3$ specimen [60]. This proves that the originally neutral domain walls indeed become charged after extensive electric cycling and could serve as trapping sites for charged point defects.
In PMN–PT, the domain walls are pinned and in turn, lose their mobility; but the overall domain morphology barely changes during fatigue. According to the proposed “domain wall pinning” model, as soon as the head-to-head or tail-to-tail domain walls are pinned, the two new domains on both sides of the pinned wall will be preserved. Eventually, the original large domain can be fragmented into a great number of smaller domains.

Simons et al. [85] speculated a domain fragmentation process from their neutron diffraction data, in which the pattern from the fatigued state becomes indistinguishable from the virgin state (Fig. 33). On top of the diffractometer, the piezoresponse force microscopy (PFM) [86] and TEM [87] both provide direct observations of the domain fragmentation process during electric fatigue, as displayed in Fig. 34 and 35, respectively.

Fig. 32. In situ TEM experiments on the 0.7Pb(Mg1/3Nb2/3)TiO3–0.3PbTiO3 ceramic. Bright field micrographs of a grain along its [101] zone-axis (a) in its virgin state, (b) under DC field of 10 kV/cm during poling, and (c) at zero field after 10^3 cycles of bipolar 10 kV/cm. (d) The selected area diffraction pattern recorded at the virgin state. The positive direction of the applied fields is indicated by the bright arrow in (b). The fatigue produced defects are marked by the bright triangle in (c). Ref [59]

Fig. 33. Neutron diffraction peak shapes for (left) (111), and (right) (200) reflections after fatigue. Ref. [85]
7) Crystal structure

Different crystal structures have distinctive fatigue behaviors. A comprehensive study has been conducted by Jiang et al. in (Pb,La)(Zr,Ti)O₃ ternary system where the crystal structure can be easily changed by slight adjustment in composition (Fig. 36) [88]. As seen in Fig. 37 & 38, PLZT of rhombohedral symmetry with composition (7/65/35) and tetragonal symmetry with composition (9.5/65/35) show little or no fatigue compared with those close to the phase boundary (8/65/35 and 8.4/65/35).

In addition, antiferroelectrics is found to usually have a stronger fatigue resistance than ferroelectrics [89].
Electric fatigue study on lead-free piezoelectric ceramics is still in its early stage and hence incomprehensive.

1) BaTiO$_3$-based ceramics

As discussed in Section 1.2.1, 0.5Ba(Zr$_{0.2}$Ti$_{0.8}$)O$_3$–0.5(Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$ (BZT–BCT), originally discovered in 2009, is a promising lead-free piezoelectric ceramic with excellent piezoelectric properties (e.g. $d_{33}$>600 pC/N). Its fatigue properties have not been studied until recent years (Fig. 39). Only <10% degradation in remanent polarization ($2P_r$) after $10^7$ bipolar cycles and <15% decrease in unipolar electro-strain ($S_{\text{max}}$) after $5\times10^6$ unipolar cycles are detected [90,91]. A PFM study compares the domain morphology before and after the intensive
electric cycling and found out that the original lamellar ferroelectric domains are no longer present in the fatigued state (Fig. 40) [92].

![Fig. 40. Domain morphology (A) before and (B) after the electric fatigue in BZT-BCT. Ref. [92]](image)

2) \((K_{1-x}Na_x)NbO_3\)-based ceramics

Zhang et al. [50] reported that the 0.95\((K_{0.5}Na_{0.5})NbO_3\)–0.05LiSbO_3 ceramic lost about 50% of its polarization after only 1,000 cycles. However, with only 1–2 wt.% addition of CaTiO_3, the ceramic showed a fatigue-free behavior up to \(10^4\) cycles, as shown in Fig. 41. Inspired by this work, CaZrO_3 addition is also used to significantly improve the fatigue resistance of \((K_{0.5}Na_{0.5})NbO_3\)-based ceramics [93-95] (Fig. 42). It should be pointed out that the

![Fig. 41. The relative change of remanent polarization during bipolar electric cycling of the undoped and CaTiO3 doped KNN-based ceramics. Ref. [50]](image)

![Electric Field (kV·mm⁻¹/scale)](image)

Fig. 42. Unipolar S-E curves of CZ doped KNN ceramics before and after \(10^4\), \(10^5\), \(10^6\), and \(10^7\) unipolar fatigue cycles. Ref. [95]
orthorhombic-tetragonal polymorphic phase transition in the 0.95(K$_{0.5}$Na$_{0.5}$)NbO$_3$–0.05LiSbO$_3$ ceramic occurs around room temperature while CaTiO$_3$ addition shifts this transition down to -40°C [51]. Apparently phase transition plays a major role in the fatigue degradation of polarization. PFM has also been used to reveal the domain morphology evolution during the electric fatigue. In MnO$_2$ doped KNN-Li ceramic, the domain structure coarsens, and the fraction of 90° domains decreases with increasing cycle number (Fig. 43) [96]. In addition, the acceptor doping has been found to significantly worsen the fatigue resistance in Cu-doped KNN [97].

3) (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-based ceramics

Studies on electric fatigue in BNT-based compositions mainly focused on the impact of the reversibility of the phase transition [98]. In the virgin state, BNT-based ceramics contain nano-sized domains. Upon the electric poling, there could be two scenarios. In non-ergodic relaxor, the nano-sized domains will transform into micron-sized lamellar domains, and these large domains can preserve after the removal of the poling field. In ergodic relaxor, on the other hand, the micron-sized lamellar domains will transform back to nano-sized domains after the poling field is removed. This nanodomain to lamellar domain transformation is
accompanied by the $P4bm$ to $R3c$ phase transition. It is found that ergodic relaxor has a much better fatigue resistance than the non-ergodic relaxor in BNT-based compositions (Fig. 44). In non-ergodic BNT-based ceramics, the domain fragmentation has been observed through X-ray and neutron diffraction measurements, which can be explained by the “domain wall pinning” fatigue model. In ergodic relaxor, the enhanced fatigue resistance is attributed to the repeated creation and destruction of the domains, rendering defect agglomeration impossible. Surprisingly, the ergodic $0.55\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3 - 0.40\text{Bi}_{1/2}\text{K}_{1/2}\text{TiO}_3 - 0.05\text{Bi}\text{Zn}_{1/2}\text{Ti}_{1/2}\text{O}_3$ exhibited large electric field-induced strains and the strain increased slightly after $10^6$ cycles of bipolar fields of 50 kV/cm (Fig. 45) [99]. Such an essentially fatigue-free behavior demonstrates that these materials have excellent potential for actuators demanding high cycle applications [100-102].

2.4 Temporal Stability --- Aging

For piezoelectric materials, aging refers to the changes in the DC bias field induced properties, including maximum polarization, remanent polarization, piezoelectric coefficient, etc., over time. Generally, aging can be classified into two categories, aging in the poled state and aging in the unpoled state. These two types of aging are distinct in, not only the fact whether the ceramic has

[Fig. 45. The fatigue-free behavior of the electro-strain in ergodic BNT-based ceramic up to $10^6$ bipolar cycles. Ref. [99]]

[Fig. 46. Characteristic $P$-$E$ loop in an aged (a) poled and (b) unpoled state. Ref. [103]]
been exposed to external electric field before aging but also the shape of the aged $P-E$ loop [103]. In an aged poled ceramic, the $P-E$ loop tends to shift horizontally, so that an internal bias is developed (Fig. 46a). In an aged unpoled ceramic, the $P-E$ loop can become pinched, with the remanent polarization suppressed (Fig. 46b). Historically, aging in the poled state received more attention, since every piezoelectric material must be electrically poled before use. Aging in the unpoled state, on the other hand, was not widely studied until Ren et al. demonstrated an ultrahigh electro-strain in an aged unpoled BaTiO$_3$-based ceramic in 2004 [104].

Compared with fatigue, aging is thought to be a much simpler process. The reason is evident: aging behavior is affected by nothing but the temperature and the composition. But in fatigue, any changes in the profile of the cyclic field can result in different fatigue degradation, as discussed before. Therefore, the study on aging effect is substantially less than fatigue. In addition, even though aging is believed correlated with charged point defect redistribution as well, the microstructure is not likely to change during aging. As a consequence, there were very few microscopy investigations on an aged piezoceramic. However, in-situ TEM could still be a suitable tool here because TEM can directly visualize the defects. Thus, we will show the first direct microscopic observation of aging phenomenon in this dissertation (Chapter 5).

### 2.4.1 Aging in poled state

Without being poled, polycrystalline ferroelectric ceramics materials cannot display piezoelectricity (Figs. 1&2). After poling, the measured piezoelectric properties are not able to remain constant as time goes by. Empirically, the aging of property $m$ with time $t$ is often described by the following logarithmic dependence [64],

$$m(t) = m(t_0) + Alog\left(\frac{t}{t_0}\right)$$

(7)
where \( t_0 \) is an arbitrary time point when the measurement starts, and constant A is the aging rate. Indeed, a linear degradation is always observed in actual aging experiments when the time is plotted in log scale (Fig. 47) [105].

In analogy to fatigue, aging in poled state is correlated with the space charges. After being poled, the domain morphology stays fixed. Driven by the depolarization field, the directional drifting of the charged point defects (Fig. 48) can eventually result in the formation of an internal bias [106]. Since the redistributed charge point defects accumulate at domain walls, this “space charge” model is also called “domain wall effect.” Derived from the model, the aging should be more severe in the compositions with higher dopant concentrations. The experimental measurements also confirmed this. As shown in Fig. 49, aging is apparently accelerated in a BaTiO\(_3\) ceramic with higher Ni\(^{2+}\) doping [107]. Meanwhile, donor doping is found to mitigate the aging degradation compared with acceptor doping (Fig. 50) because it can decrease the concentration of the charged point defects such as oxygen vacancies [108].
2.4.2 Aging in unpoled state

Different from aging in poled state, which is always regarded as a negative effect, aging in poled state could be useful to the practical applications. In 2004, Ren et al. reported an ultrahigh electro-strain >0.7% in a Fe$^{3+}$ doped BaTiO$_3$ single crystal after aged at 80 °C for 5 days (Fig. 51) [109]. Such a behavior is attributed to the reversible domain switching.

An unaged BaTiO$_3$ should display a typical square P-E loop because the switched domain won’t recover to the initial state upon the removal of the poling field (see Fig. 1). However, the domain switching process is found to be completely reversible in the aged acceptor-doped BaTiO$_3$ (Fig. 52) [110]. Later, the same group found that, even if the aging is carried out in a crystal having single domain, the domain switching in the aged state is also reversible (Fig. 53) [111]. It indicates that domain wall is not necessary for the aging effect. Thus, aging in the unpoled state is a “volume effect,” rather than “domain wall effect.”
The “volume effect” is also associated with the defects, not single charged point defect, but defect dipole. It is well known that an acceptor dopant (negatively charged) and an oxygen vacancy (positively charged) can form a defect dipole. During aging at elevated temperature, the defect dipoles are aligned with the polarization. In other words, the distribution of the charged point defects is symmetry-conforming (Fig. 54) [111].

Once the external electric field is applied, the domain switches instantaneously. However, the defect dipoles are immobile because their reorientation, or the diffusion of defects, has to take some time (see Fig. 51). As a consequence, the dipole moment of the defect dipoles will serve as a restoring force to the switched domains and make them switch back once the external field is removed.

However, the high electro-strain resulted from the aging effect may not be very stable. There could be a “de-aging” effect during cycling. As can be seen in Fig. 55, the pinched P-E loop gradually opens and eventually restore the squareness after a
few cycles [112]. This is because the repetitively reversing polarization in the lattice randomizes the defect dipoles’ orientation over time.

2.5. Thermal Stability --- Depolarization

The thermal stability of piezoelectric properties is vital because the piezoelectric ceramics are not necessarily working at room temperature only. The variation of piezoelectric coefficient as temperature increases could have multiple reasons. First, deviation from the MPB at higher temperature can sacrifice the d33, which explains why a vertical MPB is always favored. Second, the phase transition towards a nonpolar phase will definitely eliminate any piezoelectric effect. In normal ferroelectric materials, polar to nonpolar transition takes place at Curie temperature (Tc). In relaxors, depolarization temperature (Td) is the critical point. Therefore, shifting the Tc or Td to a higher temperature is the common strategy to enhance the thermal stability in piezoelectric materials.

Among the three major groups of lead-free piezoelectric ceramics (Fig. 3), BT and BNT both suffer from the poor thermal stability. Tc of the pure BaTiO3 is 120 °C. The chemically modified BZT–BCT with optimum piezoelectric properties have even lower Tc ~ 90 °C (Fig. 4). BNT-based ceramics are relaxors. So, even though their Tm are not as

![Fig. 56. Phase diagram of BNT-xBT. Ref [113]](image)

![Fig. 57. Depolarization in BNT-based ceramics. Ref. [114]](image)
low, but they have $T_d$ much below $T_m$ (Fig. 56). For example, BNT–6BT has $T_d$ around 100 °C [113]. At $T_c$ or $T_d$, piezoelectric coefficient will exhibit a sudden drop [114]. Then, the piezoelectric property will be almost lost (Fig. 57).

Increasing the $T_c$ or $T_d$ in piezoelectrics is generally realized via chemical modification.

Aberration corrected (S)TEM is capable of revealing the structure on the atomic scale. With the advanced chemical analysis techniques, EDS or EELS, the detailed elemental distribution and valence information are also detectable. Moreover, in-situ TEM using hot stage specimen holder can directly visualize the microstructural evolution upon heating. Therefore, we will take advantage of a wide variety of advanced TEM techniques to investigate the thermal depolarization process (Chapter 6).

### 2.5.1 Bismuth-containing perovskites

In 2001, Eitel et al. first reported that BiScO$_3$-PbTiO$_3$ have high $T_c$, and the value is correlated with the tolerance factor [115]. Based on this relation, multiple solid solutions with either double or triple end members have been tested (Fig. 58) [116]. However, developing lead-free high-temperature piezoceramics receives more interest nowadays.

