Development of long range cation order and its impact on dielectric properties in Pb(Mg1/3Nb2/3)O3 based relaxor ferroelectrics

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Development of long range cation order and its impact on dielectric properties in Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} based relaxor ferroelectrics

by

Xiaohui Zhao

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

DOCTOR OF PHILOSOPHY

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2008

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Dedicated to my parents, my old brother
& dearest wife
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Abstract

As the prototype of relaxor ferroelectrics, Pb(Mg_{1/3}Nb_{2/3})O_3 (PMN) has been extensively investigated for several decades. There are two types of microscopic features in PMN: cation order and electric dipole order. The development of long range cation order in PMN has proved to be challenging and the relationship between these two types of order is still open for debate. In this work, different kinds of cations and/or defects were introduced into Pb(Mg_{1/3}Nb_{2/3})O_3 to develop long range cation order. The impact of the enhanced cation order on the dielectric properties of Pb(Mg_{1/3}Nb_{2/3})O_3-based ceramics was systematically investigated. Ceramic samples were prepared via the columbite method to ensure phase purity. High temperature thermal treatments were used to manipulate the degree of cation order of the material. Dielectric and ferroelectric properties, including relative permittivity, thermal depolarization current and polarization vs. electric field hysteresis, were measured. It was shown that the cation order in these relaxor ceramics was significantly enhanced. However, different dielectric and ferroelectric properties were observed in these perovskite materials. The difference was interpreted in terms of size/charge mismatch of two B-site sublattices and size/charge difference between them. The electric field--temperature phase diagrams of PMN-based ceramics and PMN single crystals were also constructed based on electric field-induced phase transitions.
1. Introduction

The main focus of the research work presented in this dissertation is long range cation order development and its impact on electric dipole order in Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-based relaxor ferroelectrics. In this chapter, concepts and definitions for the relaxor ferroelectrics and perovskite structures will be explained followed by the introduction of cation order, electric dipole order and correlation between them in Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$. The proposed research and the organization of this dissertation will also be addressed.

1.1 Ferroelectrics

A ferroelectric material is a material that has, over a certain temperature range, a spontaneous polarization that can be reversed or reoriented by application of a sufficiently large external electric field. The displacement of cations and anions gives rise to dipole moments within each unit cell, and the resulting polarization can be measured via the material’s surface charge density. Generally a ferroelectric has one or more polar axes along which a spontaneous polarization can be developed below the material’s Curie temperature.

One distinctive characteristic of ferroelectric materials is the hysteretic behavior in the polarization vs. electric field curve. Applying a variable electric field to a ferroelectric will result in a hysteresis loop similar in a ferromagnetic metal, as seen in Figure 1.1.

![Figure 1.1 Typical hysteretic behavior of ferroelectrics. (BaTiO$_3$ at room temperature)](image1.png)
At high fields, a saturation value of polarization is reached. As the electric field returns to zero the system is left with a remnant polarization which can be flipped by applying a large enough electric field in the opposite direction. In contrast, a linear dielectric has no spontaneous polarization and its P-E curve is simply a straight line with its slope equal to the electric susceptibility. Above the Curie temperature a ferroelectric material turns to be paraelectric with higher symmetry and behaves like a linear dielectric. Some ferroelectric materials have additional ferroelectric-ferroelectric transitions (usually to lower symmetry) below the Curie temperature. For example, below its Curie temperature (approximately 130°C), BaTiO$_3$ undergoes the tetragonal $\rightarrow$ orthorhombic and orthorhombic $\rightarrow$ rhombohedral phase transition at 0°C and -80°C respectively.$^2$

Ferroelectric materials are a subgroup of piezoelectric materials. From the crystal structure point of view, 20 out of the 32 point groups are non-centrosymmetric and they exhibit the piezoelectric effect. The direct effect is defined as the appearance of the electric potential across certain faces of a crystal in response to applied mechanical stress. The converse effect refers to the production of stress and/or strain when an electric field is applied. Ten of the non-centrosymmetric groups are polar, having a dipole in their unit cell, and exhibit pyroelectricity, and spontaneous polarization will be developed in these polar crystals when cooled. If the spontaneous polarization can be reversed by the application of an electric field, the material is said to be ferroelectric.

The ability of ferroelectric materials to change their atomic structures under the influence of electric fields gives rise to extremely high values of dielectric permittivity, and hence dielectric constant. For example, lead magnesium niobate Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$, generally abbreviated as PMN, has a dielectric constant over 20,000 around room temperature. It is no wonder ferroelectric materials have been widely used in thin layer capacitors for charge storage, bypass and coupling functions.$^{3,4}$ The piezoelectric effect is another useful property of ferroelectrics. They have been largely used in making generators, actuators and
transducers. Lead zirconate titanate, Pb(Zr\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{3} or PZT, has dominated this field of application in the last five decades.\textsuperscript{5,6,7} The ability of ferroelectrics to display positive and negative permanent polarizations in the absence of electric fields has been utilized in the development of non-volatile ferroelectric memories (FeRAM).\textsuperscript{8}

1.2 Perovskite Structure

![Figure 1.2 the perovskite structure: ABO\textsubscript{3}](image)

The most commonly studied ferroelectrics have the cubic perovskite structure (in the paraelectric state) with a general chemical formula ABO\textsubscript{3}. As shown in Figure 1.2, A-site cations occupy the corners of the cube, while B-site cations sit in the center of the oxygen octahedra. Oxygen occupies the face centers of the cube. The lattice constant of the perovskite primary unit cell is always close to 4 Å due to the rigidity of the oxygen octahedra network and the well defined oxygen ionic radius of 1.40 Å.\textsuperscript{9} The tolerance factor (t) is used to determine the stability of the perovskite structure where:

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

(1-1)

And \( R_A \): ionic radii of A-site cation
RB: ionic radii of B-site cation
RO: ionic radii of oxygen anion

At the range $0.78 \leq t \leq 1.05$, the perovskite structure can be preserved.

All materials concerned in our study have the perovskite structure with slight distortions. A practical advantage of the perovskite structure is that due to the wide range of the tolerance factor, many different cations can be substituted on both A and B sites without drastically changing the overall structure. Complete solid solutions are easily formed between many cations, often across the entire range of composition. As a result, it is possible to manipulate a material’s properties, such as Curie temperature or dielectric constant, and microstructures through controlled substitution of a given cation.

1.3 Normal Ferroelectrics VS. Relaxor Ferroelectrics

Normal ferroelectrics are characterized by a sharp phase transition from the high temperature paraelectric to the low temperature ferroelectric state as seen in the dielectric constant as a function of temperature (Figure 1.3).

![Figure 1.3 Dielectric constant of barium titanate (BaTiO₃) vs. temperature.](image-url)
As for BaTiO$_3$, the ferroelectric transition occurs at 130°C (from high temperature cubic phase to low temperature tetragonal phase), which roughly corresponds to the peak in dielectric constant. Below the Curie temperature, $T_C$, the cubic structure changes to lower symmetry and there is a sharp decrease in the dielectric constant. Above the Curie temperature, the dielectric constant follows the Curie-Weiss law:

$$\varepsilon_r = \frac{A}{T - T_C}$$  \hspace{1cm} (1-2)

Where $T$ is the temperature, $A$ is a constant.

In contrast, relaxor ferroelectrics have broad dielectric constant peaks and often contain more than one cation species on the A or B-site. Lead magnesium niobate, Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$, is the prototypical relaxor ferroelectric and has been extensively studied for several decades. In the perovskite unit cell, Pb occupies the corner A-site while Mg and Nb share the B-site. A very large dielectric constant with a broad maximum and a significant frequency dispersion are the characteristics of relaxors (Figure 1.4).

![Figure 1.4](image-url)  
**Figure 1.4** Dielectric constant (left) and dielectric loss (right) of the relaxor Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ as a function of temperature.
The maximum of the dielectric constant \( \varepsilon_m \) decreases while the temperature at that maximum \( T_m \) increases with increasing measuring frequencies.

In normal ferroelectrics, the sharp transition in dielectric constant also indicates a structural phase transition as the symmetry of the crystal changes. However, for relaxors, the broad peak in dielectric constant does not correspond to a structural change. Therefore, the temperature at the maximum dielectric constant is denoted as \( T_m \) instead of \( T_C \). In the case of PMN, there are polar nanoregions that exist well above \( T_m \). However, no transition to a normal ferroelectric state can occur even down to 4 K without assistance of external electric fields. The polar nanodomains (less than 5nm in size) are slightly distorted with a local rhombohedral symmetry, but the overall long range structure remains cubic.

PMN is not only an ideal compound for fundamental scientific research due to its typical relaxor ferroelectric behavior, but also a good candidate material for advanced technologies. Both the high dielectric constant and electrostrictive coefficients have been exploited. Currently, applications of PMN are wide-ranging. The high dielectric constants are utilized in miniaturized multi-layer ceramic capacitors.\textsuperscript{12} Relaxors are especially useful in this regard not only because of their very high dielectric constants, but also because those high values occur near room temperature. Furthermore, the broad peak indicates that the high dielectric constant is attainable within a wide temperature range. In contrast, a normal ferroelectric typically has its maximum dielectric constant well above room temperature, and the sharp temperature dependence makes it unsuitable for applications. The superior electrostrictive properties over classical piezoelectric materials allow for very precise positioning control. Thus, they are employed in applications such as micropositioners, actuators, motors, biomedical instruments and surface deformable mirrors.\textsuperscript{14,15} PMN also has good electro-optic properties, so its index of refraction can be changed by applying a field. Optical shutters and switches take advantage of this effect.\textsuperscript{14}
1.4 Physical models for PMN

PMN and its characteristic behavior were discovered several decades ago. Smolenskii and Isupov first interpreted it as an indication of a “diffuse ferroelectric phase transition”.⁷ Due to the randomness that exists on the B-site in PMN, each unit cell is subjected to a different net field. This leads to a range of Curie temperatures, resulting in an overall broadened ferroelectric transition. The temperature $T_m$ would only indicate the mean Curie temperature. This simple model has been widely cited ever since, however, the physics of the relaxor behavior in PMN appears to be more complicated. There is no structure transition in the vicinity of $T_m$, and the pseudocubic structure persists down to 4K. So the nature of relaxor behavior is still open for debate, and various physical models have been proposed to describe the dispersive dielectric relaxation.

**Superparaelectric model**

Cross proposed the superparaelectric model for relaxors.⁹ Similar to the superparamagnetic state, it involves micro polar regions that are dynamically disordered above $T_m$, the mean Curie temperature of the different regions. Cation displacement continuously fluctuates among equivalent directions (for PMN it is $<111>$), activated by thermal energy. The heterogeneity caused by the mixed B-site creates locally favorable directions, so the local symmetry is lower than the global one. However, the energy barrier separating different directions is small, so macroscopic polar domains never form as in normal ferroelectrics.

**Spin-glass model**

Viehland *et al.* ¹⁷,¹⁸ showed evidence for dipolar glass-like behavior by analyzing the dielectric response using the Vogel-Fulcher relationship which also implies activated dynamics. Fitting to the Vogel-Fulcher relationship gave a freezing temperature of 217 K. This is well below the temperature $T_m$, and is the temperature below which the micro
domains can no longer change their polarization direction. The glassy nature was believed to be due to the randomly oriented dipoles and electrostrictive strain fields between superparaelectric moments. The evidence was seen in the very slow dynamics and the long time relaxation of the dielectric response with logarithmic decay, reported by Colla et al.\textsuperscript{19}

**Random field model**

Kleemann et al.\textsuperscript{20} proposed that PMN by nature is a ferroelectric, but due to the strong contribution of quenched random electric field arising from the charged composition fluctuations, the phase transition of PMN is smeared by random-field interactions. As a result, PMN shows relaxor ferroelectricity.

There are also some other models such as spherical random-bond-random-field model and the slow glassy dynamics model. However, the applicability of a given model limited to specific cases.

### 1.5 The cation order and the electric dipole order

There are two distinct types of ordered domains within PMN, both on the nanometer scale. One is the B-site cation ordered domains, giving rise to superstructure peaks in the diffraction pattern at the $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ position. The other is polar nanodomains, having local rhombohedral symmetry with size less than 10nm.\textsuperscript{21} These are the domains that give PMN its ferroelectric behavior. The characteristics of these two types of order and the correlations between them will be discussed in detail as follows.

#### 1.5.1 The cation order

In Pb(B'B'')O$_3$, which is the general formula for the complex perovskite with multiple cations at B-site, compositional fluctuations take the form of nanoscale domains of 1:1 B-site cation order.\textsuperscript{22} These domains of chemical order dispersed in the disordered matrix have been extensively imaged by the TEM technique.\textsuperscript{23} Electronegativity and ionic radii were proposed
as the two major factors controlling the cation order. This order is stoichiometric in Pb($B'^{1/2}B''^{1/2}$)O$_3$ type compounds such as Pb(Sc$^{1/2}$Ta$^{1/2}$)O$_3$ and Pb(Sc$^{1/2}$Nb$^{1/2}$)O$_3$, but nonstoichiometric in Pb($B'^{1/3}B''^{2/3}$)O$_3$ type compounds such as Pb(Mg$^{1/3}$Nb$^{2/3}$)O$_3$ and Pb(Zn$^{1/3}$Nb$^{2/3}$)O$_3$. The cation ordered nanodomains in PMN crystals are stable in terms of size (less than 5nm) and volume fraction (less than 30%). It has been indicated that thermal treatment in pure PMN can not introduce long range cation order. Thus the 1:1 order is usually interpreted with the “space charge model”, in which the ordered regions contain a 1:1 ratio of Mg and Nb, and the non-stoichiometric domains would then be embedded in a Nb rich disordered matrix in order to maintain electro-neutrality. The strong charge imbalance between the ordered domains and disordered matrix inhibits the growth of the ordered domains. However, extensive growth of the ordered domains was observed in chemically modified PMN ceramics such as A-site doping with La and B site doping with Sc cation. A new charge-balanced “random site model” was then proposed (The schematic diagram of the random site model is shown in Figure1.5).

![Figure 1.5 Schematic diagram of B-site ordered structure of PMN-based on random site model](image)
In this model, every other \{111\} plane of the B-site lattice is exclusively occupied by Nb\(^{5+}\) cations (referred to as the B''-sublattice in literature), the other \{111\} plane (referred to as the B'-sublattice) is randomly occupied by Mg\(^{2+}\) and the rest Nb\(^{5+}\) cations in a 2:1 ratio. Since one plane (B'') is ordered, the superstructure is well-defined.

In this case, there would be no charge imbalance and the entire crystal volume could be composed of these ordered domains with the chemical formula: Pb[(Mg\(_{2/3}\)Nb\(_{1/3}\))\(_{1/2}\)Nb\(_{1/2}\)]O\(_3\). The above descriptions result when adjacent unit cells have sites either occupied by different ions or with a preference for different types of ions. Effectively, this doubles the size of the unit cell, producing a superstructure that exists over small domains. And recently, this new model received support from the atomic resolutions Z-contrast TEM imaging\(^{28,29}\) and the small angle X-ray scattering study.\(^{30}\)

The stability of the 1:1 B-site cation order in the random site structure depends on (1) the average valence difference of cations occupying the B'- and the B''-sublattices, (2) the average size difference of cations occupying the two sublattices, and (3) the mismatch in the size and charge of the cations occupying the random B'-sublattice.\(^ {31,32}\) Although La and Sc were doped in different sites, the cation ordering mechanism is somewhat similar.

Sc substitutes both Mg and Nb at the B'-sublattice, the charge difference between the B'- and the B''-sublattices kept unchanged. However, the introduction of much larger Sc\(^{3+}\) cations (0.885Å) significantly stabilizes the B-site cation order by increasing the size difference between the B'- and the B''-sublattices.

