In-situ TEM investigation of the phase transitions in perovskite ferroelectrics

Weiguo Qu
Iowa State University

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In-situ TEM investigation of the phase transitions in perovskite ferroelectrics

by

Weiguo Qu

A dissertation submitted to the graduate faculty
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Xiaoli Tan, Major Professor
Vitalij K. Pecharsky
Matthew J. Kramer
Scott L. Chumbley
David K. Hsu

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Ames, Iowa
2008

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Dedicated to my parents and my wife Xuefei for their love and support during my education
Table of Contents

Abstract.................................................................................................................. vii

Chapter 1. Introduction............................................................................................. 1
  1.1 History of ferroelectrics ...................................................................................... 2
  1.2 Concepts and characteristics of Ferroelectrics ................................................ 4
    1.2.1 Concepts ..................................................................................................... 4
    1.2.2 Characteristics ............................................................................................ 6
  1.3 Applications of ferroelectric materials ............................................................... 11
    1.3.1 High dielectric permittivity—capacitors ..................................................... 11
    1.3.2 Reversible spontaneous polarization--non-volatile memories ................... 12
    1.3.3 Large piezoelectric coefficient—transducers .............................................. 13
  1.4 Perovskite structure .......................................................................................... 13
  1.5 The Pb(Zr1-xTix)O3 solid solution system ........................................................ 15
  1.6 The prototype relaxor compound Pb(Mg1/3Nb2/3)O3 .......................................... 18
    1.6.1 B-site 1:1 cation ordering .......................................................................... 18
    1.6.2 Dipole ordering ......................................................................................... 19
    1.6.3 Evolution of the electric dipole order under electric fields ......................... 20
    1.6.4 Correlations between the two types of ordering .......................................... 23
  1.7 Logic of this dissertation ................................................................................... 24
  1.8 Key experimental approach .............................................................................. 26
  1.9 References ......................................................................................................... 27

Chapter 2. High Temperature Phases in the 0.98PbZrO3–0.02Pb(Ni1/3Nb2/3)O3 Ceramic .................................................. 33
  2.1 Abstract ............................................................................................................ 33
  2.2 Introduction ....................................................................................................... 34
  2.3 Experimental procedure ................................................................................... 34
  2.4 Results and discussion ..................................................................................... 36
    2.4.1 Electrical properties .................................................................................. 36
    2.4.2 Hot state TEM ........................................................................................... 39
    2.4.3 High temperature XRD ............................................................................. 42
  2.5 Conclusion ........................................................................................................... 43
  2.6 Acknowledgements ........................................................................................... 45
  2.7 Figure list ........................................................................................................... 45
  2.8 References ......................................................................................................... 52
Chapter 3. *In-situ* Transmission Electron Microscopy Study on Nb-Doped Pb(Zr0.95Ti0.05)O3 Ceramics

3.1 Abstract
3.2 Introduction
3.3 Materials and methods
3.4 Results and discussion
  3.4.1 Structure and Electrical Properties
  3.4.2 Hot-stage *in-situ* TEM study
  3.4.3 Electric field *in-situ* TEM study
3.5 Conclusion
3.6 Acknowledgements
3.7 Figure list
3.8 References

Chapter 4. Evolution of Nanodomains During the Electric-field-induced Relaxor to Normal Ferroelectric Phase Transition in a Sc-doped Pb(Mg1/3Nb2/3)O3 Ceramic

4.1 Abstract
4.2 Introduction
4.3 Experimental procedure
4.4 Results and discussion
  4.4.1 Structure and electrical properties
  4.4.2 *In-situ* TEM study
4.5 Conclusions
4.6 Acknowledgement
4.7 Figure list
4.8 References

Chapter 5. General conclusions

Chapter 6. Recommendations for Further Study

Acknowledgements

Appendix A: Publication List

Appendix B. Texture Control and Ferroelectric Properties of Pb(Nb,Zr,Sn,Ti)O3 Thin Films Prepared by Chemical Solution method
Appendix C. *In-situ* Transmission Electron Microscopy Study of the Nanodomain Growth in a Sc-doped Lead Magnesium Niobate Ceramic ..............................................125

Appendix D. Room Temperature Magnetoelectric Multiferroism Through Cation Ordering in Complex Perovskite Solid Solutions .........................................................134
Abstract

Ferroelectrics are important materials displaying outstanding dielectric, piezoelectric, and ferroelectric properties and are widely used in capacitors, transducers, actuators, filters, sensors, and random access memories. Direct observation of the dynamic process of thermal and/or electric field-induced phase transitions in ferroelectrics is of great importance in understanding the underlying mechanisms of their peculiar properties.

In this work, thermal and electric field in-situ TEM techniques were used to study the dynamic process of antiferroelectric to normal ferroelectric, normal ferroelectric to normal ferroelectric as well as relaxor ferroelectric to normal ferroelectric phase transitions.

A thermal in-situ TEM technique was used to study the antiferroelectric to normal ferroelectric phase transition in 0.98PbZrO$_3$-0.02Pb(Ni$_{1/3}$Nb$_{2/3}$)O$_3$ ceramics during heating. The low temperature antiferroelectric phase and intermediate ferroelectric phase are characterized by the $\frac{1}{4}\{110\}_c$-type and the $\frac{1}{2}\{110\}_c$-type superlattice diffractions, respectively. An incommensurate phase with $\frac{1}{6.48}\{110\}_c$ satellite diffractions was revealed to exist within a narrow temperature range of 3$^\circ$C between the antiferroelectric and ferroelectric phases presumably as a result of the competition between two these two types of ordering. The ferroelectric phase is special not only because of its frequency dependence, but also because of its checkerboard type domain morphology.
Electric field \textit{in-situ} TEM and thermal \textit{in-situ} TEM techniques are used separately to study the FE$_{RL}$$\rightarrow$FE$_{RH}$ phase transition in Pb$_{0.99}[(Zr_{0.95}Ti_{0.05})_{0.982}Nb_{0.018}]$O$_3$ ceramics. There appear to be different ferroelectric domains associated with the $\frac{1}{2}\{111\}_c$-type and the $\frac{1}{2}\{110\}_c$-type superlattice diffraction spots. These two types of domains respond to temperature increase independently. Under the conditions used in this study (thin TEM specimen and field close to $<011>_c$), external electric fields favor the FE$_{RH}$ over the FE$_{RL}$ phase at room temperature.

A cryo electric field \textit{in-situ} TEM technique was used to study the relaxor ferroelectric to normal ferroelectric phase transition in 0.92Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$–0.08Pb(Sc$_{1/2}$Nb$_{1/2}$)O$_3$ ceramics. The dynamic phase transition process was observed under TEM for the first time. It is revealed that the electric field-induced relaxor to normal ferroelectric phase transition initiates at grain boundaries. The transition involves the gradual coalescence of polar nanoregions and the successive abrupt formation of large ferroelectric domains. The formed domain/phase walls are roughly along $\{110\}$ planes. The morphology of the cation ordered domains does not change under applied electric fields. Furthermore, no evidence for strong interactions of these chemical domains with the induced large ferroelectric domains is found in the Sc-doped PMN ceramic.
Chapter 1. Introduction

The understanding and control of the nanoscopic properties of phase transitions in ferroelectrics remains a great challenge for materials scientists and an area of active research. Multiscale phenomena in materials exhibiting ferroelectricity arise from the complex interaction of these systems with their constituent nanostructure. This local, nanoscale critical phenomena can lead to interesting and unexpected behavior, and in some cases dominate the macrostructural properties of ferroelectric materials. Observation of the dynamic process of phase transitions at the nanoscale can provide valuable information to facilitate the development of modern theories of phase transitions in ferroelectrics\(^1\).

The main focus of the research work presented in this dissertation is \textit{in-situ} TEM investigation of the phase transitions in perovskite-structured ferroelectrics. The dissertation is composed of a number of journal articles published or submitted for publication and organized as follows:

Chapter one, the introductory chapter, provides background information and a comprehensive literature review of the topics addressed in subsequent chapters. Chapter two contains a journal paper submitted to \textit{Journal of Applied Physics} concerning the antiferroelectric to normal ferroelectric (AFE-FE) phase transition in PbZrO\(_3\) based ceramics. Chapter three contains a journal paper accepted for publication by \textit{Microscopy Research and Technique} concerning the normal ferroelectric to normal ferroelectric (FE-FE) phase transition in PZT-based ceramics. Chapter four contains a journal paper published in \textit{Journal of Applied Physics} concerning the relaxor ferroelectric to normal ferroelectric (RFE-FE) phase transition
1.1 History of ferroelectrics

The phenomenon of ferroelectricity was discovered in 1921 by Professor Joseph Valasek of the University of Minnesota when he was investigating the dielectric properties of Rochelle salt (NaK\(_4\)H\(_6\)O\(_6\)•4H\(_2\)O, RS) single crystals and observed an electric field hysteresis effect as well as very high dielectric constants (~4000) within a certain temperature range. He realized that these phenomena were similar in nature to the ferromagnetic properties of iron and therefore used the term ferroelectricity in analogy to ferromagnetism to identify such behavior\(^2,3\).

Unfortunately, like many other hydrates, RS is unstable and deteriorates easily, either by dehydration or liquefaction\(^4\), which made it rather difficult to work with. In 1935, such agonies were partly relieved due to the discovery of ferroelectricity in potassium dihydrogen phosphate (KH\(_2\)PO\(_4\), KDP) series single crystals by Busch and Scherer in Zurich\(^5,6\). These crystals were more symmetric and easier to work with. However, the ferroelectricity is confined to very low temperature (<-150°C), which limited its industrial application.

The discovery of ferroelectricity in ceramic materials began in the early 1940s under a cloud of secrecy because of World War II. Stimulated by the urgent need of higher dielectric-constant capacitors, concurrent work conducted by several countries, including the United States, United Kingdom, USSR, and Japan, identified barium titanate (BaTiO\(_3\), BT) polycrystalline ceramic as a high dielectric constant material contemporarily\(^7\). The source of the high dielectric constant in BT was soon associated with its ferroelectric nature in 1945 by
Wul and Goldman in the USSR and in 1946 by von Hippel’s group from MIT. The discovery of ferroelectricity in BT ceramics was extremely important, as it demonstrated for the first time that ferroelectricity could exist in simple oxide materials rather than always associated with hydrogen bonding.

Another startling discovery in this period was made by Gray from Erie. He realized that an external electric field could orient the domains within the grains, thus producing a ceramic material that acted very similar to a single crystal possessing both ferroelectric and piezoelectric properties. This electrical aligning was named “poling” process and was identified as the key to turning an inert ceramic into an electromechanically active material with a multitude of industrial and commercial uses.

Shortly after the discovery of ferroelectricity in BT, such nature was also observed in other compounds with similar structure, namely the ABO₃ perovskite structure. However, since the number of simple perovskites is very limited, only few new ferroelectric oxides were obtained. Among them, the discovery of ferroelectricity in lead titanate (PbTiO₃, PT) by Georgii Smolenskii in USSR and G. Shirane in Japan and the discovery of antiferroelectricity in lead zirconate (PbZrO₃, PZ) by Shirane are most important. These simple perovskites opened the door to many new discoveries. In seeking of the inner relationship between PT and PZ, Shirane started to study the solid solution between them and constructed the first phase diagram for the famous lead zirconate titanate [Pb(Zr₁₋ₓTiₓ)O₃, 0≤x≤1, PZT] system. Simultaneously, Smolenskii attributed the ferroelectricity in perovskite-type materials to the “ferroelectric active” cations such as Pb²⁺. This inspired him to sinter lead containing complex perovskites and a broad series of new ferroelectric oxides were soon discovered, including lead magnesium niobate [Pb(Mg₁/₃Nb₂/₃)O₃, PMN], lead
nickel niobate \([Pb(Ni_{1/3}Nb_{2/3})O_3, PNN]\), lead scandium niobate \([Pb(Sc_{1/2}Nb_{1/2})O_3, PSN]\), and lead magnesium tungstate \([Pb(Mg_{1/2}W_{1/2})O_3, PMW]\), to name a few. Later, diffused phase transition behavior was observed in PMN\(^{19}\), and it became the prototype of a new type of ferroelectrics: relaxor ferroelectrics. Until today, although great progress has been made on the understanding of ferroelectric behavior, on the design and preparation of ferroelectric materials and on the application of ferroelectric materials, BT, PZ, PT, PZT, PMN as well as their solid solutions still dominate the research and industry of electroceramics.

### 1.2 Concepts and characteristics of Ferroelectrics

In this dissertation, many terminologies concerning ferroelectric materials are frequently used. This section provides the concept of them followed by the comparison between three types of ferroelectric materials, namely, the ferroelectrics, antiferroelectrics and relaxor ferroelectrics.

#### 1.2.1 Concepts

Depending on their geometry, crystals are commonly classified into seven systems: triclinic, monoclinic, orthorhombic, tetragonal, trigonal, hexagonal and cubic. These systems can be further divided into 32 crystal classes based on their symmetry with respect to a point. Of the 32 crystal classes, 11 are centrosymmetric and consequently possess no polar properties. Of the remaining 21 non-centrosymmetric classes, 20 exhibit electrical polarity when subject to stress. Such effect is called the piezoelectric effect. Of the 20 piezoelectric crystal classes, only 10 are polar crystals. Polar crystals exhibit electric polarity even without an external electric field, such an effect is called spontaneous polarization\(^{20,21}\).
When a material exhibits two or more spontaneous polarization states and can be shifted from one state to another by the application of an electric field, it is called a ferroelectric material. In order to distinguish it from other ferroelectrics, such materials are referred to as normal ferroelectrics hereafter. Ideally, all the dipoles are parallel orientated in ferroelectric crystals. However, due to the existence of depolarizing fields, it is energetically more preferable for different regions of the crystal to possess different polarization states. Each region with a uniform polarization state is called a domain. The resulting domain structure usually leads to almost completely compensated polarization, or in other words, very small net polarization, until an electric field strong enough to forcefully align all the dipoles is applied. Such aligning process is called poling and the state after poling when all the dipoles are aligned is referred to as the poled state.

There are two major categories of ferroelectrics: displacive and order-disorder. In displacive ferroelectrics, such as BT or PT, there are no clearly recognizable dipoles when the temperature is higher than a critical value $T_c$, which is called the Curie temperature. Such a state at high temperature is referred to as the paraelectric phase. When the system is cooled below $T_c$, spontaneous polarization is generated due to a polarization catastrophe, in which, when an ion is displaced from equilibrium position slightly, the force from the local electric fields due to the surrounding ions in the crystal increases faster than the elastic-restoring forces, resulting in an asymmetrical shift in the equilibrium ion positions and hence to a permanent dipole moment. In the order-disorder ferroelectrics, such as KDP, the permanent dipoles are randomly oriented above the transition temperature and become spontaneously ordered below transition temperature. Recent researches, however, seem to soften the strict separation...
between displacive and order-disorder ferroelectrics and suggest the co-existence of them instead\textsuperscript{23}.

Antiferroelectric materials, or antiferroelectrics, are closely related to normal ferroelectrics. An antiferroelectric material consists of an ordered array of electric dipoles, but with adjacent dipoles oriented antiparallel. The dipoles of each orientation form interpenetrating sublattices, loosely analogous to a checkerboard pattern\textsuperscript{22}.

Relaxor ferroelectric materials, or relaxor ferroelectrics, are another type of ferroelectric materials closely related to normal ferroelectrics. In contrast to normal ferroelectrics in which the dipoles are long range ordered, “soft” polar nanometer-sized regions (PNRs) appear in relaxor ferroelectrics due to composition and field inhomogeneities\textsuperscript{25}. In PNRs, unit cells can freely choose several different directions, while the direction of the total moment of the nanoregion remains the same\textsuperscript{26}.

\subsection*{1.2.2 Characteristics}

Based on their different dipole ordering arrangements, ferroelectrics, antiferroelectrics and relaxor ferroelectrics exhibit distinct electric polarization behaviors, which are shown in Fig. 1-1.

As shown in Fig 1-1(a), when an external electric field is applied across a normal ferroelectric material, all the dipoles tend to align themselves with the field direction. After the electric field is removed, the dipoles retain their polarization state. As the consequence, large remanent polarization ($P_r$) is achieved. In order to reverse such polarization, an opposite electric field higher than the coercive field ($E_c$) must be applied. The value of the spontaneous
polarization $P_s$ is obtained by extrapolating the curve onto the polarization axes\textsuperscript{27}. The area within the loop is a measure of the energy required to twice reverse the polarization\textsuperscript{21}.

Fig. 1-1 Typical electric polarization hysteresis loop for (a) normal ferroelectrics, (b) antiferroelectrics under insufficient electric field
Fig. 1-1 Typical electric polarization hysteresis loop continued for (c) antiferroelectrics under sufficient electric field and (d) relaxor ferroelectrics with active PNRs

In antiferroelectrics, when the electric field is not high enough to alter the antiparallel arrangement of nearest neighboring dipoles, the material shows a linear response just like a normal linear dielectric material, as can be seen in Fig. 1-1(b).
However, when the electric field is strong enough (>EF), all the dipoles can be forcefully aligned to the field direction. A normal ferroelectric phase is induced in this situation. The induced ferroelectric phase can be sustained with electric fields higher than EA. When the electric field is decreased below this level, the antiparallel arrangement recovers and the material shows linear response again. Similarly, all the dipoles can be aligned to the opposite direction with strong reversed electric field. Thus, a double hysteresis loop is formed, as can be seen in Fig. 1-1(c).

The situation is more complicated in relaxor ferroelectrics. Since only the polar ordered regions contribute to the nonlinearity, the hysteresis behavior of relaxor ferroelectrics is highly dependent on the size, volume fraction and activity of such polar regions, which in turn depends on the composition, temperature and electric field. Typically, when the polar region is active and nonometer-sized (PNRs), it shows a slim, nonlinear hysteresis loop with minimal or even negligible remanent polarization and coercive field, as shown in Fig. 1-1(d). However, with appropriate combination of composition and temperature/electric field history, the loop can open up or even exhibit features similar to normal ferroelectrics. In this sense, the hysteresis loop alone is not enough for distinguishing relaxor ferroelectrics from normal ferroelectrics.

In addition to hysteresis behavior, dielectric permittivity as a function of temperature and frequency is also used to characterize ferroelectrics. In this measurement, normal ferroelectrics and antiferroelectrics show similar behavior. As shown in Fig. 1-2(a), a sharp peak is observed in the vicinity of Tc. Above Tc, the system turns into paraelectric phase. Such a phase transition is accompanied with a macroscopically detectable structural change.
Fig. 1-2 Dielectric permittivity as a function of temperature and frequency for (a) normal ferroelectrics and antiferroelectrics and (b) relaxor ferroelectrics.

In relaxor ferroelectrics, as shown in Fig. 1-2(b), a broad peak in dielectric permittivity versus temperature can be observed, and the temperature at which the maximum dielectric permittivity is achieved (T_m) shifts toward higher temperature with increasing measuring frequency. This phenomenon is termed diffused phase transition (DPT) and is believed to be
related to the two types of short range ordering in relaxor ferroelectrics. Detailed discussion will be provided in section 1.6. The dielectric permittivity is typically much higher in relaxor ferroelectrics than in normal ferroelectrics or antiferroelectrics.

1.3 Applications of ferroelectric materials

Due to their extraordinary electric behavior, ferroelectric materials can be used in many applications. Conventional applications include capacitors, memories, transducers, high voltage regulators and so on, and the scope is expanding rapidly.

1.3.1 High dielectric permittivity—capacitors

A capacitor consists of a dielectric material sandwiched between two electrodes. The total capacitance for this device is given by

$$C = \frac{\varepsilon_0 \varepsilon_r A}{t}$$

where $C$ is the capacitance, $\varepsilon_0$ is the permittivity of free space, $\varepsilon_r$ is the relative dielectric permittivity of the dielectric material, $A$ is the area of electrodes and $t$ is the distance between the electrodes.

To get a high volumetric efficiency (capacitance per unit volume) the dielectric material between the electrodes should have a large dielectric constant, a large area and a small thickness. The volumetric efficiency can be further enhanced by using multilayer ceramic (MLC) capacitors consisting of alternate layers of dielectric and electrode material. Each individual dielectric layer contributes capacitance to the MLC capacitor as the electrodes terminate in a parallel configuration. Hence the effective equation for capacitance becomes
\[ C = \frac{n\varepsilon_0\varepsilon_r A}{t} \]

where \( n = \) number of dielectric layers.