BiFeO$_3$ has a high Curie temperature (>800 °C), and it can form a continuous solid solution

![Fig. 58. $T_c$ in Bi(Me)O$_3$-PT solid solutions. Ref. [116]](image)

![Fig. 59. Phase diagram of BF-BT solid solution. Ref. [117]](image)
with BaTiO$_3$. What makes it more promising is that the MPB in BF–BT solid solution resembles that in PZT (Fig. 59) [117]. However, the conventional fabrication is hard to produce high-quality BF–BT ceramic with satisfactory piezoelectric properties. In 2015, Lee et al. introduced the water quenching to the ceramic processing and managed to see both high $d_{33}$ and high $T_c$ simultaneously (Fig. 60) [117]. It should be noted that the selection of the additional dopants is also accordingly to the above-mentioned tolerance factor relation.

### 2.5.2 Composite approach

In BNT-based ceramics, forming a new solid solution or adding new dopant has been proved futile in increasing the $T_d$. In 2015, Zhang et al. reported a composite approach (Fig. 61), which successfully eliminates the $T_d$ in BNT–6BT:xZnO (Fig. 62) [118]. Using this approach, the enhanced thermal stability is seen in other types of piezoceramics as well [119].

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**Fig. 60.** Depolarization in water quenched (doped) BF-33BT ceramics. Ref. [117]

**Fig. 61.** Microstructure of the BNT–6BT:0.3ZnO composite. Ref. [118]

**Fig. 62.** Vanished $T_d$ in BNT–6BT:xZnO. Ref. [118]
Unfortunately, the underlying mechanism is still elusive, which prevents researchers from designing new composite systems to achieve an even better effect.

References


[20] D. S. Keeble, F. Benabdallah, P. A. Thomas, M. Maglione, J. Kreisel, Revised structural phase diagram of (Ba\textsubscript{0.7}Ca\textsubscript{0.3}TiO\textsubscript{3})–(BaZr\textsubscript{0.2}Ti\textsubscript{0.8}O\textsubscript{3}), Appl. Phys. Lett. 102 (2013) 092903.


[22] H. Guo, B. K. Voas, S. Zhang, C. Zhou, X. Ren, S. P. Beckman, X. Tan, Polarization alignment, phase transition, and piezoelectricity development in polycrystalline 0.5Ba(Zr\textsubscript{0.2}Ti\textsubscript{0.8})O\textsubscript{3}−0.5(Ba\textsubscript{0.7}Ca\textsubscript{0.3})TiO\textsubscript{3}, Phys. Rev. B 90 (2014) 014103.


[28] C. Ma, X. Tan, E. Dul'kin, M. Roth, Domain structure–dielectric property relationship in lead-free (1-x)(Bi\textsubscript{1/2}Na\textsubscript{1/2})TiO\textsubscript{3}–xBaTiO\textsubscript{3} ceramics, J. Appl. Phys. 108 (2010) 104105.

[29] C. Ma, H. Guo, X. Tan, A new phase boundary in (Bi\textsubscript{1/2}Na\textsubscript{1/2})TiO\textsubscript{3}–BaTiO\textsubscript{3} revealed via a novel method of electron diffraction analysis, Adv. Funct. Mater. 23 (2013) 5261-66.


[34] X. Liu, X. Tan, Giant Strains in Non-Textured (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-Based Lead-Free Ceramics, Adv. Mater. 28 (2016) 574-578.


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[92] V. Rojas, J. Koruza, E. Patterson, M. Acosta, X. Jiang, N. Liu, C. Dietz, J. Rödel, Influence of composition on the unipolar electric fatigue of Ba (Zr$_{0.2}$Ti$_{0.8}$)O$_3$-(Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$ lead-free piezoceramics, J. Am. Ceram. Soc. 100 (2017) 4699-4709.


[96] S. Tsurekawa, H. Hatao, H. Takahashi, Y. Morizono, Changes in ferroelectric domain structure with electric fatigue in Li$_{0.06}$(Na$_{0.5}$K$_{0.5}$)$_{0.94}$NbO$_3$ ceramics, Jpn. J. Appl. Phys. 50 (2011) 09NC02.


[99] E. A. Patterson, D. P. Cann, Bipolar piezoelectric fatigue of Bi(Zn$_{0.5}$Ti$_{0.3}$)O$_3$–(Bi$_{0.5}$K$_{0.3}$)TiO$_3$–(Bi$_{0.3}$Na$_{0.3}$)TiO$_3$ Pb-free ceramics, Appl. Phys. Lett. 101 (2012) 042905.

[100] N. Kumar, T. Ansell, D. Cann, Role of point defects in bipolar fatigue behavior of Bi(Mg$_{1/2}$Ti$_{1/2}$)O$_3$ modified (Bi$_{1/2}$K$_{1/2}$)TiO$_3$–(Bi$_{1/2}$Na$_{1/2}$)TiO$_3$ relaxor ceramics, J. Appl. Phys. 115 (2014) 154104.

[101] Hao, Z. Xu, R. Chu, W. Li, J. Du, P. Fu, Large strain response and fatigue-resistant behavior in lead-free Bi$_{0.5}$(Na$_{0.80}$K$_{0.20}$)$_{0.5}$TiO$_3$–(K$_{0.3}$Na$_{0.7}$)MO$_3$ (M= Sb, Ta) ceramics, RSC Adv. 5 (2015) 82605-82616.

[102] N. Kumar, D. Cann, Electromechanical strain and bipolar fatigue in Bi(Mg$_{1/2}$Ti$_{1/2}$)O$_3$–(Bi$_{1/2}$K$_{1/2}$) TiO$_3$–(Bi$_{1/2}$Na$_{1/2}$)TiO$_3$ ceramics, J. Appl. Phys. 114 (2013) 054102.


CHAPTER 3.

AN IDEAL AMPLITUDE WINDOW AGAINST ELECTRIC FATIGUE
IN BaTiO$_3$-BASED LEAD-FREE PIEZOELECTRIC MATERIALS

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3.1 Abstract

Electric fatigue has been a vexing issue for Pb(Zr,Ti)O$_3$ ceramics, the material-of-choice for piezoelectric technologies, where higher field amplitudes always lead to a more severe property degradation. Thus, piezoelectric devices must be driven under low electric fields to ensure performance reliability, which results in a low efficiency. In the past decade, the intensive worldwide research on lead-free compositions has identified a few ceramics with piezoelectric properties comparable to those of lead-containing ones. However, their resistance to electric fatigue has not been well studied. In this work, we report an abnormal amplitude dependence of electric fatigue in lead-free piezoelectrics: A BaTiO$_3$-based ceramic suffers fatigue degradation when the field amplitude is low, but exhibits an amplitude window at higher fields with essentially no fatigue. Furthermore, electric-field in-situ transmission electron microscopy (TEM) experiments up to $10^5$ cycles are conducted to clearly reveal that the degradation at low fields is due to the unique single-domain state. We, therefore, have identified an ideal amplitude window with performance at full potential and, at the same time, extremely high reliability for a lead-free piezoelectric ceramic that is promising to replace Pb(Zr,Ti)O$_3$. 
3.2 Introduction

Electric fatigue is an inevitable problem for a wide range of materials and devices, especially electric capacitors [1], ferroelectric memories [2], Li-ion batteries [3,4], and piezoelectric actuators [5], where high cycle numbers are required. In ferroelectric and piezoelectric materials, the continuous reduction of switchable polarization ($2P_r$) upon repeated electric cycling is the most commonly cited manifestation of electric fatigue [6-]. In order to mitigate fatigue-related issues, massive efforts have been made towards clarifying the effects of various factors on the fatigue behavior of piezoelectric materials, primarily the market-dominant Pb(Zr,Ti)O$_3$ ceramics. These factors include composition [9], temperature [10], cycling frequency [11], and cyclic field amplitude [12-]. While the effects of other factors are often disputable, the amplitude dependence of fatigue degradation in bulk Pb(Zr,Ti)O$_3$ ceramics is consistent in the literature: high amplitude accelerates the degradation [12-16].

Over the past decade, environmental and health concerns over the toxicity of lead have generated great interest in replacing Pb(Zr,Ti)O$_3$ ceramics with lead-free compositions. Intense worldwide research has identified the three most promising solid solution systems, (K$_{1-x}$Na$_x$)NbO$_3$-, (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-, and BaTiO$_3$-based compositions [17]. Meantime, studies on the electric fatigue of these lead-free piezoelectric ceramics started to appear in literature [18,19]. The main focus in these limited reports has been the effect of composition on fatigue behavior [20-22]. The field amplitude effect on fatigue of bulk lead-free ceramics has seldom been mentioned; but more severe degradation has been predicted when cycled at higher field
amplitudes [23]. This is confirmed by comparing fatigue behaviors reported in a few separate articles on ceramics with very close compositions. For example, the $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiSbO_3$ ceramic does not display any degradation up to $10^4$ cycles at an amplitude of 22 kV/cm while the $0.948(K_{0.5}Na_{0.5})NbO_3$–$0.052LiSbO_3$ ceramic loses 50% of its switchable polarization within $2\times10^3$ cycles of $\pm 50$ kV/cm [24]. In the present work, we conduct the first systematic study of amplitude effect on bipolar fatigue of lead-free ceramics and report an opposite trend, severe degradation at lower amplitudes while fatigue-free at higher amplitudes, in a BaTiO$_3$-based polycrystalline bulk ceramic. Furthermore, we identify a clear correlation between the abnormal macroscopic behavior and the microstructural domain evolution during electric cycling directly revealed with the in-situ TEM technique [25].

3.3 Experimental

The polycrystalline ceramic BZT–BCT was prepared through the solid-state reaction method. Stoichiometric amount of powders of BaCO$_3$ (99.8%), CaCO$_3$ (99.5%), ZrO$_2$ (99.5%), and TiO$_2$ (99.6%) were mixed and milled for 5 hours in a planetary mill using ethanol and ZrO$_2$ milling media. The suspension was then dried and the powders were calcined at 1300 °C for 2 hours. After calcination the powders were again milled, dried, and formed into disks by uniaxial hand pressing in a 10 mm diameter die, followed by cold isostatic pressing at 300 MPa. Sintering was performed at 1500 °C for 2 hours, with a heating rate of 5 °C/min.

The sintered pellets were ground to a thickness of about 0.7 mm and silver electrodes were painted and fired on at 400 °C. The bipolar fatigue tests on bulk samples were carried out at room temperature using a triangular waveform at the frequency of 10 Hz. The polarization
hysteresis loops at different cycling intervals were recorded at 4 Hz using a standardized ferroelectric test system (Precision LC II, Radiant Technologies).

For the in-situ TEM experiments, as-sintered ceramic pellets were mechanically ground and polished down to 120 μm thick, and then ultrasonically cut into disks with a diameter of 3 mm. After mechanical dimpling and polishing, the disks were annealed at 150 °C for 2 hours and Ar-ion milled to the point of electron transparency. In-situ TEM fatigue testing was performed on an FEI Tecnai G2-F20 microscope operated at 200 kV, with bipolar electric fields in a triangle waveform at a frequency of 10 Hz applied to the specimen.

### 3.4 Results

#### 3.4.1 Macroscopic fatigue behavior

Ca- and Zr-modified BaTiO$_3$ ceramics display excellent piezoelectric properties (e.g. $d_{33} > 600$ pC/N) that exceed many Pb(Zr,Ti)O$_3$ ceramics [26], and their electric fatigue behaviors have not been investigated until very recently [27-30]. The most widely studied composition, 0.5Ba(Zr$_{0.2}$Ti$_{0.8}$)O$_3$–0.5(Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$ (BZT–BCT), is found to exhibit a 7% reduction in $2P_r$ after $10^7$ bipolar cycles at the amplitude of 4.5 kV/cm.[27] In contrast, an 11% increase in $2P_r$ after $10^6$ bipolar cycles at 20 kV/cm is observed in a ceramic with a slightly different Ca and Zr content.[29] These seemingly conflicting results prompt us to conduct the first systematic study on the field amplitude dependence of electric fatigue in BZT–BCT. The evolution of switchable polarization ($2P_r$) and maximum polarization ($2P_m$) during bipolar cycling at amplitudes of 5.5 kV/cm and 18 kV/cm are depicted in Fig. 1 (error bars are exaggerated by the normalization process). Surprisingly, electric cycling at ±5.5 kV/cm results in a 6.0% reduction in $2P_r$ after $10^6$
cycles, while cycling at ±18 kV/cm leads to an 8.2% increase in $2P_r$. Similarly, an 8.3% decrease in $2P_m$ is measured at 5.5 kV/cm cycling but only 1.3% reduction is seen at 18 kV/cm cycling.

### 3.4.2 Microstructural evolution during fatigue

Such highly unusual fatigue behavior requires an explanation. It is known that BZT–BCT has several phases around room temperature, therefore field- or temperature-induced phase transitions could play a role [31-33]. Our previous *in-situ* TEM work first reported a unique single-domain state under electric fields ($E_{SD}$) ranging from 4 to 6 kV/cm [34]. At fields surpassing this range ($E_{MD}$), the single-domain state is disrupted and replaced by a multiple-domain state that is different from the virgin state [35]. The correlation appears to be obvious: The apparent fatigue degradation at the amplitude of 5.5 kV/cm might be associated with the unique single-domain state of the ceramic, while the fatigue-free behavior at 18 kV/cm might be connected with the high-field multiple-domain state. In order to verify the correlation between the abnormal amplitude dependence of fatigue resistance and different domain states, we conduct *in-situ* TEM experiments to directly visualize the domain morphology evolution during bipolar cycling at $E_{SD}$ and $E_{MD}$.