In the donor doped Pb\(_{1-x}\)La\(_x\)[Mg\(_{(1+x)/3}\)Nb\(_{(2-x)/3}\)]O\(_3\) solid solutions, the substitution of La at A-site is compensated by an increase in the overall Mg:Nb ratio at B-site. Due to the larger ionic size and lower valence of Mg (0.72 Å for Mg\(^{2+}\) vs. 0.64 Å for Nb\(^{5+}\)), both size and charge difference between B'- and the B''-sublattices increased significantly. Furthermore, the mismatch in the charge/size of the cations on the random B'-sublattice is reduced. This is believed to be the primary cause for the enhanced B-site cation ordering in La doped PMN.
1.5.2 The electric dipole order

The existence of polar nanoregions in relaxors was first confirmed by Burns and Dacol’s birefringence measurements.\(^{33}\) These polar regions start to develop at Burn’s temperature \(T_B\) (~650 K), which is several hundred degrees above \(T_m\) (265 K) in PMN crystals. More direct evidence was subsequently found from diffuse X-ray scattering and diffuse neutron scattering studies,\(^{34,35}\) which suggested that they arise from the condensation of the soft mode.\(^{36}\) On cooling, the polar nanodomains that result from an important short-range correlation of the atomic shifts along the eight equivalent \(<111>_{\text{cub}}\) directions progressively nucleate in the cubic matrix, leading to a local rhombohedral structure \((R3m)\).

The origin of the lattice distortions with the preferential rhombohedral symmetry can be explained by the chemical features of \(\text{Pb}^{2+}\) with its lone-pair electrons, which are “stereochemically active” and may stick out to one side of the lead ion by adjusting the orientation of the lone pair.\(^{37}\)

Because the local polarization is randomly oriented, the resulting average polarization remains zero. The polar clusters increase both in size and number as temperatures decrease. However, unlike normal ferroelectrics, they never coarsen into large domains. Their growth seems to be inhibited by the chemical order and the induced random electric/strain fields. At 5K, the length of the polar clusters is less than 10nm, with total volume fraction under 30% in PMN.\(^{21}\) Thus, the system can be described by polar nanoregions embedded in a cubic matrix.\(^{38,39}\) And the overall structure was named correspondingly as \textit{pseudocubic}.

1.5.3 Correlations between the two types of order

The correlations between cation order and electric dipole order has been detected and investigated in some relaxors. In the ordered regions of \(\text{Pb(Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3\) ceramics, the Sc cations and the Ta cations take the alternative \((\frac{1}{2} \frac{1}{2} \frac{1}{2})\) sites, and the degree of the order can be altered by thermal annealing.\(^{40,41}\) Long-term annealing produces a fully ordered structure.
and leads to normal ferroelectric behavior. Relaxor behavior is observed only in the Pb(Sc\textsubscript{1/2}Ta\textsubscript{1/2})O\textsubscript{3} ceramics with nanoscale cation order. In other words, increasing cation order in Pb(Sc\textsubscript{1/2}Ta\textsubscript{1/2})O\textsubscript{3} is correlated with the long range electric dipole order development. And 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 increases and, eventually, a macrodomain state of normal ferroelectric characteristics can be achieved.\textsuperscript{42} These experiments clearly indicate a firm link between the cation and electric dipole orders, and suggest that nanoscale cation order is essential to relaxor behavior in these ceramics.

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.\textsuperscript{43} Using the high-resolution TEM lattice imaging technique, Jin and his co-workers revealed that the cation-ordered domains in PMN had faceted interfaces, most of which were along \{111\} planes.\textsuperscript{44} Interestingly, it has been suggested that the phase boundary for the polar domain is parallel to \{111\} planes.\textsuperscript{45} Also, the morphology of the island-like macrodomains in Pb(Sc\textsubscript{1/2}Ta\textsubscript{1/2})O\textsubscript{3} closely resembles that of the chemical domains.\textsuperscript{23} Recent theoretical modeling also indicates that, in the temperature range from T\textsubscript{B} to 300 K, polar nanoregions coincide with the chemical nanodomains.\textsuperscript{46} Based on the above well-established facts, strong interactions between the two types of order must exist.

\textbf{1.6 Evolution of the electric dipole order under electric fields}

The impact of an electric field to the electric dipole order in relaxors was first examined in lanthanum-modified Pb(Zr,Ti)O\textsubscript{3}.\textsuperscript{47} The focus was later shifted to the Pb(B'B'\textsuperscript{\prime\prime})O\textsubscript{3}-type relaxors. When a DC field is applied along the <111>-direction in PMN single crystals, a long-range symmetry breaking from pseudocubic to rhombohedral occurs. The field-induced phase transition was verified by light scattering\textsuperscript{48} and neutron scattering\textsuperscript{49}
studies. This polar nanoregion-to-macrodomain-state transition introduces nonergodicity in relaxor behavior. An electric field vs. temperature phase diagram delimiting several states was proposed based on experimental studies of PMN single crystals, as exemplified in Figure 1.6.50

![E-T phase diagram proposed for PMN single crystal](image)

Figure 1.6 E-T phase diagram proposed for PMN single crystal 50

Pseudocubic phase with relaxor behavior (area 1), ferroelectric rhombohedral phase with reversible polarization (area 2), induced rhombohedral phase with frozen polarization (area 3), and frozen disordered phase after zero-field cooling (area 3’) were discerned. The field-induced phase transition was characterized by an intrinsic Curie temperature $T_{C0}=213\text{K}$ associated with a threshold field strength $E_{th}=1.75\text{kV/cm}$. The applied field grows the polar nanoregions by enforcing correlated ion shifts along the symmetry-preferential directions and overcoming the random local electric fields, giving rise to the formation of macrodomains. The existing polar regions averaging less than 10nm (which can be temperature dependent) were suggested to be the nuclei of the induced ferroelectric phase. Optical imaging technique with polarized light sources has been used to visualize the development of the macrodomains.51,52 However, due to the limited resolution, these observations missed the critical activities of the nanoscale polar domains.
1.7 Proposed Research

1:1 B-site cation order is believed to have a strong correlation with electric dipole order in PMN. The main focus of this research is on manipulating the cation order and examining the cation order effect on the dielectric properties of the PMN-based relaxors. By doing this, the relationship between the cation ordered structure and unique dielectric and ferroelectric properties of PMN-based ceramics can be established. As PMN is the prototype of relaxor ferroelectrics, the results of the current work can also be applied to other complex perovskite systems. We started the research with single crystal PMN due to its simplified structure and focused on the electric field-induced phase transition of the single crystal pallets with different orientations. However, since the degree of cation ordering in pure PMN is stable against thermal treatment, long range cation order can’t be developed in pure single crystal PMN. Therefore in order to achieve long range cation ordering, different cations were introduced into PMN polycrystalline ceramics as dopants. Additionally, the impact of the defects on long range cation order development in PMN was also investigated.

1.7.1 Dopant selection

La

La was doped in PMN to substitute Pb at A-site with concentration from 5 to 50 at.%. Superlattice reflections associated with the development of long range cation order were observed in X-ray diffraction patterns.\textsuperscript{24,51} So La was chosen to enhance the cation order of PMN. Meanwhile, by comparing electrical properties of La doped PMN with pure PMN, the impact of the A-site substitution of Pb on electric dipole order of PMN system will be better understood.

Sc

Sc was introduced in PMN system to form the $(1-x)\text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 -x\text{Pb(Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ solid solution with $0.1\leq x \leq 0.9$.\textsuperscript{26} In other words, Sc substitutes both Mg
and Nb at B-site. The long range B-site cation order was successfully developed with thermal annealing treatment. However, the compositions with \( x \leq 0.1 \) have never been tried, and the dielectric properties were only investigated in composition series rather than same composition with varying degrees of cation ordering.

\[ W \]

W was also introduced into PMN system because Pb(Mg\(_{1/2}\)W\(_{1/2}\))O\(_3\), which is antiferroelectric, can form the complete solid solution with Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) and this solid solution (PMN-PMW) showed composition dependent long range B-site cation order for compositions containing >20mol\% PMW, as shown in Figure 1.7.\(^{54}\)

![Figure 1.7 Lattice constant and superstructure line intensity vs. composition in PMN-PMW solid solutions.\(^{54}\)](image)

The chemical order is easy to control by varying the composition. At the same time, there will be interactions between the antiferroelectric phase and the relaxor ferroelectric phase. In this antiferroelectric-relaxor solid solution system, not only the correlations between cation order and electric dipole order will be clarified, but also the interaction or the competition between the antiferroelectric phase and relaxor phase will be studied.

In order to keep the perovskite structure of PMN unchanged and reduce the internal
strain which is caused by ion doping, only dopant concentrations less than 5 at.% were tried for all the systems above. At the same time, since the composition is changed, it was thought it might be possible to change the degree of cation order by varying thermal treatment method, so different cooling rates were also carried out after final high temperature sintering to manipulate the degree of cation order.

\textit{Zr}

Previously Zr was introduced in PMN to form \((1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbZrO}_3\) solid solution, \(\text{Zr}^{4+}\) presumably substitutes both \(\text{Mg}^{2+}\) and \(\text{Nb}^{5+}\) simultaneously. It was reported that PMN does not show any significant structure modification\(^{27,54,55}\)

\[\text{Zr}^{4+} \text{substitutes both } \text{Mg}^{2+} \text{and } \text{Nb}^{5+} \text{simultaneously.} \]

\[\text{Figure } 1.8\text{ Schematic stability diagram for PMT and PMN relaxors with } \leq 15 \text{ mol}\% \text{ solid solution additives.} \]

Lines represent the change in the stability of the 1:1 B-site cation order with the concentration of the solid solution additive. Hatched region indicates temperatures where the samples are kinetically active.\(^{55}\)

As shown in Figure 1.8, it was believed that an equilibrium 1:1 cation ordered form of PMN phase does not become stable until \(T<900^\circ\text{C}\). Therefore, to induce any change in the cation order by thermal treatment it is necessary to first raise the stability of the order to temperatures where the samples are kinetically active. Sc and La doping in PMN raises the ordering temperature drastically while Zr is somewhat less effective. So it was suggested that...
the absence of enhanced cation order in PMN-PZ system was due to the ineffectiveness of Zr substitution in extending the stability range of the ordered phase to “kinetically active” temperatures where extensive B-site cation diffusion is possible.

However, Zr\(^{4+}\) has the identical size with Mg\(^{2+}\), so it will substitute Mg\(^{2+}\) at B’-sublattice in the cation ordered structure. Not only the size/charge difference between B’ and B” sublattice will increase, but also the size/charge mismatch at B’ sublattice will be reduced with Zr modification. All of these conditions favor cation order development. Zr is still a quite promising dopant to enhance the cation order of PMN.

1.7.2 Sample Preparation

All ceramic samples were prepared with the columbite method developed by Swartz and Shrout.\(^{57}\) The starting materials were commercially available high purity (better than 99.9 wt.%) metal oxide PbO, MgO, Nb\(_2\)O\(_5\), La\(_2\)O\(_3\), Sc\(_2\)O\(_3\), ZrO\(_2\) and WO\(_3\) powders. The composition of PMN was modified by A-site La doping, B-site Sc, Zr or W doping, in conjunction with the Mg/Nb ratio properly adjusted.

![Flow chart of powder processing.](image_url)

**Figure 1.9** Flow chart of powder processing.

The flow chart of powder processing is shown in Figure 1.9. After vibratory milling
in isopropyl alcohol for 6 hours and subsequent drying, the mixed stoichiometric powders of B-site oxides were calcined at 1100°C for 4 hours. The calcined powders were then mixed with A-site doping metal oxide and/or PbO (with 2 at.% extra) powders, milled for 6 hours, and calcined at 900°C for 4 hours to form phase pure perovskite powders. The heating/cooling ramp rate is 300°C/hour. The pellets were formed by conventional sintering or hot pressing.

1. Conventional sintering. A steel die with half inch inner diameter was used for cold pressing to form the compact. Synthesized powder of 0.75-1.5 grams was mixed with one drop of poly-vinyl-alcohol binder (2 wt. % aqueous solution) and then pressed at 150 MPa (hold for 1 minute). The preformed pellets were then buried in PMN protective powder and annealed at 1200-1250°C for 3-6 hours with double crucible method (as shown in Figure 1.10). Different cooling ramp rates ranging from 10°C/hour to 1200°C/hour were used for thermal processes in order to manipulate the degree of chemical order.

![Figure 1.10 Sample sintering/annealing setup: double crucible method.](image)

2. Hot-pressing. Pressed cylinders, 15 mm in diameter by 20 mm tall, were formed by cold-isostatic pressing at 350 MPa. The preformed pellets were then hot pressed in an Al₂O₃ die at 1150°C for 2 hours in air. Thin slices from the hot pressed piece were buried in PMN powder and annealed at 1250°C for 1 hour. With an oxygen flow rate about 1000 ml/min, a second annealing was then carried out at 900°C for 6 hours in an atmosphere containing
excess PbO. A heating/cooling rate of 300°C/hour was generally used for these thermal processes.

The surface layers of the processed ceramic pellets were removed by mechanical grounding prior to structure and property characterization.

1.7.3 Structure characterization

X-ray diffraction was used to check the phase purity of the ceramics and calculate the degree of the cation ordering. Based on the intensity of superstructure peak which is around 2θ=19°, the degree of cation ordering (α) was calculated with the following equation:

$$\alpha^2 = \frac{I_{(111)\text{measured}}}{I_{(111)\text{ideal}}} \left( \frac{I_{(100)\text{measured}}}{I_{(100)\text{ideal}}} \right)^2$$

A siemens D500 x-ray diffractometer with Cu-Kα (1.51487 Å) source was used for all the structural analysis. Data were collected between 15-50° for 2θ, using a step size of 0.05° and counting time as 1 second. In order to get precise intensity of the superlattice peak, longer counting time (15 seconds) was applied at a certain angle range. Identification of the phases present and indexing of peaks were accomplished using MDI Jade 7.0 software. The ordering parameters were calculated using the lattice construction function of that software.

It is critical to obtain ceramics with high densities in order to minimize the influence of pores and cavities. The Archimedes’ method was used to determine the density of the pellet. In this method, the dry mass (D) of each pellet is compared to its mass when suspended in water (S) and when it has water saturated in all open pores (M). The actual density of material, $$\rho_{\text{exp}}$$ in grams per cubic centimeter is:

$$\rho_{\text{exp}} = \frac{D}{M - S}$$

Theoretical density is easily calculated from the unit cell volume and atomic mass, as shown in equation 1-5, and then the relative density is calculated according to equation 1-6.
\[ \rho_{th} = \frac{m_f Z}{V_{uc} N_a} \tag{1-5} \]

\[ \rho_{relative} = \frac{\rho_{exp}}{\rho_{th}} \times 100\% \tag{1-6} \]

Where \( m_f \) is the mass of one formula unit in the unit of g/mol, \( Z \) is the number of the formula unit per unit cell, \( V_{uc} \) is the volume of one unit cell in cm\(^3\), \( N_a \) is the Avogadro’s number.

Scanning electronic microscopy (JSM-606LV, JEOL) was used to observe the grain morphology of the samples. Specimens were prepared by introducing a fresh fracture surface and then sputtering gold as conducting layer for 15 seconds.

The cation ordering and polar ordering of the samples were characterized using transmission electronic microscopy (CM30, Philips). Specimens were prepared by ultrasonically cutting 3 mm diameter disks and grinding or polishing to a thickness of \( \sim 200 \mu m \). The central portions of the disks were further thinned to about \( 15 \mu m \) by mechanical dimpling. The final thinning to perforation was conducted via argon-ion milling (5 kV and 50mA, Gatan). Dark field images were obtained to visualize the cation ordered domains, while bright field images were collected to show polar domains.

After the density measurement, both sides of the sample were electroded by gold sputtering. Copper wires (\( \phi = 50 \mu m \)) were fixed by silver epoxy at the center of the platelet.

1.7.4 Property measurement

The dielectric constant is measured to investigate the relaxor behavior of the samples, and the value of \( T_m \) is determined in this measurement. An LCR meter (HP-4284A, Hewlett-Packard) or LCZ meter (Keithley 3330, Keithley) in conjunction with an environmental chamber (9023, Delta Design) were used for dielectric constant measurements. A heating/cooling rate of \( 2^\circ C/min \) was used during the measurement. Samples were
thermally annealed at 373 K before measurements in order to eliminate the possible remnant
macropolar regions. In order to further investigate the relaxation process of PMN
based-ceramics, the frequency dependence of the dielectric constant was also measured by
using a Novocontrol system (Novocontrol, Germany).