BaTiO\textsubscript{3} based normal ferroelectric ceramics, due to their high dielectric permittivity (\( \varepsilon_r \sim 2,000 \) at room temperature) and ease of preparation, have been dominating the ceramic capacitor market for decades. Relaxor ferroelectrics, e.g. PMN based ceramics, have various advantages over BaTiO\textsubscript{3} based ceramics, including much higher dielectric constants (\( \varepsilon_r \sim 15,000 \) at room temperature), much lower temperature and electric field dependence of permittivity, much finer grain sizes (\( \leq 1 \mu m \) as compared to BaTiO\textsubscript{3} ~2-5 \( \mu m \)) to get high dielectric constant with low temperature dependence and much lower sintering temperature. However, some inherent problems in relaxors still need to be overcome before they can be used for large scale production, including the high dielectric loss below Curie temperature, the frequency dependence of the dielectric permittivity, the weak mechanical properties and poor reproducibility of preparation processes.\textsuperscript{27}

1.3.2 Reversible spontaneous polarization--non-volatile memories

Semiconductor memories such as dynamic random access memories currently dominate the market. However, the disadvantage of these memories is that they are volatile, i.e. the stored information is lost when the power fails.

Based on the spontaneous polarization and its reversibility in ferroelectric materials, a new kind of memory, namely the ferroelectric random access memories (FRAMs) is proposed in which data is stored by localized polarization switching in the microscopic regions of
ferroelectric thin films. The FRAMs are non-volatile because the polarization remains in the same state after the voltage is removed.

The prospects of FRAM devices replacing the semiconductor memories in the near future are very bright. A great deal of work must still be done to obtain the optimum composition and microstructure of PZT thin films, to study the interaction of the PZT film with the electrode material and to improve the reliability of the storage device.27

1.3.3 Large piezoelectric coefficient—transducers

The excellent piezoelectric behavior of ferroelectric materials can be utilized in both active and passive transducer applications. In active transducers, the ferroelectric material serves as the generator of other types of energy in form of sound, mechanical displacement and so on, while in passive transducers, the ferroelectric material absorbs energy in the form of sound, force and so forth and converts it into an electrical signal. Active and passive functions can be combined within one device and such a principle is widely used in transducers for ultrasonic medical imaging applications.27

1.4 Perovskite structure

The word “perovskite” originally refers to a particular type of mineral with chemical formula CaTiO₃, named after Russian mineralogist, L. A. Perovski (1792-1856)22. The crystal structure of this mineral is named the perovskite structure and more generally, any material with the same structure is called a perovskite. Most perovskites are oxides with the general formula ABO₃, where A and B denote two different cations and O denotes oxygen. The size of A-site cation is larger than B-site cation.
The unit cell of an ideal perovskite structure is a cube, where the A-site cations sit on the corners of the cube, the B-site cation sits in the body center and oxygen sit in the face centers, as shown in Fig. 1-3. The structure is a network of corner-linked oxygen octahedra, with the smaller cations filling the octahedral holes and the larger cations filling the dodecahedral holes.

However, most perovskite structures are distorted and do not have such cubic symmetry, even the prototype perovskite, CaTiO$_3$. Common distortions such as cation displacements within the octahedra and tilting of the octahedra are related to the properties of the cations on the A-sites and on the B-sites. According to Victor Moritz Goldschmidt, Swiss chemist and father of modern geochemistry, the degree of distortion in ABO$_3$ perovskites can be determined using the following equation:
\[ t = \frac{R_A + R_O}{\sqrt{2(R_B + R_O)}} \]  

(1)

where \( R_A, R_B \) and \( R_O \) denote the ionic radii of the A-site cation, B-site cation and oxygen anion, respectively, and \( t \) is named as Goldschmidt tolerance factor. In an ideal cubic perovskite the A-site and B-site cations realize their equilibrium bond distances to oxygen without inducing any distortion of the unit cell and the Goldschmidt tolerance factor is equal to 1. When \( 0.78 < t < 1.05 \), a distorted perovskite structure can be stabilized.

A wide variety of cations can be substituted in the perovskite structure. As a matter of fact, the perovskite structure is one of the most common structures possessed by many ferroelectric materials. Some typical ferroelectric systems possessing perovskite will be introduced in the next sections.

### 1.5 The \( \text{Pb(Zr}_{1-x}\text{Ti}_x\text{)}\text{O}_3 \) solid solution system

Lead titanate (\( \text{PbTiO}_3 \), PT) is a prototype ferroelectric material which undergoes a first order phase transition at 493°C from cubic perovskite to a tetragonal ferroelectric phase. At room temperature, the \( c/a \) ratio is about 1.063. Due to the large ionic shift, PT exhibits a particularly large room temperature spontaneous polarization. However, the crystal growth and reproducibility problem hampers the development of this system.\(^{21}\)

Lead zirconate (\( \text{PbZrO}_3 \), PZ) is a prototype antiferroelectric material. At temperatures below 220°C, \( \text{PbZrO}_3 \) displays an orthorhombic perovskite structure with antiparallel shifts of \( \text{Pb}^{2+} \) ions along the pseudocubic \( <110> \) direction, which leads to the antiferroelectric (AFE) behavior.\(^{14,30}\) At temperatures above 230°C it possesses the prototype cubic perovskite structure and exhibits paraelectric behavior with dielectric permittivity following the Curie-Weiss law.\(^{21}\)
In between the AFE and the paraelectric phase within a narrow temperature range, there is an intermediate phase which is characterized by $1/2\{110\}_c$ type superlattice diffractions. The nature of this intermediate phase is still open for debate. It was reported to be either rhombohedral or orthorhombic, and either ferroelectric or antiferroelectric. Since $E_\text{F}$, the critical electric field level required to induce the AFE to FE phase transition, is in the range of the dielectric breakdown strength, such a phase transition can hardly be observed in pure PZ crystals.

PT and PZ form complete solid solutions Pb(Zr$_{1-x}$Ti$_x$)O$_3$ (PZT) for any $x$ value between 0 and 1. PZT shows unusual piezoelectric behavior and has been extensively studied and utilized since its discovery in the 1950s. A phase diagram of PZT solid solution system is shown in Fig. 1-4.

Except for the three phases previously observed in the two end components, namely (A) the antiferroelectric orthorhombic phase close to the PZ side, (T) the ferroelectric tetragonal phase close to the PT side and (C) the high temperature paraelectric cubic phase for all compositions, three other phases were observed: (R$_I$) the high temperature ferroelectric rhombohedral phase, (R$_{II}$) the low temperature ferroelectric rhombohedral phase, and (M) the monoclinic phase. For all the phases and compositions, a perovskite structure is retained in which Zr$^{4+}$ and Ti$^{4+}$ occupy the B-site randomly while the A-site is always occupied solely by Pb$^{2+}$. The phases are only distinguishable from each other by slight difference in the extent and/or direction of lattice distortion from the parent cubic perovskite structure.
The composition close to the morphotropic phase boundary (MPB, $x=0.48$) is of particular interest due to its extremely high dielectric permittivity and piezoelectric coefficient. These properties make PZT-based compounds some of the most prominent and useful electroceramics. The strong piezoelectric effect is believed to be the result of the increased number of allowable domain states at the MPB. At this boundary, the 6 possible $<100>$ domain states from the tetragonal phase and the 8 possible $<111>$ domain states from the rhombohedral phase are equally favorable energetically, thereby allowing a maximum 14 possible domain states.

Usually, PZT is not used in its pure form, but rather it is doped with either acceptor dopants or donor dopants. Acceptor dopants act to pin domain walls and produce hard PZT, which shows a high mechanical quality factor, low loss and low piezoelectric constant.
the contrary, donor dopants act to facilitate domain wall motion in the material. As a result, soft PZT is obtained which shows a high piezoelectric constant and large loss.

1.6 The prototype relaxor compound Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$

Fig. 1-5 Schematic representation of the double perovskite cell of the 1:1 ordered $A(B'_{1/2}B''_{1/2})O_3$ structure

1.6.1 B-site 1:1 cation ordering

Lead magnesium niobate [Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$, PMN] is a prototype relaxor ferroelectrics. At room temperature, PMN has a cubic $ABO_3$ complex perovskite structure, where Pb$^{2+}$ occupies A-sites while Mg$^{2+}$ and Nb$^{5+}$ share the B-sites (octahedral center). Within a local area, the B-site cations adopt a doubled perovskite unit cell, $A(B'_{1/2}B''_{1/2})O_3$-type "1:1" structure with
a face centered arrangement of two different (B' and B'') cation positions. As shown in Fig. 1-5, every other \{111\} plane belongs to B' sublattice while the remaining \{111\} planes belong to B'' sublattice. For simplicity, A-site cation and oxygen are omitted in this figure.

Such chemical heterogeneities in Pb(B'B'')O₃ were later confirmed by high-resolution TEM technique and conventional TEM dark-field technique with (1/2, 1/2, 1/2)-type superlattice reflections. The microstructure takes the form of nanometer scale B-site cation ordered domains which are dispersed in the disordered matrix. The cation ordered domains in pure PMN was proved to be highly stable against thermal treatments. Such lack of coarsening is believed to owe to kinetic rather than thermodynamic constraints.

The crystal chemistry of the ordered nanodomains was widely interpreted in terms of a "random site" model. This model suggested that only one of the two cation sublattices in 1:1 ordered PMN (B'') is occupied by a single type of metal ion (Nb⁵⁺), whereas the other cation sublattice (B') contains a random 2:1 distribution of Mg²⁺ and Nb⁵⁺ cations. Therefore, partial chemical ordering was still allowed while the overall stoichiometry of the bulk composition remained. According to this model, the average composition of the ordered regions is identical to that of the bulk PMN and no charge imbalance exists within the ordered regions. This model has found strong experimental support from the thermal growth of cation ordered domains in Pb(Mg₁/₃Ta₂/₃)O₃-PbZrO₃ solid solution as well as atomic resolution Z-contrast TEM imaging.

**1.6.2 Dipole ordering**

In coupling to this chemical ordering, electrical dipole ordering also exists in relaxor ferroelectrics as a result of the local destruction of the cubic symmetry due to the difference in
ionic sizes between the B-site cations. It is believed that not only the nanoscale chemical ordering but also the nanoscale electrical dipole ordering accounts the characteristic dielectric behavior in relaxor ferroelectrics.

A two component model is proposed to describe the dipole ordering in relaxor ferroelectrics.\textsuperscript{45} According to this model, anisotropic polar nanometer regions (PNRs), which assemble ferroelectric domains, are embedded in an isotropic disordered glass-like matrix.

The existence of polar nanoregions in relaxors was confirmed by multiple macroscopic techniques such as birefringence measurements\textsuperscript{45}, Raman spectroscopy\textsuperscript{46}, diffuse scattering\textsuperscript{47,48}, pair distribution function analysis\textsuperscript{49} and NMR\textsuperscript{50}. It is believed that in PMN, the PNRs are locally rhombohedral distorted along one of the eight equivalent $<111>$ directions and they are the only components in relaxors that respond to external electric fields.\textsuperscript{50}

Expected as they are, reports on TEM imaging of the polar domains in relaxor ceramics are very limited. Especially in pure PMN, because of faint contrast in bright field image and small size, the direct TEM observation of polar domains has always been difficult. In 1998, Yoshida et al finally succeeded in observing the polar domains by TEM with the help of a liquid nitrogen cooling stage, and a microscopic domain structure of the rhombohedral phase was clearly revealed at low temperatures below $T_c$.\textsuperscript{51} They also suggested that the polar domains can be contrasted in the DF image of the fundamental reflection due to the rhombohedral lattice strain in the cubic lattice of matrix.

1.6.3 Evolution of the electric dipole order under electric fields

The PNRs in relaxor ferroelectrics respond to external electric fields in a way that is similar to normal ferroelectrics. With appropriate temperature, electric field combination and
history, multiple states can be induced from relaxor ferroelectrics. An electric field-temperature (E-T) phase diagram delimiting several states was proposed based on experimental studies of PMN single crystals\textsuperscript{52}, as exemplified in Fig. 1-6.

![Fig. 1-6 Electric field–temperature phase diagram](image)

In this diagram, $E_{th}$ indicates the minimum of the threshold field. Line A delimits the disordered pseudo cubic phase (area 1) and the induced polar phase (areas 2 and 3). Strictly speaking, the symmetry in the phase field of area 1 is only pseudo-cubic, meaning that under line A, the electric field along $<111>_c$ gives rise to a slight thermodynamically-reversible distortion of the cubic phase. Line B indicates the lower limiting temperature for a given field strength, above which the frozen disordered phase (area 3) (after zero-field-cooling) can be poled and the polarization of the induced polar phase (area 3') (after FC) can be reversed with an opposite polarity of $E$ upon heating. The dashed line on the right of line B gives the temperatures above which the reverse polarization is established completely under certain field
strength in the latter case. Between lines A and B (area 2) the PMN crystals may be considered to be normal ferroelectric with reversible polarizations.

Fig. 1-7 Time dependency of the induced polarization under electric field after zero field cooling

The kinetics of the electric field-induced relaxor to normal ferroelectrics transition has been studied with a constant electric field applied at appropriate temperatures. It was discovered that an incubation time $\tau$, in which the polarization reaches a critical value, was needed before the onset of transition. Also, a threshold electric field $E_{th}$ must be satisfied before the onset of transition.

The incubation time is both temperature and field strength dependent. In the high field regime where $E>E_{th}$, an abrupt jump of polarization to a higher value was observed at a time $t=\tau$, and the incubation time appears to increase with decreasing temperature. However, in the
low field regime where \( E < E_{th} \), the polarization \( P \) remains at low values and never reaches the critical value. The long-range polar phase is never observed. It could be interpreted that the required incubation time \( \tau \) is beyond the measurable range.

The kinetic mechanism for the dynamic transition in relaxors is still open for debate. There are two major models, namely the growth mechanism\(^{54} \) and the nucleation mechanism\(^{55} \). The former proposes that the applied field grows PNRs into ferroelectric macrodomains due to the enforced correlated ion shifts along the symmetry-preferential directions, while the later suggests that the applied electric field triggers the nucleation of ferroelectric embryos and it is the number of nuclei rather than their size that is increasing. A new probing tool with sub-nanometer resolution capability is required to identify the true mechanism.

### 1.6.4 Correlations between the two types of ordering

Although the cation-ordered domains and polar nanoregions in PMN have both similar size and volume fraction at low temperatures, no direct proof has demonstrated any correspondence between these two nanoscale features. In highly ordered PST ceramics with ferroelectric macrodomains, TEM examinations indicate no strong interactions between the macrodomains and the antiphase boundaries\(^{56, 57} \). This finding, however, should by no means be interpreted as indicating that there are no strong interactions between the chemical order and the electric dipole order in relaxors, because (i) the observation was made in fully ordered areas with normal ferroelectric characteristics, (ii) the antiphase boundaries are fundamentally different from those chemical order/disorder interfaces that are structural features peculiar to true relaxors, and (iii) the chemical order/disorder interfaces in \( \text{Pb}(\text{B}'_{1/2}\text{B}''_{1/2})\text{O}_3 \)-type relaxors are presumably different from those in \( \text{Pb}(\text{B}'_{1/3}\text{B}''_{2/3})\text{O}_3 \)-type relaxors. This argument is based
on the fact that relaxor behavior is persistent in chemically modified PMN ceramics with large
chemical domains, whereas in PST ceramics with large chemical domains relaxor behavior
transforms to normal ferroelectric behavior.

Based on the following well-established facts, strong interactions between the two
types of order must exist. (a) In Ti-doped PMN solid solutions, any increase in the amount of
Ti-dopant disrupts the chemical order. At the same time, the length scale for the electric dipole
order increased and, eventually, a macrodomain state of normal ferroelectric characteristics can
be achieved\textsuperscript{48}. (b) In the PST system, nanoscale chemical order leads to relaxor behavior,
whereas full chemical order corresponds to a normal ferroelectric state. The chemical order
generates random electric/strain fields, and these nanoscale fields suppress the development of
long-range ferroelectric ordering\textsuperscript{59}. (c) Jin and his coworkers revealed that the cation-ordered
domains in PMN had faceted interfaces, most of which were along \{111\} planes\textsuperscript{60}. Interestingly, it has been suggested that the phase boundary for the polar domain is parallel to
\{111\} planes\textsuperscript{51}. Also, the morphology of the island-like macrodomains in PST closely
resembles that of the chemical domains\textsuperscript{57}. (d) First-principle-based simulation implied that the
characteristic lengthscale for polar nanoregions is the same as for chemical short-range
order\textsuperscript{61,62}

There is a need of clarifying the correlations between the two types of order in various
relaxor ceramics.

### 1.7 Logic of this dissertation

The work presented in this dissertation is based on the most widely used and studied
ferroelectric systems for the sake of providing more representative information. Bearing this in
mind, three materials systems were selected for this work: PZ, the prototype antiferroelectric material; PZT, the most widely used electroceramics; and PMN, the prototype of relaxor ferroelectric material.

Special treatments were performed for each system to facilitate the *in-situ* observation under the TEM. For the PZ system, 2mol% PNN was introduced to form a solid solution. This helps to expand the temperature range of the intermediate phase\(^6^3\) and provides a wide enough window for *in-situ* TEM observation. For the PZT system, 0.95PZ-0.05PT, which is at the AFE/FE phase boundary at ambient conditions, was chosen to be the base composition. 0.018 at% Nb was introduced in order to stabilize the FE phase in this composition\(^6^4\). As a consequence, ferroelectric→ferroelectric and ferroelectric→antiferroelectric phase transitions can be easily triggered in these ceramics. This expands the scope of *in-situ* TEM observation. In PMN, 4 at% Sc was introduced by the solid solution method in order to enlarge the 1:1 B-site cation ordered domain and promote the dipole order\(^6^5\). This reduces the difficulty of in-site TEM observation. A low dopant level was chosen to maintain the structure and characteristics of the base composition.

*In-situ* TEM observations were performed and presented in this dissertation in a sequence of increasing complexity. Thermal *in-situ* TEM, which doesn’t require special configuration of a TEM sample, is first performed in the simplest system, the PZ system. Afterwards, a more complicated system, the PZT system, is studied. In addition to the thermal *in-situ* TEM, the electric field *in-situ* TEM was also performed as a separate procedure to provide complementary information. Finally, the most complicated system, the PMN system, was studied. The phase transition in this system requires low temperature and application of electric field simultaneously, requiring the use of our special liquid nitrogen-cooled TEM
holder with electric feedthroughs can make a unique contribution. In addition to the effect of electric field and temperature, that of time is also taken into account.

1.8 Key experimental approach

In order to observe the dynamic phase transition process at the nanoscale, in-situ TEM is extensively used for the studies presented in this dissertation. This technique has been widely used in the study of ferromagnetic, ferroelectric and ferroelastic systems and proven to be quite relevant for phase transition studies provided that the samples do not damage under electron irradiation\textsuperscript{66-67}.

Thermal in-situ does not require special treatment of the sample. However, for electric field in-situ TEM study, the sample needs to be electroded in order to apply the electric field. The configuration of the TEM sample used for in-situ TEM study is shown in Fig. 1-8. Two half-circle shaped electrodes with their straight edges facing each other with a distance of 200\(\mu\)m in between are evaporated onto the flat surface of the perforated TEM specimen through a special mask. The electroded TEM samples are fixed on the bottom of the sample cup using one droplet of insulating varnish. The electric feedthroughs on the holder tip are connected to the electrodes on the TEM sample with thin platinum wires which are bent with appropriate curvature. Conductive epoxy is used to make the connections on the gold electrodes, which need to be made as far away from the central perforation as possible. The samples need to be cured for at least 24 hour before the in-situ study. The entire sample preparation and connection procedure must be performed with special care in order to avoid any mechanical stress which might lead to the failure of in-situ observation.
It should be noted that the presence of the central perforation disturbs the electric field. For an ideal circular perforation, it was shown that the actual field in the two small shaded areas at the edge of the central perforation in Fig. 1-8 is intensified and preserves the direction of the nominal field. The \textit{in-situ} TEM observations in the present study were performed in the grains within these two areas and the electric field intensity specified refers to the nominal field.

\section*{1.9 References}


Chapter 2. High Temperature Phases in the 0.98PbZrO₃–0.02Pb(Ni₁/₃Nb₂/₃)O₃ Ceramic


W. Qu¹, X. Tan¹*, N. Vittayakorn², S. Wirunchit² and M.F. Besser³

2.1 Abstract

The phase evolution with temperature in the 0.98PbZrO₃–0.02Pb(Ni₁/₃Nb₂/₃)O₃ ceramic was investigated with dielectric permittivity and polarization measurements, hot stage transmission electron microscopy (TEM) and high temperature X-ray diffraction (XRD). Below 190°C, the ceramic is in the antiferroelectric phase with characteristic \( \frac{1}{4} \{110\}_c \) superlattice diffractions. In this stage, typical antiferroelectric 180° domains were observed. Between 190 and 220°C, an intermediate phase which is characterized by \( \frac{1}{2} \{110\}_c \) -type superlattice diffractions was detected. Evidences are found to suggest that this intermediate phase is ferroelectric. The \( \frac{1}{2} \{110\}_c \) -type superlattice diffraction persists even into the paraelectric phase above 220°C. In addition, there exists an incommensurate phase between the low temperature antiferroelectric phase and the intermediate ferroelectric phase.