Accounting for the poor fatigue resistance at 5.5 kV/cm, a grain in the ceramic specimen is imaged along its [113] zone-axis while it is cycled with an amplitude of $E_{SD}$. In its virgin state, the grain contains lamellar domains with a high density of domain walls (Fig. 2a). When an electric field is applied along the marked direction indicated in Fig. 2b, those fine domains in the virgin state are replaced by new lamellar domains. Further increase in the electric field leads to the unique single-domain state where all domain walls disappear throughout the grain (Fig. 2c). Upon removal of the applied field, domains form and occupy the grain again. As displayed in Fig. 2d, large lamellar domains are present in both the top and bottom portion of the grain, and
thin lamellar domains are located close to the left grain boundary. Then, bipolar electric cycling is carried out with an amplitude of $E_{SD}$ and bright field micrographs are recorded at zero field after a certain number of cycles. After $10^2$ cycles, the large lamellar domains in the top portion of the grain are replaced by some small domains adjacent to the grain boundary (indicated by the bright arrow in Fig. 2e). After $5 \times 10^3$ cycles, the fine domains close to the left grain boundary are coarsened and disrupted, while other lamellar domains almost disappear (Fig. 2f). After $5 \times 10^4$ cycles, all large domains with straight walls disappear throughout the grain. In their place, many features with complex contrast are observed (Fig. 2g). These complex features are suspected to be a mixture of point defect clusters and disrupted domain segments (One tiny segment is pointed out by the bright arrow in Fig. 2g). After $10^5$ cycles, high density defect clusters occupy most of the grain (Fig. 2h). Therefore, our in-situ TEM results directly confirm the quick disruption of large ferroelectric domains and accumulation of defect clusters during bipolar cycling at $E_{SD}$.

Correlating with the good fatigue resistance at the amplitude of 18 kV/cm, our in-situ TEM test reveals a rather stable domain configuration against cycling at $E_{MD}$. The grain of interest is imaged along its [100] zone-axis and is initially occupied by lamellar domains (Fig. 3a). Under the poling field along the bright arrow, the domain wall density reduces significantly (Fig. 3b). The applied field appears to be very close to $E_{SD}$ and the micrograph is almost at the point where all domain walls disappear. Further increase in applied field to $E_{MD}$ leads to the formation of new sets of domains, corresponding to the multiple-domain state (Fig. 3c). These new domains have a different configuration from the virgin state and most of them are separated by edge-on $\{110\}$ planes, suggesting they are likely 90° tetragonal domains. Upon removal of the field, the domain morphology at the poled state is largely preserved with some backswitching in the middle
portion of the grain (Fig. 3d). Moreover, many nanoscale domains are seen within the microscale domains, forming the hierarchical domain structure [32,34]. At that point, bipolar cycling is carried out with an amplitude of $E_{MD}$. After $10^3$ cycles, almost all domain walls stay undisrupted and defect clusters do not form (Fig. 3e). After $5 \times 10^4$ cycles, the overall domain morphology still persists, with many large lamellar domains occupying the majority of the grain (Fig. 3f). The resilience of these large ferroelectric domains upon disruption during cycling at $E_{MD}$ is apparently the reason for the excellent fatigue resistance observed at 18 kV/cm in Fig. 1a on the bulk sample. The more complex phase transitions within each cycle at $E_{MD}$ may reset the domain structure and disrupt the defect clustering process.

3.5 Discussion

It should be noted that better fatigue performance at higher field amplitudes has been reported previously in thin films of BiFeO$_3$ and Bi-based layered perovskites [36,37]. However, those tests are performed on thin films with orders of magnitude higher electric conductivity, field amplitude and frequency. In addition, no field-induced phase transition is expected in those films. The unusual fatigue behavior in the bulk BZT–BCT specimens featured in Fig. 1 occurs in a totally different regime, and hence, through different mechanisms.

Our *in-situ* TEM results indicate that the fatigue degradation in BZT–BCT is accompanied by the accumulation of point defect clusters. The concentration of charged point defects has been proven to have crucial influence on fatigue resistance [38]. In BZT–BCT, with no volatile species or aliovalent dopants, the charged point defects are most likely oxygen vacancies with a relatively low concentration. This could explain the observation that the fatigue degradation in BZT–BCT at either 5.5 or 18 kV/cm is much lower than most lead-containing or lead-free
piezoelectric ceramics. However, the low concentration oxygen vacancies are still able to disrupt the original lamellar domains after the clusters form [39]. Even though the oxygen vacancies have like charge and strain fields, the unscreened depolarization field in ferroelectrics could be capable of overcoming their mutual repulsion and leading to their agglomeration [40]. Under intense fields, oxygen vacancies can form, migrate, and cluster into ordered structures [41,42]. In BZT–BCT, the large single domain at $E_{SD}$ (Fig. 2c) presumably possesses huge unscreened depolarization fields. In contrast, the depolarization field at $E_{MD}$ is supposed to be significantly reduced due to complex multiple domains with hierarchical structures (Fig. 3c). The driving force for the clustering of oxygen vacancies is much higher in the single-domain state than the multiple-domain state.

Our previous in-situ TEM work has recorded the blockage of domain growth by a charged point defect cluster embedded in the single-domain matrix in a fatigued BZT–BCT ceramic [43]. The fatigue mechanism at $E_{SD}$ in the present work should be the same: The formation of large lamellar domains is severely suppressed by the oxygen vacancy clusters after the fatigue. On the other hand, the increase of switchable polarization at the amplitude of 18 kV/cm is not well understood (Fig. 1a). Similar phenomena have been reproducibly observed in ergodic relaxor ceramics that have a vanished depolarization field due to the random nanosized domains [44,45], resembling the low depolarization field in the multiple-domain state with a hierarchical structure in BZT–BCT at $E_{MD}$. The lower depolarization field has also been suggested to be responsible for the better fatigue resistance in antiferroelectrics than ferroelectrics [46].

It should be made clear that, even though all fatigue tests are conducted at room temperature, different cycling amplitudes with identical frequency can give rise to different levels of self-heating in the ceramic [47], hence a possible self-annealing effect during cycling at 18 kV/cm.
Zhang et al. has monitored the temperature change during their fatigue tests on the BZT–BCT ceramic and detected an increase of less than 2 °C [27]. To further rule out the self-annealing effect, we cycled a specimen at 30 kV/cm for $10^6$ cycles and observed an apparent fatigue degradation (Fig. 4). This degradation is not due to microcracking, because annealing at 150 °C for 2 hours fully recovers the switchable polarization. If self-annealing due to the temperature rise during cycling led to the strong fatigue resistance at 18 kV/cm, the specimen cycled at 30 kV/cm would have shown an even stronger fatigue resistance. This is obviously not the case. Therefore, the temperature effect, if any, plays a trivial role here and the different fatigue behaviors observed are associated with different processes of domain disruption and defect accumulation.

In order to gain a comprehensive picture of the amplitude dependent electric fatigue in the BZT–BCT ceramic, macroscopic fatigue tests are also carried out at four field amplitudes other than 5.5 or 18 kV/cm. Practically no degradation in $2P_r$ is found after $10^6$ cycles at the amplitude of 3.5 kV/cm, which is below the single-domain field range (4 ~ 6 kV/cm). At 4.5 kV/cm, a 4.9% reduction in $2P_r$ is measured, close to that at 5.5 kV/cm. Analogous to 18 kV/cm, bipolar cycling at the amplitude of 15 kV/cm exhibits an increase in $2P_r$ (4.8%). However, the good fatigue resistance does not persist to higher amplitude. Cycling at 30 kV/cm for $10^6$ cycles renders 8.2% degradation in $2P_r$. It is reasonable to assume that more severe fatigue degradation occurs at amplitudes even higher than 30 kV/cm. These relative changes in $2P_r$ are summarized in Fig. 5. There are four different regimes in terms of the field amplitude dependence of the relative change of switchable polarization. With an amplitude below 3.5 kV/cm, the cyclic field will not induce any fatigue degradation. Around $E_{SD}$ between roughly 3.5 and 7.5 kV/cm, bipolar cycling leads to some apparent fatigue degradation. Between roughly 8 and somewhere around
24 kV/cm, the BZT–BCT ceramic displays strong fatigue resistance. At amplitudes above 24 kV/cm, large decreases in switchable polarization during bipolar cycling are expected.

Strong fatigue resistance is essential for device applications. In devices like electric capacitors, ferroelectric memories, and piezoelectric actuators [1,2,5] the magnitude of $2P_r$ is also critical. The blue curve in Fig. 5 represents the absolute value of switchable polarization as a function of field amplitude in the BZT–BCT ceramic (The data is extracted from a series of polarization hysteresis loops). It is observed that $2P_r$ increases sharply at very low fields. However, the slope abruptly drops at 6.5 kV/cm, corresponding to the transition from the single-domain to multiple-domain state. Beyond this field amplitude, $2P_r$ continues to rise, but at a much slower rate. Therefore, there exists an ideal amplitude window against electric fatigue in BZT–BCT, where not only large values of $2P_r$ can be achieved, but also no degradation in $2P_r$ is possible. This ideal amplitude window is the region highlighted in green between 8 and 24 kV/cm in Fig. 5. Such a rare combination is not possible in Pb(Zr,Ti)O$_3$, the most widely used piezoelectric materials, where larger values of $2P_r$ comes at higher field amplitudes with more severe fatigue degradation.

The existence of an ideal amplitude window against electric fatigue in BZT–BCT suggests a new strategy for the design and development of other lead-free piezoelectric materials. For instance, (K$_{1-x}$Na$_x$)NbO$_3$-based ceramics have complex phase transitions with chemical modifications and under applied electric fields [48,49]. Therefore, their fatigue behaviors at different amplitudes, and the possible existence of an ideal amplitude window against fatigue, should be pursued in the future.
3.6 Conclusions

In summary, an abnormal field amplitude dependence of electric fatigue resistance is observed in the BZT–BCT bulk ceramic samples. The electric field in-situ TEM experiments indicate that the degradation at the lower amplitudes is associated with the single-domain state, which facilitates the clustering of oxygen vacancies. The defect clusters accelerate the pinning process of domain walls and suppress the formation of large lamellar domains during electric cycling. The stronger fatigue resistance at higher amplitudes correlates with the multiple-domain state. The defect clustering in this state is slowed down due to the complex domain morphology and reduced depolarization field. As a result, an ideal field amplitude window exists in BZT–BCT with large switchable polarization and no fatigue degradation. The search for such amplitude window in other composition systems should be the focus of future research on lead-free piezoelectric materials.

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Reference


[21] N. Kumar, T. Y. Ansell, D. P. Cann, Role of point defects in bipolar fatigue behavior of Bi(Mg1/2Ti1/2)O3 modified (Bi1/2K1/2)TiO3–(Bi1/2Na1/2)TiO3 relaxor ceramics, J. Appl. Phys. 115 (2014) 154104.


[24] G. Ray, N. Sinha, S. Bhandari, B. Kumar, Achieving high piezoelectricity and fatigue free hysteresis in lead free relaxor ferroelectric ceramic 0.94[Na\textsubscript{0.5}K\textsubscript{0.5}NbO\textsubscript{3}]-0.06LiSbO\textsubscript{3}, Mater. Chem. Phys. 159 (2015) 107.


[29] N. Chaiyo, D. P. Cann, N. Vittayakorn, Lead-free (Ba,Ca)(Ti,Zr)O\textsubscript{3} ceramics within the polymorphic phase region exhibiting large, fatigue-free piezoelectric strains, Mater. Des. 133 (2017) 109-121.

[30] V. Rojas, J. Koruza, E. A. Patterson, M. Acosta, X. Jiang, N. Liu, C. Dietz, J. Rödel, Influence of composition on the unipolar electric fatigue of Ba(Zr\textsubscript{0.2}Ti\textsubscript{0.8})O\textsubscript{3}–(Ba\textsubscript{0.7}Ca\textsubscript{0.3})TiO\textsubscript{3} lead-free piezoceramics, J. Am. Ceram. Soc. 100 (2017) 4699-4709.

[31] D. S. Keeble, F. Benabdallah, P. A. Thomas, M. Maglione, J. Kreisel, Revised structural phase diagram of (Ba\textsubscript{0.7}Ca\textsubscript{0.3}TiO\textsubscript{3})–(BaZr\textsubscript{0.2}Ti\textsubscript{0.8}O\textsubscript{3}), Appl. Phys. Lett. 102 (2013) 092903.

[32] J. Gao, D. Xue, Y. Wang, D. Wang, L. Zhang, H. Wu, S. Guo, H. Bao, C. Zhou, W. Liu, S. Hou, G. Xiao, X. Ren, Microstructure basis for strong piezoelectricity in Pb-free Ba(Zr\textsubscript{0.2}Ti\textsubscript{0.8})O\textsubscript{3}–(Ba\textsubscript{0.7}Ca\textsubscript{0.3})TiO\textsubscript{3} ceramics, Appl. Phys. Lett. 99 (2011) 092901.


[34] H. Guo, B. K. Voas, S. Zhang, C. Zhou, X. Ren, S. P. Beckman, X. Tan, Polarization alignment, phase transition, and piezoelectricity development in polycrystalline 0.5Ba(Zr\textsubscript{0.2}Ti\textsubscript{0.8})O\textsubscript{3}–0.5(Ba\textsubscript{0.7}Ca\textsubscript{0.3})TiO\textsubscript{3}, Phys. Rev. B 90 (2014) 014103.


[37] D. Dimos, H. N. Al-Shareef, W. L. Warren, B. A. Tuttle, Photoinduced changes in the fatigue behavior of SrBi\textsubscript{2}Ta\textsubscript{2}O\textsubscript{9} and Pb(Zr,Ti)O\textsubscript{3} thin films, J. Appl. Phys. 80 (1996) 1682-1687.