Based on the dielectric constant measurement results, the diffuse phase transition in
these relaxor ferroelectric oxides is quantitatively evaluated with the diffuseness parameter $\delta$
determined by fitting the data (1kHz) to the following equation in the temperature range
above $T_m$ where $\varepsilon_m < 1.5 \varepsilon_r$:

$$\frac{\varepsilon_r}{\varepsilon_m} = \exp\left[ -\frac{(T - T_m)^2}{2\delta^2} \right]$$  \hspace{1cm} (1-7)

Thermal depolarization current measurement is performed with a picoammeter
(Model 486, Keithley) under the ‘zero field heating after field cooling’ condition to get the
$T_{C0}$, which marks the real phase transition of the relaxor and is believed to be the intrinsic
physical property of relaxor ferroelectrics. A bias field of 10kV/cm was applied when the
sample was cooled down to ~120 K with 4°C/min cooling rate. Then the bias field was
removed, thermal depolarization current was monitored when the sample was heated with
2°C/min to room temperature. The development of macroscopic polarization is a
manifestation of the electric-field-induced relaxor to normal ferroelectric phase transition.
The macroscopic polarization vs. temperature curve was calculated by integrating the thermal
depolarization current:

$$P = \int \frac{i}{A(dT/\text{dt})} dT$$  \hspace{1cm} (1-8)

Where $i$ is the thermal depolarization current, $A$ is the electroded area of sample and $dT/dt$ is
the heating rate.

The polarization hysteresis measurement was made with a standardized ferroelectric
test system (RT-66A, Radiant technologies). Sample was soaked in fluorinert fluid (FC-77,
3M) to avoid electrical arcing and held at the specific temperatures for 10 minutes prior to the measurement. Hysteresis loops were measured with different history conditions. In normal ferroelectrics, identical hysteresis loops are achieved despite the history of the samples, while in relaxors there will be differences between the hysteresis loops if the samples have different histories. It is believed these measurements can provide useful information about the phase boundary of the relaxor state and induced ferroelectric state in PMN-based relaxor ferroelectrics. Part of the electric field induced phase transition diagram of PMN-based relaxor ferroelectrics will be constructed.

Based on the above dielectric property measurement results, which directly correspond to the electric dipole ordering of the material, the impact of the cation ordering on the electric dipole ordering in PMN-based ceramics will be clarified through the comparison between the samples which have the same composition but only different degrees of cation order.

1.8 Dissertation Organization

This dissertation is composed of a number of journal articles published or submitted for publication. The introductory chapter contains background information and a comprehensive literature review of the topics addressed in subsequent chapters.

Chapter 2 is a paper that investigates the electric field-induced phase transition in Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ single crystals with field applied along the <111>, <110>, and <100> directions. The lowest threshold field $E_{th}$ was measured to be 3kV/cm in the (110)-oriented crystal with field applied along the <110> direction, and 5kV/cm for the (100)-oriented crystal with field along the <100> direction. An additional ferroelectric rhombohedral to ferroelectric orthorhombic phase transition is found to occur in the (110) platelet at high electric fields (~20kV/cm). An E~T phase diagram was proposed for Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ crystals with different orientations. This paper has been published in Physical Review B.
Chapter 3 contains an article that investigates the long range cation order development in A-site La-doped and B-site Sc-doped PMN relaxor ceramics. Samples were prepared with the hot pressing method and more than 5 at. % dopant was introduced. The enhanced chemical orderings showed different impacts on the dielectric and ferroelectric properties in these perovskite materials. The difference was discussed on the basis of cation size and charge imbalance. This paper has been published in *The Journal of the American Ceramic Society*.

Chapter 4 is a manuscript that focuses on long range cation order development in PMN with minimum amount of different dopants. 2 or 3 at.% La, Sc and W were doped in PMN independently to achieve long range cation order. The impact of cation order on electric dipole order was investigated by comparing dielectric properties within a wide frequency range of $10^{-2}$-$10^5$ Hz of ceramics with same composition but different degree of cation ordering. By fitting the low frequency permittivity measurement data, the relaxation processes in modified PMN ceramics are discussed. This manuscript is ready for submission to *Physical Review B*.

Chapters 5 and 6 contain articles which focus on the long range cation order development in Zr modified PMN ceramics. Different approaches are applied: One (Chapter 5) is to use $\text{Zr}^{4+}$ substituting only $\text{Nb}^{5+}$ according to the chemical formula $\text{Pb(Mg}_{1/3}\text{Zr}_{2x/3}\text{Nb}_{2(1-x)/3})\text{O}_{3-x/3}$ and introducing oxygen vacancies into the system. The other (Chapter 6) is to introduce $\text{Zr}^{4+}$ as forming the $(1-x)\text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - x\text{PbZrO}_3$ solid solution. Long range cation ordering was successfully developed in both systems. Their ordering mechanisms were discussed in detail and the dielectric properties of the ceramics were compared with each other. The first article (Chapter 5) has been published in the *Journal of the American Ceramic Society* and the second one (Chapter 6) is ready for submission to the *Journal of Physics: Condensed Matter*.

The final chapter covers the general conclusion of the dissertation summarizing the
progress this study has performed, in addition to suggested future work. Works cited are listed at the end of each chapter in which they appear.

1.9 References


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2. Electric Field-induced Phase Transitions in (111)-, (110)-, and (100)-oriented Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ Single Crystals


Xiaohui Zhao, Weiguo Qu, Xiaoli Tan*, A. A. Bokov¶ and Z.-G. Ye¶

2.1 Abstract

Electric field-induced phase transitions were investigated in (111), (110) and (100) thin platelets of relaxor ferroelectric Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ single crystals with electric fields applied along the <111>, <110> and <100> directions, respectively. Temperature dependences of complex dielectric permittivity, pyroelectric current and dielectric hysteresis loops were investigated. Electric field-temperature (E-T) phase diagrams were proposed for the different directions of the field. Alongside with the high-temperature ergodic relaxor phase and the low-temperature glassy nonergodic relaxor phase existing at E=0, the ferroelectric phase may appear in the diagram at the fields higher than the threshold field (E$_{th}$). The temperature of the first-order transition between ergodic relaxor and ferroelectric phases (T$_C$) was located in field-cooling and field-heating after field-cooling regimes. For the <111> field direction, T$_C$ is higher and E$_{th}$ is lower than for the other directions. For the<100> direction, T$_C$ is the lowest and E$_{th}$ is the highest. The critical point bounding the T$_C$(E) line when the field is applied in <111> direction [Z. Kutnjak, J. Petzelt, and R. Blinc, Department of Materials Science & Engineering, Iowa State University, Ames, IA, 50011

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Nature 441, 956 (2006) is not observed in the <110> and <100> directions up to the highest applied field of 7.5 kV/cm. Extrapolation of experimental data suggests that the critical point for the <110> and <100> directions (if any) can be expected only at much higher fields. In the hysteresis loops experiments performed after zero-field cooling, the lower temperature limit is determined above which a ferroelectric phase can be induced from the frozen glassy state at a given field strength or the polarization of the induced ferroelectric phase can be reversed. This limit is located at much lower temperatures in the (100) platelet than in the (110) or (111) platelets. An additional ferroelectric rhombohedral to ferroelectric orthorhombic phase transition occurs in the (110) platelet at high electric fields (~ 20kV/cm). The mechanisms of the field-induced transformation from the glassy nonergodic relaxor phase or the ergodic relaxor phase to the ferroelectric phase are discussed.

**Keywords:** Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}, relaxor ferroelectric, electric field-induced phase transition, dielectric permittivity
2.2 Introduction

Complex perovskite Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} (PMN), a prototype relaxor ferroelectric compound, exhibits both a strong frequency dispersion and a high relative permittivity with a broad dielectric peak around $T_m = 265\text{K}$.\textsuperscript{1,2} The origin of the relaxor ferroelectric behavior can be traced back to the structure of the compound, where nanometer scale ($< 5\text{nm}$) 1:1 cation ordering exists on the B-site of the ABO\textsubscript{3} perovskite.\textsuperscript{3-7} Superimposed on the nanoscale chemical ordering is the nanoscale polar ordering in PMN crystals.\textsuperscript{8} The polar nanoregions nucleate at the Burns temperature $T_B \approx 650\text{K}$. Upon cooling below about 300K, the polar nanoregions begin to grow, reaching about 7nm at 10K, with the most significant growth taking place around the intrinsic Curie temperature $T_{C0} = 213\text{K}$.\textsuperscript{9-15} The structure of the polar regions is slightly distorted along the $<111>$ direction, yet the long-range structure preserves cubic symmetry without any phase transition down to liquid He temperature.\textsuperscript{9-15} Recent first principles-based simulations showed that in the temperature range from $T_B$ to 300K, the polar nanoregions are essentially the same as the cation ordered domains.\textsuperscript{16,17}

The most fascinating aspect of PMN lies in its nonergodic states under bias electric fields.\textsuperscript{18-29} The polar nanoregions in PMN can grow into micrometer-sized ferroelectric domains when driven by external electric fields, which corresponds to a field-induced phase transition.\textsuperscript{20,30,31} The transition kinetics study has shown that when a static field is applied to a zero-field-cooled crystal along the $<111>$ direction, the phase transition takes place abruptly after an incubation period.\textsuperscript{23-26} During incubation under 3 kV/cm at 175K, the polar nanoregions coarsen up to $\sim 70\text{nm}$; the percolation of the coarsened polar regions leads to the ferroelectric state with a rhombohedral symmetry.\textsuperscript{26} The polarization in the induced ferroelectric state is reversible only within a temperature range, bounded by the upper limit of Curie temperature $T_C$ and the lower limit of the temperature below which the ferroelectric spontaneous polarization is clamped. Both these limits are functions of bias field.\textsuperscript{19-21}
intrinsic Curie temperature $T_{C0}$ (determined by zero-field-heating after field-cooling), 213K, lies in between the clamping temperature and $T_C$. The lowest threshold bias field $E_{th}$ to trigger the relaxor cubic to the ferroelectric rhombohedral transition is found around the temperature $T_{C0}$. When the field is applied along the $<111>$ direction, $E_{th}$ was observed to be 1.75kV/cm.20

The current understanding of the electric field-induced phase transition in Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ is built almost entirely on experimental observations of (111) thin crystals with the field along the $<111>$ direction. Limited, though inconsistent reports on (110) and (100) crystals have clearly shown that they behave differently from (111) crystals under electric fields. Schmidt et al.29 observed that when the electric field was applied along the $<100>$ direction, $T_{C0}$ was 13 K lower than when the field was along the $<110>$ and $<111>$ directions. In addition, the hysteresis loop measurements indicated different remanent polarization $P_r$ and coercive field $E_c$ among the three directions. Arndt et al.30 noticed that a ferroelectric rhombohedral phase could be induced at 180K with a bias field of 10kV/cm along $<111>$ or $<110>$, but not along $<100>$. Westphal and colleagues18 observed a number of optically detected Barkhausen jumps under a reversed field of 3.3kV/cm along the $<110>$ direction at 221K. Ye and Schmid20 observed the electric field-induced phase transition in all (111), (110), and (100) platelets. A monodomain state was realized in (111) platelets under a field as low as 2.2 kV/cm (in the $<111>$ direction) around $T_{C0}$, but a multidomain state invariably resulted in the (100) platelet even under 150 kV/cm (in the $<100>$ direction). Recently, Lushnikov et al.32 measured the phonon velocity in PMN crystals under a bias field of 5 kV/cm along the $<111>$, $<110>$, and $<100>$ directions and speculated that different phases may have been triggered by electrical stimuli.

Compared with the phase transition induced by electric fields along the $<111>$ direction, the transition under $<110>$ or $<100>$ fields is expected to be more complicated because the external field is not aligned with the local polarization axis of the polar
nanoregions. As a result, the electric field (E) vs. temperature (T) phase diagrams with fields applied along the <110> and the <100> directions in PMN crystals have yet to be established. The present work studied the orientation dependence of the electric field-induced phase transition in PMN single crystals and proposed the E-T phase diagrams for (110)- and (100)-oriented crystals poled along the <110> and <100> directions, respectively.

2.3 Experimental Procedure

\[ \text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 \] single crystals were grown via a high temperature solution process from the flux of PbO-B_2O_3. Thin slices with broad faces parallel to the (111), (110), and (100) crystallographic planes were cut and polished. Gold electrodes measuring approximately 6 mm² were deposited by sputtering. The electric field was applied across the thickness, which was around 0.3 mm, of the thin slices.

Dielectric permittivity and loss as a function of temperature were measured under bias fields of 0, 3.0, 5.0 and 7.5 kV/cm with LCR meters (HP-4284A or Keithley 3330) in conjunction with a Delta 9023 environmental chamber. A heating/cooling rate of 2 K/minute was used during measurements. The bias field was switched on at room temperature, and immediately after that the crystal was cooled down to 123 K (field-cooling test) and heated up back to the room temperature (field-heating after field-cooling test). Between measurements with different bias fields, crystal samples were thermally annealed at 373 K to eliminate possible history effect. Thermal depolarization current was measured using a picoammeter (Keithley 486) at a heating rate of 2 K/min. The polarization hysteresis loops of the crystal platelets were displayed by a RT-66A ferroelectric test system (Radiant Technologies). For hysteresis loop measurements, the crystals were first cooled to 123 K without electric field at a cooling rate of 4K/min. Then the temperature was set, in sequence, to 153, 173, 193, 213, and 233K to let the chamber warm up. When the temperature was stabilized for 10 minutes at the setpoint, a hysteresis loop was measured at a peak-to-peak
field of ±20 kV/cm.

2.4 Experimental Results

2.4.1 Dielectric properties under zero bias

The dielectric permittivity of the (111), (110), and (100) single crystal platelets upon cooling without bias field is shown in Fig. 1. The characteristic broad peaks and strong frequency dispersion are clearly seen. The \( T_m \) at 1 kHz was found to be 268 K for all three orientations.

2.4.2 Thermal depolarization measurement

The Curie temperature under zero-field heating after field-cooling (intrinsic Curie temperature), \( T_{C0} \), was measured by monitoring the thermal depolarization current of 10 kV/cm field-cooled crystals. From the measurement, \( T_{C0} \) is found to be ~217 K for the (111) and (100) platelets, and ~213 K for the (110) platelet. The integration of the current with respect to time indicates the development of macroscopic polarization. Such an integration process leads to the polarization vs. temperature curves shown in Fig. 2. The macroscopic polarization developed by 10kV/cm field cooling from room temperature to 183K was measured as 33, 28, and 21 \( \mu \)C/cm\(^2\) for the (111), (110), and (100) platelets, respectively. The development of macroscopic polarization is a manifestation of the electric field-induced relaxor to normal ferroelectric phase transition. Furthermore, the polarization values support a rhombohedral structure with \( <111>_{\text{cubic}} \) polar direction.\(^{19} \) This can be seen from the fact that

\[
33(\mu\text{C/cm}^2) \times \cos 35.3^\circ = 27(\mu\text{C/cm}^2) \approx 28(\mu\text{C/cm}^2); \quad 33(\mu\text{C/cm}^2) \times \cos 54.7^\circ = 20(\mu\text{C/cm}^2) \approx 21(\mu\text{C/cm}^2),
\]

where 35.3\(^\circ\) is the angle between the \( <110>_{\text{cubic}} \) and \( <111>_{\text{cubic}} \) directions, and 54.7\(^\circ\) between the \( <100>_{\text{cubic}} \) and \( <111>_{\text{cubic}} \) directions.
2.4.3 Dielectric property upon field-cooling

The field-induced phase transition is further characterized by detailed dielectric measurements. The temperature dependence of dielectric permittivity and loss under field cooling conditions for the (111), (110), and (100) crystals are shown in Fig. 3. With the electric field applied along the <111> direction, a sharp dielectric anomaly was detected at 222 K under $E = 3.0$ kV/cm, indicating a first-order induced phase transition. With the field increased to 5.0 kV/cm, the dielectric anomaly occurred at a higher temperature, 238K, and became broader. At a still higher field of 7.5kV/cm, the dielectric anomaly immersed into the broad dielectric peak around $T_m$ (Fig. 3(a)). These results are consistent with previous studies that showed a correlation between increasing field strength and a smoother induced phase transition process.20,22

When the field was applied along the <110> direction, much weaker dielectric anomalies were detected at 197K under 3.0kV/cm and 222K under 5.0kV/cm. At the field level of 7.5kV/cm, a dielectric anomaly can be barely detected at 232K (Fig. 3(b)). For the (100) crystal platelet, no apparent anomaly was observed on the relative permittivity $\varepsilon_r$ vs. $T$ curves under 3.0, 5.0, or 7.5kV/cm. However, anomalies did appear on the $\tan\delta$ vs. $T$ curves at 204K under 5.0kV/cm, and 215K under 7.5kV/cm (Fig. 3(c)).