1. Department of Materials Science & Engineering, Iowa State University, Ames, IA 50011, USA
2. Department of Chemistry, King Mongkut’s Institute of Technology Ladkrabang, Bangkok 10502, Thailand
3. Materials and Engineering Physics Program, Ames Laboratory, U.S.-DOE, Ames, IA 50011, USA
* Author to whom correspondence should be directed
2.2 Introduction

The classic antiferroelectric compound lead zirconate (PbZrO₃ or PZ) has been extensively studied since 1950s. At temperatures below 220°C, PbZrO₃ displays an orthorhombic perovskite structure with antiparallel shifts of Pb²⁺ ions along the pseudocubic <110> direction, which leads to the antiferroelectric (AFE) behavior. The space group for the low temperature AFE phase was determined to be $P_{bam}$. At temperatures above 230°C, PbZrO₃ is in the paraelectric phase with the cubic $m\overline{3}m$ symmetry. In between the AFE and the paraelectric phase within a narrow temperature range, there is an intermediate phase which is characterized by $\frac{1}{2}[110]$-type superlattice diffractions. However, the nature of this intermediate phase is still open for debate. Experimental evidences have found to support either a ferroelectric or an antiferroelectric phase.

In our previous study, it has been found that by introducing minor amounts (2~6 mol.%) of relaxor ferroelectric Pb(Ni$_{1/3}$Nb$_{2/3}$)O₃ (PNN) into PZ, the temperature range is expanded for an intermediate phase which is characterized by an evident frequency dispersion in dielectric permittivity. As a consequence, a series of striking phase transitions was revealed by the dielectric measurement. In the present work, the 0.98PbZrO₃–0.02Pb(Ni$_{1/3}$Nb$_{2/3}$)O₃ (PZ98-PNN2) ceramic was selected to further investigate the phase evolution sequence during heating up to 300°C with hot stage TEM and high temperature X-ray diffraction.

2.3 Experimental procedure

The phase pure PZ98-PNN2 ceramic was prepared using the columbite precursor method in order to avoid the pyrochlore phase formation. Detailed preparation procedures have
been reported in our previous publications. The relative density of the as-sintered ceramic was measured using the Archimedes method to be 98%. The grain size was examined by scanning electron microscopy (SEM, JEOL JSM-606LV). As shown in Fig. 2-1, the freshly fractured cross section of the PZ98-PNN2 ceramic is almost free of pores and the grain size is in the range of 2-5μm.

The surface layers of the sintered pellets were removed by mechanical grinding. X-ray diffraction analysis was performed with Cu Kα radiation at a series of temperatures up to 300°C on a PANalytical X-Pert Pro diffraction system to investigate the structural evolution. Dielectric properties were measured with an LCR meter (HP-4284A, Hewlett-Packard) on a Au-electroded specimen during heating from room temperature to 300°C at a rate of 2°C/min. The electrical polarization versus field hysteresis loops were recorded at a series of temperature with a standardized ferroelectric test system (RT-66A, Radiant Technologies). The peak field was maintained at 20kV/cm during measurement.

Thin disks with a diameter of 3mm were cut from the as-sintered ceramic pellet, ground and polished to a thickness of 0.15mm for TEM specimen preparation. The central portion of the disks was further thinned and polished by mechanical dimpling. Argon ion mill was then used to perforate the disk at the center. Hot-stage TEM observations were performed with a heating rate less than 2°C/min on a Philips CM30 instrument operating at 300kV. Bright field images and selected area electron diffraction patterns were recorded ten minutes after the temperature was stabilized.
2.4 Results and discussion

2.4.1 Electrical properties

The temperature dependence of relative dielectric permittivity and loss tangent was measured at frequencies of 100Hz, 1kHz and 10kHz during heating from 30 to 300°C and the results are displayed in Fig 2. Clearly, there are two abrupt changes in both relative permittivity and loss tangent in the PZ98-PNN2 ceramic. The first one occurred at around 190°C where both relative permittivity and loss tangent increased by one order of magnitude. The second abrupt change took place at the Curie temperature 220°C where significant suppression of loss tangent is seen. Therefore, the dielectric response in the PZ98-PNN2 ceramic can be divided into three stages. At temperatures below 190°C, the relative permittivity and the loss tangent both have low values and show negligible increases with increasing temperatures. At temperatures above 220°C, the relative permittivity starts to decrease following the Curie-Weiss law, \( \varepsilon_r = \frac{C}{T - T_0} \), where \( \varepsilon_r \) is the relative permittivity, \( T \) is the temperature, \( C \) and \( T_0 \) are Curie constant and Curie point, respectively. By fitting the data between 220 and 300°C in Fig. 2-2, \( C \) and \( T_0 \) were determined to be 1.89×10^5 °C and 185.8°C, respectively. In the intermediate temperature range (190 to 220°C), the relative permittivity increases dramatically while the loss tangent remains high around 0.1. The most remarkable feature of the dielectric behavior in this temperature range is the evident frequency dispersion of both relative permittivity and loss tangent, resembling that in relaxor ferroelectric ceramics. \( T_{\text{max}} \), the temperature at which the maximum dielectric permittivity is achieved, was measured to be 219.4°C at 100Hz, 220.1°C
at 1kHz, and 220.4°C at 10kHz, respectively, shifting slightly toward higher temperatures with increasing frequency.

To further clarify the dielectric behavior of the different phases in the PZ98-PNN2 ceramic, electrical polarization hysteresis loop measurements were performed under a peak field of 20kV/cm at a series of temperatures. During heating, the two electrodes were shortened. The loop was recorded after the temperature was stabilized for at least five minutes. As shown in Fig. 2-3(a), very small polarizations can be induced by the applied electric field in the ceramic at room temperature. This is typical for an AFE ceramic subjected to electric fields that are not sufficient to induce the AFE to ferroelectric phase transition. Such a linear behavior with minimum polarization remains at temperatures up to 170°C.

When the temperature further increases, a hysteretic behavior starts to develop. As shown in Fig. 2-3(b), a regular hysteresis loop with a coercive field $E_c$ of 3.9kV/cm was recorded at 173°C. However, the observed hysteresis loop does not indicate the presence of a ferroelectric phase. Close examination of the loop in Fig. 2-3(b) reveals that slight distortions occurred at ~5kV/cm, marked with the two dashed circles on the hysteresis loop. Similar distortions on hysteresis loops were found in Pb$_{0.99}$Nb$_{0.02}$(Zr$_{0.57}$Sn$_{0.43}$)$_{1-y}$Ti$_y$O$_{3}$ ceramics and have been attributed to the onset of the electric field-induced AFE to ferroelectric phase transition. Therefore, the PZ98-PNN2 ceramic at this temperature is still in the antiferroelectric phase. It should be noted that the distortions marked in Fig. 3(b) indicate the antiferroelectric-to-ferroelectric phase transition. The distortion associated with the backward ferroelectric-to-antiferroelectric transition was not seen because it may overlap with the coercive field of the induced ferroelectric phase. The observed large polarization is due to the
induced ferroelectric phase by the applied field of 20kV/cm, which is much higher than the critical electric field $E_F$ of ~5kV/cm.

Further increase in temperature leads to the decrease in the critical field $E_F$ and the increase in both the saturation polarization $P_s$ and the remanent polarization $P_r$. $P_r$ saturates at 25µC/cm² when the temperature reaches 177°C and stays unchanged up to 186°C. It should be noted that the coercive field $E_c$ (not the critical field $E_F$) remains the same at 3.9 kV/cm in the temperature range of 172~186°C. The results suggest that the volume fraction of the ferroelectric phase induced by a field of 20kV/cm in the ceramic increases with increasing temperatures between 172 and 177°C. In the temperature range of 177~186°C, the whole piece of sample was forced into a ferroelectric phase by the external electric field of 20kV/cm. Therefore, the $P_r$ saturates in this temperature range.

Dramatic change in the coercive field $E_c$ was observed at 186°C. At this temperature, although a well defined hysteresis loop was still observed, $E_c$ abruptly reduced to 2.4kV/cm, indicating the appearance of a new phase. Up to 200°C, the hysteresis loop remains largely unchanged, with the one at 200°C shown in Fig. 2-3(c).

Combined with the results presented in Fig. 2-2, we believe that the abrupt change in $E_c$ at 186°C marks the phase transition at 190°C revealed by the dielectric measurement. The discrepancy in temperature is due to the different test conditions. In the dielectric measurement, the ceramic sample was subjected to continuous heating at a rate of 2°C/min while in the polarization measurement, the hysteresis loops were recorded after at least five minutes the temperature is stabilized. In summary, the macroscopic property measurements reveal that at temperatures below 190°C, the PZ98-PNN2 ceramic is antiferroelectric with stable and low
dielectric permittivity and loss tangent. Under applied electric fields, the antiferroelectric phase can be transformed into a ferroelectric phase at temperatures slightly below the transition temperature. An intermediate phase exists between 190 and 220°C. The increased loss tangent and the well defined hysteresis loops with reduced coercive fields $E_c$ seem to suggest that this phase is ferroelectric. Further supporting evidence is found in our previous study where the intermediate phase is stabilized down below room temperature in the PZ90-PNN10 ceramic and an undistorted hysteresis loop was observed in this ceramic at room temperature. However, this intermediate phase is a unique ferroelectric phase with evident frequency dispersion in its dielectric behavior.

2.4.2 Hot state TEM

The temperature induced phase transitions were visualized by hot stage TEM during heating. One grain about 3μm in size was tilted so that its <001> zone-axis was aligned with the electron beam direction. The evolution of the selected area electron diffraction (SAED) pattern with temperature is exemplified in Fig. 2-4. At room temperature, the primary feature is the presence of the $\frac{1}{4}\{110\}_c$ -type superlattice diffraction spots [Fig. 2-4(a)], where the subscript $c$ indicates that the indices are based on the parent cubic perovskite unit cell. The superlattice structure is identical to that of PbZrO$_3$ at room temperature. Therefore, adding 2mol% of PNN does not change the crystal structure of PbZrO$_3$. The SAED pattern with the $\frac{1}{4}\{110\}_c$ superlattice spots does not change with increasing temperature up to 179°C.
At 179°C, the \( \frac{1}{4}\{110\}_c \) superlattice spots disappeared, as shown in Fig. 2-4(b). Instead, incommensurate superlattice diffraction spots emerged. These extra diffraction spots are of the \( \frac{1}{n}\{110\}_c \)-type where \( n \) is not an integer. The value of \( n \) is determined to be 6.48 for the PZ98-PNN2 ceramic from Fig. 2-4(b). The incommensurate superlattice diffraction spots only existed over a narrow temperature range of \( \sim\)3°C and completely disappeared at 181°C. This type of incommensurate superlattice diffraction has been previously observed in PbZrO\(_3\) and was attributed to the competition between the low temperature antiferroelectric phase and the intermediate ferroelectric phase.\(^6\)

In the temperature range of 181–212°C, the primary feature in SAED patterns is the presence of \( \frac{1}{2}\{110\}_c \)-type superlattice diffraction, as exemplified by the diffraction pattern recorded at 194°C shown in Fig. 2-4(c). The \( \frac{1}{2}\{110\}_c \) superlattice diffraction was reported previously and has been considered as the signature of the intermediate phase in PbZrO\(_3\).\(^2,5-8\) However, considerable controversy remains concerning the symmetry and the nature of the intermediate phase. It was reported to be either rhombohedral\(^6\) or orthorhombic\(^5,7\), either ferroelectric\(^2,6,7\) or antiferroelectric\(^5,8\).

The \( \frac{1}{2}\{110\}_c \) superlattice diffraction started to become weaker and diffuse at 212°C and finally vanished at 240°C. Further increase in temperature up to 300°C did not lead to any change in the diffraction pattern. The SAED pattern at 240°C is shown in Fig. 2-4(d) and can be indexed with the parent cubic perovskite structure.
Corresponding changes in the bright field image of the same grain were observed as well, as shown in Fig. 2-5. From room temperature to 179°C, one set of lamellar 180° antiferroelectric domains was observed in the grain [Fig. 2-5(a)], consistent with the one set of \( \frac{1}{4} \{110\}_c \) superlattice spots in the diffraction pattern. These lamellar domains became thinner as temperature was increased. At 179°C, corresponding to the appearance of the \( \frac{1}{n} \{110\}_c \) incommensurate and the disappearance of the \( \frac{1}{4} \{110\}_c \) superlattice diffraction, the 180° antiferroelectric domains in the whole grain were replaced by wedge-shaped domains near grain boundaries. The tip of one wedge-shaped domain is marked by an arrow in Fig. 2-5(b).

In the temperature range of 181~212°C, corresponding to the \( \frac{1}{2} \{110\}_c \) -type superlattice diffraction in SAED patterns, the grain displays a checkerboard-like domain morphology with domain walls primarily on \( \{100\}_c \) planes. The domain walls of the large domain with bright contrast are indicated by arrows in Fig. 2-5(c). Such domain morphology is a reminiscence of the antiferroelectric domains in lead zirconate stannate titanate ceramics. The walls of these checkerboard-like domains started to move and disappear at 212°C and completely vanished at 224°C. This grain remains contrast free during the further heating up to 300°C, as shown in Fig. 2-5(d).

Compared with the results from dielectric measurement in bulk samples, the in-situ TEM heating experiment reveals almost the same phase transition sequence. Below 179°C, the PZ98-PNN2 ceramic is in the antiferroelectric phase that is isostructural to PbZrO\(_3\). Between 181°C and 212°C, the ceramic is in the intermediate ferroelectric phase, characterized by the
$1/2\{110\}$-type superlattice diffraction and the checkerboard-like domains. Above 212°C, the ceramic is in the paraelectric phase. However, the $1/2\{110\}$-type superlattice diffraction and the checkerboard domain morphology persists up to 224°C in the paraelectric phase. The persistence of the $1/2\{110\}$ superlattice into paraelectric phase was noticed before in PbZrO$_3$.$^{2,6}$ The difference in the transition temperatures between the TEM experiment and the dielectric measurement is due primarily to the different sample geometries. The advantage of the *in-situ* TEM study over the dielectric measurement is manifested in the revealing of the transient incommensurate phase around 179°C between the low temperature AFE phase and the intermediate phase.

### 2.4.3 High temperature XRD

The crystal structure of the PZ98-PNN2 ceramic was further analyzed with XRD at a series of temperatures during the heating process. Four temperatures were selected to record the diffraction pattern: 25°C where the AFE phase isostructural to PbZrO$_3$ is expected, 190°C where the incommensurate phase is expected in the bulk sample, 210°C where the intermediate phase is expected, and 240°C where the paraelectric phase should be dominant. All the patterns were recorded after the temperature was stabilized at the desired temperature for at least 10 minutes. The results are shown in Fig 6, where the major peaks are indexed based on a cubic unit cell.

At 25°C, the diffraction pattern fits the space group $Pbam$, the same as PbZrO$_3$ at room temperature.$^{3-5}$ The peaks marked by the asterisks indicate the peaks that belong to this
symmetry but are forbidden in the cubic structure. All these peaks can be indexed as $\frac{1}{4} [110]_c$-type superlattice diffractions. When the temperature increased to 190°C, orthorhombic $Pbam$ symmetry was remained, as indicated by the asterisks. However, two additional peaks, one on each side of the $\{110\}_c$ peak, emerged at 25.4° and 35.0°, respectively. They are marked with squares in Fig. 2-6. These additional peaks cannot be indexed with either cubic or orthorhombic symmetry. Considering the observed incommensurate phase observed in TEM, these two peaks may be the satellite diffraction peaks of the strongest $\{110\}_c$ peak. This is indeed the case. They can be indexed as $\{110\}_c - \frac{1}{n} [110]_c$ and $\{110\}_c + \frac{1}{n} [110]_c$, respectively, with $n = 6.48$. This value of $n$ is exactly the same as determined by the TEM result. The observation of the incommensurate modulation with XRD is significant because so far it has been only revealed by electron diffraction in TEM in PbZrO$_3$-based ceramics.\textsuperscript{14}

On further heating to 200°C, the $\frac{1}{4} [110]_c$-type superlattice peaks became weaker and some of them even disappeared. While an orthorhombic symmetry was reserved, the overall pattern fits better with the space group $P2cb$. To our surprise, the incommensurate superlattice peaks can still be clearly observed. This appears to disagree with the TEM result shown in Fig. 2-4, where the incommensurate satellite spots existed over a very narrow temperature range of less than 3°C. This discrepancy can be explained by considering the difference in the experimental conditions. In the TEM experiment, observations were made in a single grain while in XRD, hundreds of thousands of grains were exposed to the X-ray beam. The un-synergized phase transition of each individual grain leads to a much wider temperature range for the incommensurate phase.
At 240°C where the PZ98-PNN2 ceramic is supposed to be in the high temperature paraelectric phase, the major peaks can be indexed with a cubic symmetry. However, close examination revealed the presence of trace amount of the orthorhombic phase.

2.5 Conclusion

By introducing 2 mol.% Pb(Ni\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} into PbZrO\textsubscript{3}, a series of phase transitions occurred above room temperature. The high temperature phases show distinct crystal structures and domain morphologies, as well as distinct dielectric and ferroelectric properties. Below 190°C, the ceramic is in the \textit{Pbam} symmetry with antiferroelectric 180° domains. Both the dielectric permittivity and the loss tangent are low and stable against temperature change. Around 190°C, one order of magnitude increase in dielectric permittivity and loss tangent occurs within a narrow temperature range. Corresponding to the dramatic change in dielectric property is the presence of an incommensurate phase with \(\frac{1}{6.48}[\text{110}]_c\) satellite diffractions. In the temperature range of 190~220°C, the ceramic is in an intermediate phase, which is believed to be ferroelectric. This phase is characterized by the fast increasing dielectric permittivity, stable and high loss tangent, well defined polarization hysteresis loops, and the \(\frac{1}{2}[\text{110}]_c\) superlattice diffraction. This ferroelectric intermediate phase is unique because of the frequency dispersion in its dielectric properties, the checkerboard-like morphology of its domain structure, and the orthorhombic space group of \textit{P2cb}. Above 220°C, the ceramic is in the cubic paraelectric phase with the relative permittivity following the Curie-Weiss law. However, the structural change at the Curie point is by no means abrupt. Some residual orthorhombic phase persists even at temperatures several tens of degrees above 220°C.
2.6 Acknowledgements

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2.7 Figure list

FIG. 2-1 SEM micrograph of the freshly fractured cross section of the PZ98-PNN2 ceramic.

FIG. 2-2 Dielectric properties during heating at 100Hz, 1kHz, and 10kHz in a bulk PZ98-PNN2 ceramic.

FIG. 2-3 Polarization hysteresis loops recorded from a bulk PZ98-PNN2 ceramic at 4Hz during heating at (a) 25°C, (b) 173°C, and (c) 200°C.

FIG. 2-4 Hot stage in-situ TEM experiment on a thin foil specimen of the PZ98-PNN2 ceramic. The <001>-zone axis SAED patterns observed during heating at (a) 25°C, (b) 179°C, (c) 194°C, and (d) 240°C.

FIG. 2-5 The bright field micrographs under the <001>-zone axis of the grain used for the electric diffraction study in Fig. 2-4 at (a) 148°C, (b) 179°C, (c) 186°C, and (d) 300°C.

FIG. 2-6 X-ray diffraction patterns of a bulk PZ98-PNN2 ceramic during heating at 25, 190, 200, and 240°C.
FIG. 2-1 SEM micrograph of the freshly fractured cross section of the PZ98-PNN2 ceramic
FIG. 2-2 Dielectric properties during heating at 100Hz, 1kHz, and 10kHz in a bulk PZ98-PNN2 ceramic
FIG. 2-3 Polarization hysteresis loops recorded from a bulk PZ98-PNN2 ceramic at 4Hz during heating at (a) 25°C, (b) 173°C, and (c) 200°C
FIG. 2-4 Hot stage in-situ TEM experiment on a thin foil specimen of the PZ98-PNN2 ceramic. The $<001>$-zone axis SAED patterns observed during heating at (a) 25°C, (b) 179°C, (c) 194°C, and (d) 240°C.
FIG. 2-5 The bright field micrographs under the <001>-zone axis of the grain used for the electric diffraction study in Fig. 2-4 at (a) 148°C, (b) 179°C, (c) 186°C, and (d) 300°C.
FIG. 2-6 X-ray diffraction patterns of a bulk PZ98-PNN2 ceramic during heating at 25, 190, 200, and 240°C.
2.8 References

Chapter 3. *In-situ* Transmission Electron Microscopy Study on Nb-Doped Pb(Zr$_{0.95}$Ti$_{0.05}$)O$_3$ Ceramics

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W. Qu$^1$, X. Tan$^1$* and P. Yang$^2$

3.1 Abstract

The ferroelectric-to-ferroelectric phase transition between the high temperature (FE$_{RH}$) and the low temperature (FE$_{RL}$) rhombohedral phases in a Nb-doped Pb(Zr$_{0.95}$Ti$_{0.05}$)O$_3$ ceramic was investigated with transmission electron microscopy (TEM). Both bright field images and electron diffraction patterns were monitored as a function of temperature as well as dc electric fields. A special TEM specimen holder that permits the application of electric voltage up to 600V was employed for the study of electric field-induced phase transition. It was found that both $\frac{1}{2}(011)_c$- and $\frac{1}{2}(111)_c$-type superlattice diffraction spots were present at room temperature when the specimen was under no electric field. The $\frac{1}{2}(111)_c$-type superlattice spots were observed to disappear during heating above the phase transition temperature. When dc electric fields were applied at room temperature, the $\frac{1}{2}(111)_c$-type superlattice spots vanished as the electric field-induced FE$_{RL}$$\rightarrow$FE$_{RH}$ phase transition occurred.