Fig. 3.1 The evolution of normalized (a) switchable polarization, $2P_r$, and (b) maximum polarization, $2P_m$, during bipolar cycling at field amplitudes of 5.5 and 18 kV/cm in BZT–BCT bulk ceramic samples.
**Fig. 3.2** Electric field *in-situ* TEM observation on the domain morphology change during (a)-(d) the initial loading to the single-domain state and (e)-(h) the subsequent bipolar cycling at the field amplitude of $E_{SD}$. Bright field micrographs at (a) virgin state, (b) $E < E_{SD}$, (c) $E = E_{SD}$, (d) $E = 0$ after field is removed; and after bipolar cycling at $E_{SD}$ for (e) $1 \times 10^2$, (f) $5 \times 10^3$, (g) $5 \times 10^4$, (h) $1 \times 10^5$ cycles. Images in (e) through (h) are recorded under no applied bias. The electron diffraction pattern of the virgin state is shown in the inset in (a). No noticeable changes in the diffraction pattern are observed during either the initial loading or the bipolar cycling. The positive direction of applied field in the *in-situ* TEM experiment is indicated by the bright arrow in (b).
Fig. 3.3 Electric field *in-situ* TEM observation on the domain morphology change during (a)-(d) the initial loading to the multiple-domain state, and (e) and (f) the subsequent bipolar cycling at the field amplitude of $E_{MD}$. Bright field micrographs at (a) virgin state, (b) $E \approx E_{SD}$, (c) $E = E_{MD}$, (d) $E = 0$ after field is removed; and after bipolar cycling at $E_{MD}$ for (e) $1 \times 10^3$ and (f) $5 \times 10^4$ cycles. Images in (e) and (f) are recorded under no applied bias. The electron diffraction pattern of the virgin state is shown in the inset in (a). No noticeable changes in the diffraction pattern are observed during either the initial loading or the bipolar cycling. The positive direction of applied field in the *in-situ* TEM experiment is indicated by the bright arrow in (b).
Fig. 3.4 The full recovery of the polarization hysteresis loop by annealing at 150 °C for 2 hours of the specimen after $10^6$ bipolar cycles at the field amplitude of 30 kV/cm.
Fig. 3.5 Summary of the electric field amplitude dependence of the relative change in switchable polarization, $\Delta 2P_r$, between that of after $10^6$ cycles and the first cycle in BZT–BCT bulk ceramic samples. The black line is schematically drawn to guide the eye. For direct reference, the absolute value of $2P_r$ of the first cycle is also displayed. The error bars are smaller than the symbol size on the blue curve.
CHAPTER 4.

A COMPARATIVE STUDY OF THE POLARIZATION DEGRADATION MECHANISMS DURING ELECTRIC CYCLING IN 

\((\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\)-BASED RELAXORS

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4.1 Abstract

The polarization degradation during electric field cycling in a ferroelectric ceramic is closely related to the phase composition. In the present work, electric biasing \textit{in-situ} transmission electron microscopy (TEM) fatigue tests are conducted on relaxors of \((1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3-x\text{SrTiO}_3\). It is directly observed that the ceramic of \(x = 0.25\) features an irreversible relaxor-ferroelectric phase transition and the domain walls in the metastable ferroelectric phase sweep shorter and shorter distances during cycling. In contrast, the ceramic of \(x = 0.27\) features a reversible relaxor-ferroelectric transition and the domain walls in the transient ferroelectric phase remain highly mobile even after \(10^4\) cycles.

\textit{Keywords}: \textit{in-situ} TEM, electric fatigue, ferroelectric domains, relaxor-ferroelectric transition

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Polarization fatigue, as it can devastatingly affect the device performance, has been regarded as a key issue of ferroelectric ceramics [1,2]. An important research topic is to identify the factors that have critical impacts on their fatigue behavior; these include the external factors such as field amplitude [3], cycling frequency [4], and test temperature [5]. However, factors that are inherent to ferroelectric ceramics are thought to be more crucial. For example, addition of aliovalent dopants and changes in phase compositions can lead to distinct fatigue behaviors in lead zirconate titanate ceramics with similar chemical composition [6,7]. Lead-free piezoelectric ceramics are known to have complex phase transitions in the electric field-temperature space, their phase composition presumably plays a decisive role on their fatigue behavior.

Discussions on the phase composition-fatigue behavior relation have been made in all three major lead-free piezoelectric ceramic systems. In BaTiO$_3$-based ceramics, electric cycling in the orthorhombic phase exhibits a worse fatigue resistance than in the tetragonal phase [8]. In (K$_{0.5}$Na$_{0.5}$)NbO$_3$-based solid solutions, polarization degradation is considerably mitigated after getting rid of the polymorphic phase transition [9]. In (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-based relaxors, a fatigue-free or even anti-fatigue phenomenon is observed when the relaxor-ferroelectric transition is reversible [10-12]. Nevertheless, given the fact that the polarization fatigue is closely related to the domain dynamics under cyclic electric field, experiments that can directly reveal the microstructural evolution during cycling would be more insightful than bulk measurements. In the present study, the electric biasing in-situ TEM is employed to compare the different polarization degradation mechanisms in two (1-x)(Bi$_{1/2}$Na$_{1/2}$)TiO$_3$–xSrTiO$_3$ (BNST100x, x = 0.25 and 0.27) relaxors [13,14].

BNST25 and BNST27 ceramics were fabricated using the solid-state reaction method, with starting powders of Bi$_2$O$_3$ (99.9%), Na$_2$CO$_3$ (99.9%), SrCO$_3$ (99.99%) and TiO$_2$ (99.99%).
batched powders were mixed in a vibratory mill in ethanol for 6 hours, and dried in oven at 90 °C. Calcination was performed at 850 °C for 2 hours while sintering was carried out at 1100 °C or 1125 °C for 2 hours. The temperature-dependent loss tangent was measured at a heating rate of 4 °C/min using an LCZ meter (Model 3330; Keithley, Cleveland, OH). The polarization hysteresis loops were recorded at 1 Hz using a standardized ferroelectric test system (Precision LC II, Radiant Technologies). For the in-situ TEM experiments on a FEI Tecnai G2-F20 microscope, as-sintered pellets were mechanically ground and polished to 120 µm thickness. Disks of 3 mm in diameter were ultrasonically cut and the center portion was thinned to 10 µm by mechanical dimpling. The dimpled disks were annealed at 250 °C for 1 hour to minimize the residual stress before Ar-ion milling until perforation. During the fatigue tests on bulk ceramics and with in-situ TEM, cyclic electric fields in a triangular waveform of 1 Hz were applied.

What is the difference between BNST25 and BNST27 in terms of the phase nature? Since BNST25 has been discussed in detail recently [15], Fig. 1 focuses on BNST27 only. In the virgin state (Fig. 1a), the entire grain is occupied with the nanoscale domains. The \([1\bar{1}2]_c\) zone-axis diffraction pattern contains two sets of superlattice spots, \(\frac{1}{2}\{000\}\) and \(\frac{1}{2}\{00e\}\) type marked by the bright circle and arrow, respectively. It means that, BNST27 is a mixture of the rhombohedral \(R3c\) phase and the tetragonal \(P4bm\) phase [16]. Subjected to a voltage of 420 V (Fig. 1b), the nanoscale domains near the top corner of the grain transform into thin tweed-like domains. In the corresponding diffraction pattern, the \(\frac{1}{2}\{00e\}\) spots disappear while the \(\frac{1}{2}\{000\}\) spots become more discrete. Such events are interpreted as the field-induced \(P4bm\) to \(R3c\) phase transition. Once the voltage is removed (Fig. 1c), not only the domain morphology, but also the diffraction pattern resumes to the initial state, indicating that the phase transition is reversible. On the contrary, BNST25 is known to undergo a field-induced irreversible relaxor-ferroelectric
phase transition and is not accompanied with any change in the crystal structure [15]. In other words, the 2 mol.% more of Sr$^{2+}$ in BNST27 has shifted the depolarization temperature ($T_d$) down towards room temperature (Fig. 2a); so that the induced long-range ferroelectric order in BNST27 is disrupted upon removal of the field [17,18].

Does a reversible phase transition in BNST27 really correspond to a better fatigue resistance, as similar to other (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-based relaxors? As can be seen in Fig. 2b, the polarization-electric field ($P$-$E$) loop of BNST25 changes much more dramatically than that of BNST27 during electric cycling. After $10^4$ bipolar cycles at ±40 kV/cm, the maximum polarization ($2P_m$) drops 38% in BNST25 while only 4% in BNST27 (Fig. 2c). On the other hand, the switchable polarization ($2P_r$) decreases by 39% in BNST25 but increases by 5% in BNST27. Note that BNST27 displays a non-zero $P_r$ (Fig. 1c$_2$), indicating the presence of ferroelectric phase. This can traces its origin to the fact that roughly 20% of the grains in BNST27 contain a Sr-deficient core full of lamellar ferroelectric domains [19].

In order to reveal the micromechanism for the strong fatigue resistance in BNST27, *in-situ* TEM fatigue test is conducted on another [1$ar{1}$0]$_c$ zone-axis aligned grain (Fig. 3). The reversible relaxor-ferroelectric phase transition takes place in the center of the observed area under 420 V (Fig. 3a-c). After $2 \times 10^3$ cycles, the same reversible process is seen (Fig. 3d-f). It should be noted that the cyclic bias of 420 V used here is unipolar. Due to the reversible nature of the phase transition, the responses under +420 V and -420 V are presumably symmetric. As a result, $N$ cycles of bipolar fields would lead to an equal amount of degradation in BNST27 as to $2N$ cycles of unipolar fields. After $10^4$ cycles, the tweed-like domains with almost identical appearance can still be induced at 420 V (Fig. 3g-i). Such a stable microstructural response during electric
cycling is perfectly consistent with the excellent fatigue resistance observed in the BNST27 bulk ceramic.

The situation in BNST25 is completely different. In the virgin state, the grain observed along its [001]$_c$ zone-axis is full of nanoscale domains (Fig. 4a). When a voltage of 300 V is applied, the relaxor to ferroelectric phase transition occurs and wedge-shaped large domains form (Fig. 4b) [15]. The long domain walls trace along the $<100>_{c}$ direction, suggesting that they are very likely on inclined {110}$_c$ planes. As the voltage increases, the two major wedge domains grow in size, at the cost of the matrix in between (Fig. 4c). It implies that the wedge domains have the polarization favored by the applied field, while the matrix domain does not. Subsequently, the two long domain walls continue moving toward each other until their middle sections merge (Fig. 4d). The voltage is then removed, but the domain morphology hardly changes (Fig. 4e). Then, the voltage reverses the polarity. The merged domain walls first detach apart (Fig. 4f), followed by the contraction of the two major wedge domains and the growth of the matrix in between (Fig. 4g). After the voltage returns to 0 V from the negative peak value, the domain morphology, again, mostly remains unchanged (Fig. 4h).

Unlike BNST27, the cyclic fields used for the fatigue test in BNST25 are selected to be bipolar rather than unipolar. The reason is that, unipolar fields only lead to the cycling between the remanent state and the poled state in the same polarity ($P_s \approx P_m$ in BNST25), but the severe fatigue degradation is often associated with a more complete polarization reversal process [20,21]. Therefore, the domain switching dynamics is checked after $3\times10^3$ bipolar cycles at $\pm 420$ V. As shown in Fig. 4i, those two major wedge domains are still present at 0 V. Under $+420$ V, they do grow, but the growth is suppressed, i.e. the long domain walls are no longer able to merge (Fig. 4j). Under $-420$ V, similarly, the domain wall motion occurs, but it sweeps a shorter
distance (Fig. 4k). Upon the removal of the voltage, the domain morphology at 0 V prior to this checking cycle is restored (Fig. 4l). Apparently, such a suppression of the domain wall mobility in the form of reduced sweeping distance is the fundamental reason for the degradation of ferroelectric properties in the BNST25 ceramic.

What causes the distinctive fatigue behaviors in BNST25 and BNST27? Although particular allovalent dopants have been found beneficial to the fatigue resistance in (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-based ceramics [22-24], the subtle difference in Sr$^{2+}$ concentration, which is equivalent to an isovalent dopant on A-site in the ABO$_3$ perovskite structure, is unlikely to create an impactful difference in defect concentration between BNST25 and BNST27 [25]. It is noted that charged point defects, such as $V_G$, $V_{Bi}''$ and $V_{Na}'$, exist in both ceramics due to the loss of Bi$_2$O$_3$ and Na$_2$O during thermal processing [17,26]. When BNST25 is subject to bipolar cyclic fields, the long walls of the wedge domains sweep back and forth (Fig. 4). It is known that the sidewise motion of domain wall during polarization reversal initiates from a section stepping out from the wall [27]. The head-to-head or tail-to-tail dipole configuration will be formed between the step-out section and the matrix domain [28], giving rise to a local depolarization field ($E_d$). During the continuous sweeping, the long domain walls have numerous opportunities to trap the charged point defects at the $E_d$ sites, and eventually are pinned [21]. In the present TEM experiment, no observable defect clusters are found attaching to the domain wall in the fatigued state because the domain wall mobility degrades so quickly that the trapped defects do not have enough time to accumulate [29].

In BNST27, there exist at least two main differences. First, the relaxor-ferroelectric phase transition takes place in each and every electric cycle. The ferroelectric phase nucleates from the relaxor phase and the formed relaxor/ferroelectric interface also bears uncompensated $E_d$. 
However, the magnitude should be only a half of that in BNST25 since the nanoscale domains on the relaxor side do not possess net polarization [30]. As a consequence, the driving force for the defect accumulation is significantly reduced in BNST27. Second, there is no polarization reversal in the induced ferroelectric phase in BNST27. During the reversible relaxor-ferroelectric transition, the induced ferroelectric phase is of transient nature and exists only within a very short period of time when the applied field is in the vicinity of its peak value; it disappears before the unloading is complete. Even if the polarization alignment/domain switching occurs during this transient period [31,32], the defect accumulation process would be interrupted whenever the loading/unloading is below the critical fields. As polarization reversal is essential for fatigue degradation, BNST27 hence exhibits a much stronger degradation resistance. It should be pointed out that BNST27 is not a single relaxor phase at zero field, the ferroelectric phase contributing to the $P_r$ will eventually lead to overall polarization degradation after prolonged electric cycling.