2.4.4 Dielectric property upon field-heating after field-cooling

After the field-cooling tests, field-heating tests were conducted under the same field level. Dielectric permittivity and loss as a function of temperature were measured and are shown in Fig. 4. For the (111) crystal, an anomaly associated with the ferroelectric to relaxor transition upon heating occurs at 230 K under 3.0 kV/cm and 242 K under 5.0 kV/cm, and immerses into the dielectric peak under 7.5 kV/cm (Fig. 4(a)). For the (110) platelet, the transition occurs at 222K under 3.0 kV/cm, 230 K under 5.0 kV/cm, and 238K under 7.5 kV/cm (Fig. 4(b)). For the (100) platelet, the phase transition can barely be detected from the
dielectric loss curve at 218K under 3.0 kV/cm, but is clearly observed at 226 K under 5.0 kV/cm and at 229 K under 7.5 kV/cm (Fig. 4(c)).

2.4.5 Polarization hysteresis measurements

The reversibility of polarization in the field-induced ferroelectric phase was evaluated by polarization vs. field (P~E) hysteresis loop measurement at temperatures below $T_m$ with a peak-to-peak field of ±20kV/cm. As shown in Fig. 5, all three platelets show well-defined ferroelectric hysteresis loops, indicating reversible macroscopic polarizations within the test temperature range. However, a close examination shows significant differences between the three orientations. For the (111) platelet, the reversible polarization was significantly suppressed at 153 K, compared to that at 173 K (the remanent polarization $P_r$ is 6.0 $\mu$C/cm$^2$ at 153 K and 25.5 $\mu$C/cm$^2$ at 173 K). Obviously, a large fraction of the polarization was frozen at 153 K in the (111) platelet, giving rise to a much higher coercive field and a much lower remanent polarization. Increasing the temperature from 173K to 193K and to 213K did not significantly change $P_r$ (Fig. 5(a)).

The P~E hysteresis loops at different temperatures in the (110) thin crystal show distinct features (Fig. 5(b)). At 153K, large reversible polarization can still be seen but it requires a high coercive field $E_c$. The hysteresis loop is not saturated at the 20kV/cm field level. Increasing the temperature to 173K increases the switchable polarization and reduces the coercive field. Further increasing the temperature to 193K, however, leads to a significant decrease in the $P_r$, from 26.2 to 12.3 $\mu$C/cm$^2$. The low $P_r$ persists up to 213K. For the (100) platelet, fully developed P~E hysteresis loops were observed at all four test temperatures (Fig. 5(c)). The coercive field $E_c$ decreases dramatically, but the remanent polarization $P_r$ remains almost constant as temperature increases from 153K to 213K.

The remanent polarization $P_r$ and coercive field $E_c$ measured from the P~E hysteresis loops in Fig. 5, as well as from the hysteresis loops measured at 233K under 20kV/cm (not
shown) are plotted against temperature in Fig. 6. It is evident that $E_c$ decreases as temperature increases for all three orientations. However, there exists a strong orientation dependence of the remanent polarization $P_r$. At the highest test temperature (233K), slim loops with low $P_r$ were recorded for all three crystal slices.

2.5 Discussion

The experimental data shown in Figs. 2 through 6 revealed the electric field-induced phase transition in PMN single crystals. As noted in the Introduction section, phase transition in PMN has been largely studied in (111) thin crystals with the field applied along the $<111>$ direction. Different phases stabilized with combined electric field and temperature conditions are presented in E~T phase diagrams for such experimental configuration. However, such phase diagrams for the (110)- and (100)-oriented PMN single crystals have not yet been reported. Strong orientation dependence of the electric field-induced phase transition has been observed in normal ferroelectrics with the perovskite structure, such as BaTiO$_3$, as well as in relaxor-based solid solutions Pb[(Mg$_{1/3}$Nb$_{2/3}$)$_{1-x}$Ti$_x$]O$_3$. The orientation dependence in these ferroelectric oxides has been clearly illustrated by their distinct E~T phase diagrams. As seen in Section III, significantly different dielectric and ferroelectric behavior has also been observed in pure PMN crystals with different orientations. Therefore, E~T phase diagrams for the (110)- and (100)-oriented crystals are distinctly different from those for the (111)-oriented crystals.

The relaxors at low temperatures are known to be nonergodic, so that many different thermodynamically metastable states (or even different phases) may correspond to the same set of thermodynamic parameters (T and E in our case). The phase diagram obtained from experiment is expected to be affected by thermal and field history and different diagrams can be constructed, depending on the paths by which the points of the diagram are reached. It is sensible to choose the state at $T >> T_m$ as “reference point”: this
state is ergodic, and thus truly in equilibrium regardless the history. For that reason we always started the new experiment after annealing the crystal at 373 K >> T_m.

2.5.1 Constant field E~T phase diagram

Fig. 7 (a) presents the E~T phase diagram for the <111> direction based on the results of field-cooling and field-heating after field-cooling runs at constant fields. Alongside with the T_C values found in the dielectric measurements of the present work (Figs. 3, 4), the data for T_C extracted from the pyroelectric measurements in Refs. 26 and 31 are also shown. The lowest threshold field level E_{th} that triggers a ferroelectric state in a (111) thin crystal was measured to be 1.75kV/cm before, thus the low-field boundary of the ferroelectric phase is shown by the horizontal line at this field. The intrinsic Curie temperature T_C0 (i.e. zero-field-heating after field-cooling value of T_C) determined in Sec. II B is shown by the arrow. As reported previously, it coincides with the glassy freezing temperature T_f separating the ergodic and the glassy nonergodic relaxor phases in the zero-field-cooling regime. The boundary between these two phases at non-zero fields is not known and we can only tentatively mark it by the vertical dashed line. Note that one more phase boundary between the “paraelectric” and “glasslike” states (a nearly vertical line at ~240 K) was reported previously based on the measurements of nonlinear dielectric permittivity. However, we have not found in this work any experimental data that would confirm the existence of such a boundary. Thus, it is not shown in Fig. 7(a).

One can see in Fig. 7(a) that the transition temperature between the ferroelectric and ergodic relaxor phases, T_C, is significantly lower on cooling than on subsequent heating (shown by the thick horizontal arrows). Such kind of hysteresis indicates a first-order phase transition. For the position of T_m (which is also shown in Fig. 7(a)) the hysteresis is practically absent. The hysteresis of T_C dramatically decreases with increasing field. At the highest applied field the dielectric anomaly corresponding to T_C can hardly be seen; even if it
exists it is smoothed out and immersed into the dielectric peak at $T_m$ [Fig. 3(a) and Fig. 4(a)]. However, at high fields the thermal hysteresis further decreases as can be concluded from the comparison of dielectric curves on heating and cooling at 7.5 kV/cm. According to Ref. 28 decreasing hysteresis and smearing anomaly in response to increasing field in PMN and Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ solid solution signify the approaching to a critical end point at which the line of the first-order phase transitions in the E-T phase diagram terminates. At fields above the critical one the difference between high- and low-temperature phases disappears.

In the (110) and (100) platelets, however, dielectric anomalies are still detected under 7.5kV/cm [Figs. 3(b, c) and 4(b, c)] and the line of the first-order phase transitions at $T_C$ can be reliably constructed up to this field as shown in Figs. 7(b) and (c). It is apparent that the boundary of the ferroelectric region is significantly shifted to lower temperatures under electric fields with directions in the sequence of $<111>$, $<110>$ and $<100>$. Besides, the thermal hysteresis of $T_C$ increases in the same sequence. Cooling and heating $T_C$ lines in the cases of (110) and (110) samples become nearly parallel with increasing field, suggesting that the hysteresis disappears only at very high field (if at all). Therefore, when the field is applied along the $<110>$ or $<100>$ direction, the ferroelectric transition remains far from the critical point even at the highest applied fields and may not reach it at all.

From Figs. 3 and 4, it can be seen that at low fields the dielectric anomalies at $T_C$ are much more smeared for the (110) platelet and especially for the (100) platelet, than for the (111) one. The smearing at low fields suggests the proximity of $E_{th}$. Again, $E_{th}$ seems to increase in crystals with the field applied in the direction sequence of $<111>$, $<110>$ and $<100>$. The values of $E_{th}$ are tentatively shown in Fig. 7 (b) and (c) by dashed line.

To explain the peculiarities of the E-T phase diagrams depicted in Fig. 7, we apply the two-stage kinetic model of first-order diffuse phase transitions in compositionally disordered crystals, with the implication that in the PMN relaxor the diffuse ferroelectric
transition begins on cooling at Burns temperature. At this temperature the polar nanoregions (PNRs) start to nucleate in the non-polar matrix, however, the development of the ferroelectric phase is prevented by the compositional disorder, i.e. PMN can be considered as an incipient ferroelectric. This model has been successfully used for the interpretations of the structural changes and T-x phase diagram in the system of (1-x)Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$−xPbTiO$_3$ solid solutions$^{42}$ and the dielectric and elastic properties in this system.$^{43}$ The model predicts that in the first, high-temperature, stage of the phase transition upon zero-field-cooling, a PNR is characterized by a specific dependence of its free energy (F) on its size (R). Namely, F first decreases with increasing R and then increases so that the minimum at $R_{\text{min}}$ exists which determines the equilibrium size of the PNR. The value of $R_{\text{min}}$ can be different for different PNRs and generally increases on cooling. As the equilibrium size of every PNR ($=R_{\text{min}}$) is a single-valued function of temperature, the temperature hysteresis is absent at this stage. The PNR can be considered as an individual dipole moment with the magnitude (which is expected to be roughly proportional to R) determined by $R_{\text{min}}$ and the direction allowed by the symmetry (eight possible <111> directions in the case of rhombohedral symmetry of PNRs). Therefore the PNR is characterized by an energy structure with eight potential wells separated by barriers. If the temperature is high enough ($T>>T_f$), the PNRs may be reoriented by thermal fluctuations among the allowed directions (potential wells) and the orientational polarization and relaxation of PNRs in the electric field gives rise to the familiar diffuse and dispersive dielectric maximum at $T_m$ (see Fig. 1). In spite of the fact that the transition is a first-order one, the maximum is non-hysteretic according to the model, which has been confirmed in the experiments.

In the second stage which begins when the crystal is cooled closer to the mean temperature of phase transition, a maximum appears in the F(R) dependences for some (not all) PNRs alongside with the minimum (see Ref. 41 for details). The maximum is located at $R_{\text{max}} > R_{\text{min}}$ and F(R) becomes a decreasing function for $R>R_{\text{max}}$. Such kind of PNRs are
therefore metastable. The magnitude of the maximum decreases on further cooling so that at a certain temperature the thermally activated jump over the maximum from the (metastable) state with $R=R_{\text{min}}$ to the state with lower energy at $R>> R_{\text{max}}$ becomes possible. This process is analogous to the process of critical nucleation and growth of the new phase in the case of a normal first-order phase transition (see e.g. Ref. 44) and it is associated with thermal hysteresis. However, in contrast to a normal transition, the activation energy for the formation of the critical nucleus of the ferroelectric phase from the metastable PNR [i.e. the magnitude of $F(R)$ maximum] can be very different for different PNRs, so that the nucleation process is smeared out over a wide temperature range. Besides, the extensive growth of nucleus is impossible because a large number of closely located neighboring PNRs and nuclei hinder the growth. The directions of PNR dipole moments are random. Merging of PNRs into single ferroelectric (macroscopic) domain requires in most cases reorientation of the dipole moments to align them in the same direction. However, the dipole moments are effectively frozen due to the glassy interactions and/or the low temperature (approaching $T_f$), and their flipping is practically forbidden. As a result, the ferroelectric phase (i.e. the state with macroscopic ferroelectric domains) cannot develop.

When a strong dc field is applied to the crystal at $T>> T_f$ in the $<111>$ direction, one of the eight potential wells becomes much deeper, and consequently the preferable $<111>$ orientation for PNRs appears. This state can be frozen in the field-cooling process. If the field is high enough, all or almost all PNRs are oriented along the direction of the field (i.e. the subsystem of PNRs is completely poled). Therefore, at the second stage of the transition the growth and mergence of critical nuclei from the metastable PNRs can easily lead to large domains at $T_C$, giving rise to the formation of the ferroelectric state. Due to the above-mentioned distribution of the temperatures of critical nuclei formation, the transition is diffuse and no sharp anomalies of permittivity and other properties appear. Upon subsequent heating (field-heating after field-cooling) the crystal transforms back to the ergodic relaxor
state with the temperature hysteresis inherent in the first-order transition.

If the dc field is not high enough, PNRs are poled incompletely during field-cooling, i.e. some of them retain at \( T > T_C \) the directions different from the direction of the field and thereby hinder the growth of ferroelectric phase. As a result, a structure consisting of differently oriented frozen PNRs, supercritical ferroelectric nuclei and non-polar regions appears. This structure implies the existence of large internal stresses and electric fields which increase on cooling when more and more nuclei form. The stresses and electric fields can be significantly released by the transformation into the state with large ferroelectric domains; however, there exists an energy barrier to the transformation which is related to the (necessary) reorientation of the dipole moments of the structure inside the frozen “unpoled” PNRs. The reorientation (phase transformation) may happen via the flipping of PNR dipole moments and/or via the motion of the boundaries of ferroelectric phase regions in such a way that their volume fraction increases at the expense of “unpoled” (energetically unfavorable) regions. This appears to be possible if \( E > E_{th} \) (the amount of “unpoled” PNRs, and thus the transformation energy barrier, are comparatively small), or impossible if \( E < E_{th} \). Nevertheless, the transformation temperature is decreased as compared to the \( T_C \) expected in a completely poled crystal at the same field.

Whatever the strength of the field in the field-cooling process, the induced ferroelectric phase is qualitatively the same. Therefore \( T_C \) on heating after field-cooling is expected to be independent of the field strength on cooling. The increase in the field-heating \( T_C \) with \( E \) is of the same origin as in the case of any normal ferroelectric transition (see e.g. Ref. 45). The field-cooling \( T_C \), in contrast, depends also on the PNR reorientation conditions: as discussed above, if \( E \) is not high enough, some PNRs need to be reoriented at the transition, which leads to an additional decrease of \( T_C \). This explains the significant enlargement of the temperature hysteresis of \( T_C \) with decreasing field (Fig. 7).

If the dc field is applied along \(<110>\) or \(<100>\), complete poling of PNRs in the
course of field-cooling at $T>T_C$ is impossible. Indeed, out of the eight $<111>$ directions allowed for the dipole moment of PNRs by the rhombohedral symmetry, two or four directions correspond to the same energy in the case of $<110>$ or $<100>$ field, respectively. Therefore, when the crystal is cooled to $T_C$, the inevitable PNR reorientations should accompany the process of PNR merging into ferroelectric domains at any field strength. As a result, $E_{th}$ and thermal hysteresis are increased and $T_C$ is decreased [Fig. 7(b) and (c)]. In particular even in highest $<100>$ fields, when the maximum possible degree of PNR polarization is achieved at $T>T_C$, additional $71^\circ$ and $109^\circ$ reorientations are needed to form the ferroelectric state at $T_C$. In the $<110>$ field, only $71^\circ$ reorientations are required, so that the energy barriers are lower than in the $<100>$ case and the effect on $T_C$, $E_{th}$ and thermal hysteresis is smaller.