1. Department of Materials Science & Engineering, Iowa State University, Ames, IA 50011
2. Sandia National Laboratories, Albuquerque, NM87185
* Author to whom correspondence should be directed
3.2 Introduction

Pb(Zr$_{1-x}$Ti$_x$)O$_3$ ceramics have found wide applications in engineering technologies due to their unique dielectric, piezoelectric and ferroelectric properties. The ferroelectric-to-ferroelectric phase transition from a high temperature (FE$_{RH}$) to a low temperature (FE$_{RL}$) rhombohedral phase covers a wide range of composition in the PbZrO$_3$ rich side of the Pb(Zr$_{1-x}$Ti$_x$)O$_3$ solid solution system (Jaffe et al., 1971). It has been shown that the FE$_{RH}$ $\rightarrow$ FE$_{RL}$ transition is manifested by the doubling of the perovskite unit cell, with the space group changing from $R3m$ to $R3c$ (Glazer et al., 1978). In compositions that are further closer to PbZrO$_3$, an antiferroelectric phase with the space group $Pbam$ becomes stable (Jaffe et al., 1971; Woodward et al., 2005). At ambient conditions, Pb(Zr$_{0.95}$Ti$_{0.05}$)O$_3$ is at the antiferroelectric/ferroelectric phase boundary. A small amount of Nb (usually 2 at.%) is often used to stabilize the ferroelectric phase in this composition (Yang, 2005). As a consequence, ferroelectric$\leftrightarrow$ferroelectric, and ferroelectric$\leftrightarrow$antiferroelectric phase transitions can be easily triggered in these ceramics.

External electric fields are known to be capable of triggering antiferroelectric-to-ferroelectric (Pan et al., 1989; Yang and Payne, 1992; He and Tan, 2005) and relaxor-to-ferroelectric (Ye and Schmid 1993; Qu et al., 2007) phase transitions in various Pb-based perovskite compounds. In these field-induced transitions, the electric field aligns the short range ordered electrical dipoles to the external field direction, stabilizing the ferroelectric phase with long range dipole order. In ferroelectric single crystals, strong electric fields along a non-polar axis have been found to rotate the polarization vector. The rotation of the polar axis changes the symmetry of the crystal, leading to a field-induced ferroelectric-to-ferroelectric...
phase transition (Park and Shrout, 1997; Wada et al., 1999; Zhao et al., 2007). However, the scenario becomes less clear when external electric fields are applied to polycrystalline ferroelectric ceramic specimens, especially to such ceramics as used in the present study for the $F_{ERH}/F_{ERL}$ phase transition. Both ferroelectric phases show a long range dipole order with a polar axis along the same pseudocubic $<111>_c$ direction (the subscript $c$ denotes the indices are based on the pseudocubic parent structure). When electric fields are applied to a polycrystalline ceramic specimen with random oriented grains, either $F_{ERH}$ or $F_{ERL}$ phase could be favored. A previous study with X-ray diffraction indicated that near the $F_{ERH}/F_{ERL}$ phase transition temperature the application of an electrical field favors the $F_{ERL}$ phase and expands its stable region to a higher temperature in a bulk Sn-modified lead zirconate titanate ceramic (Yang et al., 2004a). In the present study, the $F_{ERH} \leftrightarrow F_{ERL}$ phase transition triggered by temperature and electric field was investigated by electron diffraction in transmission electron microscopy (TEM) in thin foils of a Nb-doped lead zirconate titanate ceramic.

3.3 Materials and methods

Powder of nominal composition $\text{Pb}_{0.99}[(\text{Zr}_{0.95}\text{Ti}_{0.05})_{0.982}\text{Nb}_{0.018}]\text{O}_3$, abbreviated as PZT95/5(1.8Nb), was prepared by precipitating a lead acetate and Zr, Ti, Nb n-butoxide-glacial acetic acid solution with an oxalic acid-n-propanol solution (Voigt et al., 1999). An excess of 2 at.% lead was added to the formulation to compensate for lead loss during the subsequent high temperature process. The chemically prepared powder was first pyrolyzed at 400°C and then calcined at 900°C for 16 hours. An appropriate amount of pore former (Lucite - spherical polymerized methyl methacrylate, with average diameter of 15 µm) was added and mixed with the dry calcined PZT powder, then a 2 wt.% binder solution, was sprayed into the tumbling
powder. The purpose of adding the pore former was to control the final sintering density of the ceramic for optimizing device performance. Approximately 70 grams of the granulated powder was then fed into tool steel die and uniaxially pressed at 96 MPa. Ceramic compacts were slowly heated up to 750°C and held for 4 hours to burn out all the organic additives. To prevent lead loss during the high temperature sintering, a double crucible technique with the same composition powder was used to provide a Pb-rich atmosphere. Sintering was performed at 1350°C for 6 hours. Typical sintering weight loss after organic burn-out was controlled to less than 0.2 wt%. The Archimedes method was used to measure the densities of the specimens. These sintered billets were then ground, sliced and electroded with a fired on silver paste for electrical characterization.

The phases of the calcined powders were examined using X-ray diffractometry with a 2θ angle range from 20° to 100°. The composition of the powder was determined by an induction coupled plasma (ICP) technique, using a reference powder batch to monitor the variation from batch to batch. The temperature dependence of the dielectric constant was measured at a temperature range from -20°C to 115°C with a heating and cooling rate of 3°C/min at 100 kHz. Ferroelectric polarization hysteresis measurements were made with a modified Sawyer-Tower circuit at room temperature.

Thin disks with diameter of 3mm were cut from the sintered ceramics pellets, and then were ground and polished to a thickness ~150μm. The central portion of the disks was further thinned and polished by mechanical dimpling. Argon ion milling was then used to perforate the disk at the center. For the hot-stage in-situ TEM study, a heating and cooling rate lower than 2°C/min was used. Bright field images and selected area electron diffraction patterns were recorded ten minutes after the temperature was stabilized. For the electric field in-situ TEM
observation, two half-circle shaped Au-electrodes were evaporated directly onto the TEM
specimen surface, as illustrated in Fig. 3-1. A special TEM specimen holder with two electric
feedthroughs was used to supply the electrical voltage. Experimental details can be found in
our previous publications (Tan et al., 2000, Tan and Shang, 2002, Tan et al., 2005, He and Tan,
2005, Qu et al., 2007). All the TEM observations were carried out on a Phillips CM30
instrument operated at 300kV.

3.4 Results and discussion

3.4.1 Structure and Electrical Properties

The chemical composition after calcination was analyzed by ICP. The molar ratio of
the cation elements are Pb 0.958, Zr 0.957, Ti 0.043, Nb 0.0177, respectively. The bulk density
of sintered pellets is 7.26 g/cm³. Fig. 3-2 shows a representative micrograph of polished and
chemically etched PZT95/5(1.8Nb) ceramic pellets. It is evident that in addition to those large
intergranular pores, small circular intragranular pores can be clearly seen. The grain size is
determined to be 10.3 μm. Refinement of the x-ray diffraction spectrum obtained at room
temperature from the sintered PZT95/5(1.8Nb) ceramic pellet indicates a space group of \( R\overline{3}c \)
with lattice parameters of \( a=5.8486 \) Å and \( c=14.4230 \) Å (Avdeev et al., 2006).

The results of the dielectric property measurement are shown in Fig. 3-3. During
cooling the \( FE_{RH} \rightarrow FE_{RL} \) transition occurs at 43°C, as indicated by the anomalies in both
dielectric constant and dielectric loss curves. There is an abrupt increase in dielectric loss as the
\( FE_{RH} \) phase transforms to the \( FE_{RL} \) phase. The ferroelectric polarization measurement from
sintered pellets at room temperature revealed a very smooth and quite square loop (Fig. 3-4).
The squareness can be attributed to the Nb addition which effectively lowers the coercive field (Yang et al., 2005). The results from Fig. 3-4 indicate a remanent polarization \( P_r \) of 33.2\( \mu \)C/cm\(^2\) and a coercive field \( E_c \) of 12.3kV/cm. The absence of obvious kinks on the hysteresis loop seems to suggest that electric fields up to 40kV/cm did not trigger any phase transitions.

**3.4.2 Hot-stage *in-situ* TEM study**

The sintered pellet contained many circular pores of different sizes, as revealed by optical microscopy shown in Fig. 3-2. A grain that was at the edge of a circular pore was focused for the hot stage *in-situ* TEM study. The specimen was tilted to make the <110>\(_c\) direction of this grain parallel to the electron beam direction. Then the specimen was heated from room temperature to 80°C with several steps. At each step (a setpoint) after the temperature was stabilized for ten minutes, selected area electron diffraction patterns as well as bright field images were recorded. Careful attempts were made to maintain identical recording conditions for electric diffraction patterns at different temperatures. The evolution of the <110>\(_c\) zone-axis diffraction pattern is shown in Fig. 3-5. It is interesting to notice that the diffraction pattern contains both \( \frac{1}{2}(011)\_c\) and \( \frac{1}{2}(111)\_c\)-type superlattice diffraction spots at room temperature [Fig. 3-5(a)]. The space group was determined before for bulk PZT95/5(1.8Nb) ceramic to be \( R3c \) (Avdeev et al., 2006). However, the \( \frac{1}{2}(011)\_c\)-type superlattice spots are forbidden from \( R3c \) (Woodward et al., 2005). Therefore, the local symmetry revealed by electron diffraction is inconsistent with the overall symmetry revealed by x-ray diffraction. Such discrepancy has been seen before and was attributed to either local composition fluctuation (Woodward et al., 2005) or surface effect of TEM specimens (Ricote...
The coprecipitation process route used in this study ensures a homogeneous composition. Therefore, it is more likely that the $\frac{1}{2}(011)_c$-type superlattice spots appear as a consequence of the thin geometry of TEM specimens. These spots are believed to be mainly originated from antiparallel Pb$^{2+}$ displacements (Woodward et al., 2005).

When heated, the intensity of the $\frac{1}{2}(011)_c$-type superlattice spots increases slightly. However, most dramatic changes are found for the $\frac{1}{2}(111)_c$-type superlattice spots. They get weaker continuously from room temperature up to $48^\circ C$ and disappear completely at $55^\circ C$. This indicates that the FE$_{RL}$ phase transforms completely to the FE$_{RH}$ phase at a temperature between $48^\circ C$ and $55^\circ C$ upon heating. Compared with the dielectric measurement data shown in Fig. 3-3, it is clear that the phase transition shows a thermal hysteresis between heating and cooling, consistent with the fact that this phase transition is of first order in nature. The in-situ TEM study results also imply that the temperature change in the specimen from electron beam is quite small.

The domain morphology of the same grain for the electron diffraction patterns was also monitored and recorded, as shown in Fig. 3-6. At room temperature, two sets of domains coexist. The main set takes a lamellar morphology with domain walls on $\{100\}_c$ planes, while the second set takes an irregular shape and runs across the main set. When heated to $40^\circ C$, the contrast of the main set becomes weaker and the second set can be clearly seen [Fig. 3-6(b)]. At $55^\circ C$, the main set disappears completely while the contrast for the second set becomes sharper. The second set of domains persists at even higher temperatures.

Results shown in Figs. 3-5 and 3-6 seem to suggest that $\frac{1}{2}(011)_c$- and $\frac{1}{2}(111)_c$-type superlattice spots are originated from two different sets of domains. Specifically, the $\frac{1}{2}(111)_c$-type spots appear to be associated with the main set domains while the $\frac{1}{2}(011)_c$-type
corresponds to the second set. Therefore, the $\text{FE}_{\text{RL}} \rightarrow \text{FE}_{\text{RH}}$ phase transition during heating in
the PZT95/5(1.8Nb) ceramic is manifested as the diminishing of the $\frac{1}{2}(111)_c$ superlattice
diffraction spots and the disappearance of one set of ferroelectric domains with straight walls
along the $\{100\}_c$ planes. As suggested before, the $\frac{1}{2}(111)_c$ superlattice spots are resulted from
the oxygen octahedra tilting while the $\frac{1}{2}(011)_c$-type superlattice spots are mainly attributed to
the antiparallel Pb$^{2+}$ displacements (Woodward et al., 2005). Therefore, the results presented in
Figs. 3-5 and 3-6 indicate that the antiparallel Pb$^{2+}$ displacements persist to higher temperature
than the oxygen octahedra tilting due to the different boundary conditions present in a thin
TEM specimen. However, a full interpretation of the appearance of the $\frac{1}{2}(011)_c$-type
superlattice spots still awaits detailed investigations.

### 3.4.3 Electric field *in-situ* TEM study

In addition to the temperature induced phase transition, electric field-induced
ferroelectric-to-ferroelectric phase transition was also studied with TEM. In this experiment,
crack-free TEM specimens were selected for electroding with Au films (see Fig. 1 for
specimen geometry). Static electric fields were applied to these TEM specimens in a stepwise
manner. It should be noted that the presence of the central hole in the TEM specimen disturbs
the electric field within the specimen. In the two shaded areas at the edge of the perforation
shown in Fig. 3-1, the direction of the actual field remains unchanged but the magnitude is
intensified. If an ideal circular hole is assumed, the intensification ratio is 2 (Tan et al., 2005).
So the actual electric field mentioned in the following is estimated by doubling the nominal
field. The nominal field is calculated with the applied voltage and the electrode spacing (200
$\mu$m).
A grain was tilted with its $<211>_{c}$ zone-axis along the electron beam direction. The evolution of the selected area electron diffraction pattern under electric field is shown in Fig. 3-7. Consistent with Fig. 3-5(a), both $\frac{1}{2}(111)_{c}$- and $\frac{1}{2}(011)_{c}$-type superlattice spots are present, with the $\frac{1}{2}(111)_{c}$-type spots stronger. The static electric field was then applied along the direction marked in the diffraction pattern shown in Fig. 3-7(b), close ($\sim$6° off) to the $<011>_{c}$ crystallographic direction. Recording conditions for electric diffraction patterns at different field levels were maintained the same. Starting at the actual field level of 28kV/cm, the $\frac{1}{2}(111)_{c}$-type spots get weakened while the $\frac{1}{2}(011)_{c}$-type spots get strengthened. The trend continues at 32kV/cm where the $\frac{1}{2}(111)_{c}$-type superlattice spots can be barely seen. When the actual field level reaches 36kV/cm, the $\frac{1}{2}(111)_{c}$-type spots completely disappear. Strong $\frac{1}{2}(011)_{c}$ superlattice spots are still seen at even higher field levels [Fig. 3-7(f)].

The domain morphology in the same grain under the same tilting conditions was monitored and recorded, as shown in Fig. 3-8. In this grain there are two types of domains, a large domain with straight domain walls and many small domains. Under strong electric fields, the domain wall for small domains disappears. At the same time, the large domain in Fig. 3-8 grows slightly (the width increased) and furthermore, the fine contrast within it disappears.

The results shown in Fig. 3-7 are the first time ever observations of the electric field-induced phase transition made by TEM in a rhombohedral ferroelectric perovskite. Compared to the in-situ TEM heating experiments data shown in Figs. 3-5 and 3-6, the applied external electric field seems to function in a similar way to heating as to the ferroelectric-to-ferroelectric phase transition. External electric fields are also capable of triggering the $\text{FE}_{\text{RL}} \rightarrow \text{FE}_{\text{RH}}$ phase transition in this grain. However, the observations shown in Figs. 3-7 and 3-8 may be closely associated with the thin geometry of the TEM specimen and most importantly, with the
specific electric field direction in this particular grain. Extreme caution should be exercised in making the observed trend general. As shown in Fig. 3-4, the polarization hysteresis loop measurement up to 40kV/cm in a circular disk bulk sample did not reveal any distortions that may suggest a phase change. Furthermore, there are experimental evidences that in a bulk ceramic with rhombohedral symmetry electric fields stabilizes the FE_{RL} phase (Yang et al., 2004) while in BaTiO$_3$ single crystals, the ferroelectric-to-ferroelectric phase transition is dictated by the direction of the electric field (Wada et al., 1999).

Although we believe the different electrical/mechanical boundary conditions in our TEM study are primarily responsible for the observed structure and phase transition route, other factors may also cause the discrepancy from bulk samples. For example, it is often reported that ion milling of Pb-based ceramics preferentially removes Pb which might result in a Pb-deficient TEM specimen. Our previous study on bulk ceramic samples has indicated that losing Pb in this ceramic increases the FE_{RL}-FE_{RH} transition temperature, i.e. stabilizes the FE_{RL} phase (Yang et al., 2004b). However, composition analysis with X-ray energy dispersive spectroscopy in TEM did not detect any Pb-deficiency in our TEM specimens. Further, our in situ TEM experiments indicate that the FE_{RL} phase is destabilized upon heating and applying electric fields.

The electric field-induced FE$_{RL}\rightarrow$FE$_{RH}$ phase transition in this grain is reversible and no obvious time delay was detected during the in-situ TEM study. When the electric field was decreased, the $\frac{1}{2}$(111)-type superlattice spots reappeared. When the field was increased again, they disappeared again.
3.5 Conclusion

In-situ TEM study confirmed the $\text{FE}_{\text{RL}} \rightarrow \text{FE}_{\text{RH}}$ phase transition in PZT95/5(1.8Nb) during heating. There appear to be different ferroelectric domains associated with the $\frac{1}{2}(111)_{c}$-type and the $\frac{1}{2}(011)_{c}$-type superlattice diffraction spots. These two types of domains respond to temperature increase independently. Under conditions used in this study (thin TEM specimen and field is close to $<011>_c$), external electric fields favor the FE$_{\text{RH}}$ over the FE$_{\text{RL}}$ phase at room temperature in the PZT95/5(1.8Nb) ceramic.

3.6 Acknowledgements

Weiguo Qu and Xiaoli Tan acknowledge the financial support from Sandia National Laboratories through contract 679766. The in-situ TEM experiments were carried out at the Materials & Engineering Physics Program, Ames Laboratory which is supported by the Department of Energy of U.S., Office of Basic Energy Sciences, under Contract No. DE-AC02-07CH11358. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

3.7 Figure list

Fig. 3-1 Schematic diagram of the TEM specimen for the electric field in-situ study. The specimen was fixed to the specimen holder with the nominal electric field perpendicular to the primary axis of holder. The two dark areas at the edge of the central perforation indicate the areas where observations were made in this study.

Fig. 3-2 Optical micrograph of polished and chemically etched PZT95/5(1.8Nb) ceramic.
Fig. 3-3 Variation of dielectric constant and loss tangent as a function of temperature for the PZT95/5(1.8Nb) ceramic (data were recorded at 100 kHz on cooling).

Fig. 3-4 The polarization vs. electric field hysteresis loop measured from the PZT95/5(1.8Nb) ceramic at room temperature at 1 Hz.

Fig. 3-5 The <011>-zone axis selected area electron diffraction pattern of the PZT95/5(1.8Nb) ceramic during heating. (a) Room temperature, (b) 40°C, (c) 44°C, (d) 46°C, (e) 48°C, (f) 55°C.

Fig. 3-6 The evolution of the domain morphology in the same grain as Fig. 3-4 during heating. (a) Room temperature. One of the lamellar domains is indicated by the bright arrow in the left. One of the domains of the secondary set is indicated by the bright triangle in the lower part. (b) 40°C, (c) 55°C.

Fig. 3-7 The <211>-zone axis selected area electron diffraction pattern of the PZT95/5(1.8Nb) ceramic under static electric fields at room temperature. (a) 0kV/cm, (b) 20kV/cm, (c) 28kV/cm, (d) 32kV/cm, (e) 36kV/cm, (f) 40kV/cm.

Fig. 3-8 The evolution of the domain morphology in the same grain as Fig. 3-6 under static electric fields at room temperature. (a) 0kV/cm, (b) 40kV/cm.
Fig. 3-1 Schematic diagram of the TEM specimen for the electric field *in-situ* study. The specimen was fixed to the specimen holder with the nominal electric field perpendicular to the primary axis of holder. The two dark areas at the edge of the central perforation indicate the areas where observations were made in this study.
Fig. 3-2 Optical micrograph of polished and chemically etched PZT95/5(1.8Nb) ceramic.
Fig. 3-3 Variation of dielectric constant and loss tangent as a function of temperature for the PZT95/5(1.8Nb) ceramic (data were recorded at 100 kHz on cooling).
Fig. 3-4 The polarization vs. electric field hysteresis loop measured from the PZT95/5(1.8Nb) ceramic at room temperature at 1 Hz.
Fig. 3-5 The \(<0\bar{1}l>\)-zone axis selected area electron diffraction pattern of the PZT95/5(1.8Nb) ceramic during heating. (a) Room temperature, (b) 40°C, (c) 44°C, (d) 46°C, (e) 48°C, (f) 55°C.
Fig. 3-6 The evolution of the domain morphology in the same grain as Fig. 3-4 during heating.