In summary, the correlation between the polarization degradation and the phase transition reversibility in (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-based relaxors has been verified. The greater depolarization field generated during the repeating polarization reversal under cyclic fields in the metastable ferroelectric phase accounts for the more severe fatigue degradation in BNST25 where the relaxor-ferroelectric transition is irreversible. In comparison, in BNST27 where the transition is reversible, no polarization reversal occurs in the transient induced ferroelectric phase and the relaxor/ferroelectric interface exhibits a reduced depolarization field, rendering a much stronger fatigue resistance.
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**Reference**


Figures

Fig. 4.1 The reversible relaxor-ferroelectric phase transition in BNST27. TEM bright-field micrographs taken at (a) virgin state, (b) 420 V, (c) 0 V. The insets display the selected area electron diffraction patterns recorded from the top corner of the grain. The bright circles mark the $\frac{1}{2}\{000\}$ superlattice spots while the bright arrow highlights a $\frac{1}{2}\{ooe\}$ spot. The long arrow in (b) indicates the direction of the applied electric field.
**Fig. 4.2** Electric characterization on bulk ceramic samples. Loss tangent curves measured during heating on poled (a₁) BNST25 and (a₂) BNST27 ceramics. The evolution of the $P$-$E$ hysteresis loops during bipolar electric cycling at ± 40 kV/cm in (b₁) BNST25 and (b₂) BNST27 ceramics. (c₁), (c₂) the variation of $2P_m$ and $2P_r$ with cycling number $N$, extracted from (b₁) and (b₂), respectively.
**Fig. 4.3** *In-situ* TEM fatigue test on BNST27. (a)-(c) The microstructural responses in a grain observed along [110] zone-axis during the first unipolar cycle. (d)-(f) The responses after $2 \times 10^3$ unipolar cycles at 420V. (g)-(i) The responses after $10^4$ unipolar cycles at 420 V. The arrow in (b) represents the direction of the applied/cyclic fields.
Fig. 4.4 *In-situ* TEM fatigue test on BNST25. The domain morphology in a [001]c zone-axis aligned grain at (a) virgin state, (b) 300 V, (c) 360 V, (d) 420 V, (e) 0 V, (f) -180 V, (g) -420 V, (h) 0 V during the first bipolar cycle. The bright arrow in (b) indicates the positive direction of the applied field. (i)-(l) The domain dynamics after $3 \times 10^3$ bipolar cycles at ±420 V.
CHAPTER 5.
MECHANISMS OF ENHANCED THERMAL STABILITY OF
POLARIZATION IN LEAD-FREE \(\text{(Bi}_{1/2}\text{Na}_{1/2})_{0.94}\text{Ba}_{0.06}\text{TiO}_3/ZnO}\)
CERAMICS COMPOSITE

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5.1 Abstract

\((\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\)-based solid solutions, one of the major systems of lead-free piezoelectric ceramics, exhibit a low thermal depolarization temperature \((T_d \sim 100 \, ^\circ\text{C})\). It was reported that by incorporating 30 mol% ZnO particles to form a ceramic composite of \((\text{Bi}_{1/2}\text{Na}_{1/2})_{0.94}\text{Ba}_{0.06}\text{TiO}_3/ZnO\), the depolarization process can be shifted up to \(\sim 250 \, ^\circ\text{C}\). In the present work, a variety of advanced transmission electron microscopy techniques, including \textit{in-situ} heating, annular bright-field, high-angle annular dark-field, geometric phase analysis, energy-dispersive spectrum and electron energy-loss spectroscopy, are employed to investigate the underlying mechanisms for the enhanced thermal stability of polarization in the composite. It
is found that the abrupt depolarization in \((\text{Bi}_{1/2}\text{Na}_{1/2})_{0.94}\text{Ba}_{0.06}\text{TiO}_3\) at \(T_d\) becomes diffused over a wide temperature window up to the temperature at maximum dielectric constant \((T_m)\) under the combined actions of the incorporation of Zn into the perovskite lattice, the presence of residual stresses, and the pinning effect on micron-sized domains provided by ZnO particles.

### 5.2 Introduction

Lead-free ceramics have been the worldwide focus for research in the piezoelectrics community over the past fifteen years, motivated by the search for replacement of the health/environment unfriendly lead-containing ceramics [1]. According to their chemical compositions, lead-free piezoceramics are classified into three groups, \(\text{BaTiO}_3\)-based, \((\text{K}_{1-x}\text{Na}_x)\text{NbO}_3\)-based, and \((\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\)-based [2]. Each of these groups possesses specific advantages and shortcomings in comparison with the market-dominating \(\text{Pb(Zr}_{1-x}\text{Ti}_x)\text{O}_3\) ceramics. Generally speaking, \(\text{BaTiO}_3\)-based ceramics exhibit outstanding small signal piezoelectric properties (e.g. \(d_{33} > 600 \text{ pC/N}\)), while their working temperature is quite limited due to their low Curie point \((T_c \sim 100 ^\circ\text{C})\) [3-5]; Modified \((\text{K}_{1-x}\text{Na}_x)\text{NbO}_3\) compositions can achieve values of \(d_{33}\) comparable to \(\text{Pb(Zr}_{1-x}\text{Ti}_x)\text{O}_3\) and have a moderate Curie point \((T_c > 200 ^\circ\text{C})\), in spite of the concerns on processing and reproducibility [6-8]; \((\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\)-based polycrystalline ceramics show a mediocre \(d_{33}\) but are capable of developing giant electro-strains [9,10]. However, they suffer from the restriction in working temperature as well. For example, the prototypical \((\text{Bi}_{1/2}\text{Na}_{1/2})_{0.94}\text{Ba}_{0.06}\text{TiO}_3\) (BNBT6) undergoes a thermal depolarization at the \(T_d\) about 100 \(^\circ\text{C}\), above which the micron-sized ferroelectric domains and the associated piezoelectricity vanish [11,12]. The thermal depolarization in \((\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\)-based ceramics is a manifestation of their complex phase transitions, most of which are still not fully understood.
Massive efforts have been invested in overcoming the shortcomings without sacrificing the advantages in these lead-free composition systems. Recently, we reported a novel method to eliminate the thermal depolarization in BNBT6, that is to form composites with ZnO particles (BNBT6/0.3ZnO) [13]. A “space charge” model was hypothesized to explain the influence of ZnO particle on $T_d$: the poling-induced micron-sized ferroelectric domains in BNBT6 are stabilized by charges in the ZnO particles, so that the depolarization of the ferroelectric phase can be significantly delayed. Following the initial work, various research groups have attempted to reproduce the BNBT6/ZnO composites and offered two new interpretations. Riemer et al. suggested the “stress field” model: the difference in thermal expansion coefficients of BNBT6 and ZnO leads to compressive stresses in the BNBT6 matrix when cooling down from the sintering temperature, hence the stress-induced relaxor → ferroelectric phase transition takes place in BNBT6 [14]. Mahajan et al., on the other hand, proposed that the increase in $T_d$ of BNBT6/ZnO is essentially a result of Zn incorporation into BNBT6 lattice which stabilizes the ferroelectric phases to a higher temperature; that is the “Zn doping” model [15].

Despite the plausibility of all three models, none of them have been unambiguously corroborated. In the present work, advanced transmission electron microscopy (TEM) techniques are utilized to unravel the exact mechanisms of the absence of the low temperature thermal depolarization at $T_d$ in the piezoelectric BNBT6/0.3ZnO composite.

5.3 Experimental

Sample preparation: Single phase BNBT6 was prepared first. Stoichiometric Bi$_2$O$_3$ (99.8%), BaCO$_3$ (99.0%), Na$_2$CO$_3$ (99.8%) and TiO$_2$ (99.0%, all from Alfa Aesar), were weighed and ball milled in ethanol for 24 h. The dried slurries were calcined at 900 °C for 3 h, ground manually
for 0.5 h, ball milled again in ethanol for 24 h, followed by a drying process. The powders were sintered in covered alumina crucibles at 1,100 °C for 3 h.

To fabricate the BNBT6/0.3ZnO composite, the sintered single phase BNBT6 was first ground into powder manually for 1 h. Afterwards, both the prepared BNBT6 powder and the commercial ZnO nanoparticles with the size of 25 nm (PlasmaChem, Germany) were weighed according to the formula. The mixture was ball milled again in ethanol for 24 h, dried and subsequently pressed into green disks with a diameter of 10 mm under 40 MPa. Sintering was carried out in covered alumina crucibles at 1,050 °C for 1 h with a ramp rate of 9 °C min⁻¹.

*Electrical properties measurement:* The disk samples with a diameter of ~8.5 mm and a thickness of ~0.5 mm were electroded with a thin layer of silver paste fired at 550 °C for 30 min. Dielectric constant (\(\varepsilon_r\)) and loss tangent (\(\tan\delta\)) were measured using an impedance analyzer (HP4294A) at 100 kHz in a temperature range from 30 to 320 °C on poled samples.

*Electron Microscopy:* An overall microstructure and element distribution were analyzed by SEM (FEI Helios NanoLab DualBeam). For TEM experiments, as-sintered ceramic pellets were mechanically ground and polished down to 120 μm thick, and then ultrasonically cut into disks with a diameter of 3 mm. After mechanical dimpling and polishing, the disks were annealed at 350 °C for 0.5 hour and Ar-ion milled to perforation. The *in-situ* heating tests were performed on a TEM of FEI Tecnai G2-F20. The detailed morphology, structure and element characterizations were performed on an aberration-corrected S/TEM (FEI Titan Themis).
5.4 Results and Discussion

5.4.1 Thermal Depolarization at $T_d$: Delayed or Diffused?

There are multiple ways to determine the depolarization temperature in (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-based piezoceramics, among which the anomaly in dielectric permittivity is most commonly used [16]. The temperature dependent dielectric constant ($\varepsilon_r$) and loss tangent (tan$\delta$) measured in poled BNBT6/0.3ZnO composite and single phase BNBT6 are compared in Fig. 1. Single phase BNBT6 shows a $T_d$ around 115 $^\circ$C, manifested by the steep increase of $\varepsilon_r$ and a raised plateau between 120 and 140 $^\circ$C in tan$\delta$. In contrast, $\varepsilon_r$ and tan$\delta$ increase continuously until $T_m$ in the BNBT6/0.3ZnO composite. It should be noted that the difference between $T_m$ and the temperature of the tan$\delta$ peak is typical for relaxor ferroelectrics [17].

There could be two interpretations of the absence of $T_d$ in dielectric curves of BNBT6/0.3ZnO. The first possibility is that $T_d$ is so much delayed that it merges with $T_m$. The other possible scenario is that the thermal depolarization becomes diffused and spreads over the temperature window of $T_d \sim T_m$. Owing to the capability of tracking the evolution of microstructure with temperature, in-situ heating TEM should be able to provide direct evidences to discern these two possible interpretations [18]. Here we use a Gatan heating holder with a tantalum furnace to heat the specimen in TEM. In order to correlate the temperature in in-situ TEM experiments with those during dielectric measurements on bulk specimens, TEM experiments are first carried out on the single phase BNBT6 (Fig. 2), of which the $T_d$ has been determined to be 115 $^\circ$C from the dielectric measurement. It has been shown that ~40% of the grains in BNBT6 display a core-shell structure where the core contains micron-sized domains and the shell is filled with nano-sized domains (Fig. 2a) [19]. The crystal symmetry of the core and shell can be analyzed using the selected area electron diffraction (SAED). According to
previous studies on (Bi$1/2$Na$1/2$)TiO$_3$ and its solid solutions [11,20,21], superlattice diffraction spots in SAED patterns can be used to identify possible space groups [22]. The [11$ar{2}$] zone-axis SAED recorded from the core shows discrete $\frac{1}{2}\{000\}$ superlattice spots (highlighted by the bright circle in the inset in Fig. 2a), indicating the $R3c$ phase of the micron-sized domains within the core. In contrast, the SAED (the upper right inset in Fig. 2a) from the shell region displays clear $\frac{1}{2}\{00e\}$ superlattice spots, suggesting the possible $P4bm$ symmetry of the nano-sized domains. As the specimen is heated up to 140 °C, the core starts to shrink in volume (Fig. 2b). At 170 °C, the core has been completely replaced by nano-sized domains and the SAED pattern recorded from the same position no longer shows the $\frac{1}{2}\{000\}$ superlattice spots (Fig. 2c). It can be concluded that, first, temperature discrepancy exists between the in-situ heating TEM experiment and the dielectric measurement on bulk specimens; second, the thermal depolarization in single phase BNBT6 occurs within such a narrow temperature window that corresponds well to the raised plateau in the tan$\delta$ curve in Fig. 1b.

To prepare for the in-situ heating TEM experiments on the BNBT6/0.3ZnO composite, we first analyze its representative microstructure (Fig. 3). There are three distinguishable phases from the contrast in the scanning electron microscopy (SEM) backscattered electrons micrograph: the bright matrix phase, the grey secondary phase and the dark secondary phase (Fig. 3a). The element distribution mapping recorded from the same area reveals that, the matrix phase is BNBT6; the grey secondary phase contains only Zn and O while the dark secondary phase contains Zn, Ti, and O. A close examination of the three phases is conducted with TEM. Fig. 3b displays the annular bright-field scanning transmission electron microscopy (ABF-STEM) image of the BNBT6 matrix viewed along its [001] zone-axis. The sites occupied by Bi (Na, Ba), Ti, and O atoms are respectively highlighted with purple, green and blue dots. Fig. 3c
and 3d shows the morphology of the two types of Zn-containing secondary phases. Even though indistinguishable in the bright field contrast, the two secondary phases are determined to be ZnO (Fig. 3c) and Zn$_2$TiO$_4$ (Fig. 3d) based on the corresponding energy-dispersive spectrum (EDS) displayed in Fig. 3(c1) and 3(d1). Interestingly, the microstructure of BNBT6 is altered by forming the composite. As shown in Fig. 2a, single phase BNBT6 is dominantly occupied with nano-sized domains with minor amounts of micron-sized domains in the central portion of some grains [11]. In BNBT6/0.3ZnO, on the contrary, a great number of micron-sized domains exist in BNBT6 grains close to the particle/matrix interface. It is found that the regions occupied by micron-sized domains vary in volume, some are confined in a narrow zone along the interface (Fig. 3c) while others can expand deep into the grain interior (Fig. 3d). It should be noted that there seems to be no correlation between the size of the region of micron-sized domains and the type of the secondary phase (ZnO or Zn$_2$TiO$_4$).