2.5.2 Constant-temperature after zero-field-cooling $E$-$T$ phase diagram

Another type of $E$-$T$ phase diagram can be roughly estimated from the hysteresis loops results (Figs. 5 and 6), namely, the diagram resulting from field application at constant temperature after zero-field-cooling. Note that the $E$-$T$ phase diagram constructed after zero-field-cooling for the PMN (111) platelet in different modes is known. In that diagram the temperature $T_{ph}$ at which the glassy nonergodic relaxor state transforms to the ferroelectric state was determined after zero-field-cooling down to very low temperature during the constant-field-heating tests. The ferroelectric state appears in the diagram within a U-shaped region, bounded by the $T_{ph}(E)$ line at low temperatures and the $T_C(E)$ line at high temperatures. The latter line coincides with the $T_C(E)$ line in the field-heating after field-cooling diagram and above $T_C$ the ergodic relaxor state is stable. Based on the results of the present work we try to locate the line separating the cubic glassy phase and the ferroelectric phase in the experiments with isothermal field applied after zero-field-cooling. It is expected to coincide with the $T_{ph}(E)$ line, at least approximately.
For the (111) platelet, the reversible polarization determined from the hysteresis loops at 153K is significantly smaller than that at 173K. This can be explained in different ways. The first possible explanation is that the crystal remains in the glassy phase (at least partially), i.e. for the field of 20 kV/cm (peak value of E) the temperature of experiment (153 K) is lower than T_{ph}. Alternatively, one may expect that the crystal is in the ferroelectric phase (T_{ph} < 153 K at 20 kV/cm) but the peak field is smaller than the coercive field so that the polarization cannot be fully switched. However, it was experimentally confirmed for the <111> direction in PMN, that the T_{ph}(E) line in the phase diagram coincides with the E_c(T) line,^{20} i.e. the minimum field needed to induce the ferroelectric phase from the glassy one at some temperature after zero-field-cooling equals the coercive field of the ferroelectric phase at this temperature. Therefore, the first explanation is valid, implying that 153K is lower than the temperature T_{ph} at 20kV/cm.

The hysteresis loops for the <111> field at higher temperatures (shown in Fig. 5a) are saturated, i.e. the peak field applied is higher than E_c and the E_c value can be measured (as the intersection of the loop with the abscissa axis) and subsequently used for determining the line of phase transition from the glassy phase to the ferroelectric phase. As explained above, it is the same as the E_c(T) line.

For the (110) platelet, the reversible polarization is only slightly suppressed at 153K while for the (100) crystal, the reversible polarization is not at all suppressed at 153K. Therefore, the T_{ph}(E) line for the (100)-oriented crystal should be located at lower temperatures than that for the (110)-oriented crystals, and both of them are at lower temperatures than the (111)-oriented crystals. In order to more accurately locate the T_{ph}(E) line for the <100> field orientation, the (100) crystal platelet was further tested for reversible polarization at liquid nitrogen temperature (77K). The results are shown in Fig. 8. It is evident that the polar order is completely frozen and cannot be reversed at ±20kV/cm. A saturated P~E hysteresis loop cannot be achieved even under ±40kV/cm (only a very small P_r
of 1.2μC/cm² is measured from the loop). Therefore, the $T_{ph}(E)$ line for the (100)-oriented PMN crystal should lie above 77K for electric fields below 40kV/cm.

The above discussion is summarized in Fig. 9. Alongside with $T_C(E)$, the diagrams establish the $T_{ph}(E)$ lines for different orientations of the field. The diagrams include the following features: (a) the ferroelectric state with reversible polarization is confined within a U-shaped region for all three orientations; (b) below this region the ergodic relaxor phase is observed at temperatures above $\sim T_f$; at lower temperatures the state can be nonergodic relaxor (before the first field application) or ferroelectric with non-reversible polarization (if $E>E_c$ has already been applied) and (c) the U-shaped region shifts to lower temperatures and to higher fields in crystals with orientations in the sequence of (111), (110), and (100).

One can notice that the easiest way to induce the ferroelectric phase from the high-temperature ergodic relaxor phase is to apply the field in the $<111>$ direction. In particular, $E_{th}$ for this direction is smaller and $T_C$ (at the same E) is higher than for other directions. On the contrary, for the ferroelectric transition from the glassy phase at $T<<T_f$ the $<111>$ direction is the “hardest” one. This behavior can be understood from the fact that the PNRs are completely frozen at $T<<T_f$ and the mechanisms of transformation discussed in Section IV.A implying the flipping of PNR dipole moments no longer work. It seems that the process of field-induced merging of nanoscale polar regions of glassy phase into large domains of ferroelectric phase is similar to the poling process in normal ferroelectrics. In the latter case the dipole moments of domains are also frozen and it is the motions of domain walls that allow the crystal to be poled effectively rather than the switching of the whole domains.\(^{45}\) Likewise, the polar regions of glassy relaxor phase whose dipole moment directions are parallel (or close) to the direction of the poling field grow and absorb the other polar regions. This mechanism is in agreement with the above mentioned finding that at $T<<T_f$ the same lowest field is needed to reverse the polarization in the ferroelectric phase (i.e. $E_c$) and to induce the ferroelectric phase from the glassy one.
2.5.3 Further ferroelectric to ferroelectric phase transitions

The electric field-induced phase transition in PMN is presumably different from that in normal ferroelectrics such as BaTiO$_3$ because of the distinct nature of their polar structures. The polar nanoregions in PMN are known to have local rhombohedral symmetry with polarization fluctuating along all the eight $<111>$ directions.$^{2,9-15}$ It is highly probable that if the field is not very high the electric field-induced phase transition in PMN is a cubic to rhombohedral structural transition, regardless of the direction of the applied electric fields. In fact, such field-induced macroscopic rhombohedral structure was speculated by Schmidt et al$^{29}$ in 1980 in their pioneering studies on (111), (110), and (100) PMN crystals. It was later found that when the field was applied along the $<111>$ direction, a monodomain state could be easily achieved, while the fields applied in the $<110>$ and $<100>$ directions always result in a multidomain state.$^{20,31}$ As mentioned in Section III B, the values of the induced-polarization under 10kV/cm field cooling support the idea of the cubic to rhombohedral phase change.

Further ferroelectric to ferroelectric phase transition may occur in PMN single crystals under strong electric fields. It has been theoretically shown that in normal ferroelectrics with the perovskite structure, the rhombohedral, orthorhombic, and tetragonal phases have close free energies and, depending on the field direction, external electric fields can stabilize any one of them.$^{36,46,47}$ The transition is realized through a polarization rotation process, which often leads to intermediate monoclinic phases.$^{46,47}$ We believe that it is also possible for further ferroelectric to ferroelectric transitions to occur in PMN at high electric fields. For the (111)-oriented crystal with field applied along the $<111>$ direction, the rhombohedral structure will be stable and since the field direction is parallel to the polarization direction, there will be no further ferroelectric to ferroelectric transition. For the (110) platelet with field applied along the $<110>$ direction, a further ferroelectric rhombohedral to ferroelectric orthorhombic phase transition may be triggered. While for the
(100) platelet, a further ferroelectric rhombohedral to ferroelectric tetragonal transition may be triggered under high electric fields. These transitions were previously suggested to account for the ultrahigh piezoelectric strains in rhombohedral Pb\((\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\)O\(_3\) single crystals.\(^{28,48,49}\)

The abnormal change in the remanent polarization \(P_r\) in the (110)-oriented crystal shown in Fig. 5(b) and Fig. 6 suggests that the ferroelectric rhombohedral to ferroelectric orthorhombic transition actually may have occurred in the (110) platelet. The hysteresis loops presented in Fig. 5(b) appear to indicate that the 20kV/cm electric field stabilizes an orthorhombic phase at 153K and 173K, but a rhombohedral phase at 193K and 213K. Therefore, there is an additional line delimiting the ferroelectric rhombohedral and the ferroelectric orthorhombic phases within the U-shaped region in the E~T phase diagram for the (110)-oriented crystal (Fig. 9). This line passes the point (183K, 20kV/cm), where 183K is the midpoint between 173K and 193K. The orthorhombic phase is favored at high electric fields while the rhombohedral phase is favored at low electric fields.

In order to locate a second point on the rhombohedral/orthorhombic phase boundary line, the remanent polarization \(P_r\) in the (110) crystal platelet was further measured at 213K under electric fields of ±25, ±30, ±35, and ±40kV/cm along the <110> direction. The P~E hysteresis loops are shown in Fig. 10. Consistent with the proposed rhombohedral to orthorhombic phase transition, \(P_r\) abruptly increases from 9.9\(\mu\)C/cm\(^2\) under ±20kV/cm to 25.2\(\mu\)C/cm\(^2\) under ±25kV/cm at this temperature. The \(P_r\) value remains around 25\(\mu\)C/cm\(^2\) under ±30, ±35, and ±40kV/cm. Therefore, the rhombohedral/orthorhombic phase boundary line in the E~T phase diagram for the (110) crystal platelet passes a second point (213K, 22.5kV/cm). These two experimentally determined data points are marked in Fig. 9 as open circles.

In the following, we analyze the values of the remanent polarization to further support the proposed ferroelectric rhombohedral to ferroelectric orthorhombic phase transition in the
(110)-oriented crystal. At 173K, a ferroelectric orthorhombic phase is resulted from the ferroelectric rhombohedral phase under 20kV/cm. This transition presumably leads to a polarization vector parallel to the direction of the applied field, the <110> cubic direction. Therefore, a high \( P_r \) is expected. From Fig.6, it can be seen that the \( P_r \) for the induced orthorhombic phase (26.2\( \mu \)C/cm\(^2\) at 173K) is indeed high and is comparable to that of the monodomain rhombohedral phase (25.5\( \mu \)C/cm\(^2\) at 173K).

However, in the present study, the ferroelectric rhombohedral to the ferroelectric tetragonal phase transition was not observed with field up to 40kV/cm in the (100) platelet crystal, indicating that such transition may require a much higher field.

### 2.6 Conclusions

The electric field-induced phase transition was investigated in Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) single crystals with the field applied along the <111>, <110>, and <100> directions and E-T phase diagrams have been constructed. Because of nonergodicity effects the low-temperature part of the diagram depends dramatically on the history of the crystal. The diagrams based on the results of field-cooling and field-heating after field-cooling experiments are shown in Fig. 7. The diagrams in Fig. 9 depict for all three directions the U-shaped region of the ferroelectric state which was found in experiments with isothermal field application after zero-field-cooling. The Curie temperature \( T_C \) (the upper boundary of the U-shaped region) and the lower boundary of the U-shaped region are shifted to lower temperatures in the crystal under field directions in the sequence of <111>, <110>, and <100>. The electric field along the <111> and <100> directions trigger only the relaxor cubic to ferroelectric rhombohedral phase transition. Fields along the <110> direction with a magnitude around 20kV/cm trigger a further ferroelectric rhombohedral to ferroelectric orthorhombic transition after the initial relaxor cubic to ferroelectric rhombohedral transition.
The lowest threshold field $E_{th}$ needed to induce ferroelectric phase was measured in the field-cooling experiments. It is found to be the largest in the (100)-oriented crystal with field applied along the $<100>$ direction, and the smallest for the (111)-oriented crystal with field along the $<111>$ direction. In the field-cooling and field-heating after field-cooling experiments for the $<100>$ and $<110>$ field directions, significant dielectric anomalies and large hysteresis of $T_C$ are revealed which do not vanish even at the highest applied field of 7.5 kV/cm, in contrast to the $<111>$ field direction where the disappearance of anomalies and hysteresis is known to be the result of the critical end point existing on the $T_C(E)$ line of the first-order phase transitions. As one can judge from the character of $T_C(E)$ dependences, the critical point for non-$<111>$ directions is probably also absent at fields higher than 7.5 kV/cm.

It is suggested that the mechanisms of the field-induced transformation to the ferroelectric phase from the glassy nonergodic relaxor phase and from the ergodic relaxor phase are different. In the former case the motions of the boundaries between polar nanoregions are the main origin. In the latter case the flipping of the dipole moments of the polar nanoregions are involved. The behavior is explained in terms of the two-stage kinetic model of the first-order phase transitions in compositionally disordered crystals.\textsuperscript{41,42}

Note that far reaching implications are attached to our conclusion about the critical point in the E-T phase diagram. It was recently suggested that the origin of the giant electromechanical response in ferroelectric relaxors was related to the existence of the critical point at which enhanced piezoelectric coefficients were expected\textsuperscript{28,50} and practically observed.\textsuperscript{28} All the experiments related to the critical point were conducted in Ref. 28 for the $<111>$ direction of the field only. On the other hand, the electromechanical response in this direction is comparatively moderate; only when the field is applied along $<100>$ it becomes extraordinary large.\textsuperscript{48} However, in the present work we do not find the critical point in the $<100>$ direction. Therefore, the relation between the giant electromechanical response and
the critical behavior becomes questionable and more experimental efforts are needed to elucidate this intriguing issue.

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2.8 Figure list

Fig. 1. Dielectric properties of Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) single crystals measured during cooling under zero bias field. (a) (111), (b) (110), and (c) (100) platelets.

Fig. 2. Development of macroscopic polarization as a function of temperature. The curve is integrated from the thermal depolarization current during zero-field-heating after 10kV/cm field-cooling.

Fig. 3. Dielectric properties of Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) single crystals measured during field cooling at 1kHz. (a) (111), (b) (110), and (c) (100) platelets.

Fig. 4. Dielectric properties of Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) single crystals measured during field heating after field cooling at 1kHz. (a) (111), (b) (110), and (c) (100) platelets.

Fig. 5. Polarization vs. electric field hysteresis loops measured at 4Hz under a ±20kV/cm peak-to-peak field in Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) single crystals. (a) (111), (b) (110), and (c) (100) platelets.

Fig. 6. Remanent polarization \(P_r\) and coercive field \(E_c\) as a function of temperature in the Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) single crystals. The \(E_c(T)\) lines will be re-plotted in Fig. 9 to delimit the ferroelectric phase from the glassy non-ergodic relaxor phase.

Fig. 7. The E-T phase diagrams for Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) single crystals established based on the processes of field-cooling at a constant field and subsequent heating at the same field applied along (a) <111>, (b) <110> and (c) <100> directions. The directions of the thermal paths are shown by the thick arrows. The values of \(T_C\) upon cooling and heating are shown by triangles and circles, respectively. Solid and dashed lines indicate the boundaries between the ferroelectric, ergodic relaxor and nonergodic relaxor phases. Squares and dot-dashed line show \(T_m\) at 1 kHz. Filled symbols are the results of the present work while open symbols in (a) represent the data from Refs. 26 and 31.
Fig. 8. Polarization vs. electric field hysteresis loops measured at 4Hz under ±20kV/cm and ±40kV/cm peak-to-peak fields in the (100)-oriented Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ crystal at 77K.

Fig. 9. The E-T phase diagrams of Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ single crystals obtained from data presented in Figs. 6 and 7. The $E_c(T)$ or $T_{ph}(E)$ lines, delimiting the ferroelectric phase from the glassy nonergodic phase were attained from the measurement of ferroelectric hysteresis loops in different directions after zero-field-cooling. The directions of the employed E-T path are shown by thick arrows.