(a) Room temperature. One of the lamellar domains is indicated by the bright arrow in the left. One of the domains of the secondary set is indicated by the bright triangle in the lower part. (b) 40°C, (c) 55°C.
Fig. 3-7 The $<2\bar{1}\bar{1}>$-zone axis selected area electron diffraction pattern of the PZT95/5(1.8Nb) ceramic under static electric fields at room temperature. (a) 0kV/cm, (b) 20kV/cm, (c) 28kV/cm, (d) 32kV/cm, (e) 36kV/cm, (f) 40kV/cm.
Fig. 3-8 The evolution of the domain morphology in the same grain as Fig. 3-6 under static electric fields at room temperature. (a) 0kV/cm, (b) 40kV/cm.
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Chapter 4. Evolution of Nanodomains During the Electric-field-induced Relaxor to Normal Ferroelectric Phase Transition in a Sc-doped Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ Ceramic


W. Qu, X. Zhao and X. Tan*

4.1 Abstract

Sc doping in Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ enhances the B-site 1:1 cation order significantly but promotes the ferroelectric polar order moderately. At low doping levels, the electrical polar domains remain at the nanometer scale and the relaxor ferroelectric behavior is preserved. A normal ferroelectric state can be triggered with electric fields from the relaxor state at lower temperatures. This electric-field-induced phase transition process was directly observed with an *in-situ* transmission electron microscopy technique in a 4 at.% Sc-doped Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ polycrystalline ceramic under different conditions. It was found that the phase transition started at the grain boundary and took two steps to complete: the gradual coalescence of the polar nanodomains and the abrupt formation of the long-range ferroelectric domains. During the growth of the polar nanodomains, the morphology of the cation ordered chemical domains does not change. Furthermore, these chemical domains seem to have no strong resistance to the growth of polar domains in Sc-doped Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$.

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

*Author to whom correspondence should be directed
4.2 Introduction

Relaxor ferroelectrics have been extensively studied due to their extraordinary dielectric, ferroelectric and electrostrictive properties and accordingly their applications in multilayer capacitors, actuators and electro-optic devices.\textsuperscript{1} The most distinctive features of this type of ferroelectrics are the diffuse phase transition, the frequency dispersion in dielectric response, and the electric field-induced relaxor to normal ferroelectric phase transition.\textsuperscript{2}

Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} (PMN), has been considered as the prototype relaxor ferroelectrics since its discovery by Smolenskii in 1958.\textsuperscript{3} At room temperature, it has a cubic ABO\textsubscript{3} perovskite structure, where Pb\textsuperscript{2+} occupies the A-site while Mg\textsuperscript{2+} and Nb\textsuperscript{5+} share the B-site. The structure inevitably involves local compositional fluctuations in the distribution of the Mg and Nb cations on the B-site sublattice. Such fluctuations typically manifest themselves as the 1:1 cation order on the B-site sublattice by unit cell doubling at the nanometer scale.\textsuperscript{4} This cation ordering was suggested to account for the diffuse phase transition and the strong frequency dispersion in dielectric permittivity.\textsuperscript{5} Transmission electron microscopy (TEM) study by Krause et al.\textsuperscript{6} and Hilton\textsuperscript{7} directly imaged the B-site cation ordered nanometer-scaled domains. The nonstoichiometric chemical ordering in PMN-based 1:2 complex perovskites is described by the "random site" model.\textsuperscript{8} In this model, every other {111} planes of the B-site sublattice are occupied exclusively by Nb\textsuperscript{5+} while the remaining {111} planes are occupied by a random 2:1 distribution of Mg\textsuperscript{2+} and Nb\textsuperscript{5+}. The “random site” model has obtained direct support from the atomic resolution Z-contrast imaging study.\textsuperscript{9} According to this model, there is no charge imbalance between the B-site 1:1 cation ordered domains and the disordered matrix. The stability of the B-site cation ordered domains is believed to be caused by kinetics constrains.\textsuperscript{4}
By introducing appropriate dopants, such kinetics constraints could be overcome and long range cation ordering can be realized.\textsuperscript{10}

The relaxor ferroelectric PMN contains electrical dipoles as well. In contrast to normal ferroelectrics, the ordered regions of these electrical dipoles are confined at the nanometer-scale, forming the so-called polar nanoregions (PNRs). The PNRs persist up to the temperature $T_d$ of Burns and Docol, which is several hundred degrees above the dielectric permittivity peak temperature $T_m$.\textsuperscript{11} The origin of PNRs in relaxor ferroelectrics can also be traced back to the intrinsic chemical fluctuations and the resulting charge and strain inhomogeneity.\textsuperscript{12,13} The PNRs have been characterized by many techniques, such as biprism refractive index measurement,\textsuperscript{11} pair distribution function (PDF) analysis,\textsuperscript{14} as well as TEM.\textsuperscript{15,16} In PMN, the electrical dipole ordered PNRs are structurally distorted along the $<111>$ direction, and the polar vector randomly fluctuates among the eight equivalent $<111>$ directions.\textsuperscript{1,17} On cooling without electric fields, the PNRs remain less than 10 nm in size.\textsuperscript{13,18} However, various phases can be developed in the electric field-temperature space in PMN relaxor ferroelectrics, which correspond to various electric field-induced phase transitions.\textsuperscript{2}

Both the B-site cation ordering and the electrical dipole ordering are believed to play important roles in determining the peculiar ferroelectric behavior of PMN.\textsuperscript{19} Therefore, observing the evolution of both the chemical and electrical domains under applied electric fields is highly expected to reveal the interrelationship and the interactions between them. However, due to technical difficulties, there have been no publications on the direct observation of such evolution at the nanoscale with TEM until recently we briefly reported the growth of polar nanodomains during a field-cooling process.\textsuperscript{20} In the present paper, more detailed results are reported, including the macroscopic properties measurement, the polar
nanodomain growth during a poling process, the response of chemical nanodomains to applied electric fields, and the interactions of the growing polar domains with the chemical cation ordered domains.

### 4.3 Experimental procedure

The Sc-dopant is introduced through forming a solid solution of Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ with Pb(Sc$_{1/2}$Nb$_{1/2}$)O$_3$ (PSN). The composition of the ceramic used in this study is 0.92PMN–0.08PSN (abbreviated as PSMN8 hereafter), containing 4at.% Sc$^{3+}$ on the B-site. A two step solid state reaction method was employed to prepare the polycrystalline ceramic. The starting materials used in this work were commercially available and high purity (better than 99.9 wt.%) PbO, MgO, Nb$_2$O$_5$, and Sc$_2$O$_3$ powders. After vibratory milling in isopropyl alcohol for 6 h and subsequent drying, the well-mixed stoichiometric powders of B-site oxides were calcined at 1100°C for 4 h. The calcined powders were then combined with PbO powder, milled for 6 h, and calcined at 900°C for 4 h to form phase pure perovskite powder. Cold-pressing formed disks were then sintered at 1250°C for 3 h in controlled atmosphere. At the end of sintering, a slow cooling rate of 12°C/h to 900°C was used to achieve long range cation ordering in the ceramic.

The surface layers of the sintered pellets were removed and the x-ray diffraction was performed on a Siemens D500 diffractometer to check the phase purity and the cation ordering. The cation ordering was also examined by TEM dark field imaging. Then, the dielectric characterization was performed with an LCR meter (HP-4284A, Hewlett-Packard) in conjunction with an environmental chamber (9023, Delta Design). A heating/cooling rate of 2°C/min was used during this measurement. Electric field-induced phase transition was then
evaluated by the thermal depolarization current measurement with a picoammeter (Model 486, Keithley) and the polarization hysteresis measurement with a standardized ferroelectric test system (RT-66A, Radiant Technologies).

The in-situ TEM experiment was carried out on a JEOL 2010 TEM operating at 200 kV with a special specimen holder. The holder has two electrical leads at the tip and a liquid nitrogen Dewar to cool the specimen to cryogenic temperatures. Detailed specimen preparation procedure for the in-situ study can be found in previous reports. The sample geometry is schematically shown in Fig. 4-1. Two half-circle shaped electrodes with their straight edges facing each other and a distance of 200 μm in between were evaporated onto the flat surface of the perforated TEM specimen with the help of a special mask. It should be noted that the presence of the central perforation disturbs the electric field. For an ideal circular perforation, it was shown that the actual field in the two small shaded areas at the edge of the central perforation in Fig. 4-1 is intensified and preserves the direction of the nominal field. The in-situ TEM observations in the present study were performed in the grains within these two areas and the electric field intensity specified refers to the nominal field.

4.4 Results and discussion

4.4.1 Structure and electrical properties

The x-ray diffraction pattern of the PSMN8 ceramic (cooled at 12°C/h after sintering) is shown in Fig. 4-2. For comparison, the diffraction result for a pure PMN ceramic is also included. It is evident that PSMN8 still possesses a pseudocubic structure as pure PMN. The lattice parameter for PSMN8 is 4.0608 Å, increased from 4.0509 Å for the pure PMN ceramic. The increase in the unit cell size is caused by the larger ionic radius of Sc³⁺. In addition to the
major diffractions from the simple cubic perovskite structure, two extra weak peaks at ~19° and ~37° respectively are noticeable in the PSMN8 ceramic. These two peaks correspond to the d-spacing values twice those of the (111) and (311) major diffraction, respectively. The two superlattice peaks do not appear in the pure PMN ceramic. The comparison is more apparent in the inset of Fig. 4-2 for the ½(111) peak. Therefore, the x-ray diffraction results indicate a considerable enhancement of the B-site 1:1 cation ordering as a result of Sc-doping. The introduction of larger Sc³⁺ cations (0.745Å versus 0.72Å of Mg²⁺) promotes the B-site cation order by increasing the size difference between the cations on the two B-site sublattices.²⁵,²⁶

The relative dielectric permittivity as a function of temperature of PSMN8 is plotted in Fig. 4-3. Broad peaks and strong frequency dispersions are clearly seen, indicating that the characteristic relaxor ferroelectric behavior is still preserved after 4 at.% Sc-doping. For comparison, the dielectric constant for pure PMN measured at 1kHz is also plotted as the solid line in Fig. 4-3. At 1 kHz, the maximum relative permittivity εₘ was measured as 21,440 at the Tₘ of -5°C for PSMN8. Compared with the Tₘ of -10°C for pure PMN, Sc-doping shifted the Tₘ slightly to a higher temperature.

For relaxor ferroelectrics, at temperatures above Tₘ and when εₘ<1.5ε, the dielectric constant versus temperature relationship can be approximately expressed as follows:²⁷

\[
\frac{\varepsilon}{\varepsilon_m} = \exp \left[ -\frac{(T - T_m)^2}{2\delta^2} \right]
\]  

(1)

where εₘ is the maximum dielectric constant, Tₘ is the temperature at which εₘ is measured, T and ε are the temperature and the dielectric constant at this temperature, respectively. The parameter δ is the diffuseness parameter which was introduced by Smolenskii²⁸ to characterize the diffuse phase transition of relaxor ferroelectrics. By fitting the
1kHz dielectric constant data to Eq. (1), the diffuseness parameter $\delta$ was determined to be 32.5K for PSMN8 and 35.2K for pure PMN. The lower $\delta$ in PSMN8 indicates an enhanced ferroelectric behavior after Sc-doping.

Thermal depolarization measurement was carried out on a PSMN8 sample during zero-field heating after it had been cooled under an electric field of 10 kV/cm. The result is shown as the inset in Fig. 4-4. By integrating the depolarization current over the entire temperature range, the change of the polarization during zero-field-heating is plotted in Fig. 4-4 as a function of temperature. The spike of depolarization current corresponds to the sudden release of the polarization developed during the initial field cooling, indicating a first order phase transition. This phase transition is believed to be the intrinsic phase transition from the induced normal ferroelectric phase to the ergodic relaxor phase. The intrinsic phase transition temperature $T_{C0}$ was determined to be $-38^\circ$C for the PSMN8 ceramic, increased significantly from $-60^\circ$C for pure PMN. It is worthy of noting that the gap between $T_m$ and $T_{C0}$ is 33 °C for PSMN8 and 50 °C for pure PMN. In other words, Sc doping reduced the difference between $T_m$ and $T_{C0}$. It should be pointed out that $T_m$ and $T_{C0}$ converge at $T_C$, the Curie point, in normal ferroelectrics. Therefore, the smaller temperature gap in PSMN8 also indicates an enhanced ferroelectric behavior. The enhanced ferroelectric behavior can be explained by taking into consideration the larger ionic size and higher ferroelectric activity of Sc$^{3+}$ in comparison to Mg$^{2+}$. When larger Sc$^{3+}$ is introduced to the B site, the lattice is more open for Nb$^{5+}$ to shuffle in response to external electric fields. In addition, Sc$^{3+}$ is ferroelectrically more active than Mg$^{2+}$. Therefore, not only is the chemical ordering enhanced, but also the electrical dipole ordering is moderately improved in the Sc-doped PMN relaxor ferroelectrics.
The electric field-induced relaxor to normal ferroelectric phase transition was further characterized with the hysteresis loop measurement at different temperatures. In each measurement, the sample was cooled from room temperature at 2 °C/min to the desired temperature without electric fields. Then the polarization versus electric field hysteresis loop was measured at a peak field of 40 kV/cm. As shown in Fig. 4-5, the sample showed fully developed hysteresis loops at all the measuring temperatures (-50, -80, -100, -120, and -150°C), indicating a normal ferroelectric phase has been developed in PSMN8 under 40kV/cm at these temperatures. The coercive field $E_c$ increases as the temperature decreases. The remanent polarization $P_r$, however, initially increases when temperature decreases from -50°C to -120°C, then decreases at -150°C. Such decrease in polarization indicates that electrical dipoles in some ferroelectric domains are frozen and cannot be switched anymore at -150°C.

It was suggested that the coercive field measured under such condition in PMN-based relaxor ferroelectrics is approximately identical to the critical electric field delimiting the nonergodic relaxor phase from the induced normal ferroelectric phase. Therefore, the coercive field $E_c$ measured from Fig. 4-5 can be used to construct the $E$-$T$ phase diagram of PSMN8, as shown in Fig. 4-6. The solid line that connects the measured $E_c$ data points denotes the boundary between the nonergodic phase and the induced normal ferroelectric phase with switchable polarizations. The intrinsic phase transition temperature $T_{C0}$ determined from the thermal depolarization measurement is indicated by the arrow in Fig. 4-6. According to Ye, there is another phase boundary which delimits the ergodic relaxor phase and the induced normal ferroelectric phase. This phase boundary is not experimentally determined in the present study and is only schematically indicated by the dashed line.
4.4.2 In-situ TEM study

Finally, in-situ TEM study was conducted for the PSMN8 ceramic to directly observe the electric field-induced relaxor-to-normal ferroelectric phase transition at the nanometer scale. As shown in the E-T phase diagram in Fig. 4-6, the normal ferroelectric phase with switchable polarization can be developed through either a field cooling process, route (a), or a poling process at a low temperature, route (b). In the present in-situ TEM study, both routes were carried out.

Route (a) in Fig. 4-6 was followed in the in-situ TEM study by field cooling a PSMN8 TEM specimen under a static electric field of 10 kV/cm from room temperature. One grain with its <110> direction close to the electron beam was focused on, as shown in Fig. 4-7. At room temperature, very faint contrast of polar nanoregions is noticed associated with bending contours [Fig. 4-7(a)]. The inset shows the <110> zone-axis electron diffraction pattern, where the \( \frac{1}{2}(111) \) superlattice diffraction spots are clearly seen. The in-plane directions <001> and <\( \tilde{1}1\tilde{0} \)> are indicated by bright arrows in Fig. 4-7(a). In this micrograph, the grain boundary is also noted by the bright dashed line at the top.

A fixed static electric field of 10 kV/cm, with the direction indicated by the bright arrow in Fig. 4-7(b), was then applied. The direction of the applied field happened to be very close to the <001> direction. No detectable morphological changes of the polar nanoregions were observed at room temperature under the static field. However, when temperatures goes down to \(-50^\circ\)C, evident changes were noticed in the area close to the grain boundary, as shown in Fig. 4-7(b). It is clear that clustering of the polar nanoregions occurred. The coalescence of the polar nanodomains continues during the further cooling to \(-55^\circ\)C [Fig. 4-7(c)]. Until this
temperature, the morphology of the nanodomains remains irregular-shaped without well
defined domain walls. When the temperature reaches -70°C, a dramatic change in the domain
morphology is observed [Fig. 4-7(d)]. Large ferroelectric domains (>200nm) with flat domain
walls close to the \{1\bar{1}0\} plane appeared in the close vicinity of the grain boundary. Further
cooling to -90°C leads the growth of existing large domains and appearing of new large
domains [Fig. 4-7(e)]. The temperature was then held constant at -90°C. After 30 minutes,
further growth of the large domains was noticed [Fig. 4-7(f)].

The results shown in Fig. 4-7 indicate that the field-induced relaxor to normal
ferroelectric phase transition takes two stages, the gradual coalescence of polar nanodomains
and the abrupt formation of long-range ferroelectric domains. This process is very similar to
the one in <111>-oriented Pb(Mg_{1/3}Nb_{2/3})O_3 single crystals depicted by x-ray diffraction and
polarization measurement.\textsuperscript{30,31} It should be noted that the current observation was made with an
individual grain in a polycrystalline ceramic. In contrast, polarization measurements from
polycrystalline ceramic samples are not able to show such a two stage process. This is where
TEM can make unique contributions.

Figure 4-7 also shows that the coalescence of polar nanodomains and formation of
wedge-shaped domains take place in the vicinity of a grain boundary. The result is consistent
with the random field model for relaxor ferroelectrics, where the polar ordering is controlled by
the quenched random electric fields originating from charged point defects.\textsuperscript{32} At grain
boundaries, periodic packing of atoms is disrupted and impurity species are concentrated. This
may lower the energy barrier for the alignment of local electrical dipoles at longer range.
Consequently, grain boundaries are preferred sites for the initiation of the field-induced normal
ferroelectric phase.
Route (b) in Fig. 4-6 was realized in the *in-situ* TEM study by cooling another TEM specimen at 2°C/min to -70°C under zero electric field, then applying static electric fields up to 16 kV/cm at -70°C. The polar domain growth during this poling process was recorded with dark field images with the <100> primary diffraction spot. After zero-field-cooling to -70°C, the PSMN8 ceramic preserves polar nanodomains, as shown in Fig. 4-8(a). A grain boundary was found at the upper right corner of the micrograph. While the temperature was maintained at -70°C, an electric field was applied along the direction indicated by the bright arrow in Fig. 4-8(b). When the applied electric field was below the critical field for phase transition, coalescence of polar nanodomains occurred in the vicinity of the grain boundary. When the electric field was increased to 6kV/cm, abrupt changes in the morphology of polar domains were observed, as shown in Fig. 4-8(b). Large ferroelectric domains on the order of 100 nm formed with the domain walls parallel to the {001} crystallographic planes. The tips of these large polar domains are marked with bright arrows in Fig. 4-8(b). This indicates that the electric field-induced phase transition has occurred. It is noted from the E-T phase diagram in Fig. 4-6, the critical field is ~7kV/cm to trigger the relaxor to normal ferroelectric phase transition at -70°C. Upon further increase in electric field, a new set of domain walls appeared (with tips marked by bright arrows), replacing the existing one, as shown in Fig. 4-8(c). At the higher level of applied electric field [Fig. 4-8(c)], the new domain walls are close to the {110} plane, consistent with the observations in the Route-(a).

The electric field-induced normal ferroelectric phase presumably possesses a rhombohedral structure with spontaneous polarization along one of the <111> directions. By considering the electric field to be applied along the [100] direction, the [111], [111], and [111] directions should be equally favored and multiple domains are expected. However, under
the present experimental conditions, the direction of the applied electric fields deviates slightly from the [100] crystallographic direction. As a result, some of the <111> directions are favored over others. With the increasing electric field, domains with polarization directions along one of the favored <111> directions will grow by consuming domains with polarization directions along one of the disfavored <111> directions. The observed {110} domain walls are therefore electrically charged. It should be pointed out here that there is an alternative interpretation of these domain walls. Close examination of Figs. 4-7(f) and 4-8(c) shows that the multiple domains may merge to a single domain as they grow. Therefore, these domain walls could possibly be the rhombohedral/pseudocubic phase boundary.

Figures 4-7 and 4-8 indicate that the field-cooling process, route (a), and the low temperature poling process, route (b), share some common features as for the relaxor to normal ferroelectric phase transition. First, the transition initiates at grain boundaries in both routes. Second, the transition takes two stages to complete during the decrease in temperature in route (a) or the increase in electric field in route (b): The gradual coalescence of polar nanodomains and the abrupt formation of micrometer-sized ferroelectric domains. Third, the domains walls are roughly along {110} planes and they are the rhombohedral/pseudocubic phase boundary at the same time.