Then *in-situ* heating TEM experiments are conducted on the BNBT6/0.3ZnO composite to reveal the thermal depolarization process. A grain with a large region of micron-sized domains in the BNBT6 matrix is observed along the $\overline{1}10$ zone-axis during heating (Fig. 4). At room temperature, the BNBT6 grain is filled with micron-sized domains, and the ZnO particle resides at the grain boundary triple junction (Fig. 4a). The presence of the $\frac{1}{2}\{000\}$ superlattice spot, marked by the bright circle on the SAED pattern in the inset, indicates the $R3c$ crystal symmetry of the micron-sized domains [11]. When the specimen is heated up in TEM, the domain morphology remains unchanged until 150 °C, when the micron-sized domains start to be replaced by nano-sized domains from the left edge of the observed area (Fig. 4b). According to the results shown in Fig. 2, these nano-sized domains are of $P4bm$ symmetry. At 170 °C, the micron-sized domains in the top left part completely disappear (Fig. 4c). As temperature reaches
190 °C, the micron-sized domains near the bottom edge of the observed area transform into
nano-sized domains (Fig. 4d). At 210 °C, the volume occupied by micron-sized domains
continues to shrink (Fig. 4e). At 220 °C, only a few micron-sized domains can be seen in the
vicinity of the interface (Fig. 4f). Eventually, the observed area is entirely free of micron-sized
domains at 240 °C (Fig. 4g). In the meantime, the \( \frac{1}{2} \{ ooo \} \) superlattice spot in the corresponding
SAED pattern shown in the inset disappears. It can be easily derived from the in-situ heating
TEM experiment that the thermal depolarization in the BNBT6/0.3ZnO composite starts at a
temperature more or less the same as single phase BNBT6, so \( T_d \) is not delayed. Instead, the
thermal depolarization process is found to become gradual and spreads over a temperature range
spanning approximately 90 °C, much broader than that in the single phase BNBT6. Moreover,
the thermal depolarization in BNBT6/0.3ZnO seems to follow a spatial sequence. The micron-
sized domains in the BNBT6 grain interior depolarize and disappear first while those closer to
the ZnO particle are able to survive at higher temperatures and depolarize later.

The spatially sequenced thermal depolarization process in BNBT6/0.3ZnO is confirmed in
another [110] aligned BNBT6 grain (Fig. 5). The grain of interest is again filled with micron-
sized domains at room temperature (Fig. 5a). When the temperature increases, the thermal
depolarization starts at 117 °C (Fig. 5b). At 137 °C, the micron-sized domains in the left portion
completely disappear (Fig. 5c). As the temperature reaches 181 °C, the central portion of the
BNBT6 grain becomes free of micron-sized domains (Fig. 5d). At 230 °C, no micron-sized
domains are observable except for a few residuals near the ZnO/matrix interface (highlighted by
the yellow circle in Fig. 5e). These lamellar domains do not vanish until 271 °C, above which the
BNBT6 grain is completely occupied by nano-sized domains (Fig. 5f). In this particular grain,
the thermal depolarization process takes more than 150 °C (from 117 °C to 271 °C) to complete.
Similar to Fig. 4, the disappearance of micron-sized domains follows the unambiguous spatial sequence, from the region away from the ZnO particle towards the region in contact with the ZnO particle.

**5.4.2 Impact of ZnO on the Diffused Thermal Depolarization**

The introduction of ZnO particles as a secondary phase indeed makes the thermal depolarization in BNBT6 matrix diffused over a much broader temperature range. More importantly, the ZnO particles seem to have a pinning action to the micron-sized domains and, understandably, the “pinning force” must be stronger at the position closer to them. As a result, the weakly pinned micron-sized domains away from ZnO particles depolarize earlier and those in the region in contact with ZnO particles, which are strongly pinned, remain polarized till much higher temperatures. This is basically in agreement with our “space charge” model proposed in our original report [13]. However, there are still two critical questions to be answered. First, are there evidences to support the “stress field” and the “Zn doping” models? Second, what is the nature of the “pinning force” provided by ZnO particles?

The interface mismatch strain in ferroelectric thin films has been proved capable of enhancing ferroelectricity in BaTiO$_3$ [23]. Similar effect can even create ferroelectricity at room temperature in originally non-polar SrTiO$_3$ thin film [24]. In the BNBT6/0.3ZnO composite, according to Riemer *et al.* [14], a compressive stress in BNBT6 matrix is resulted from its higher thermal expansion coefficient than ZnO particles during the cooling process from the sintering temperature. Recently, a compressive stress induced relaxor (pseudocubic) → ferroelectric (R3c + P4mm) phase transition is observed in the BNBT6 bulk ceramic through systematic dielectric and X-ray diffraction studies [25]. Accordingly, the “stress field” model claims that micron-sized
ferroelectric domains are formed in the BNBT6 matrix through a stress-induced phase transition [14].

In order to find evidence for the “stress field” model, the strain field in the BNBT6 matrix grain was analyzed. Geometric phase analysis (GPA) is a powerful image-based strain measurement method used in high-resolution STEM micrographs. The basic idea is to calculate and illustrate the deviation of a real local lattice with respect to a reference lattice generated from the electron diffraction pattern [26]. Fig. 6a and 6b display the high-angle annular dark-field scanning transmission microscopy (HAADF-STEM) images of the BNBT6 matrix in contact with ZnO and Zn$_2$TiO$_4$ particles respectively, both of which are viewed along the [001] zone-axis. The GPA results (in-plane strain, $\varepsilon_{xx}$) are shown to the right of each HAADF-STEM images. It should be noted that the color contrast of strain mapping in the ZnO and the Zn$_2$TiO$_4$ particle do not represent the real strain there because the reference lattice used for GPA is also BNBT6 rather than ZnO or Zn$_2$TiO$_4$. In BNBT6, the strain values are uniformly below 1% across the examined area. Similar results are obtained in $\varepsilon_{yy}$ (out-of-plane) and $\varepsilon_{xy}$ (shear strain) mapping as well. It has been shown previously that strains of <1% can have a significant impact on the ferroelectric phase transitions [27,28]. Therefore, our GPA results seem not able to rule out the stress effect from contributing to the diffused thermal depolarization in the BNBT6/0.3ZnO composite.

Replacement of Ti$^{4+}$ by Zn$^{2+}$ on the B site of perovskite is likely to strengthen the dipole moment in BO$_6$ octahedra, hence stabilizes the long-range ferroelectric order in BNBT6 at room temperature [29,30]. The enhanced ferroelectric order can be a direct result of the strong tendency of Zn$^{2+}$ off-center displacement in BO$_6$ octahedra. In addition, Zn$^{2+}$ is an acceptor dopant for Ti$^{4+}$ on the B-site, which can be compensated by oxygen vacancies. Therefore,
(Zn\textsuperscript{\textit{\text{2+}}}\textsubscript{\textit{Ti}} - V\textsubscript{\text{O}}) defect dipoles are likely to be formed. It has been shown that other acceptor dopants, such as Fe\textsuperscript{3+} and Cu\textsuperscript{2+}, harden the ferroelectric behavior in (Bi\textsubscript{1/2}Na\textsubscript{1/2})TiO\textsubscript{3}-based ceramics and influence their thermal depolarization [31,32]. Accordingly, Mahajan \textit{et al.} attributed the higher $T_d$ in their BNBT6/ZnO composites to the diffusion of Zn into the lattice of BNBT6 matrix, namely the “Zn doping” model [15]. During the sintering process of composite materials, the inter-diffusion between different phases is certainly possible. So Zn doping probably also occurs in our BNBT6/0.3ZnO composite. However, when reviewing the works which support the “Zn doping” model, we notice that the thermal depolarization anomaly at $T_d$ in dielectric permittivity vs. temperature plots is still observable in BNBT6/ZnO composites, but is consistently ~30 $^\circ$C higher than the single phase BNBT6 [15,29,33]. So, the diffused thermal depolarization which causes the absence of that particular anomaly in our dielectric measurement cannot be solely attributed to Zn doping.

In order to obtain the exact picture of Zn distribution in the BNBT6 matrix, careful element analysis is conducted. Two points close to the interface are selected in Fig. 6a and 6b, of which \textit{Point 1} is located 4 nm from the ZnO/matrix interface and \textit{Point 2} has a 7 nm distance to the Zn\textsubscript{2}TiO\textsubscript{4}/matrix interface. The EDS patterns collected from the two points are shown for comparison in Fig. 6c. Since Zn L-line overlaps with Na K-line, only Zn K-line is displayed for illustration. It can be clearly seen that there is no Zn at \textit{Point 1} while Zn does exist at \textit{Point 2}. Since ZnO nanoparticle is the raw material used in the composite processing, it can be known that there is barely no Zn diffusion from ZnO into BNBT6 lattice during the sintering. This might be due to the relatively low sintering temperature and the fast heating/cooling rate. On the other hand, Zn\textsubscript{2}TiO\textsubscript{4} is very likely formed through the reaction between ZnO and BNBT6 at high temperatures [34]. The reaction can be expressed as follows (using BNT to represent BNBT6),
8ZnO + 4(Bi\textsubscript{1/2}Na\textsubscript{1/2})TiO\textsubscript{3} \rightarrow 4Zn\textsubscript{2}TiO\textsubscript{4} + Bi\textsubscript{2}O\textsubscript{3} + Na\textsubscript{2}O \quad (1)

This is supported by further element analysis in the vicinity of Zn\textsubscript{2}TiO\textsubscript{4}/matrix interface. Since Na and Zn are hard to distinguish in EDS, electron energy-loss spectroscopy (EELS) is employed for Na detection. As shown in Fig. 6d, Na L-edge is seen at Point 2 as expected, but is absent at Point 3 which is < 2nm away from the interface, implying the existence of a Na deficiency layer in BNBT6 matrix along the Zn\textsubscript{2}TiO\textsubscript{4}/matrix interface. Additional EDS analysis on Bi also indicates an even thicker Bi deficiency layer close to the interface. Such an A-site cation deficiency layer can be directly observed in the zoomed-in HAADF-STEM image of the BNBT6 matrix, in which the A-site columns (pointed by the yellow arrow in the inset of Fig. 6b) become apparently dimmer at the interface (left side). Because Na and Bi are volatile elements, BNBT6 might have lost some Na/Bi at elevated temperatures. After BNBT6 becomes deficient in Na/Bi, the reaction between ZnO and BNBT6 (shown in equation (1)) might be promoted, producing Zn\textsubscript{2}TiO\textsubscript{4}. Other products of this reaction, Bi\textsubscript{2}O\textsubscript{3} (T\textsubscript{m} = 817 °C) and Na\textsubscript{2}O (T\textsubscript{m} = 1132 °C), might then be evaporated during sintering. Thus, there exists a Na/Bi deficiency layer at the interface but no Bi\textsubscript{2}O\textsubscript{3} or Na\textsubscript{2}O segregation is found.

Concluding from the above EDS and EELS results, the ZnO nanoparticles in the raw mixture of the composite can be divided into two groups, the first group simply agglomerates into large particles, while the second group reacts with BNBT6. The fact that Zn is only detected in BNBT6 near Zn\textsubscript{2}TiO\textsubscript{4} reflects that Zn doping into BNBT6 lattice is accomplished during the reaction (1), rather than the direct diffusion of ZnO into BNBT6 lattice as was claimed in previous works. In other words, the second group of the ZnO nanoparticles can be regarded as the Zn source, leading to an increase in T\textsubscript{d} of the BNBT6 matrix. Even though the magnitude of this increase is moderate, e.g. ~30 °C, the reduced thermal disturbance to the dipole alignment
can still provide a big chance for the long-range ferroelectric order in micron-sized domains to form out of the nano-sized domains at room temperature [35].

As discussed in the last section, micron-sized domains occupy a larger volume fraction in BNBT6 grains in the BNBT6/0.3ZnO composite at room temperature than those in the single phase BNBT6 because of Zn doping via reaction (1). Nevertheless, such an effect is not able to render the thermal depolarization gradual and diffused, which is exactly how the BNBT6/0.3ZnO composite behaves. It becomes clear below that the group of ZnO nanoparticles that do not participate in the chemical reaction (1) play a critical role.

When we originally proposed the pinning effect from ZnO using the “space charge” model [13], there was a sufficient condition of DC field poling. The poling field not only induces the micron-sized domains in BNBT6 matrix, but also the redistribution of the charges in the semiconductor ZnO at the ZnO/matrix interface. Those charges compensate the depolarization field within the micron-sized domains across the interface, so their transition back into nano-sized domains during temperature increasing is suppressed. It is well known that ZnO with the wurtzite structure possesses a spontaneous polarization along the polar [0001] axis [36-38]. This provides bound charges along the ZnO/matrix interface even without any externally applied field. This explains why the pinning effect can be clearly observed during our in-situ heating TEM experiments conducted on unpoled specimens (Figs. 4 and 5).

Since the pinning force stems from the spontaneous polarization in ZnO, it should be highly anisotropic. In other word, the “space charge” model can be indirectly proved if the anisotropy in the pinning effect is verified. For this purpose, a circular shaped ZnO particle with a diameter of ~1 µm is deliberately chosen to be viewed along its [3302] zone-axis during another in-situ heating TEM experiment (Fig. 7). The polar [0001] direction in ZnO is projected onto the
micrograph plane and marked by the red arrow in Fig. 7a. The projection angle is 31.7° (Fig. 7a$_1$). At room temperature, two clusters of micron-sized domains are present in the BNBT6 matrix, respectively located close to the lower (Fig. 7a) and the left part of the ZnO inclusion (Fig. 7a$_2$). From room temperature to 150 °C, neither of the two clusters of domains depolarize (Fig. 7b). At 160 °C, the domains close to the left side of the ZnO inclusion disappear while the other domains close to the lower side of ZnO persist (Fig. 7c). When the temperature reaches 230 °C, the straight domain walls are still observable in that particular region close to the lower side of ZnO (Fig. 7d). As the specimen is further heated up to 300 °C, all the micron-sized domains disappear (Fig. 7e). It should be noted that the changes in the contrast and shape of the ZnO particle in Fig. 7 is due to the slight adjustment of tilting to optimize the domain contrast in the BNBT6 matrix; therefore, they do not reflect real changes of the ZnO particle in this temperature range.

These two clusters of micron-sized domains are very likely formed due to the same reasons as for the ferroelectric core in Fig. 2. The domains close to the left side of the ZnO inclusion disappear at the temperature almost the same as for the ferroelectric core in Fig. 2b and for the domains far away from the ZnO particles in Fig. 4b and 5b. It indicates that in spite of the very short distance, the domains close to the left side of the ZnO inclusion do not receive any pinning force from ZnO at all. On the contrary, the domains close to the lower side of the ZnO inclusion are indeed pinned up to the temperature that is roughly the same as the final stage of the diffused thermal depolarization process (Fig.s 4f and 5e). It should be noted that the projected direction of the polar [0001] axis of ZnO exactly points to this set of micron-sized domains (Fig. 7a).