Fig. 10. Polarization vs. electric field hysteresis loops measured at 4Hz under ±20kV/cm and ±25kV/cm peak-to-peak fields in the (110)-oriented Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ crystal at 213K.
Fig. 1. Dielectric properties of Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ single crystals measured during cooling under zero bias field. (a) (111) and (b) (110) platelets.
Fig. 1. Dielectric properties of Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ single crystals measured during cooling under zero bias field. (c) (100) platelet.
Fig. 2. Development of macroscopic polarization as a function of temperature. The curve is integrated from the thermal depolarization current during zero-field-heating after 10kV/cm field-cooling.
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Fig. 3. Dielectric properties of Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ single crystals measured during field cooling at 1kHz. (c) (100) platelet.
Fig. 4. Dielectric properties of Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ single crystals measured during field heating after field cooling at 1kHz. (a) (111) and (b) (110) platelets.
Fig. 4. Dielectric properties of Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ single crystals measured during field heating after field cooling at 1kHz. (c) (100) platelet.
Fig. 5. Polarization vs. electric field hysteresis loops measured at 4Hz under a ±20 kV/cm peak-to-peak field in Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} single crystals. (a) (111) and (b) (110).
Fig. 5. Polarization vs. electric field hysteresis loops measured at 4Hz under a ±20kV/cm peak-to-peak field in Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} single crystals. (c) (100) platelet.
Fig. 6. Remanent polarization $P_r$ and coercive field $E_c$ as a function of temperature in the Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ single crystal.
Fig. 7. (a), (b)
Fig. 7. The E-T phase diagrams for Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} single crystals established based on the processes of field-cooling at a constant field and subsequent heating at the same field applied along (a) <111>, (b) <110> and (c) <100> directions. The directions of the thermal paths are shown by the thick arrows. The values of $T_C$ upon cooling and heating are shown by triangles and circles, respectively. Solid and dashed lines indicate the boundaries between the ferroelectric, ergodic relaxor and nonergodic relaxor phases. Squares and dot-dashed line show $T_m$ at 1 kHz. Filled symbols are the results of the present work while open symbols in (a) represent the data from Refs. 26 and 31.
Fig. 8. Polarization vs. electric field hysteresis loops measured at 4Hz under $\pm 20kV/cm$ and $\pm 40kV/cm$ peak-to-peak fields in the (100)-oriented Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ crystal at 77K.
Fig. 9. The E-T phase diagrams of Pb(Mg_{1/3}Nb_{2/3})O_3 single crystals obtained from data presented in Figs. 6 and 7. The $E_c(T)$ or $T_{ph}(E)$ lines, delimiting the ferroelectric phase from the glassy nonergodic phase were attained from the measurement of ferroelectric hysteresis loops in different directions after zero-field-cooling. The directions of the employed E-T path are shown by thick arrows.
Fig. 10. Polarization vs. electric field hysteresis loops measured at 4Hz under ±20kV/cm and ±25kV/cm peak-to-peak fields in the (110)-oriented Pb(Mg₁/₃Nb₂/₃)O₃ crystal at 213K.
2.9 References


3. Influence of Cation Order on the Electric Field-induced Phase Transition in Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-Based Relaxor Ferroelectrics


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3.1 Abstract

The effect of cation ordering on the electric field-induced relaxor to normal ferroelectric phase transition in Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-based ceramics was investigated. Both A-site La-doping and B-site Sc-doping was found to enhance the chemical ordering in these relaxor ceramics. However, the enhanced chemical orderings showed different impacts on the dielectric and ferroelectric properties in these perovskite materials. The 5% La-doping was observed to shift the dielectric maximum temperature (T\(_{\text{max}}\)) to a significantly lower temperature and suppress the electric field-induced transition to a ferroelectric phase. In contrast, the 5% and 10% Sc-doping showed little effect on T\(_{\text{max}}\) but strengthened the ferroelectric coupling. The difference is discussed on the basis of cation size and charge imbalance. An electric field-temperature phase diagram is also proposed for the 0.90Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)–0.10Pb(Sc\(_{1/2}\)Nb\(_{1/2}\))O\(_3\) based on its history dependence of the electric field-induced phase transition.

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3.2 Introduction

Complex perovskite Pb(Mg_{1/3}Nb_{2/3})O_3 (PMN)-based relaxor ferroelectrics have been extensively studied for several decades due to their unique dielectric, ferroelectric, and electrostrictive properties.\textsuperscript{1-3} The characteristic diffuse phase transition was initially suggested to be caused by microscale compositional fluctuations.\textsuperscript{1} Such chemical heterogeneities were later confirmed by transmission electron microscopy investigations, taking the form of nanometer scale B-site cation ordered domains.\textsuperscript{4-7} In coupling to this chemical ordering, electrical dipole ordering also exists in the form of polar nanoregions in these relaxor ferroelectrics and these nanoscale polar domains persist well above the diffuse phase transition temperature $T_{\text{max}}$.\textsuperscript{8}

The B-site 1:1 cation ordered domains in PMN are highly stable against extended thermal annealing.\textsuperscript{5-7} Two models have been proposed to interpret the nonstoichiometric chemical ordering in these PMN-based 1:2 complex perovskites. One is the “space charge model” where Mg and Nb occupy the \{111\} plane alternatively.\textsuperscript{2-6} This model suggests that the cation ordered domains carry negative space charges. The disordered matrix is Nb-rich and hence positively charged. The space charge prevents the growth of the cation ordered domains during thermal annealing. The other B-site cation ordering model is the recently proposed “random site model” and seems to have gained more experimental support.\textsuperscript{7,9-14} In this model, every other \{111\} plane of the B-site sublattice is occupied solely by Nb cations. The rest \{111\} planes of the B-site sublattice are occupied randomly by Mg and Nb cations at a ratio of 2:1. This model preserves the charge neutrality of the cation ordered domains and the growth of the chemically ordered domains is limited by kinetics considerations.\textsuperscript{9-12}

The electrical dipole ordered nanoregions in PMN are structurally distorted along the <111> directions and the polar axis of these nanodomains is randomly fluctuating among the eight equivalent directions.\textsuperscript{2,3} External electric fields can strengthen the dipole ordering and
grow the polar nanoregions into large domains.\textsuperscript{15-24} This process corresponds to a first order relaxor to normal ferroelectric phase transition. Presumably, the nanoscale cation ordering should have strong interactions with the nanoscale dipole ordering and the cation ordering would not be affected by external electric fields. However, information on such interactions is still lacking and the effect of cation order on the electric field-induced polar nanoregion coarsening in the PMN-based relaxor ferroelectrics is still not clear.\textsuperscript{12,25,26} The present work investigates the influence of chemical ordering on the field-induced phase transition in La-doped and Sc-doped PMN ceramics.

### 3.3 Experimental Procedure

\[ \text{Pb}_{1-x}\text{La}_x\text{(Mg}_{1/3}\text{Nb}_{2/3})_3\text{O}_3 \quad (x = 0.05, \text{ abbreviated as PLMN5 hereafter}) \]

\[ (1-x)\text{Pb(Mg}_{1/3}\text{Nb}_{2/3})_3\text{O}_3-x\text{Pb(Sc}_{1/2}\text{Nb}_{1/2})_3 \quad (x = 0.05, 0.10, \text{ abbreviated as PSMN5 and PSMN10 hereafter, respectively}) \]

Ceramics were prepared via the columbite method developed by Swartz and Shrout.\textsuperscript{27} The starting materials used in this work were commercially available high purity (better than 99.9 wt.\%) PbO, MgO, Nb\textsubscript{2}O\textsubscript{5}, La\textsubscript{2}O\textsubscript{3}, and Sc\textsubscript{2}O\textsubscript{3} powders. After vibratory milling in isopropyl alcohol for 6 hours and subsequent drying, the mixed stoichiometric powders of B-site oxides were calcined at 1100°C for 6 hours. The calcined powders were then mixed with La\textsubscript{2}O\textsubscript{3} and/or PbO powders, milled for 6 hours, and calcined at 900°C for 4 hours to form phase pure perovskite powders. Pressed cylinders, 15 mm in diameter by 20 mm thick, were formed by cold-isostatic pressing at 350 MPa. The preformed pellets were then hot pressed in an Al\textsubscript{2}O\textsubscript{3} die at 1150°C for 2 hours in air. Thin slices from the hot pressed piece were buried in PMN powder and annealed at 1250°C for 1 hour. With an oxygen flow rate about 1000 ml/min, a second annealing was then carried out at 900°C for 6 hours in an atmosphere containing excess PbO. A heating/cooling ramp rate of 300°C/hour was generally used for these thermal processes. One slice of the 0.90Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})\textsubscript{3}O\textsubscript{3}–0.10Pb(Sc\textsubscript{1/2}Nb\textsubscript{1/2})\textsubscript{3}O\textsubscript{3} ceramic was further thermally
treated at 1250°C for 3 hours and slowly cooled to 900°C at 10°C/hour. This slow-cooled sample is referred to as “PSMN10 ordered” ceramic hereafter.

Density of these ceramics was measured by the Archimedes’ method and the grain size was examined by scanning electron microscopy (SEM). The surface layers of the annealed slices were removed by mechanical grounding and x-ray diffraction was used to check the phase purity and cation ordering. The cation ordering was also examined by dark field imaging in a transmission electron microscope (TEM). 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 3°C/min was used during measurement. Electric field-induced phase transition was evaluated by the thermal depolarization measurement with a picoammeter (Model 484, Keithley) and the polarization hysteresis measurement with a standardized ferroelectric test system (RT-66A, Radiant technologies).

3.4 Results and Discussion

Density measurement indicates that all four ceramics had relative densities in the range of 95~98%. SEM examination confirmed the high relative density and also revealed the grain size in these ceramics. As shown in Fig. 1, PSMN5, PSMN10 and PLMN5 have fine grains (average grain size <5μm) while the “PSMN10 ordered” ceramic has larger grains (average grain size ~8μm). X-ray diffraction confirmed that phase pure perovskite was formed in all compositions. Fig. 2 shows the diffraction spectrum with 2θ from 15° to 25°. The appearance of the (½ ½ ½) peak in the “PSMN10 ordered” and PLMN5 ceramics is indicative of an enhanced ordering on the B-site cation sublattice. It has been reported before that doping by La at A-site and Sc at B-site are both capable of coarsening B-site cation ordering domains in PMN. 5,11,12,28 It is evident from Fig. 2 that the effect of Sc-doping on enhancing the chemical ordering is more moderate compared to La-doping. Strong cation
ordering that is detectable to x-ray diffraction only developed in the slowly cooled PSMN10 sample (the “PSMN10 ordered” ceramic). The ordering parameter \( \alpha \) evaluated according to the common procedure used in literature\(^{11} \) for the “PSMN10 ordered” and PLMN5 ceramic is 0.9 and 0.7, respectively. The strong 1:1 cation ordering in these two ceramics was further confirmed by TEM analysis. Figure 3 shows the dark field images formed with the \((\frac{1}{2} \frac{1}{2} \frac{1}{2})\) superlattice spot in the \(<110>-z\) axis electron diffraction pattern. Chemical domains on the order of 100 nm were observed in both ceramics with those in the “PSMN10 ordered” ceramic slightly larger than those in the PLMN5 ceramic.

Although both grain size and cation ordering are distinct in these four ceramics, it is believed that the cation ordering plays a decisive role in determining their dielectric and ferroelectric properties. This argument is made based on the experimental results of undoped PMN. In this prototype relaxor ferroelectric ceramic, extended high temperature annealing presumably develops larger grains. However, no noticeable change in dielectric properties was observed since the degree of cation ordering was not altered during the annealing.\(^ {5-7} \) In the following, the discussion is therefore, focused on the cation ordering effect on the dielectric and ferroelectric properties.

The dielectric properties of these ceramics are shown in Fig. 4. The relative permittivity of all samples exhibits a broad peak and shows strong frequency dispersion, which are characteristics of a typical relaxor behavior. All four ceramics showed comparable dielectric loss at \( T_{\text{max}} \). In PLMN5, the relative permittivity was dramatically suppressed and the temperature at dielectric maxima \( T_{\text{max}} \) shifted considerably to a lower temperature (-80.3°C at 1 kHz). The results are consistent with previous studies.\(^ {5,28} \) The shift in \( T_{\text{max}} \) was suggested to be caused by the smaller size of La\(^ {3+} \) cations and the deviation of Mg:Nb ratio from 1:2.\(^ {5} \) In contrast, little change in \( T_{\text{max}} \) was noted in both PSMN5 and PSMN10. Increasing Sc-dopants from 5% to 10% led to an increase in \( T_{\text{max}} \) about 4.8°C at 1kHz and a decrease in relative permittivity. At the same Sc-doping level of 10%, it is interesting to
notice that the $T_{\text{max}}$ in the “PSMN10 ordered” ceramic was about 9.3°C lower at 1kHz than that in the PSMN10 ceramic, together with a further decrease in the permittivity. In these Sc-doped PMN ceramics, the degree of chemical ordering presumably increases in the sequence of PSMN5, PSMN10, and “PSMN10 ordered”. Results from Fig. 4 indicate that such an increase in cation order leads to a decrease in the relative permittivity. In this respect, the PLMN5 follows the same trend. It has strong chemical order but weak dielectric response.

It is known that several ferroelectric states exist in PMN-based relaxor ferroelectrics under different temperature/electric field conditions.15-24 One of the most important parameters that delineate these states is the thermal depolarization temperature $T_{C0}$ under the “zero-field-heating after field-cooling” condition. The temperature $T_{C0}$ is typically several tens of degrees lower than the diffuse phase transition temperature $T_{\text{max}}$ and marks a real phase transition. Therefore, it has been considered as an intrinsic material property for relaxor ceramics.22 $T_{C0}$ is typically measured by monitoring the thermal depolarization current of a field cooled sample. Figure 5 shows the results of such measurement on the four hot-pressed ceramics. The PSMN5, PSMN10 and “PSMN10 ordered” ceramics were field-cooled with 10 kV/cm down to -150°C and the PLMN5 ceramic was cooled with the same field down to -185°C before the measurement. Again, the PLMN5 ceramic showed a completely different behavior from that of Sc-doped ceramics. A very weak and broad current peak was detected at -155°C during heating. In sharp contrast, strong peaks were detected in all three Sc-doped ceramics. The thermal depolarization process in both PSMN5 and PSMN10 occurred in a relatively wide temperature range compared to that in the “PSMN10 ordered” ceramic. The measured $T_{C0}$ is -66.2°C, -63.5°C, and -51.4°C for PSMN5, PSMN10, and “PSMN10 ordered”, respectively, and is listed in Table 1 with other dielectric properties.

It is worth of comparing the $T_{\text{max}}$ and $T_{C0}$ of PSMN10 with those of “PSMN10
ordered”. Slow cooling enhanced the cation order in the “PSMN10 ordered” ceramic. The strengthened chemical ordering increased the $T_{C0}$ from -63.5°C to -51.4°C and decreased the $T_{max}$ from -7.5°C to -16.8°C. In other words, the enhanced chemical ordering in “PSMN10 ordered” reduced the gap between $T_{C0}$ and $T_{max}$. It should be pointed out that $T_{C0}$ and $T_{max}$ converge to the Curie temperature $T_c$ in normal ferroelectrics with long range dipole order. Therefore, increasing the lengthscale of the chemical ordering in Sc-doped PMN leads to an increase in the lengthscale of the electric dipole order as well.12

The electric field-induced relaxor to normal ferroelectric phase transition was characterized by the polarization hysteresis measurement at temperatures below $T_{max}$. The result for PLMN5 at 30kV/cm is shown in Fig. 6. It is evident that a normal ferroelectric phase could hardly be forced to form by external fields. Very low remanent polarization $P_r$ and saturation polarization $P_s$ was measured, which is consistent with the thermal depolarization measurement. The A-site La-doping shifted both $T_{max}$ and $T_{C0}$ significantly down to lower temperatures. In general, a normal ferroelectric phase could be induced by electric fields in relaxor ferroelectrics at temperatures in the vicinity of $T_{C0}$. The polarization hysteresis loop did open up slightly at -150°C, which is close to $T_{C0}$ (-155°C). However, it seems that the electrical dipoles in the random polar nanodomains are frozen and cannot be aligned by external electric fields at such low temperatures.

In contrast, the polarization hysteresis measurements on PSMN5, PSMN10, and “PSMN10 ordered” showed a very well defined relaxor to normal ferroelectric phase transition, as demonstrated in Fig. 7. It is clear that square hysteresis loops, indicating the presence of a normal ferroelectric phase, can be induced by external electric fields at temperatures around $T_{C0}$. The enhanced chemical ordering in Sc-doped PMN at least preserves, if not enhances, the electric field-induced relaxor to normal ferroelectric phase transition.

Ferroelectric properties, the remanent polarization $P_r$ and the coercive field $E_c$, were
measured from the hysteresis loops and are plotted in Fig. 8. Sharp contrast is seen again between the PLMN5 and the three Sc-doped ceramics. The PLMN5 ceramic showed a minimal $P_r$ and a low $E_c$. The three Sc-doped ceramics showed a peak in $P_r$ at $-120^\circ$C, indicating the optimum temperature to align most of the electrical dipoles. A high $P_r$ (>15$\mu$C/cm$^2$) was observed to persist at $-50^\circ$C in the slow cooled “PSMN10 ordered” ceramic. At $-20^\circ$C, which is close to their $T_{\text{max}}$, $P_r$ was found to diminish for all three Sc-doped ceramics. A monotonic decrease in the coercive field $E_c$ with increasing temperature is shown in Fig. 8(b). This indicates a higher resistance for the polarization switching at lower temperatures and is consistent with previous observations.$^{19-22}$ Compared to PSMN5 and PSMN10, “PSMN10 ordered” shows a higher $E_c$ at temperatures below $T_{C0}$. This could be a result of the larger polar nanodomains in this ceramic. A larger polar domain needs a higher field to switch its polarization.