During the field-cooling process shown in Fig. 4-7, cation ordered domains in the same grain were also recorded under each field level through dark field imaging with the ½{111} superlattice diffraction. The original morphology of these chemical domains at room temperature and that at -65°C under 10kV/cm are shown in Fig. 4-9. It can be seen that the cation ordered domains in PSMN8 are on the order of 100nm, much larger than that in pure PMN. The comparison between Fig. 4-9(a) and Fig. 4-9(b) reveals that the size and
morphology of the cation ordered domains remain unchanged during the field-induced relaxor to normal ferroelectric phase transition process. However, close examination indicates that there are obvious changes in the contrast of some cation ordered domains. For example, domain A in Fig. 4-9(a) has a bright contrast; it changes to a dark domain A' in Fig. 4-9(b). The dark domain B in Fig. 4-9(a) turns into a bright domain B" in Fig. 4-9(b). There are also many cation ordered domains with unchanged contrast [e.g., C in Fig. 4-9(a) versus C' in Fig. 4-9(b)].

The persistence of the morphology of cation ordered domains during the electric field-induced relaxor to ferroelectric phase transition is anticipated because the diffusion activities of B-site cations are extremely limited at these low temperatures. The change in contrast of some chemical domains was not initially expected and can be explained as follows. In PMN-based complex perovskite oxides, the B-site cations are packed periodically on {111} planes in the ordered domains. Therefore, the cation ordered domains have four variants: \( \frac{1}{2}(111) \), \( \frac{1}{2}(-111) \), \( \frac{1}{2}(1\bar{1}1) \), and \( \frac{1}{2}(\bar{1}1\bar{1}) \). During electron diffraction, we consider dynamical conditions which permit the double diffraction route,\(^{33}\) for example,

\[
\begin{bmatrix}
1 \\
2 \\
2
\end{bmatrix}
\begin{bmatrix}
1 \\
2 \\
2
\end{bmatrix}
+ \{110\} = \begin{bmatrix}
1 \\
1 \\
2 \\
2
\end{bmatrix}
\]

That is to say, the \( \frac{1}{2}(111) \) superlattice diffraction spot used for dark field imaging could have contributions from cation ordered domain variants of both \( \frac{1}{2}(111) \) and \( \frac{1}{2}(-111) \). Upon application of external electric fields, the double diffraction route may be modified. As a
consequence, the $\frac{1}{2}(\overline{1}11)$ domain variant turns into a dark contrast, such as domain A in Fig. 4-9(a). At the same time, other domain variants, $\frac{1}{2}(\overline{1}11)$ and/or $\frac{1}{2}(\overline{1}11)$, may become favored for double diffraction to the $\frac{1}{2}(111)$ superlattice spot. This leads to the brightening in contrast of these domains, such as domain B in Fig. 4-9(a). However, it needs to be clarified that these changes are only the changes in imaging conditions. There are no physical changes in the cation ordered domains under conditions in the present *in-situ* TEM study.

As mentioned in the Introduction, the interactions between the cation ordered chemical domains and the growing polar domains would be of high interest. In the PSMN8 ceramic studied here, large cation ordered domains facilitate the direct observation on such interactions under electric fields. Fig. 4-10 shows a dark field micrograph of the cation ordered domains in exactly the same area within the same grain as the micrographs shown in Fig. 4-7. Close comparison of Figs. 4-7(d) and 4-7(f) with Fig. 4-10 indicates that neither the initiation of large polar domains nor the advancement of the walls of the polar domains shows a clear correlation with the underlying cation ordered domains. In other words, the chemical domains appear not to have strong interactions with the large ferroelectric domains in the 4 at.% Sc-doped PMN ceramic.

### 4.5 Conclusions

By introducing 4 at.% Sc$^{3+}$ to the B-site sublattice in Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$, the pseudocubic perovskite structure and the characteristic relaxor behavior are preserved in the resulting PSMN8 ceramic. In the meanwhile, the B-site 1:1 cation order is significantly
enhanced while the ferroelectric polar order is slightly promoted. Direct observation with the
\textit{in-situ} TEM technique reveals that the electric-field-induced relaxor to normal ferroelectric
phase transition initiates at grain boundaries. The transition involves the gradual coalescence of
polar nanoregions and the successive abrupt formation of large ferroelectric domains. The
formed domain/phase walls are roughly along \{110\} planes. The morphology of the cation
ordered domains does not change under applied electric fields. Furthermore, no evidence for
strong interactions of these chemical domains with the induced large ferroelectric domains is
found in the Sc-doped PMN ceramic.

\textbf{4.6 Acknowledgement}

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\textbf{4.7 Figure list}

FIG. 4-1. Schematic diagram of the TEM specimen for the electric field \textit{in-situ} study. The
specimen was fixed to the specimen holder with the nominal electric field
perpendicular to the primary axis of holder. The two dark areas at the edge of the
central perforation indicate the areas where observations were made in this study.

FIG. 4-2. X-ray diffraction spectra of the pure PMN and the PSMN8 ceramics. The inset
shows a close look in the range between 18° and 20° of 2θ.

FIG. 4-3. Dielectric properties of the PSMN8 ceramic as a function of temperature at 100 Hz,
1 kHz, 10 kHz and 100 kHz. The solid line shows the dielectric constant vs.
temperature for the pure PMN ceramic at 1 kHz.
FIG. 4-4. Polarization of the PSMN8 ceramic obtained by integrating the depolarization current (inset) during zero field heating after field cooling at 10 kV/cm over the measurement temperature range.

FIG. 4-5. Polarization versus electric field hysteresis loops measured at 4 Hz for the PSMN8 ceramic at different temperatures under a 40 kV/cm peak electric field.

FIG. 4-6. E–T phase diagram proposed for the PSMN8 ceramic with long range cation order. The dotted lines mark the routes used for the \textit{in-situ} TEM experiments. Route-(a) represents a field-cooling process while Route-(b) represents a poling process at a low temperature.

FIG. 4-7. The morphological evolution of the polar nanodomains during the field cooling process under 10 kV/cm revealed by the \textit{in-situ} TEM technique. The applied field direction is shown by the arrow in (b). (a) The initial polar nanoregions at room temperature. The inset shows the <110> zone-axis selected area electron diffraction (SAED) pattern. (b) -50 °C, (c) -55 °C, (d) -70 °C, (e) -90 °C, and (f) -90 °C after 30 min.

FIG. 4-8. The morphological evolution of the polar nanodomains during the poling process at -70°C revealed by the \textit{in-situ} TEM technique. The applied field direction is shown by the arrow in (b). (a) 0 kV/cm at -70°C. The inset shows the <110> zone-axis SAED pattern. (b) 6 kV/cm, (c) 16 kV/cm.

FIG. 4-9. The change in the contrast of the cation ordered domains in the same grain as in Fig. 4-7 during the field-induced relaxor to normal ferroelectric phase transition. (a) 10 kV/cm at room temperature, and (b) 10 kV/cm at -65°C.
FIG. 4-10. Dark field imaging of the cation ordered domains in the exactly same area within the same grain as those micrographs shown in Fig. 4-7.
FIG. 4-1. Schematic diagram of the TEM specimen for the electric field *in-situ* study. The specimen was fixed to the specimen holder with the nominal electric field perpendicular to the primary axis of holder. The two dark areas at the edge of the central perforation indicate the areas where observations were made in this study.
FIG. 4-2. X-ray diffraction spectra of the pure PMN and the PSMN8 ceramics. The inset shows a close look in the range between 18° and 20° of 2θ.
FIG. 4-3. Dielectric properties of the PSMN8 ceramic as a function of temperature at 100 Hz, 1 kHz, 10 kHz and 100 kHz. The solid line shows the dielectric constant vs. temperature for the pure PMN ceramic at 1 kHz.
FIG. 4-4. Polarization of the PSMN8 ceramic obtained by integrating the depolarization current (inset) during zero field heating after field cooling at 10 kV/cm over the measurement temperature range.
FIG. 4-5. Polarization versus electric field hysteresis loops measured at 4 Hz for the PSMN8 ceramic at different temperatures under a 40 kV/cm peak electric field.
FIG. 4-6. E–T phase diagram proposed for the PSMN8 ceramic with long range cation order. The dotted lines mark the routes used for the *in-situ* TEM experiments. Route-(a) represents a field-cooling process while Route-(b) represents a poling process at a low temperature.
FIG. 4-7. The morphological evolution of the polar nanodomains during the field cooling process under 10 kV/cm revealed by the *in-situ* TEM technique. The applied field direction is shown by the arrow in (b). (a) The initial polar nanoregions at room temperature. The inset shows the <110> zone-axis selected area electron diffraction (SAED) pattern. (b) -50 °C, (c) -55 °C, (d) -70 °C, (e) -90 °C, and (f) -90 °C after 30 min.
FIG. 4-8. The morphological evolution of the polar nanodomains during the poling process at -70°C revealed by the *in-situ* TEM technique. The applied field direction is shown by the arrow in (b). (a) 0 kV/cm at -70°C. The inset shows the <110> zone-axis SAED pattern. (b) 6 kV/cm, (c) 16 kV/cm.
FIG. 4-9. The change in the contrast of the cation ordered domains in the same grain as in Fig. 4-7 during the field-induced relaxor to normal ferroelectric phase transition. (a) 10 kV/cm at room temperature, and (b) 10 kV/cm at -65°C.
FIG. 4-10. Dark field imaging of the cation ordered domains in the exactly same area within the same grain as those micrographs shown in Fig. 4-7.
4.8 References


Chapter 5. General conclusions

The primary objective of the work presented in this dissertation was to investigate the dynamic process of phase transitions in prototype ferroelectric materials at nanoscale and provide useful information to facilitate better understanding of the ferroelectric behaviors.

It has been shown that with carefully designed experiment conditions based on knowledge of macroscopic behavior, the temperature and/or electric field in-situ TEM technique could be extremely powerful in revealing underlying physics mechanisms of distinct behaviors in ferroelectric materials.

In the prototype antiferroelectric PbZrO$_3$ system, by introducing 2 mol.% Pb(Ni$_{1/3}$Nb$_{2/3}$)O$_3$, a series of phase transitions occurred above room temperature. Electric property measurement suggests that three distinct phases can be developed within different temperature region: an antiferroelectric low temperature phase below 190$^\circ$C, a paraelectric high temperature phase above 220$^\circ$C and a ferroelectric phase with slight frequency dependence in the intermediate region. Thermal in-situ TEM observation confirmed the antiferroelectric nature of the low temperature phase by the existence of characteristic $1/4\{110\}_c$ type superlattice reflections and 180$^\circ$ AFE domain morphology. Complementary information was obtained for the intermediate ferroelectric phase. The domain was found to posses checkerboard morphology, resembles that of 90$^\circ$ AFE domains. Furthermore, the presence of an incommensurate phase with $\frac{1}{6.48}\{110\}_c$ satellite diffractions was visualized within a narrow temperature range of 3$^\circ$C between the low temperature AFE phase and the intermediate FE phase. Such incommensurate diffractions were then observed with X-ray
diffraction for the first time. The presence of the incommensurate diffractions is believed to be a result of the competition of AFE and FE ordering.

In 1.8%Nb doped PZT95/5 ceramics, the \( \text{FE}_{\text{RL}} \rightarrow \text{FE}_{\text{RH}} \) phase transition was confirmed with thermal \textit{in-situ} TEM and electrical \textit{in-situ} TEM respectively. There appear to be different ferroelectric domains associated with the \( \frac{1}{2}(111)_{c} \)-type and the \( \frac{1}{2}(011)_{c} \)-type superlattice diffraction spots. These two types of domains respond to temperature increase independently. Under conditions used in this study (thin TEM specimen and field is close to \(<011>_c\)), external electric fields favor the \( \text{FE}_{\text{RH}} \) over the \( \text{FE}_{\text{RL}} \) phase at room temperature in the PZT95/5(1.8Nb) ceramic.

In the prototype relaxor ferroelectric \( \text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 \) system, by introducing 4 at.% \( \text{Sc}^{3+} \) to the B-site sublattice in, the pseudocubic perovskite structure and the characteristic relaxor behavior are preserved in the resulted PSMN8 ceramic. In the meanwhile, the B-site 1:1 cation order is significantly enhanced while the ferroelectric polar order is slightly promoted. With our special holder with the capability of applying electric field to the sample and cooling the sample simultaneously, the dynamic phase transition process was observed under TEM for the first time. It is revealed that the electric field-induced relaxor to normal ferroelectric phase transition initiates at grain boundaries. The transition involves the gradual coalescence of polar nanoregions and the successive abrupt formation of large ferroelectric domains. The formed domain/phase walls are roughly along \{110\} planes. The morphology of the cation ordered domains does not change under applied electric fields. Furthermore, no evidence for strong interactions of these chemical domains with the induced large ferroelectric domains is found in the Sc-doped PMN ceramic.
Chapter 6. Recommendations for Further Study

This work has proved that in-situ TEM is a powerful technique to study the dynamic processes in ferroelectric materials. The application of this technique can be further extended.

Based on current capability (cooling, heating, electric field, cooling + electric field) and materials system, more work can be done:

A) In (1-x)PZ-xPNN system, x=0.08 is an interesting composition. It is close to the morphotropic phase boundary between orthorhombic and rhombohedral phases. The AFE to FE phase transition temperature is around 105°C, close to room temperature. The AFE to FE phase transition should be easily induced by a moderate electric field at room temperature. Electric field in-situ TEM study on this composition is expected in order to better understand the extraordinary behavior of ferroelectrics near MPB.

B) In PZT system, our in-situ TEM observation implied that different phase preference with the application of electric field might be a result of sample geometry. Such effect is increasingly important due to the ceaseless miniaturization of electric devices and needs to be further clarified.

C) In PMN system, our result indicated that the electric field induced RFE to FE phase transition tends to start close to defects such as domain boundaries. Furthermore, our attempts on single crystals with similar composition turned out to be fruitless. This, again, might be a result of lacking of defects. Thus, defects seem to play an important role in the electric field induced phase transition. In-situ TEM study on PMN based samples with intentionally introduced defects, such as ferroelectric inactive second phase particles, inner grain pores and
so on, might provide deeper insight into the E-induced phase transition process in relaxor ferroelectrics.

In addition to the current studied systems, the application of in-situ TEM techniques can be extended into much wider scope. A good example is the electromagnetic multiferroelectric systems, such as PFW-BF solid solution. With our current capability, it is promising to observe the response of magnetic domains to the applied electric field at low temperature, which is essential to understanding the multiferroic behavior.

Furthermore, since most applications of ferroelectric materials require transition temperature higher than room temperature and inevitably involve application of electric field, it is more desirable to have a new configuration of in-situ TEM stage with the capability of heating and applying electric field simultaneously. With such capability, the material systems could be studied is remarkably expanded and more importantly, dynamic process of real application situation could be directly observed.
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Appendix A: Publication List


5. **W. Qu**, X. Zhao and X. Tan, Evolution of nanodomains during the electric-field-induced relaxor to normal ferroelectric phase transition in a Sc-doped Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ ceramic, *J. Appl. Phys.*, **102**, 084101 (2007)

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Appendix B. Texture Control and Ferroelectric Properties of Pb(Nb,Zr,Sn,Ti)O$_3$ Thin Films Prepared by Chemical Solution method


Weiguo Qu and Xiaoli Tan*

Abstract

A chelating and spin-coating procedure was used to prepare antiferroelectric thin films of Pb$_{0.99}$Nb$_{0.02}$(Zr$_{0.84}$Sn$_{0.16}$)$_{0.982}$Ti$_{0.018}$O$_3$. By controlling substrate and thermal processing conditions, films with strong (100) and (111) textures, as well as without textures, were prepared. These antiferroelectric films showed the characteristic double hysteresis polarization vs. electric field loops. An orientation dependence of the critical field for the antiferroelectric-to-ferroelectric phase transition was also observed. In addition, when the applied voltage exceeded a critical level during the first “ramp up”, an abnormal reduction in the area of the hysteresis loop was noticed in the (100) and (111) textured films.

Introduction

The wide use of PbZrO$_3$-based antiferroelectric ceramics in microelectromechanical systems and high energy-density capacitors makes them of great technological importance [1–5]. The electric field-induced antiferroelectric-to-ferroelectric phase transition is the underlying physical mechanism for these applications. However, the transition requires such a strong electric field in the prototype antiferroelectric PbZrO$_3$ that dielectric breakdown occurs instead. Therefore, for many engineering applications, Sn and Ti in conjunction with small amounts of Nb or La are added to most antiferroelectric ceramics to reduce the critical field and optimize the properties [1–5].

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

*Author to whom correspondence should be directed
A thin film is often needed to integrate the functionality of antiferroelectrics into devices. However, unlike ferroelectric lead zirconate titanate films, which are widely covered in literature, only a limited amount of information is available on the preparation procedure and property characterization for antiferroelectric ceramic thin films [6–24]. In many previous studies, wet chemical methods were used to prepare antiferroelectric Pb(Nb,Zr,Sn,Ti)O$_3$ films [9–24]. These studies demonstrated that the microstructure and dielectric/ferroelectric properties of the films are strongly dependent on a number of factors, including chemical composition, starting wet chemicals, solution preparation route, stock solution age, pyrolysis and crystallization procedure, film thickness, etc. However, one important issue that has not been fully addressed is texture control and its effects on properties [22–24]. It is known that the polar axis is along specific crystallographic orientations in these perovskite ceramics and electric fields force the polar vectors to align along the field direction during the antiferroelectric-to-ferroelectric transition. Therefore, films with different texture orientations are expected to have different responses to external fields during field-induced transition.

It has been previously shown that surface treatment of the substrate profoundly influences the structure and properties of Pb(Nb,Zr,Sn,Ti)O$_3$ films [21–24]. It is believed that the effects are due to changes in the state of stress as well as the preferred crystallographic orientation of the grains in the film. Therefore, the substrate surface treatment provides a means to control the nucleation and growth stage during film crystallization and hence to tailor the preferred orientations in the resulted films [21,25–27]. Since bulk single crystal growth in Pb(Zr,Ti)O$_3$ or Pb(Nb,Zr,Sn,Ti)O$_3$ is technologically impractical, textured thin films have the unique advantage of allowing researchers to study the orientation dependence of the ferroelectric properties.

In this paper, we report on antiferroelectric Pb(Nb,Zr,Sn,Ti)O$_3$ thin films with different texture orientations prepared through a chelating and spin-coating process and compare their ferroelectric properties.

**Experimental details**

Antiferroelectric thin films were prepared according to the chemical formula Pb$_{0.99}$Nb$_{0.02}$(Zr$_{0.84}$Sn$_{0.16}$)$_{0.982}$Ti$_{0.018}$O$_{3}$, (abbreviated as PNZST 16/1.8/2). Starting
chemicals were lead acetate trihydrate, niobium ethoxide, tin acetate and titanium isopropoxide from Alfa Aesar Co., and zirconium isopropoxide solution from Sigma-Aldrich Co. A chelating process was used to prepare the solution. First, titanium isopropoxide was added to hot acetic acid (80°C). After 10 min, niobium ethoxide was added to the mixture. Ten minutes later, zirconium isopropoxide was added. To reduce moisture sensibility, the titanium isopropoxide, niobium ethoxide, and zirconium isopropoxide mixture was then kept at 80°C for 30 min, which allowed exchanges between the alkoxy groups and the acetate group. After the exchanging reaction, excess acid was neutralized with isopropanol and the solution was heated to 120°C. Next, hydrolyzation was carried out by introducing de-ionized water. Lead acetate trihydrate and tin acetate were then added to the hydrolyzed solution at 120°C. To compensate for lead loss during high temperature crystallization, the amount of lead acetate trihydrate was adjusted to provide 15 mol% extra PbO in the solution. The temperature of the solution was maintained at 120°C until it turned clear. The solution was then diluted to 0.3 M with acetic acid and isopropanol (volume ratio 1:2) and cooled to room temperature. To adjust the viscosity of the solution, prevent cracking and increase the surface smoothness of the films, a small amount (1~5 vol.%) of ethylene glycol was added to the clear solution.

A stock solution for the PbZrO₃ seed layer was also prepared using a procedure similar to that described above for the PNZST 16/1.8/2 stock solution.

Thin films were prepared using a spin-coating procedure on 1×1 cm platinized silicon substrates. The substrates were pretreated differently in order to achieve different textures in the films to be deposited. The first substrate used was an untreated Pt/Ti/SiO₂/Si. The second was the PbZrO₃-coated platinized silicon substrate. The PbZrO₃ seed layer with a thickness around 100 nm was deposited by spin coating. The third substrate was Ti-coated platinized silicon. The thin Ti layer (~1 nm) was deposited by electron beam evaporation.

After the stock solution was aged for 24 h, it was dropped onto a spinning substrate using a syringe with a 0.2 μm filter. After receiving the droplet, the substrate continued spinning at 3000 rpm for 30 s. The coated substrate was then inserted directly into a preheated tube furnace for pyrolysis. After two minutes, the coated substrate was cooled to room temperature. This spin-pyrolysis procedure was repeated for five times to achieve the final
film thickness. After a final step, the film was annealed for one hour at temperatures of 700 °C and 750 °C.