Therefore, the anisotropy in the pinning effect is experimentally verified in Fig. 7 and is further schematically illustrated in Fig. 8. The 2-D diagram can be regarded as the micrograph plane in
Fig. 7 after it is tilted for 31.7° to have the [0001] polar axis (bright arrow) in-plane. The polarization in the micron-sized domains in the BNBT6 matrix are drawn in accordance with the most common configuration in rhombohedral ferroelectric crystals. The positive and negative charges are separated along the [0001] polar axis and respectively bound at the bottom and top ZnO/matrix interface. On the other hand, there is no spontaneous polarization along the direction perpendicular to [0001] in ZnO. Thereby no bound charges at the left or right side of the ZnO/matrix interface. As a result, the domains located close to the bottom interface are pinned by the bound charges but the domains in contact with the left interface have no chance to receive any pinning force. When the temperature is above $T_d$, the unpinned domains in the left side disappear while the pinned ones close to the bottom interface persist. Such an anisotropy in the pinning effect strongly supports our original “space charge” model and further indicates that the spontaneous polarization of ZnO is the source of pinning charges.

However, there are several points that need to be made clear. First, the presence of spontaneous polarization in ZnO seems not sufficient to trigger the formation of micron-sized domains, but is sufficient to stabilize the already formed micron-sized domains. This explains the fact that there are no micron-sized domains close to the top ZnO/matrix interface, even though there exist bond charges from the spontaneous polarization of the ZnO inclusion. These bond charges, however, are capable of stabilizing the existing micron-sized domains close to the bottom interface. Second, since our GPA results do not rule out the “stress field” model, there could be tensile stresses in the ZnO inclusion to balance the compressive stresses in the BNBT6 matrix [14]. Through the piezoelectric effect of ZnO, such residual stresses are expected to increase the bound charges at the ZnO/matrix interface, which in turn will strengthen the “pinning effect” on the micron-sized domains. Third, even though the model shown in Fig. 8 is
plausible, we admit it is an oversimplified illustration and ignores some details. For example, the polarization directions of those lamellar domains are not experimentally determined and there are segments on the BNBT6/ZnO interface with the “head-to-head” polarization configuration. Further studies are still needed to improve the model.

5.5 Conclusions

In summary, extensive TEM experiments are conducted to reveal the mechanisms of the thermal depolarization in the BNBT6/0.3ZnO composite. In-situ heating TEM indicates that the thermal depolarization in the composite is not just simply shifted to higher temperatures, rather it becomes gradual and diffused. GPA results suggest a strain field of magnitude <1% is present in the BNBT6 matrix. Combined EDS and EELS analysis indicate that the existence of high volume fraction of micron-sized ferroelectric domains in BNBT6 grains in the composite at room temperature is likely due to Zn doping into the BNBT6 perovskite lattice, which is accomplished through the chemical reaction between ZnO and BNBT6. Once the micron-sized domains are formed in the BNBT6 grain, they are pinned by the charges in ZnO originated from its spontaneous polarization. Correspondingly, the pinning effect displays a strong anisotropy with respect to the [0001] polar axis of ZnO. It is observed that the thermal depolarization process in the BNBT6 matrix starts from positions farther away from ZnO and gradually progresses to the ZnO/BNBT6 interface, a continuous process spanning over a wide temperature range of more than 100 °C.
Acknowledgements

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Reference


**Figures**

![Graph](image_url)

**FIG. 5.1** Temperature dependent (a) dielectric constant and (b) loss tangent measured at 100 kHz on the single phase BNBT6 ceramic and the BNBT6/0.3ZnO composite.
FIG. 5.2 *In-situ* TEM observation of the thermal depolarization in the BNBT6 ceramic. (a)

Bright field micrograph of a [112] aligned grain with core-shell structure at room temperature. The SAED pattern recorded from the ferroelectric core is displayed in the lower left inset. The $\frac{1}{2}\{ooo\}$ superlattice spot is highlighted with the bright circle. The SAED from the shell is displayed in the upper right inset with the $\frac{1}{2}\{ooe\}$ superlattice spot indicated with the bright arrow. The same area at (b) 140 °C, and (c) 170 °C. The inset in (c) is the SAED pattern recorded from the same position as in (a).
FIG. 5.3 (a) SEM backscattered electrons image of the overall microstructure of the BNBT6/0.3ZnO composite and the corresponding EDS element maps. (b) ABF-STEM image of the BNBT6 matrix viewed along its [001] zone axis. Bi (Na, Ba), Ti and O atom columns are marked with colored dots. (c) TEM bright field image of the domain morphology around a ZnO particle (EDS pattern shown in c₁). (d) TEM bright field image of the domain morphology around a Zn₂TiO₄ particle (EDS pattern shown in d₁). Insets of (c) and (d) show the corresponding EDS mapping of Bi (green) and Zn (red).
FIG. 5.4 *In-situ* TEM observation of the diffused thermal depolarization in the BNBT6/0.3ZnO composite. The composition is verified with EDS analysis. Bright field images of the domain morphology in a [110] aligned BNBT6 grain around a ZnO particle at (a) 25 °C, (b) 150 °C, (c) 170 °C, (d) 190 °C, (e) 210 °C, (f) 220 °C, and (g) 240 °C. The SAED patterns are displayed as insets in (a) and (g). The ½{000} superlattice spot is highlighted with the bright circle in (a).
FIG. 5.5 *In-situ* TEM observation of the diffused thermal depolarization in another specimen of the BNBT6/0.3ZnO composite. Bright field images of the domain morphology in another [110] aligned BNBT6 grain around a ZnO particle at (a) 25 °C, (b) 117 °C, (c) 137 °C, (d) 181 °C, (e) 230 °C, and (f) 271 °C. The yellow circle in (e) surrounds the preserved micron-sized domains close to the interface. The SAED patterns are displayed as insets in (a) and (f). The ½{000} superlattice spot is highlighted with the bright circle in (a).
FIG. 5.6 HAADF-STEM micrographs of BNBT6 grains along their [001] zone-axis in contact with a (a) ZnO, and (b) Zn$_2$TiO$_4$ particle. Corresponding GPA mapping of the in-plane strain ($\varepsilon_{xx}$) is displayed to the right of each micrograph. The inset in (b) shows the zoomed-in HAADF-STEM image of the BNBT6 grain close to the interface, in which the yellow arrow points at one of the A-site columns. (c) The Zn K-line extracted from the EDS recorded from Point 1 in (a) and Point 2 in (b). (d) The Na L-edge extracted from the EELS recorded from Point 2 and Point 3 in (b).
FIG. 5.7 The anisotropy of the “pinning effect” from a ZnO particle embedded in a BNBT6 grain. (a) Bright field image of two clusters of micron-sized domains around a [3302] aligned ZnO particle at (a) 25 °C, (c) 160 °C, (d) 230 °C, and (e) 300 °C. The corresponding SAED pattern recorded from the ZnO particle is shown in (a1). (a2) and (b) display the close-up views of the domain cluster in the left at 25 °C and 150 °C, respectively.
FIG. 5.8 Schematic illustration of the anisotropic pinning effect from a ZnO particle on the lamellar ferroelectric domains in the BNBT6 matrix. The upper panel depicts the situation at temperatures below $T_d$ while the lower panel illustrates the situation at temperatures between $T_d$ and $T_m$. The polar [0001] direction of ZnO is marked with the bright arrow.
CHAPTER 6.

IN-SITU TEM STUDY OF THE AGING MICROMECHANISMS IN A BATIO$_3$-BASED LEAD-FREE PIEZOELECTRIC CERAMIC

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6.1 Abstract

Aging and fatigue are the two main concerns regarding the performance reliability of piezoelectric ceramics. Compared with fatigue, less efforts have been made towards clarifying the micromechanisms of aging. In this report, we employ electric field in-situ transmission electron microscopy (TEM) to directly visualize the domain structure evolution during fatigue and the subsequent aging process in the 0.5Ba(Zr$_{0.2}$Ti$_{0.8}$)O$_3$–0.5(Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$ (BZT–BCT) polycrystalline ceramic. The macroscopic aging behaviors, including the development of internal bias field ($E_{\text{bias}}$) and the degradation in switchable polarization ($2P_1$), are correlated with the microscopic domain wall clamping and domain disruption resulted from the redistribution of oxygen vacancies driven by depolarization field.

Keywords: aging, fatigue, in-situ TEM, BZT–BCT, domain disruption

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6.2 Introduction

Piezoelectric ceramics have found applications in a variety of devices including sensors, transducers, and actuators [1,2]. The primary pursuit in optimizing the piezoelectric ceramic composition is to achieve high functional properties, most importantly the piezoelectric coefficient ($d_{33}$). Piezoelectric properties inevitably degrade due to electric fatigue during electrical cycling or aging with time even without any applied fields [3]. Actually, real piezoelectric devices suffer from both fatigue and aging because they are subjected to cyclic fields while working and zero fields while sitting idle. It has been realized that long-term performance stability and reliability is of equal importance as high properties to practical devices. Therefore, investigations on the micromechanisms of fatigue and aging are critical to composition optimization and device design.

In fact, electric fatigue has been studied more comprehensively than aging in the literature. Various experimental methods are employed to uncover the microstructural origin of the fatigue degradation. Piezoresponse force microscopy has been extensively used to reveal the change in domain morphology before and after electrical cycling [4-6]. TEM, capable of providing chemical and crystallographic information and imaging nanoscale defects, starts to make contributions to electric fatigue research. Our previous electric field in-situ TEM experiments have successfully identified various microstructural mechanisms of fatigue degradation, including domain fragmentation [7], domain formation blockage [8], and microcrack initiation [9].

In contrast, the research on aging degradation has been mainly focused on interpretations of macroscopic results and analytical modelling of the experimental data [3]. Aging in piezoelectric ceramics can be generally classified into two categories, aging in the unpoled state and aging in
the poled state. Aging in the unpoled state can result in the “pinching” of polarization-electric field \((P-E)\) hysteresis loop, whereas aging in the poled state leads to the shift of the \(P-E\) loop [3]. Three major models have been proposed to explain these aging phenomena. Volume effect is associated with the symmetry-conforming defect dipoles, consisting of oxygen vacancy and acceptor cation pairs, that align themselves during aging with the spontaneous polarization in a ferroelectric domain [10]. The volume effect has succeeded in explaining the recoverable electro-strain and the double \(P-E\) loops in aged unpoled ceramics [11]. Domain wall effect, where domain walls are gradually pinned by charged point defects during aging, is more extensively discussed as the cause of fatigue than of aging [12-14]. Grain boundary effect, or the space charge model, describes the accumulation of charged point defects at grain boundaries during aging, which stabilizes the existing domain configuration [15,16]. The space charge model has been rather effective in reproducing the time dependence of the internal bias field \((E_{\text{bias}})\) development during aging of poled ceramics [17,18].

In spite of the considerable experimental and modelling efforts, direct observation on microstructure evolution during aging has not yet been reported. In the present work, a test profile that mimics the intermittent working conditions of practical piezoelectric devices, i.e., aging after cyclic electrical loadings, is applied to BZT–BCT, a BaTiO\(_3\)-based lead-free ceramic with outstanding piezoelectric properties [19-22]. \textit{In-situ} TEM is employed to directly visualize the microstructure evolution corresponding to the macroscopic fatigue and aging degradation.
6.3 Materials and methods

The BZT–BCT polycrystalline ceramic was prepared through the solid-state reaction method. Stoichiometric amount of powders of BaCO$_3$ (99.8%), CaCO$_3$ (99.5%), ZrO$_2$ (99.5%), and TiO$_2$ (99.6%) were mixed and milled for 5 hours in a planetary mill using ethanol and ZrO$_2$ milling media. The slurry was then dried and the powders were calcined at 1300 °C for 2 hours. The calcined powder was again milled, dried, and formed into disks by uniaxial pressing in a 10 mm diameter die, followed by cold isostatic pressing at 300 MPa. Sintering was carried out at 1500 °C for 2 hours, with a heating rate of 5 °C/min.

The sintered pellets were ground to a thickness of about 0.7 mm and silver electrodes were painted and fired on at 400 °C. The bipolar fatigue tests on bulk samples were conducted at room temperature using a triangular waveform at a frequency of 10 Hz. After fatigued for $10^6$ cycles at ±3.5 kV/cm, the sample was kept in air at room temperature for aging. The $P$-$E$ hysteresis loops were recorded during the fatigue as well as the aging tests using a standardized ferroelectric test system (Precision LC II, Radiant Technologies).

As-sintered ceramic pellets were mechanically ground and polished down to 120 μm thick, and then ultrasonically cut into disks with a diameter of 3 mm. After dimpling and polishing, the disks were annealed at 150 °C for 2 hours and Ar-ion milled until perforation. The *in-situ* TEM fatigue test was performed on an FEI Tecnai G2-F20 microscope operated at 200 kV, with bipolar electric fields in a triangle waveform at a frequency of 10 Hz applied to the specimen. The same TEM specimen, after subjected to $10^5$ bipolar cycles at ±60 V, was aged in air at room temperature. The specimen was then loaded to the TEM at a series of aging time to have its domain morphology examined and recorded.
In this work, we quote the applied voltage instead of the nominal electric field (applied voltage divided by the electrode spacing of 120 \( \mu \text{m} \)) because the TEM specimen contains many pores which either intensify or dilute the actual field and make the calculated nominal field misleading \[23\]. However, the magnitude of applied voltage was not arbitrarily chosen \[24\]. The voltage that can induce the single-domain state in the grain-of-interest is 108 V (Fig. 4a), while the electric field for the single-domain state in bulk samples is roughly 6 kV/cm \[25\]. To be consistent with the cycling condition (±3.5 kV/cm) in bulk measurement, ±60 V is used as the cyclic voltage for the \textit{in-situ} TEM experiment.