Strong dependence of the field-induced phase transition in undoped PMN upon temperature/electric field history has been previously reported.$^{19-23}$ Such history dependence was also examined in the PSMN10 and the “PSMN10 ordered” ceramics with the polarization hysteresis measurement. Three temperature/electric field conditions were used and compared. In the first condition, the sample was initially heated to $150^\circ$C and held for one hour and then zero-field cooled down to the desired temperature for the hysteresis measurement. At this temperature, the measurement was performed at electric fields in the sequence of 5, 10, 15, 20, 30, and 40 kV/cm, respectively. This condition is referred to as “zero-field-cooled” condition in the following. In the second condition, the hysteresis measurement was carried out right after the measurement under the first condition at the same temperatures at the same field sequence. The second condition is referred to as “poled” condition in the following discussion. In the third condition, the sample was initially heated to $150^\circ$C for one hour and then zero-field cooled to $-150^\circ$C. At $-150^\circ$C, a ferroelectric phase was induced by applying a full cycle of AC field of 40kV/cm. Then the sample was zero-field
heated to desired temperatures for polarization hysteresis measurement at fields in the sequence of 5, 10, 15, 20, 30 and 40 kV/cm.

Identical polarization hysteresis loops were observed under the second and the third conditions at all field levels in both the PSMN10 and the “PSMN10 ordered” ceramics. However, significant difference was noticed in the hysteresis loops measured under the first condition when the field was below a critical level. Figure 9 shows the comparison between the “zero-field cooled” and the “poled” conditions in the PSMN10 ceramic. At -120°C, a lower $P_r$ was observed under the “poled” condition at field levels of 5, 10, and 15 kV/cm. However, the situation was reversed at 20kV/cm where a higher $P_r$ was measured under the “poled” condition, as shown in Fig. 9 (a) and (b). Identical hysteresis loops under these two conditions were observed at 30 and 40 kV/cm field levels at this temperature. The electric field level marking the different appearance of the hysteresis loops (taken as 25 kV/cm for this temperature) is termed the critical electric field in discussion followed. At -100°C and -80°C, a higher $P_r$ was measured under the “poled” condition at fields below the critical electric field, as shown in Fig. 9 (c) and (d). The critical field was roughly determined to be 12.5kV/cm at -100°C and 7.5kV/cm at -80°C.

Similar plots for the “PSMN10 ordered” ceramic under the “zero-field cooled” and “poled” conditions are shown in Fig. 10. Again, a higher $P_r$ was measured under the “poled” condition at fields below a critical electric field. At -120°C and -80°C, a significant difference in $P_r$ was noticed. The critical electric field was determined as 25kV/cm at -120°C, 12.5kV/cm at -80°C, and 7.5kV/cm at -50°C, respectively.

The critical field can be considered as a threshold field for transforming the relaxor ferroelectric state to the normal ferroelectric state. This is best illustrated by the hysteresis loops displayed in Fig. 9(d), Fig. 10(a), and Fig. 10(b). The hysteresis loops in these figures under the “poled” condition are asymmetric, with one corner sharp and one round. Such loops strongly resemble those in poled normal ferroelectric ceramics, such as piezoelectric
lead zirconate titanate ceramics. According to previous studies on undoped PMN and Pb(Zn\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3},\textsuperscript{22,29} the PSMN10 and the “PSMN ordered” ceramics are believed to be at a “frozen macrodomain” state at electric fields below the critical electric field and at a “normal ferroelectric” state at fields above the critical levels. Therefore, an electric field vs. temperature phase diagram can be constructed for the PSMN10 and the “PSMN10 ordered” ceramics based on the values of the critical electric fields at different temperatures (Fig. 11). The “frozen macrodomain” state (FR) and the “normal ferroelectric” state (FE) are delineated by the boundary line that defines the critical electric field. Both states are bounded at the upper temperature end by the characteristic T\textsubscript{C0}. At temperatures above T\textsubscript{C0}, a typical relaxor behavior (R) with polar nanodomains is expected. It is evident from Fig. 11 that the “FE” state in the “PSMN10 ordered” ceramic is shifted to higher temperatures.

Previous studies have shown that both La-doping and Sc-doping are capable of enhancing the B-site cation ordering.\textsuperscript{5,9-12,28} However, such enhanced chemical ordering seems to have different effects on the electrical dipole ordering in the polar nanoregions. Such difference may be caused by the different chemical ordering mechanisms. The A-site La-doped PMN takes the chemical formula Pb\textsubscript{1-x}La\textsubscript{x}(Mg\textsubscript{1+y}Nb\textsubscript{2-y})O\textsubscript{3}. La\textsuperscript{3+} cation (1.50Å), which has a smaller ionic radius than Pb\textsuperscript{2+} (1.63Å), substitutes Pb cation on the A site sublattice as a donor dopant. The smaller size of the La cation in the A-site and the increased molar fraction of the larger B-site Mg cation are believed to be the primary cause for the enhanced B-site cation ordering.\textsuperscript{10,30,31} The smaller La\textsuperscript{3+} also leads to a more compact unit cell which in turn leads to a higher resistance for the shuffling of the ferroelectric active Nb\textsuperscript{5+} in response to external fields. In addition, the increased Mg/Nb ratio in PLMN5 also contributes to the weak ferroelectric response since Mg is ferroelectric inactive.\textsuperscript{30,31} Therefore, the field-induced transition to a ferroelectric phase is suppressed in this material.

The ordering mechanism for the Sc-doping is somewhat different. The introduction of larger Sc\textsuperscript{3+} cations (0.885Å) stabilizes the B-site cation order by increasing the size
difference between the two B-site sublattices.\textsuperscript{30,31} At the same time, the lattice is more open for Nb$^{5+}$ to shuffle in response to external electric fields. In addition, Sc is ferroelectrically more active than Mg.\textsuperscript{31} Therefore, both chemical ordering and electrical dipole ordering are enhanced in the Sc-doped PMN relaxor ferroelectrics.

### 3.5 Conclusions

Both A-site La doping and B-site Sc doping enhance the B-site cation order in PMN-based relaxor ferroelectrics. However, the enhanced chemical ordering has distinct effects on the electrical dipole ordering in these oxides. In the La-doped PMN (PLMN5) ceramic, the dielectric and ferroelectric responses were deeply suppressed. In contrast, the Sc-doped PMN (PSMN5, PSMN10, and “PSMN10 ordered”) ceramics display a normal ferroelectric state within a wide temperature range. Both the chemical ordering and the electrical dipole ordering are strengthened at the same time by Sc-doping.
3.6 Figure list

Fig. 1. SEM micrographs of the fresh fracture surfaces of the four hot-pressed ceramics. (a) PSMN5, (b) PSMN10, (c) PSMN10 ordered, and (d) PLMN5.

Fig. 2. X-ray diffraction spectra of the PSMN5, PSMN10, PSMN10 ordered, and PLMN5 ceramics. The 1:1 cation order is detected in the “PSMN10 ordered” and PLMN5 ceramics.

Fig. 3. TEM dark field imaging with the $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ superlattice spot in the $<110>$-zone axis electron diffraction pattern. (a) PSMN10 ordered, and (b) PLMN5.

Fig. 4. Dielectric properties of the PSMN5, PSMN10, “PSMN10 ordered”, and PLMN5 ceramics. (a) Relative permittivity vs. temperature plot at 1kHz, 10kHz, and 100kHz. (b) Dielectric loss vs. temperature plot at 1kHz, 10kHz, and 100kHz.

Fig. 5. Depolarization current measurement under zero-field heating of the hot-pressed ceramics after field-cooling at 10kV/cm.

Fig. 6. Polarization vs. electric field curves measured at 4 Hz with the PLMN5 ceramic at (a) -100°C, (b) -120°C, (c) -150°C, and (d) -196°C.

Fig. 7. Polarization vs. electric field curves measured at 4 Hz at -50°C, -80°C, -120°C, and -150°C, respectively. (a) PSMN5, (b) PSMN10, (c) PSMN10 ordered.

Fig. 8. Ferroelectric properties of the four ceramics measured from the P–E hysteresis loops. (a) Remanent polarization $P_r$, and (b) coercive field $E_c$.

Fig. 9. History dependence of the ferroelectric behavior in the relaxor ferroelectric PSMN10 ceramic. ○: the “zero-field cooled” condition; ●: the “poled” condition. (a) 15kV/cm at -120°C, (b) 20kV/cm at -120°C, (c) 10kV/cm at -100°C, and (d) 5kV/cm at -80°C.

Fig. 10. History dependence of the ferroelectric behavior in the relaxor ferroelectric “PSMN10 ordered” ceramic. ○: the “zero-field cooled” condition; ●: the “poled” condition. (a) 19kV/cm at -120°C, (b) 10kV/cm at -80°C, and (c) 5kV/cm at -50°C.
Fig. 11. The electric field-temperature phase diagram proposed for the relaxor ferroelectric PSMN10 and “PSMN10 ordered” ceramics based on the history dependence. “R” denotes the relaxor ferroelectric nanodomain state, “FE” denotes the normal ferroelectric macrodomain state, and “FR” denotes the frozen ferroelectric macrodomain state.
Fig. 1. SEM micrographs of the fresh fracture surfaces of the four hot-pressed ceramics. (a) PSMN5, (b) PSMN10, (c) PSMN10 ordered, and (d) PLMN5.
Fig. 2. X-ray diffraction spectra of the PSMN5, PSMN10, PSMN10 ordered, and PLMN5 ceramics. The 1:1 cation order is detected in the “PSMN10 ordered” and PLMN5 ceramics.
Fig. 3. TEM dark field imaging with the $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ superlattice spot in the $<110>$-zone axis electron diffraction pattern. (a) PSMN10 ordered, and (b) PLMN5.
Fig. 4. Dielectric properties of the PSMN5, PSMN10, “PSMN10 ordered”, and PLMN5 ceramics. (a) Relative permittivity vs. temperature plot at 1kHz, 10kHz, and 100kHz. (b) Dielectric loss vs. temperature plot at 1kHz, 10kHz, and 100kHz.
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Fig. 6. Polarization vs. electric field curves measured at 4 Hz with the PLMN5 ceramic at (a) -100°C, (b) -120°C, (c) -150°C, and (d) -196°C.
Fig. 7. Polarization vs. electric field curves measured at 4 Hz at -50°C, -80°C, -120°C, and -150°C, respectively. (a) PSMN5, (b) PSMN10
Fig. 7. Polarization vs. electric field curves measured at 4 Hz at -50°C, -80°C, -120°C, and -150°C, respectively. (c) PSMN10 ordered.
Fig. 8. Ferroelectric properties of the four ceramics measured from the P–E hysteresis loops.

(a) Remanent polarization $P_r$, and (b) coercive field $E_c$. 
Fig. 9. History dependence of the ferroelectric behavior in the relaxor ferroelectric PSMN10 ceramic. ○: the “zero-field cooled” condition; ●: the “poled” condition. (a) 15kV/cm at -120°C, (b) 20kV/cm at -120°C.
Fig. 9. History dependence of the ferroelectric behavior in the relaxor ferroelectric PSMN10 ceramic. ○: the “zero-field cooled” condition; ●: the “poled” condition. (c) 10kV/cm at -100°C, and (d) 5kV/cm at -80°C.
Fig. 10. History dependence of the ferroelectric behavior in the relaxor ferroelectric “PSMN10 ordered” ceramic. ○: the “zero-field cooled” condition; ●: the “poled” condition. (a) 19kV/cm at -120°C, (b) 10kV/cm at -80°C, and (c) 5kV/cm at -50°C.
Fig. 11. The electric field-temperature phase diagram proposed for the relaxor ferroelectric PSMN10 and “PSMN10 ordered” ceramics based on the history dependence. “R” denotes the relaxor ferroelectric nanodomain state, “FE” denotes the normal ferroelectric macrodomain state, and “FR” denotes the frozen ferroelectric macrodomain state.
Table 1. Dielectric properties of the Sc-doped and La-doped PMN ceramics.

<table>
<thead>
<tr>
<th>Ceramic</th>
<th>$\varepsilon_{r,\text{max}}$ @ 1kHz</th>
<th>Peak loss @ 1kHz</th>
<th>$T_{\text{max}}$ @ 1kHz (°C)</th>
<th>$T_{C0}$ (°C)</th>
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3.7 References


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4. Doped Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ Ceramics with Long Range Cation Order

A paper to be submitted to Physical Review B

Xiaohui Zhao, Weiguo Qu, and Xiaoli Tan

4.1 Abstract

The B-site cation order in Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ ceramics was significantly enhanced by doping of minor amount of La, Sc or W (less than 3 at.%). Transmission electron microscopy examination confirmed the presence of large cation ordered domains. Although relaxor characteristics have been preserved, distinct dielectric/ferroelectric properties were observed in these ordered ceramics with different dopants. Doping with Sc seems to enhance the dielectric properties while doping with La and W just shows the opposite effect. The observed difference in properties can be traced back to the ordering mechanism in these ceramics.

Keywords: lead magnesium niobate, cation order, relaxor ferroelectric
4.2 Introduction

Complex perovskite Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} (PMN) has been extensively investigated since 1958 due to its unique relaxor ferroelectric behavior\textsuperscript{1-3}. The ferroelectric domains in PMN manifest themselves as polar nanoregions, which nucleate at the Burns temperature $T_B \approx 650$K. Upon cooling, the polar nanoregions begin to grow, reaching about 7nm at 10K, with the most significant growth taking place around the intrinsic Curie temperature $T_{C0} = 213$K. The structure of the polar regions is slightly distorted along the $<111>$ direction, yet the long-range structure preserves cubic symmetry without any phase transition down to liquid He temperature. The polar axis of these nanodomains is randomly fluctuating among the eight equivalent directions\textsuperscript{3}. The polar nanoregions can grow into micrometer sized ferroelectric domains under external electric fields during cooling, which corresponds to a first order relaxor to normal ferroelectric phase transition\textsuperscript{4-11}.

It is believed that the relaxor behavior of PMN is associated with the 1:1 B-site cation order. The cation ordered domains, ranging from 2 to 5 nm in size, are embedded in the disordered matrix and do not grow upon thermal treatment. In the ordered domains, every other {111} plane of the B-site sublattice is solely occupied by Nb cations, the other {111} plane is randomly occupied by Mg and the rest Nb cations. This “random site model”\textsuperscript{12} keeps the composition the same and preserves the charge neutrality between the ordered and disordered regions. It is suggested that the growth of the cation ordered domains is constrained by kinetic limitations. Presumably, the B-site cation order has strong interactions with the nanoscale electrical dipole order in PMN, which can be revealed by dielectric and ferroelectric measurements.

It has been reported previously that La (>4 at.%) or Sc (>5 at.%) doping can enhance the degree of cation order in PMN\textsuperscript{13-17}. W, when incorporated in PMN at >10 at.%, can also lead to the formation of long range cation order\textsuperscript{18}. In the present work, we demonstrate that,
combined with appropriate thermal treatment, only 2 or 3 at.% doping of La, Sc or W can develop large cation ordered domains in PMN. However, the cation ordered PMN ceramics display completely different dielectric/ferroelectric behaviors, indicating complex interactions between the cation order and the electrical dipole order.

4.3 Experimental

La, Sc and W were introduced into PMN separately, at 2 or 3 at.% level, through forming solid solutions of Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})\textsubscript{O}\textsubscript{3} with La(Mg\textsubscript{2/3}Nb\textsubscript{1/3})\textsubscript{O}\textsubscript{3}, Pb(Sc\textsubscript{1/2}Nb\textsubscript{1/2})\textsubscript{O}\textsubscript{3}, and Pb(Mg\textsubscript{1/2}W\textsubscript{1/2})\textsubscript{O}\textsubscript{3}. The detailed chemical formulae are as follows:

- 0.97Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})\textsubscript{O}\textsubscript{3}–0.03La(Mg\textsubscript{2/3}Nb\textsubscript{1/3})\textsubscript{O}\textsubscript{3} (referred to as La3)
- 0.94 Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})\textsubscript{O}\textsubscript{3}–0.06Pb(Sc\textsubscript{1/2}Nb\textsubscript{1/2})\textsubscript{O}\textsubscript{3} (referred to as Sc3)
- 0.96Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})\textsubscript{O}\textsubscript{3}–0.04Pb(Mg\textsubscript{1/2}W\textsubscript{1/2})\textsubscript{O}\textsubscript{3} (referred to as W2).