X-ray diffraction with Cu-Kα radiation was used to examine the phase purity and texture development of the crystallized films. The diffraction spectrum was recorded at 3°/min for the 2h in the range of 20° to 60°. The morphology and thickness of the films were characterized with scanning electron microscopy on freshly fractured film/substrate cross sections. The field induced antiferroelectric-to-ferroelectric phase transition was monitored by the polarization hysteresis measurement with an RT66A standardized ferroelectric testing system. For the electrical polarization measurement, square Au pads with dimensions of 470×470μm were sputtered on the top surfaces of the films as top electrodes. The electric field was applied along the film thickness direction between the top Au-electrode and the bottom Pt-electrode.

**Results and discussion**

X-ray diffraction was used to examine texture development in films processed at different conditions (see Figs. B-1 through B-3). Within the X-ray diffraction detection limit, it is evident that all of the films deposited on different substrates under different process conditions have a single perovskite phase. For the sake of simplicity, all of the peaks in Figs. B-1 through B-3 are indexed and discussed based on the parent pseudocubic structure. For the PNZST 16/1.8/2 films deposited on the untreated substrate (Fig. B-1), pyrolysis at 650°C appeared to slightly suppress the (110) peak. Higher temperature (750°C) pyrolysis was necessary to develop thin films with random oriented grains.

In contrast, for the thin films deposited on the PbZrO3-coated substrate, high temperature pyrolysis at 750°C led to well developed (100) texture (Fig. B-2). Compared to the 750°C annealing, the 700°C annealing produced stronger (100) texture. Similarly, for the PNZST 16/1.8/2 films deposited on the Ti-coated substrate, high pyrolysis temperature (750°C) was needed to develop strong (111) texture (Fig. B-3). Pyrolysis at 650°C produced films with random oriented grains. Under the 750°C pyrolysis condition, the film annealed at 700°C showed a stronger (111) texture than those annealed at 750°C.
The results showed that phase pure PNZST 16/1.8/2 thin films with controlled texture were successfully prepared on differently treated Pt/Ti/SiO₂/Si substrates. For the Ti-coated substrate, it is believed that a thin layer of Pt₃Ti is formed during ceramic film crystallization, which favors the (111) texture in the PNZST 16/1.8/2 film [12,28]. The thermal procedure of two minutes pyrolysis at 750°C followed by one hour of annealing at 700°C seems to be the best procedure for developing films with random, (100) textured, and (111) textured grains.
(Figs. B-1a through B-3a). Therefore, further characterizations are focused on these PNZST 16/1.8/2 films prepared with this procedure.

Fig. B-2. X-ray diffraction of the PNZST 16/1.8/2 thin films deposited on platinized Si substrate with a PbZrO3 seed layer. (a) 2 min pyrolysis at 750°C and 1 h annealing at 700°C; (b) 2 min pyrolysis at 750°C and 1 h annealing at 750°C; (c) 2 min pyrolysis at 650°C and 1 h annealing at 700°C.

Scanning electron microscopy was used to examine the cross section morphology of these films (see Fig. B-4). The films were smooth and free of pores, with noticeable columnar growth features. The thickness was about 910 nm for the random oriented film, 1100 nm for the (100) textured film and 870 nm for the (111) textured film. Since the
preparation procedures were identical, the difference in thickness may be due to the different substrate surface conditions.

Fig. B-3. X-ray diffraction of the PNZST 16/1.8/2 thin films deposited on platinized Si substrate coated with a thin Ti layer. (a) 2 min pyrolysis at 750°C and 1 h annealing at 700°C; (b) 2 min pyrolysis at 750°C and 1 h annealing at 750°C; (c) 2 min pyrolysis at 650°C and 1 h annealing at 700°C.

The electric field-induced phase transition in these antiferroelectric thin films was characterized by the polarization hysteresis measurement at a series of peak voltages at an approximate frequency of 4 Hz. The electric field was applied along the thickness direction of the films. During the measurement, the peak voltage was applied in the following sequence, which is termed as a variation hereafter: 20, 25, 30, 40, 45, 50, 45, 40, 35, 30, 25,
and 20 V. The voltages from 20 to 50 V are referred to as the “ramp up” segment of the variation while those from 50 to 20 V are the “ramp down” segment.

Fig. B-4. Cross section morphology of the PNZST 16/1.8/2 films prepared with a procedure of 2 min pyrolysis at 750°C and 1 h annealing at 700°C. (a) The random oriented; (b) the (100) textured; and (c) the (111) textured.
Fig. B-5. The electric field-induced antiferroelectric-to-ferroelectric phase transition revealed by the polarization hysteresis measurement at 4 Hz in the PNZST 16/1.8/2 thin films prepared with a procedure of 2 min pyrolysis at 750°C and 1 h annealing at 700°C. (a) The random oriented; (b) the (100) textured; and (c) the (111) textured.

Fig. B-5 shows the characteristic double hysteresis loops at three selected peak voltages in the ramp up segment of the very first variation. The field-induced polarization $P_{FS}$ (the saturation value of polarization extrapolated to zero field from the double hysteresis loops) of the induced ferroelectric phase increased with applied voltage. At the peak voltage 50 V, $P_{FS}$ in the film with random oriented grains reached 33 $\mu$C/cm$^2$ (Fig. B-5a). At the peak voltage 45 V, $P_{FS}$ reached 30$\mu$C/cm$^2$ in the film with (100) texture and 34 $\mu$C/cm$^2$ in the film
with (111) texture. The critical electric field for the antiferroelectric-to-ferroelectric phase transition was measured for the three films from the hysteresis loops at the peak voltage of 40 V. The critical field was 120 kV/cm for the film with random oriented grains, 220 kV/cm for the film with (100) texture, and 150 kV/cm for the film with (111) texture. Therefore, a strong orientation dependence of the critical field for the antiferroelectric-to-ferroelectric transition was observed.

The orientation dependence of the critical field may be explained as follows. In the PNZST antiferroelectric ceramics, the Pb cation is displaced along the pseudocubic [110] direction. The field-induced phase transition starts with aligning the Pb cation to the external field direction [29]. When the field is applied along the [110] displacement direction, the alignment process resembles that in the 180° polarization reverse in normal ferroelectrics. Therefore, a film with (110) texture would display the lowest critical field and least hysteresis compared to films with other textures. The film with random oriented grains prepared in this study showed a very strong (110) X-ray diffraction peak (Fig. B-1). This peak was slightly stronger than that in a polycrystalline aggregate with completely random oriented grains. In other words, the “film with random oriented grains” in this study actually displayed, to some extent, the (110) texture. Indeed, this film showed the lowest critical field and the least hysteresis. For films with (100) and (111) textures, the applied field may be resolved into the [110] direction. Doing so would result in a higher critical field in the film with (100) texture than in that with (111) texture. And this was indeed observed experimentally. Another contribution to the high critical field in the film with (100) texture may come from the PbZrO3 seed layer which is known to have a very high critical field.

One interesting phenomenon worth noting is the abnormal reduction in the critical field for the antiferroelectric-to-ferroelectric phase transition at 45 V in the films with (100) and (111) textures during the ramp up segment of the first voltage variation (see Fig. B-5). At the same time, the field level at which the induced ferroelectric phase switches back to the antiferroelectric phase increased. In other words, the hysteresis for the electric field-induced phase switching was suppressed at this peak voltage level.

Such suppression can be better illustrated by the plot of the energy dissipation with respect to the voltage sequence, as shown in Fig. B-6. The dissipated energy in Fig. B-6 was
calculated by integrating the area of one component hysteresis loop. It is evident that the curve for the film with random oriented grains seems to be symmetrical about the maximum voltage 50 V. The loop area measured at voltages of the ramp up segment is almost the same as the area measured at the same voltages of the ramp down segment of the first variation. On the contrary, for the films with (100) and (111) textures, there was a significant drop in the dissipated energy at 45 V compared with that at 40 V during the ramp up segment. Increasing the voltage to 50 V yielded a slight increase in the dissipated energy. Interestingly, in the ramp down segment of the first variation of peak voltage, the abnormal change in the energy dissipation was no longer observed. Instead, a monotonic decrease in the dissipated energy in the ramp down segment was noticed. The abnormal reduction in energy dissipation was no longer observed in the second variation of peak voltage. The hysteresis loop at 45 V in the ramp up segment of the second variation was identical to that in the ramp down segment of the first voltage variation. It is suggested that the suppression of the hysteresis is a result of reorientation of the antiferroelectric domains in these two films.

Fig. B-6. The dissipated electrical energy calculated from the hysteresis loops in the PNZST 16/1.8/2 thin films at a series of peak voltages in the first voltage variation.
Conclusions

Phase pure PNZST 16/1.8/2 films with random oriented grains, (100) oriented grains, and (111) oriented grains were prepared using a chelating and spin-coating procedure on differently treated platinized silicon substrates. The antiferroelectric films displayed the characteristic double hysteresis loops. The electric field-induced antiferroelectric-to-ferroelectric phase transition was observed at 120 kV/cm in the film with random oriented grains, 220 kV/cm in the film with (100) texture, 150 kV/cm in the film with (111) texture. The strong orientation dependence of the critical field can be explained by the antiparallel Pb-cation displacement along the [110] direction in the antiferroelectric perovskite. In the (100) and (111) textured films, an abnormal reduction in the hysteresis for the phase switching was also observed at 45 V during the first voltage ramp up.

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References

Appendix C. *In-situ* Transmission Electron Microscopy Study of the Nanodomain Growth in a Sc-doped Lead Magnesium Niobate Ceramic


W. Qu, X. Zhao and X. Tan*

Abstract

Sc doping enhances the $B$-site 1:1 cation ordering in the Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$ ceramic. At low doping levels, the electrical polar domains remain at the nanometer scale and the relaxor ferroelectric behavior persists. The electric field-induced relaxor to normal ferroelectric phase transition process was directly observed with an *in-situ* transmission electron microscopy technique in a Sc-doped Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$ polycrystalline sample. It was found that the phase transition started at the grain boundary and took two steps to complete: the gradual coalescence of the polar nanodomains and the abrupt formation of the large wedge-shaped ferroelectric domains.

Introduction

The dielectric property of Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$, the prototype relaxor ferroelectric compound, displays a high relative permittivity, a broad dielectric peak, and a strong frequency dispersion.$^{1,2}$ The origin of the relaxor ferroelectric behavior traces back to the structure of the compound, where nanometer scale ($<5$ nm) 1:1 cation ordering exists on the $B$ site of the $ABO_3$ perovskite.$^{3-5}$ In addition to the nanoscale chemical ordering, this compound contains nanoscale polar ordering as well.$^6$ Despite extensive theoretical and experimental studies for several decades, the relation between these two types of nanoscale ordering is still unclear.$^{2,7,8}$
The polar nanoregions in Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} can grow into micrometer-sized ferroelectric domains when driven by external electric fields, which correspond to a field-induced first order phase transition.\textsuperscript{9-14} Measurements of the field induced polarization and the x-ray diffraction peak shifts under bias at low temperatures suggested that the phase transition takes place abruptly after an incubation period.\textsuperscript{11-13} It is inferred that the polar nanoregions get coarsened during the incubation period.\textsuperscript{12-13} However, the morphological evolution of the polar nanodomains during the phase transition has never been directly imaged at the nanometer scale. Furthermore, the time-delayed phase transition has only been observed in high quality pure Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} single crystals.

Transmission electron microscope (TEM) has long been used to image both polar and chemical nanodomains in relaxor ferroelectric compounds.\textsuperscript{3-5} Obviously, TEM equipped with a specimen holder with electrical bias and cooling capabilities would be ideal for studying the electric field induced relaxor to normal ferroelectric phase transition. As a proof-of-concept for such a study, we explored polycrystalline specimens of a Sc-doped Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} ceramic. Sc doping was shown to strongly enhance the cation ordering and slightly enhance the polar ordering in Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} ceramic.\textsuperscript{15-17} At low doping levels, large cation ordered domains can be obtained with the relaxor behavior retained. This facilitates the direct observation on the interaction between the chemical domains and the growing polar domains. With the \textit{in-situ} TEM technique, we visualized the electric field-induced phase transition process in a relaxor ferroelectric compound at the nanometer scale.

**Experimental details**

The Sc dopant is incorporated through solid solution of Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} with Pb(Sc\textsubscript{1/2}Nb\textsubscript{1/2})O\textsubscript{3}. The composition of the ceramic used in this study is 0.92 Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}–0.08 Pb(Sc\textsubscript{1/2}Nb\textsubscript{1/2})O\textsubscript{3} (abbreviated as PSMN8). A two step solid state reaction method was employed to prepare the ceramic. The starting materials used in this work were commercially available and high purity (better than 99.9 wt %) PbO, MgO, Nb\textsubscript{2}O\textsubscript{5}, and Sc\textsubscript{2}O\textsubscript{3} powders. After vibratory milling in isopropyl alcohol for 6 h and subsequent drying, the well-mixed stoichiometric powders of \textit{B}-site oxides were calcined at 1100 °C for 4 h. The calcined powders were then combined with PbO powder, milled for 6 h, and calcined at 900 °C for 4 h to form phase pure perovskite powder. Pressed disks, 12 mm in
diameter by 2 mm thick, were formed by cold pressing. The preformed pellets were then sintered at 1250 °C for 3 h and cooled slowly to 900 °C at the rate of 10 °C/h in controlled atmosphere.

The surface layers of the sintered pellets were removed and x-ray diffraction was used to check the phase purity and the cation ordering. The cation ordering was also examined by dark field imaging in a JEOL 2010 TEM, operating at 200 keV. The dielectric characterization was performed with an LCR meter (HP-4284A, Hewlett-Packard) in conjunction with an environmental chamber (9023, Delta Design). A cooling rate of 2 °C/min was used during this measurement.

Electric field-induced phase transition was then evaluated by the thermal depolarization measurement with a picoammeter (Model 486, Keithley) and the polarization hysteresis measurement with a standardized ferroelectric test system (RT-66A, Radiant technologies). The in-situ TEM experiment was carried out on the same JEOL 2010 TEM with a special specimen holder. The holder has two electrical leads at the tip and the specimen can be cooled by liquid nitrogen. Detailed specimen preparation procedure and electrode configuration for the in-situ study can be found in previous reports. Starting at room temperature, an electrical voltage of 200 V, corresponding to a field of 10 kV/cm, was applied and maintained. The specimen was then cooled at a rate of 2 °C/min. Bright/dark field images as well as selected area electron diffraction patterns were recorded by a charge-coupled device (CCD) camera at certain temperatures.

Results and discussion

X-ray diffraction showed an evident superlattice peak which indicates a strong 1:1 B-site cation ordering. The ordering parameter $\alpha$ for the ceramic, evaluated according to the common procedure used in literature, is 0.9. The x-ray diffraction also indicated a pseudocubic structure with a lattice parameter of 4.0608 Å. Compared with the lattice parameter of 4.0509 Å for the undoped Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$, Sc doping increased the unit cell size due to the larger Sc$^{3+}$ ion radius. The strong 1:1 cation ordering in the ceramic is further confirmed by TEM analysis. Chemical domains with average size on the order of 100 nm were clearly seen.
The dielectric properties of the ceramic are shown in Fig. C-1. The permittivity exhibits characteristics of a relaxor ferroelectric, namely, a broad peak and a strong frequency dispersion. At 1 kHz, the maximum relative permittivity $\varepsilon_{\text{max}}$ was measured as $21,441$ at the $T_{\text{max}}$ of $-5$ °C. The thermal depolarization measurement was carried out on a sample during zero-field heating after it had been cooled under a field of $10$ kV/cm. The $T_{\text{d0}}$ was measured to be $-38$ °C. Compared with the $T_{\text{max}}$ of $-10$ °C and the $T_{\text{d0}}$ of $-60$ °C in pure Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$, Sc doping shifts both $T_{\text{max}}$ and $T_{\text{d0}}$ to higher temperatures, indicative of an enhanced ferroelectric polar order. In accordance with this, the $\varepsilon_{\text{max}}$ decreases slightly compared to that of the undoped Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ ceramic ($22,870$ at $1$ kHz).

The electric field-induced relaxor to normal ferroelectric phase transition in the ceramic was characterized by the polarization hysteresis measurement on a bulk circular plate sample with diameter of $10$ mm and thickness of $0.2$ mm, with the field applied along the thickness direction. As expected, at room temperature, the PSMN8 ceramic showed a nonlinear $P$–$E$ relation with no hysteresis, as shown in Fig. C-2. However, a well-defined square hysteresis loop was observed at $-50$ °C, with coercive field $E_c$ of $5.2$ kV/cm and remanent polarization $P_r$ of $26$ $\mu$C/cm$^2$. Further decreasing in temperature leads to the increase in both $E_c$ and $P_r$. The appearance of the square hysteresis loops at low temperatures indicates the presence of a normal ferroelectric phase in PSMN8.
In order to determine the field level needed for the in-situ TEM study and assess the sample geometry effect on the field-induced phase transition, a TEM specimenlike sample (a 100 μm thick disk with diameter of 3 mm) was tested for the hysteresis measurement too. In this configuration, two half-circle shaped electrodes were deposited on a flat surface of the disk with a gap of 200 μm.\textsuperscript{18-20} Therefore, in-plane electric fields were applied and the result is also plotted in Fig. C-2. Compared to the conventional circular plate sample with electric field applied along the thickness direction, the TEM specimenlike disk shows a higher $E_c$ (8.2 kV/cm) and a lower remanent polarization. Furthermore, the hysteresis loop is no longer symmetrical.

![Fig. C-2 Electric field-induced polarization measurement at 4 Hz of a bulk circular plate sample and an unperforated TEM specimen.](image)

The electric field-induced phase transition was then directly visualized inside a TEM on a specimen during a cooling process under 10 kV/cm static electric field, as shown in Fig. C-3. One grain with its $<110>$ direction close to the electron beam was focused. Strong cation ordering was observed with dark field imaging in this grain. At room temperature, very faint contrast of polar nanoregions, associated with bending contours, is noticed [Fig. C-3(a)]. The inset in Fig. C-3(a) shows the $<110>$ zone-axis electron diffraction pattern. The in-
plane directions <001> and <110> are indicated by bright arrows in this micrograph. A grain boundary is also noted by the bright dashed line at the top.

Fig. C-3 The morphological evolution of the polar nanodomains during field cooling under 10 kV/cm revealed by the *in-situ* TEM technique. The applied field direction is shown by the arrow in (b). (a) The initial polar nanoregions at room temperature. The inset shows the <110> zone-axis selected area electron diffraction (SAED) pattern. (b) −50 °C, (c) −55 °C, (d) −70 °C, (e) −90 °C, and (f) −90 °C after 30 min

Then the polycrystalline specimen was subjected to a field-cooling process, with the direction indicated by the bright arrow in Fig. C-3(b). The field direction happened to be very close to the <001> direction. No detectable morphological changes of the polar nanoregions were observed at room temperature under the static field. However, when the temperature reached −50 °C, evident changes were noticed in the area close to the grain boundary, as shown in Fig. C-3(b). It is clear that clustering of the polar nanoregions occurred. The coalescence of the polar nanodomains continued during the further cooling to −55 °C [Fig. C-3(c)]. Up to this temperature, the morphology of the nanodomains remained irregular shaped without well-defined domain walls. When the temperature reached −70 °C, a dramatic change in the domain morphology was observed [Fig. C-3(d)]. Large wedge-shaped
ferroelectric domains (>200 nm) with straight domain walls appeared in the close vicinity of the grain boundary. The domain walls are close to the \{110\} plane. Further cooling to \(-90^\circ\)C led to the growth of existing large domains and the emergence of additional large domains [Fig. C-3(e)]. At this temperature \((-90^\circ\)C), the specimen was held for 30 min under the applied bias. Further growth of the large domains was seen [Fig. C-3(f)].

The results shown in Fig. C-3 indicate that there are two stages for the evolution of the polar nanodomains under electric field, the gradual coalescence of nanodomains and the abrupt formation of wedge-shaped large domains. This observation is very similar to the transition process depicted by x-ray diffraction and polarization measurement in <111>-oriented Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) single crystals.\(^{12,13}\) It should be noted that the current observation was made with one individual grain in a polycrystalline ceramic. It implies that the field-induced phase transition behavior of individual grains in a polycrystalline aggregate resembles that of single crystals. However, the macroscopic polarization measurement in polycrystalline ceramics was not able to reveal the two-stage process.

Figure C-3 also shows that the coalescence of polar nanodomains and the formation of wedge-shaped large domains take place in the vicinity of a grain boundary. The result is consistent with the random field model for relaxor ferroelectrics, where the polar ordering is controlled by the quenched random electric fields originating from charged point defects.\(^{21}\) At grain boundaries, higher concentration of point defects is expected. Therefore, grain boundaries are preferred sites for the initiation of the field-induced phase transition.