6.4 Results

6.4.1 Macroscopic behavior of fatigue and aging

The \(P-E\) hysteresis loops measured before fatigue, after fatigue, and after aging are displayed in Fig. 1a. The switchable polarization \(2P_r\) hardly changes during fatigue but exhibits apparent degradation during aging (Fig. 1b). \(2P_r\) decreases monotonically with the aging time, following the empirical logarithmic dependence \[26\]. In addition to the property decay, an obvious bump can be seen in the lower branch \(E > 0\) of the \(P-E\) loop in the aged state (Fig. 1a). The red dashed curve is created through the central inversion of the upper branch of the loop, in order to highlight this bump. The development of this bump shifts the \(P-E\) loop to the right, gradually building an internal bias field \(E_{\text{bias}}\), as depicted in Fig. 1c. It needs to be clarified that the observed shape change in the \(P-E\) loop is different from the “pinching” commonly seen in aged unpoled samples. They may even have different mechanisms, considering the following facts. First, defect dipoles must be rare in BZT–BCT due to absence of aliovalent dopants; second, there is no anomaly present in the \(P-E\) loop measured in the same sample which has been
annealed and then aged for the same time period (144 hours). The rightward shift of the $P$-$E$ loop (Fig. 1a) and $E_{\text{bias}}$ with negative values (Fig. 1c) imply that the aging process after electric cycling resembles that of a negatively poled sample [27]. This is reasonable because the last bipolar cycle stops when the negative voltage returns to zero. The voltage the sample sees last is with a negative polarity. Similar aging-induced changes in the shape of $P$-$E$ loops have been previously reported in other “poled” BaTiO$_3$-based ceramics [28,29], where “poling” was completed simply by application of one cycle of unipolar fields rather than a dc voltage for an extended time.

6.4.2 In-situ TEM observation of fatigue and aging

In order to uncover the microstructural origin of the macroscopic aging behavior, a grain along its $[\bar{1}10]$ zone-axis is selected for the in-situ TEM observation (Fig. 2). In our previous in-situ TEM studies, the crystal symmetry is inferred primarily from the superlattice diffraction spots [30,31]. However, the various phases in BZT–BCT ($P4mm$, $R3m$, $Amm2$, $Pm\bar{3}m$) do not have superlattice spots in their electron diffraction patterns. Therefore, the diffraction patterns here are only used to assist the determination of the crystallographic information of the domain walls (inset of Fig. 2a). In the virgin state, a few long lamellar domains with domain walls tracing along $<11\bar{1}>$ directions are embedded in the matrix (can be considered as a large domain, Fig. 2a). Crystallographic analysis indicates that the domain walls are very likely on $\{110\}$ planes, suggesting the 71° rhombohedral domain walls. In addition to the lamellar domains, a feature of $\sim 2$ μm in size with an irregular shape and complex strain contrasts exists in the center of the observed area. The nature of this feature will be discussed in detail later. At the poling voltage of 36 V, some of the original domain walls which trace along the $[1\bar{1}1]$ direction are
replaced by new domain walls tracing along the [111] direction, indicating the applied field is above the coercive field and domain switching starts to occur (Fig. 2b). Upon further increase of the poling voltage to 60 V, further changes in the domain configuration is noticed (Fig. 2c). After the voltage is removed, the domain morphology developed at 60 V is largely preserved (Fig. 2d).

The same area shown in Fig. 2 is monitored during the subsequent bipolar cycling with the peak voltage of 60 V and bright field micrographs are recorded after a certain number of cycles. It is noted that the applied voltage changes from –60 to 0 V at the end of bipolar cycling. During the first 10 cycles (Fig. 3a), a set of new domains are formed in the lower part of the observed area, which may be an indication of the domain instability in the initial stage of cycling [32]. However, domains in the rest part largely remain unchanged. Further application of bipolar fields to $10^5$ cycles induces only minor changes in the domain configuration (Fig. 3b). Then, this specimen is kept on the TEM holder and is aged in air at room temperature. After 18 hours aging (Fig. 3c), the overall domain morphology survives. But signs of aging start to emerge: several straight domain walls in the lower part of the observed area are partially disrupted by some complex features. After 42 hours aging (Fig. 3d), the domain morphology changes significantly. A substantial number of long lamellar domains have been disrupted to various degrees and are replaced by complex features. These complex features have identical appearances to the pre-existing large feature in the center of the observed area.

6.4.3 The nature of the features with complex contrast

Our previous in-situ TEM studies have reproducibly proved the existence of a unique single-domain state in the BZT–BCT ceramic at certain applied fields [8,33,34]. In this report, we take
advantage of the transition towards the single-domain state to clarify the nature of those features with a complex contrast.

Voltages beyond 60 V are applied to the aged TEM specimen and the same area shown in Figs. 2 and 3 is focused. When the applied voltage reaches 108 V, all the long lamellar domains in the aged state (Fig. 3d) disappear completely (Fig. 4a), indicating a possible phase transition from the rhombohedral ($R3m$) to the orthorhombic phase ($Amm2$) [35]. It is worth noting that those complex features, both the pre-existing and the newly formed during aging, display obvious changes as well. The formerly complex contrasts become much cleaner while only some dark spots retain. Removal of the 108 V leads to the reappearance of large lamellar domains, but with a totally different configuration (Fig. 4b). Interestingly, the complex contrast of those features are recovered. Therefore, it can be deduced that those complex features are the mixture of clusters of charged point defects (most likely oxygen vacancies in BZT–BCT) and small fragmented domains. The oxygen vacancy clusters will not change under a single triangular field cycle, hence appear as the dark spots in Fig. 4a. On the other hand, the small fragmented domains can align their polarizations to merge with the matrix large domain at 108 V and reappear at the removal of the applied voltage.

6.5 Discussion

The in-situ TEM observations on the domain structure evolution correlate well with the macroscopic behavior in the bulk measurement. The stable domain configuration against bipolar cycling at ±60 V (Fig. 3a and 3b) is apparently the reason for the good fatigue resistance at ±3.5 kV/cm in the bulk sample. Since the peak voltage for cycling (60 V) is way below the voltage needed to produce the single-domain state (108 V for the monitored grain, Fig. 4a), repeated
domain switching rather than phase transition is expected to take place during bipolar cycling. In such a situation, domain fragmentation would be the most common consequence of electric fatigue [7,36]. However, the resilience of the long lamellar domains against fragmentation during cycling at ±60 V can be attributed to the incomplete domain switching under the low applied fields. Baek et al. has shown in rhombohedral BiFeO$_3$ that fatigue degradation can only be rendered by complete 180° domain switching but not partial 71° domain switching [37]. So, ±60 V, or ±3.5 kV/cm, may not be sufficient to induce complete domain switching, thereby no obvious electric fatigue degradation is detected.

On the other hand, the apparent macroscopic aging in the bulk sample can be associated with the significant domain morphology change during the 42-hour-aging in TEM. The development of the internal bias field during aging obeys the linear logarithmic time law, as shown by the fitted dashed line in Fig. 1c [17,38,39]. It has been widely hypothesized that, it is the depolarization field that drives the redistribution of oxygen vacancies and builds the $E_{\text{bias}}$ [40,41]. Our in-situ TEM observations have provided strong support to this hypothesis. The domain morphology is quite stable against bipolar cycling but vulnerable to disruption with time in absence of applied fields. Similar phenomenon has been previously reported in ferroelectric thin films [42]. The depolarization field is reversed as the applied field changes polarity during cycling, which will redistribute the oxygen vacancies toward self-compensation. On the contrary, the depolarization field maintains its polarity during aging, hence forces a directional drift of oxygen vacancies and eventually builds the internal bias field. The disruption of lamellar domains with defect clusters during aging is a direct evidence that the depolarization field, instead of the applied field, is the driving force for oxygen vacancies’ redistribution.
A close examination of the micrographs shown in Figs. 3 and 4 indicates that they further reveal the impact of domains on oxygen vacancy clustering. As pointed by the bright arrow in Fig. 3d, a circular-shaped feature with a diameter of \( \sim 0.4 \, \mu \text{m} \) forms at the tip of a domain after 42 hours aging. For clarity, the same location is also marked in Fig. 3c where this feature has not formed yet. Also highlighted in Fig. 4a, this circular feature remains unchanged in shape and size under applied voltage of 108 V, indicating that it is a big cluster of oxygen vacancies. The high local electrostatic and elastic distortion energy at the domain tip accelerates the clustering process of oxygen vacancies. Clustered oxygen vacancies will in turn clamp the domain walls and suppress their responses to the applied fields [8]. In addition to being clamped at the tips, many lamellar domains are found to be disrupted and replaced by the mixture of oxygen vacancy clusters and fragmented domains after aging (Fig. 3d). This “domain disruption” during aging, even though appears in resemblance to the fatigue induced “domain fragmentation” [7], is resulted from completely different mechanisms. The clustering of oxygen vacancies at domain tips during aging is likely to be the first step. The accumulation of point defects at the tip then leads to the retraction of lamellar domains. As the aging process continues, domains will eventually be disrupted. This explains the observation in Fig. 3d that disruption primarily occurs to those relatively smaller lamellar domains having tips in the interior of the matrix large domain. The interactions of oxygen vacancy clusters at the tip with lamellar domains and the strong association of disrupted domains with point defects are apparently the micromechanisms for the degradation in switchable polarization \( (2P_r) \) during aging. Such a degradation in \( 2P_r \) is generally accompanied with the building up of \( E_{\text{bias}} \) [43]. The positive correlation is confirmed by the linear relation between \( 2P_r \) and \( E_{\text{bias}} \) shown in the inset of Fig. 1c.
6.6 Conclusions

The micromechanisms of aging in piezoelectric ceramics are investigated with in-situ TEM for the first time. Through contrasting the stability of domain morphology during fatigue and aging, depolarization field is proved to be the driving force for the redistribution of oxygen vacancies. During aging, oxygen vacancy clusters are directly observed to build up at the domain tips and then disrupt the lamellar domains into small fragments. As a result, the switchable polarization degrades apparently and an internal bias field builds up in the aged sample.

Acknowledgements

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Reference


[4] V. Rojas, J. Koruza, E. A. Patterson, M. Acosta, X. Jiang, N. Liu, C. Dietz, J. Rödel, Influence of composition on the unipolar electric fatigue of Ba(Zr0.2Ti0.8)O3-(Ba0.7Ca0.3)TiO3 lead-free piezoceramics, J. Am. Ceram. Soc. 100 (2017) 4699.

[5] S. Tsurekawa, H. Hatao, H. Takahashi, Y. Morizono, Changes in ferroelectric domain structure with electric fatigue in Li0.06(Na0.3K0.5)0.94NbO3 ceramics, Jpn. J. Appl. Phys. 50 (2011) 09NC02.


[25] H. Guo, B. K. Voas, S. Zhang, C. Zhou, X. Ren, S. P. Beckman, X. Tan, Polarization alignment, phase transition, and piezoelectricity development in polycrystalline 0.5Ba(Zr$_{0.2}$Ti$_{0.8}$)O$_3$–0.5(Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$, Phys. Rev. B 90 (2014) 014103.


[31] X. Liu, H. Guo, 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 (2014) 2997-3006.


[34] M. Zakhozheva, L. A. Schmitt, M. Acosta, H. Guo, W. Jo, R. Schierholz, H. J. Kleebe, X. Tan, Wide compositional range in situ electric field investigations on lead-free Ba(Zr$_{0.2}$Ti$_{0.8}$)O$_3$-xBa$_{0.7}$Ca$_{0.3}$TiO$_3$ piezoceramic, Phys. Rev. Appl. 3 (2015) 064018.


**Figures**

![P-E loops](image1.png)

![Switchable polarization](image2.png)

![Internal bias field](image3.png)

Fig. 6.1 (a) P-E loops measured before fatigue (black), after fatigue (blue) and after aging (red).

(b) Evolution of the switchable polarization ($2P_r$) depending on the fatigue cycles and the aging time. (c) The aging time dependence of the internal bias field ($E_{bias}$); (inset) correlation between $E_{bias}$ and $2P_r$. 
Fig. 6.2 *In-situ* TEM observations of the domain evolution in a grain during the initial poling. (a) Bright field micrograph along the $[\bar{1}10]$ zone axis (a) in the virgin state, (b) at 36 V, (c) at 60 V and (d) after the applied voltage is removed. The inset in (a) is the electron diffraction pattern recorded at the virgin state. The long bright arrow in (b) is the positive direction of the applied voltage.
Fig. 6.3 Bright field micrographs of the same area in Fig. 2 under 0 V after (a) 10, (b) $10^5$ bipolar cycles and (c) 18, (d) 42 hours aging.
Fig. 6.4 Clarification of the nature of complex features. Bright field micrographs of the same area in Fig. 2 (a) at 108 V and (b) after the voltage is removed.
CHAPTER 7. CONCLUSIONS

With the primary motivation to elucidate the micromechanisms of the performance instability in lead-free piezoelectric ceramics, this dissertation presents the in-situ TEM results on electric fatigue, aging, and thermal depolarization phenomena.

The fatigue resistance is proved dependent on the phase composition. Electric cycling in different phases leads to completely different fatigue behaviors. Because the phase nature is tunable while the field amplitude is changed or the chemical composition is modified, the relation between the electric fatigue and the cycling amplitude or the chemical composition is identified.

Aging effect can be more destructive than fatigue in piezoelectric ceramics. The charged point defects are observed to quickly segregate at the domain walls during aging. The affected domains are then disrupted into smaller fragments.

The mechanism underlying the enhanced thermal stability in the BNT-based composite is found to be very complicated. The thermal depolarization process is significantly diffused via the combined doping effect and pinning effect provided by the ZnO particles.

In the future, similar studies can also be conducted on KNN-based ceramics. Presumably, the results could be more interesting, owing to the presence of more complicated phases. Subjected to the poling field, the domain morphology changes significantly and continuously, accompanied by the phase transitions. Additionally, unlike BaTiO$_3$ or BNT that have a morphotropic phase boundary (MPB), KNN-based piezoceramics possess the polymorphic phase transition (PPT). Therefore, such rich physics could engender KNN a better system to study the micromechanisms of the electric fatigue or the thermal stability.