The electric field-induced normal-ferroelectric phase presumably possesses a rhombohedral structure with spontaneous polarization along the <111>.\(^{10}\) Under current experimental conditions, the electric field is applied along a direction close to the <001>. Therefore, domains with polarization vectors [111], [\(1\bar{1}\)1], [\(\bar{1}\)11], and [\(\bar{1}\bar{1}\)1] should be almost equally favored and multiple domains are expected. This is indeed the case as confirmed in Fig. C-3. The observed \{110\} domain walls are therefore electrically charged. It should be pointed out here that there is an alternative interpretation of these domain walls. Close examination of Figs. C-3(e) and C-3(f) shows that the multiple domains may merge to a
single domain as they grow. Therefore, these domain walls could possibly be the rhombohedral/pseudocubic phase boundary.

**Conclusion**

To summarize, strong 1:1 \( B \)-site cation ordering is present in the \( 0.92\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 – 0.08\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3 \) solid solution. This chemically ordered ceramic retains the characteristics of the relaxor behavior but with an enhanced ferroelectric polar order. At lower temperatures, a relaxor to normal ferroelectric phase transition can be triggered by external electric fields. Direct observation with an in-situ TEM technique reveals that the phase transition process is initiated at the grain boundary. The polar nanoregions gradually coalesce and then abruptly transform into wedge-shaped large ferroelectric domains. The large domains merge into a single domain as they grow.

**Acknowledgement**

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**References**

Appendix D. Room Temperature Magnetoelectric Multiferroism

Through Cation Ordering in Complex Perovskite Solid Solutions


W. Qu1, X. Tan1*, R. W. McCallum1,2, D. P. Cann3 and E. Ustundag1

Abstract

A strategy for developing ferrimagnetism through B-site cation ordering in thermodynamically stable ferroelectric complex perovskites is described, with the aim of realizing both a spontaneous polarization and magnetization at room temperature. Specifically, solid solutions of the complex perovskites Pb(Fe2/3W1/3)O3, Sr(Fe2/3W1/3)O3, and Ba(Fe2/3W1/3)O3 with BiFeO3 are considered. Preliminary data on the 0.75 Pb(Fe2/3W1/3)O3–0.25 BiFeO3 ceramic show promising results.

Introduction

Magnetoelectric multiferroic materials are multifunctional materials with simultaneous ferroelectric and magnetic properties [1–3]. Combining ferroelectricity and magnetism in a single-phase compound would obviously be of tremendous interest not only for practical applications but also for fundamental physics [1–8]. The intrinsic ability to couple the electrical polarization to the magnetization allows an additional degree of freedom in the design of conventional devices. A range of new applications is envisaged that takes advantage of this unique material characteristic. This great potential has launched an intensive worldwide research effort into new multiferroic materials and devices [1–8].

1. Department of Materials Science & Engineering, Iowa State University, Ames, IA 50011, USA
2. Materials and Engineering Physics Program, Ames Laboratory, Ames, IA 50011, USA
3. Department of Mechanical Engineering, Oregon State University, Corvallis, OR 97331, USA

* Author to whom correspondence should be directed
Experimental confirmation of magnetoelectric multiferroism in single-phase compounds was accomplished in the early 1960s [9, 10]. However, limited progress has been made during the last several decades for the following reasons. First, coupling in existing single-phase compounds was too weak to be of practical use. Secondly, there were very few compounds displaying the magnetoelectric coupling. Furthermore, the Curie or Neél temperature of most of the compounds was far below room temperature. Therefore, an alternative approach of combining magnetostrictive and piezoelectric compounds to form composites has been attempted [11]. In this situation, magnetoelectric coupling is realized through an extrinsic strain. The first artificial magnetoelectric composite was synthesized by unidirectional solidification of the eutectic composite of ferroelectric BaTiO₃ and magnetic CoFe₂O₄ compounds [12]. Recently, research on magnetoelectric composites has been focused on laminated structures, such as the lead zirconate titanate (PZT)/Terfenol-D laminates, in which giant magnetoelectric coupling was observed at room temperature [13–15].

However, the significant technological achievement in the laminated composites offers no insight into the intriguing intrinsic magnetoelectric coupling in single-phase compounds. Most importantly, there are technical concerns about the magnetoelectric composite approach. First of all, the giant magnetoelectric coupling effect can only be observed within a narrow frequency range centered at the natural resonance frequency of the structure [3, 13–15]. In addition, the magnetostrictive components used in these composites are electrically semiconductive or even conductive. This creates difficulties in retaining the electrical polarization developed in the ferroelectric phase and the composite structure would be too lossy when driven by ac electric fields. As a result, these composites have only been tested under ac magnetic fields [13–15].

Therefore, there remains a critical need to find new single-phase materials with strong magnetoelectric coupling at room temperature for practical applications. Recently, first principles calculations have shown that it is more realistic to have ferrimagnetism, instead of ferromagnetism, through B-site cation ordering in the multiferroic perovskite compounds [16]. In fact, the necessity of having cation ordering for the development of spontaneous magnetization, but at a temperature much lower than room temperature, has been
experimentally demonstrated by Smolenskii et al [9]. A noticeable spontaneous magnetization at temperatures below 170 K in the solid solution of 0.7Pb(Fe2/3W1/3)O3-0.3Pb(Mg1/2W1/2)O3 was detected. The Mg2+ and W6+ cations in the complex perovskite Pb(Mg1/2W1/2)O3 are fully ordered. The magnetically active Fe3+ ions in the solid solution of (1-x)Pb(Fe2/3W1/3)O3-xPb(Mg1/2W1/2)O3 are distributed in both B-site sublattices as

\[
Pb[Fe_{(1-x)2}Mg_{x2}][Fe_{(1-x)6}W_{(2+x)6}]O3.
\]

The compounds display a G-type antiferromagnetic super-exchange structure. Since the two sublattices contain a different number of Fe3+ cations, the compound as a whole exhibits a net magnetic moment.

In this paper, we examine three complex perovskite compounds with different degrees of B-site cation ordering. With the aim of realizing room temperature coupling, their solid solutions with BiFeO3 are proposed. We have demonstrated the solid solution approach in the Pb(Fe2/3W1/3)O3-BiFeO3 system.

**Cation, dipole and spin order**

The strategy of introducing magnetic behaviour into ferroelectric compounds is to incorporate magnetically active species, such as Cr3+, Mn3+, Fe3+, Co2+, Ni2+, and rare earth ions into the lattice [1–10]. Of particular importance are the compounds with the perovskite ABO3 crystal structure, such as Pb(Fe2/3W1/3)O3 [17–21], Sr(Fe2/3W1/3)O3 [22, 23], and BiFeO3 [24–31] and the Ba(Fe2/3W1/3)O3 compound with the hexagonal perovskite structure [32, 33]. Their magnetic and ferroelectric properties are summarized in table D-1. Obviously they display high transition temperatures for both ferroelectric and magnetic behaviour.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Pb(Fe2/3W1/3)O3</th>
<th>Sr(Fe2/3W1/3)O3</th>
<th>BiFeO3</th>
<th>Ba(Fe2/3W1/3)O3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td>Cubic</td>
<td>Tetragonal</td>
<td>Rhombohedral</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>Magnetic behavior</td>
<td>AFM</td>
<td>FIM</td>
<td>AFM</td>
<td>FIM</td>
</tr>
<tr>
<td>(T_N = 370K)</td>
<td>(T_C = 370K)</td>
<td>(T_N = 650K)</td>
<td>(T_C = 210K)</td>
<td></td>
</tr>
<tr>
<td>Ferroelectric behavior</td>
<td>RFE</td>
<td>AFE</td>
<td>FE</td>
<td>AFE</td>
</tr>
<tr>
<td>(T_C = 170K)</td>
<td>(T_C = 470K)</td>
<td>(T_C = 1120K)</td>
<td>(T_C = 570K)</td>
<td></td>
</tr>
<tr>
<td>B-site order</td>
<td>Nanoscale order</td>
<td>Partially order</td>
<td>N/A</td>
<td>Complete order</td>
</tr>
</tbody>
</table>

(Note: AFM-antiferromagnetic; FIM-ferrimagnetic; RFE-relaxor ferroelectric; AFE-antiferroelectric; FE-ferroelectric; \(T_C\)-Curie temperature; \(T_N\)-Neél temperature.)
It should also be noted that Pb(Fe\textsubscript{2/3}W\textsubscript{1/3})O\textsubscript{3} displays a nanoscale 1:1 B-site cation order similar to that observed in the well characterized system Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} [34]. Sr(Fe\textsubscript{2/3}W\textsubscript{1/3})O\textsubscript{3} displays partial 1:1 cation ordering on a length-scale greater than that of Pb(Fe\textsubscript{2/3}W\textsubscript{1/3})O\textsubscript{3}. Ba(Fe\textsubscript{2/3}W\textsubscript{1/3})O\textsubscript{3} exhibits a significant degree of long-range ordering in which the face-sharing oxygen octahedra are occupied by both Fe\textsuperscript{3+} and W\textsuperscript{6+} and the corner-sharing ones are exclusively occupied by Fe\textsuperscript{3+}, resulting in hexagonal symmetry [33]. As a result, Pb(Fe\textsubscript{2/3}W\textsubscript{1/3})O\textsubscript{3} shows antiferromagnetic behaviour while the partially ordered Sr(Fe\textsubscript{2/3}W\textsubscript{1/3})O\textsubscript{3} and completely ordered Ba(Fe\textsubscript{2/3}W\textsubscript{1/3})O\textsubscript{3} display ferrimagnetic behaviour with a spontaneous magnetization.

As expected, BiFeO\textsubscript{3} has the highest magnetic critical temperature because it is the most concentrated compound with the magnetically active Fe\textsuperscript{3+} species. Dilution of the magnetic species by one-third in the compounds leads to a decrease of 280 K in the critical temperature, as is evident in both Pb(Fe\textsubscript{2/3}W\textsubscript{1/3})O\textsubscript{3} and Sr(Fe\textsubscript{2/3}W\textsubscript{1/3})O\textsubscript{3}. The decrease in Ba(Fe\textsubscript{2/3}W\textsubscript{1/3})O\textsubscript{3} is even more dramatic since it has a different crystal structure from the other three compounds [33].

The ferroelectric behaviour in these four compounds is also distinct from each other. Pb(Fe\textsubscript{2/3}W\textsubscript{1/3})O\textsubscript{3} is a relaxor ferroelectric with a strong frequency dispersion in its dielectric response [17]. Both Sr(Fe\textsubscript{2/3}W\textsubscript{1/3})O\textsubscript{3} and Ba(Fe\textsubscript{2/3}W\textsubscript{1/3})O\textsubscript{3} are antiferroelectric and only BiFeO\textsubscript{3} is a normal ferroelectric. Due to its high critical temperature, BiFeO\textsubscript{3} has received extensive attention in recent years [24–31]. Unfortunately it is an antiferromagnetic compound with a negligible spontaneous magnetization at room temperature. In addition, the ferroelectric Curie temperature is too high and the spontaneous electric polarization is very hard to switch at room temperature. Furthermore, the electronic conductivity is relatively high even in the phase pure BiFeO\textsubscript{3} compound, making it very difficult to sustain the high electric fields necessary for polarization switching [31].

Therefore, the most plausible approach to realize room temperature coupling of a high remanent electric polarization and spontaneous magnetization is to form solid solutions of Pb(Fe\textsubscript{2/3}W\textsubscript{1/3})O\textsubscript{3}, Sr(Fe\textsubscript{2/3}W\textsubscript{1/3})O\textsubscript{3}, and Sr(Fe\textsubscript{2/3}W\textsubscript{1/3})O\textsubscript{3} with BiFeO\textsubscript{3}. It should be noted that solid solutions in these systems have not been reported before in the literature. In many applications utilizing ferroelectrics, the solid solution approach has been widely used for
many decades to adjust the Curie temperature, enhance the normal ferroelectric behaviour, and manipulate the B-site cation order [34, 35]. In the compound Pb(Fe_{2/3}W_{1/3})O_3, a solid solution with Li(Fe_{1/3}W_{2/3})O_3 strengthens the B-site ordering dramatically [19]. In addition, Fe-rich stoichiometries in the Pb(Fe_{2/3}W_{1/3})O_3 system have been found to favour B-site cation ordering [20]. By incorporating BiFeO_3 into Pb(Fe_{2/3}W_{1/3})O_3 the overall composition becomes Fe-rich. Based on the previous results, an enhancement in cation ordering would be expected in the solid solution Pb(Fe_{2/3}W_{1/3})O_3-BiFeO_3. Also, B-site cation ordering can be engineered in the solid solution of Ba(Fe_{2/3}W_{1/3})O_3 with BiFeO_3. Since Ba(Fe_{2/3}W_{1/3})O_3 displays complete B-site ordering and a distorted perovskite (hexagonal) crystal structure, solid solutions of (1-x) Ba(Fe_{2/3}W_{1/3})O_3-xBiFeO_3 should have a morphotropic phase boundary (MPB) and a composition-dependent degree of B-site cation ordering.

**Experimental procedure**

The solid solution approach described above was demonstrated experimentally with a ceramic of composition 0.75Pb(Fe_{2/3}W_{1/3})O_3-0.25BiFeO_3. Starting with high purity (>99.9 wt%) PbO, Bi_2O_3, Fe_2O_3, and WO_6 powders, a two-step method was utilized to synthesize phase pure ceramics [36]. Stoichiometric amounts of Fe_2O_3 and WO_6 powders were first mixed and milled with zirconia media in a plastic bottle for six hours. After drying in an oven at 150°C for 24 h, the mixture was calcined at 1000°C for 4 h. The A-site oxides PbO and Bi_2O_3 were then mixed with the calcined B-site compound and the mixture was milled again for 6 h. After drying, the mixture was calcined at 890°C for 2 h. Finally, pellets were cold-pressed and sintered at 910°C for 2 h.

The surface layers of the sintered discs were removed by mechanical grinding and X-ray diffraction was used to verify the phase purity. Fresh fracture surfaces were examined with a scanning electron microscope (SEM) to reveal the grain morphology. The ferroelectric domain structure as well as cation ordering was examined with a Phillips CM30 transmission electron microscope (TEM) operated at 300 keV. Dielectric characterization was performed with an LCR meter (HP-4284A, Hewlett-Packard) in conjunction with an environmental chamber (9023, Delta Design). A heating rate of 3°C min^{-1} was used during measurement. The polarization hysteresis measurement was carried out with a standardized ferroelectric test system (RT-66A, Radiant Technologies). A Quantum Design PPMS 9T equipped with
the vibrating sample magnetometer VSM option with furnace was used for magnetic characterization.

**Results and discussion**

![X-ray diffraction pattern](image)

**Fig. D-1** X-ray diffraction pattern of the sintered 0.75Pb(Fe<sub>2/3</sub>W<sub>1/3</sub>)O<sub>3</sub>-0.25BiFeO<sub>3</sub> ceramic.

The as-sintered ceramic is phase pure and possesses a pseudocubic perovskite structure with the lattice parameter of 4.0011 Å, as evidenced by the x-ray diffraction spectrum shown in Fig. D-1. SEM examination indicates that the ceramic is dense, with grain size around 5 μm (see Fig. D-2).

![Scanning electron microscope image](image)

**Fig. D-2** Scanning electron microscope image of the 0.75Pb(Fe<sub>2/3</sub>W<sub>1/3</sub>)O<sub>3</sub>-0.25BiFeO<sub>3</sub> ceramic.
TEM analysis reveals that the primary microstructure feature is mottled polar domains, typical of relaxor ferroelectric oxides (Fig. D-3). The inset in Fig. D-3 shows the \(<110>\) zone axis selected area electron diffraction pattern. Very faint and diffused contrast is noticed at \{1/2, 1/2, 1/2\}-type superlattice spot positions. Two examples are pointed out by the dark arrows. These \{1/2, 1/2, 1/2\}-type superlattice spots were too weak to allow dark field imaging. In complex perovskite compounds, such superlattice spots are indicative of 1:1 B-site cation ordering or oxygen octahedra tilting [34, 35, 37, 38]. However, from the x-ray diffraction pattern shown in Fig. D-1, the ceramic has a cubic structure with one ABO_{3} formula unit in the unit cell with a lattice parameter around 4 Å. It is not likely that oxygen octahedra are tilted in the structure. Therefore, the B-site cations are ordered in the as-prepared 0.75Pb(Fe_{2/3}W_{1/3})O_{3}-0.25BiFeO_{3} ceramic, but to a very limited extent. Further optimization of processing conditions and/or chemical compositions is needed to enhance such cation order. The inset shows the \(<1\overline{1}0>\) zone axis selected area electron diffraction pattern. Diffuse contrast at \{1/2, 1/2, 1/2\}-type superlattice positions is indicative of weak B-site cation ordering.

The dielectric response of this phase pure pellet was also examined and the result is shown in Fig. D-4. It is interesting to note that a broad peak appears around 320 K. The maximum relative permittivity is measured to be 1550 at 10 kHz. Strong frequency dispersion is noticed both below and above the dielectric peak temperature, different from
that of typical relaxor ferroelectric ceramics. The dielectric loss (tanδ) measurement indicates a value of less than 0.1 within 220-475 K under both 10 and 100 kHz. At room temperature (300 K), tanδ was measured to be 0.014 under 10 kHz and 0.021 under 100 kHz. Therefore, incorporating BiFeO₃ into Pb(Fe₂/₃W₁/₃)O₃ raised the ferroelectric transition temperature to above room temperature. However, the frequency dispersion behaviour does not resemble that of a typical relaxor ferroelectric.

Fig. D-4 Relative permittivity and dielectric loss of the 0.75Pb(Fe₂/₃W₁/₃)O₃-0.25BiFeO₃ ceramic as a function of temperature at 10 and 100 kHz.

The low dielectric loss measured from the ceramic pellet implies a high electrical resistivity that could sustain high electric fields for polarization switching. The electric polarization versus electric field hysteresis loop was evaluated at 4 Hz at room temperature. As shown in Fig. D-5, an unsaturated loop was recorded. An electric polarization of 6.6μC·cm⁻² was measured at the peak electric field 33 kV·cm⁻¹. Therefore, the 0.75Pb(Fe₂/₃W₁/₃)O₃-0.25BiFeO₃ composition demonstrated that the solid solution approach is effective in adjusting the ferroelectric transition temperature and developing spontaneous polarizations.

The magnetization as a function of temperature for the as-prepared ceramic is given in Fig. D-6. There is a clear transition from paramagnetic to ferrimagnetic at ~660 K. Heating the sample above 800 K in the measurement vacuum results in the introduction of a significant amount of a second magnetic phase with an ordering temperature of about 850 K.
As a result, it is not possible to analyze the behavior of the magnetization above $T_c$ in terms of a Curie-Weiss law.

Fig. D-5 Polarization versus electric field hysteresis loop measured at 4 Hz at room temperature in the 0.75Pb(Fe$_{2/3}$W$_{1/3}$)O$_3$-0.25BiFeO$_3$ ceramic.

![Polarization versus electric field hysteresis loop](image)

Fig. D-6. Magnetization versus temperature during cooling from 800 K to room temperature under 1 kOe in the 0.75Pb(Fe$_{2/3}$W$_{1/3}$)O$_3$-0.25BiFeO$_3$ ceramic.

![Magnetization versus temperature](image)

The room temperature magnetic hysteresis loop of the as-prepared ceramic is shown in Fig. D-7. The magnetization at 5 T is 0.958 emu·g$^{-1}$, which corresponds to 0.0589 $\mu_B$ per formula unit or 0.0785 $\mu_B$ per Fe. The remnant magnetization of the randomly oriented
The ceramic sample is 0.276 emu·g⁻¹ (0.017 μB per formula unit) at room temperature, comparable to those of other perovskite multiferroic compounds [3]. The material exhibits a room temperature coercive field of 1.35 kOe. Again, the solid solution approach proves to be capable of adjusting the magnetization transition temperature and developing spontaneous magnetization. A much higher spontaneous magnetization is expected if the cation ordering is further enhanced in the oxide ceramic.

Figure 7. Magnetization versus magnetic field hysteresis loop measured at room temperature in the 0.75Pb(Fe₂/₃W¹/₃)O₃–0.25BiFeO₃ ceramic.

Conclusions

Solid solutions of Pb(Fe₂/₃W¹/₃)O₃, Sr(Fe₂/₃W¹/₃)O₃, and Ba(Fe₂/₃W¹/₃)O₃ with BiFeO₃ are proposed as suitable candidates to achieve room temperature magnetoelectric multiferroism. By manipulating the B-site cation order in these complex perovskite-based ceramics, large spontaneous electric polarization and magnetic moments can be achieved at room temperature. The net magnetization is realized through uncompensated antiferromagnetic moments due to cation ordering. This approach is demonstrated in the 0.75Pb(Fe₂/₃W¹/₃)O₃–0.25BiFeO₃ ceramic, where weak cation ordering is present. The ceramic undergoes a ferroelectric transition at ~320 K and a magnetic transition at ~660 K, with a spontaneous magnetization of 0.017 μB per formula unit at room temperature.
Acknowledgments

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