Ceramic samples were prepared with the columbite method developed by Swartz and Shrout.\textsuperscript{19} High purity (>99.9 wt. %) oxide powders of PbO, MgO, Nb\textsubscript{2}O\textsubscript{5}, La\textsubscript{2}O\textsubscript{3}, Sc\textsubscript{2}O\textsubscript{3} and WO\textsubscript{3} were used as the starting materials. Before weighing and mixing, the powders were baked at high temperatures to remove moisture and organic impurities to ensure precise stoichiometry. The B-site oxide powders were first mixed and milled with yttrium stabilized zirconia media (TOSOH, OH, USA) in isopropyl alcohol within plastic bottles on a vibratory mill for 3 hours. Next, the mixed stoichiometric powders were calcined at 1100°C for 4 hours in alumina crucibles. The calcined powders were then mixed with PbO and/or La\textsubscript{2}O\textsubscript{3} powders, milled for 3 hours, and calcined at 900°C for 4 hours to form phase pure perovskite powders. A uniaxial pressure of 150MP was applied to the perovskite powder, added with polyvinyl alcohol binder (2 wt.% aqueous solution), to form pellets. The pressed pellets were then buried in PMN protective powder and sintered at various temperatures (1200°C~1250°C) for 3 hours. A heating/cooling ramp rate of 600°C/hour was used to obtain “disordered” samples. To obtain “ordered” samples, a much slower cooling rate (10°C/hour) was applied from the
sintering temperature down to 900°C. These slow-cooled samples are referred to as “La3 ordered”, “Sc3 ordered” and “W2 ordered”, respectively. A pellet of pure PMN was also prepared with the slow cooled procedure as a reference sample.

After the surface layer was removed, the density of these ceramics was measured by the Archimedes method and the grain size was examined by scanning electron microscopy (SEM). X-ray diffraction tests were performed on sintered pellets to check the phase purity and degree of cation order. The cation ordered domains were also directly imaged with dark field technique in a transmission electron microscope (CM30, Philips). Dielectric characterization was carried out 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 the measurements. The thermal depolarization current was measured during zero-field-heating with a picoammeter (Model 486, Keithley) from field-cooled (10kV/cm) samples. The polarization hysteresis was measured with a standardized ferroelectric test system (RT-66A, Radiant technologies).

4.4 Results

4.4.1 Cation order in ceramics

Density measurement shows that all ceramic samples have a relative density in the range of 92~96%. SEM examination confirmed the high relative density and revealed the grain size of the ceramics. Fig. 1 shows the SEM micrographs of the La3 ordered and Sc3 ordered ceramics, from which the grain size is determined to be 6.4μm for La3 ordered and 7.1μm for Sc3 ordered. The grain size of all ceramics is listed in Table I, where all the doped ceramics have similar values. X-ray diffraction experiments indicate a pure perovskite phase in all ceramics. In the “La3 ordered”, “Sc3 ordered” and “W2 ordered” samples, the (½ ½ ½) superlattice peak appears, as shown in Fig. 2. The presence of (½ ½ ½) superlattice peak in
complex perovskite is an indication of the development 1:1 B-site cation order.\textsuperscript{14} Therefore, the cation order in PMN can be enhanced significantly even with only 2 or 3 at.% level substitution. The enhanced cation order is further confirmed by transmission electron microscopy (TEM) analysis. Fig. 3 shows dark field images formed with the (½ ½ ½) superlattice spot in the <110>-zone axis electron diffraction pattern. Large cation ordered domains were observed in all of the slow cooled ceramics. The size of these cation ordered domains is about 100 nm for both “La3 ordered” and “Sc3 ordered” ceramics, while slightly smaller (40 nm) for the “W2 ordered” ceramic.

4.4.2 Dielectric properties

The dielectric constant of these ceramics as a function of temperature was measured at 100Hz, 1kHz, 10kHz, and 100kHz. As shown in Fig. 4, all “disordered” and “ordered” samples exhibit a broad dielectric constant peak with strong frequency dispersion, indicating that the relaxor ferroelectric behavior is preserved, even in samples with long range cation order. The dielectric loss is relatively low and comparable to each other. The four plots in Fig. 4 were presented with the same scale on abscissa and ordinate, respectively, for direct visual comparison. It is evident that doping with La significantly and with W slightly suppresses the dielectric permittivity. In contrast, doping with Sc enhances the permittivity. At the same time, the development of long range cation order in W doped PMN can recover the dielectric property slightly.

The dielectric constant measured at 1kHz was replotted in Fig. 5 for clarity. It is clear that the dielectric constant ($\varepsilon_r$) was severely suppressed and the temperature at dielectric maxima ($T_m$) shifted considerably to a lower temperature in both La3 and “La3 ordered” ceramics. For the W2 ceramics, enhanced B-site cation order leads to a significant increase in maximum dielectric constant $\varepsilon_m$ and slight shift of $T_m$ to higher temperatures. In contrast, little change in dielectric constant and $T_m$ was observed when compared the Sc3 with the
“Sc3 ordered” ceramic. The dielectric properties are listed in Table 1 for complete comparison.

The diffuse phase transition in these relaxor ferroelectric oxides is further quantitatively characterized by evaluating the diffuseness parameter $\delta$ according to the following equation in the temperature range above $T_m$ where $\varepsilon_m < 1.5 \varepsilon_r^{2.20}$

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

(1)

By fitting the experimental data measured at 1kHz to this equation, the diffuseness parameter can be determined. The results are also listed in Table 1. It is evident that Sc-doping does not change $\delta$ much, while La- and W-doping increases the parameter significantly. For both Sc- and W-doping, the “ordered” ceramic shows a smaller diffuseness parameter when compared to the “disordered” ceramic with the same composition.

### 4.4.3 Thermal depolarization behavior

PMN-based relaxor ferroelectrics can be stabilized in several ferroelectric states under different temperature/electric field conditions.\textsuperscript{4-11} One of the most important parameters that delineate these states is the thermal depolarization temperature $T_{C0}$ under the “zero-field-heating after field-cooling” condition, which marks a real phase transition from the induced ferroelectric phase to the ergodic relaxor phase. $T_{C0}$ has been considered as an intrinsic property of relaxor ferroelectric materials since it is independent from the applied field strength during the “field-cooling”. In the current study, $T_{C0}$ was measured by monitoring the thermal depolarization current after the sample was cooled down to low temperatures under 10 kV/cm. As shown in Fig. 6, very weak and broad depolarization current peaks were recorded for La- and W-doped ceramics. In contrast, strong and sharp peaks were detected in Sc-doped ceramics. $T_{C0}$ is read from Fig. 6 as the temperature at the current peaks and is also listed in Table 1.
The difference between $T_m$ and $T_{C0}$ of a ferroelectric material is suggested to be indicative of the degree of dielectric relaxation.\textsuperscript{17} For a relaxor ferroelectric material, $T_{C0}$ is much lower than $T_m$. While for a normal ferroelectric material, these two temperatures converge into a single temperature, the Curie point. The measured difference of $T_m$ and $T_{C0}$ in all the ceramics is listed in the last column of Table 1. It is evident that Sc-doping reduced the gap between the two temperatures, while La- and W-doping widens the temperature gap. In other words, compared with pure PMN, Sc-doping slightly suppresses the dielectric relaxation while La- and W-doping enhances the relaxation. However, for the ceramics with same compositions, enhanced cation order seems have no obvious impact on the temperature gap.

The electric field-induced relaxor to normal ferroelectric phase transition was further characterized by the polarization hysteresis measurement at low temperatures. The measurements recorded well-defined hysteresis loops at temperatures below $T_m$ for all the compositions, the results of ordered samples are shown in Fig. 7. The remnant polarization $P_r$ and the coercive field $E_c$ were read from the hysteresis loops and are plotted as a function of temperature in Fig. 8. The square hysteresis loops and the large $P_r$ values confirm the formation of a normal ferroelectric phase under electric fields below the temperature $T_{C0}$. As shown in Fig. 8(a), in both Sc and W doped PMN ceramics, the cation ordered samples have relatively larger $P_r$ than their disordered counterparts especially at low temperature range. The coercive field $E_c$ has been considered as the critical field for the relaxor-to-ferroelectric phase transition.\textsuperscript{17} Fig. 8(b) indicates that for all of the ceramics, the critical field needed for the phase transition increases dramatically with decreasing temperature. It should be also pointed out that the electric field-induced relaxor to normal ferroelectric phase transition persists in the long range cation ordered ceramics.
4.5 Discussion

4.5.1 Cation order mechanism

As evidenced by x-ray diffraction as well as dark field imaging shown in Figs. 2 and 3, long range B-site cation order was successfully developed in PMN polycrystalline ceramics with a dopant concentration as low as 2 or 3 at.%. However, for all of the fast cooled ceramics, no obvious B-cation ordering enhancement was detected, indicating that chemical modification alone is not capable of producing long range cation order. In other words, the enhanced B-site cation order observed in slow cooled samples was resulted from combined chemical modification and the slow cooling procedure.

Although all the slow cooled ceramics show enhanced cation ordering, the mechanism for causing the enhancement is different. La substitutes Pb at the A site as a donor dopant. The smaller size of the La$^{3+}$ cation (1.36Å vs. 1.50Å of Pb$^{2+}$) makes the unit cell more compact. In addition, introducing La$^{3+}$ increases the molar fraction of the larger Mg$^{2+}$ cation on the B-site. Consequently, the size difference between B' and B''-sublattice increases and the size and charge mismatch at B'-sublattice are reduced. These two factors are believed to be the primary causes for the enhanced cation order in La doped PMN.

Sc substitutes Mg and Nb on the B'-sublattice, and B''-sublattice is solely occupied by smaller Nb. The introduction of larger Sc$^{3+}$ cations (0.745Å vs. 0.72Å of Mg$^{2+}$ and 0.64Å of Nb$^{5+}$) increases the size difference between B' and B''-sublattice, at the same time, the size and charge mismatch at B'-sublattice are reduced. All these conditions favor the long range B-site cation order.

W substitutes Nb on the B''-sublattice and increases both the charge difference and the size difference (0.60Å vs. 0.64Å of Nb$^{5+}$) between the two B-site sublattices. In addition, the mismatch of cations on the B' sublattice is reduced. These factors are believed to be responsible for the development of long range cation order.
4.5.2 Dielectric behavior

As shown in Figs. 5 and 6, extended thermal treatment at elevated temperatures leads to noticeable changes in dielectric properties from the disordered ceramics with the same chemical composition. It should be pointed out that those slow cooled ceramics have a different grain size when compared with their counterparts. Previous investigations in PMN suggested that the grain size has negligible effects on dielectric properties.\textsuperscript{24,25} Therefore, it is plausible that the observed changes in dielectric behavior are originated from the development of cation order.

La\textsuperscript{3} can be considered as a solid solution between Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} and La(Mg\textsubscript{2/3}Nb\textsubscript{1/3})O\textsubscript{3}. La(Mg\textsubscript{2/3}Nb\textsubscript{1/3})O\textsubscript{3}, which holds a rhombohedral perovskite structure with complete 1:1 B-site cation order, is a non-ferroelectric material with a low dielectric constant about 27.\textsuperscript{26} The smaller La\textsuperscript{3+} leads to a more compact unit cell which in turn leads to a higher resistance for the shuffling of the ferroelectric active Nb\textsuperscript{5+} in response to external fields. In addition, the increased Mg/Nb ratio also contributes to the weak ferroelectric response since Mg is ferroelectric inactive.\textsuperscript{22,23} Therefore, the dielectric behavior of La3 is more diffuse and the development of electrical polarization in the induced ferroelectric phase is severely suppressed.

Sc\textsuperscript{3} is a solid solution between PMN and Pb(Sc\textsubscript{1/2}Nb\textsubscript{1/2})O\textsubscript{3}. Long range B-site cation order can be developed in the complex perovskite Pb(Sc\textsubscript{1/2}Nb\textsubscript{1/2})O\textsubscript{3} by extended annealing. The ordered Pb(Sc\textsubscript{1/2}Nb\textsubscript{1/2})O\textsubscript{3} shows a normal ferroelectric behavior with a sharp first order ferroelectric to paraelectric transition occurring at 78\textdegree C.\textsuperscript{27} In Sc3, the introduction of larger Sc\textsuperscript{3+} cations to the B-site sublattice leads to more open space for Nb\textsuperscript{5+} to shuffle in response to external electric fields. In addition, Sc is ferroelectrically more active than Mg.\textsuperscript{23} Therefore, both chemical cation order and electrical dipole order are enhanced in the Sc-doped PMN relaxor ferroelectrics.

Pb(Mg\textsubscript{1/2}W\textsubscript{1/2})O\textsubscript{3} is an antiferroelectric perovskite with a complete Mg:W cation order,
a Curie temperature at 39°C, and a dielectric constant of 150 at room temperature.\textsuperscript{28} W2, therefore, is a solid solution between a relaxor and an antiferroelectric. Not only the cation order, but also the competition between the relaxor and the antiferroelectric polar order dictates the dielectric behavior. The dielectric permittivity is suppressed in the disordered W2 but is improved when cation order is developed. The enhanced permittivity is accompanied with the significant decrease in the diffuseness parameter $\delta$.

In Sc and W doped PMN ceramics, $T_{C_0}$ doesn’t change with the degree of cation order. However, the thermal depolarization current becomes stronger and the diffuseness parameter $\delta$ is reduced in ordered samples. Furthermore, the remanent polarization of the induced ferroelectric phase increases with increasing cation ordering. All these indicate that the ferroelectricity of the Sc and W doped PMN ceramics are strengthened with the development of long range cation order.

### 4.6 Conclusions

Long range B-site cation order has been successfully developed in Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} ceramics with only 2 or 3 at. % of La, Sc or W. These doped ceramics show distinct dielectric properties. In both the La-doped and W-doped PMN ceramics, the dielectric permittivity is significantly suppressed. In contrast, the electrical dipole order is strengthened by Sc-doping.
4.7 Figure list

Fig. 1. SEM micrographs of the fracture surfaces of the La3 ceramics. (a) La3 ordered, (b) Sc3 ordered.

Fig. 2. X-ray diffraction spectra of La3 ordered, Sc3 ordered, W2 ordered and PMN ceramics. The weak peak at ~19° is the (½ ½ ½) superlattice peak.

Fig. 3. TEM dark field images formed with the (½ ½ ½) superlattice spot in the <110>-zone axis electron diffraction pattern. (a) La3 ordered, (b) Sc3 ordered, (c) W2 ordered.

Fig. 4. Dielectric properties as a function of temperature measured at 100Hz, 1kHz, 10kHz, and 100kHz. (a) PMN, (b) La3 and La3 ordered, (c) Sc3 and Sc3 ordered, (d) W2 and W2 ordered.

Fig. 5. Dielectric constant $\varepsilon_r$ vs. temperature relationship at 1 kHz in all the prepared ceramics.

Fig. 6. Thermal depolarization current measurement under zero-field heating of the ceramics after field-cooling at 10kV/cm.

Fig. 7. Polarization vs. electric field curves measured at 4 Hz at different temperatures. (a) La3 ordered, (b) Sc3 ordered, (c) W2 ordered.

Fig. 8. Ferroelectric properties of all the ceramics measured from the P~E hysteresis loops. (a) Remanent polarization $P_r$, and (b) coercive field $E_c$. 
Fig. 1. SEM micrographs of the fracture surfaces of the La₃ ceramics. (a) La₃ disordered, (b) La₃ ordered.
Fig. 2. X-ray diffraction spectra of La3 ordered, Sc3 ordered, W2 ordered and PMN ceramics. The weak peak at ~19° is the ($\frac{1}{2} \frac{1}{2} \frac{1}{2}$) superlattice peak.
Fig. 3. TEM dark field images formed with the (½ ½ ½) superlattice spot in the <110>-zone axis electron diffraction pattern. (a) La3 ordered, (b) Sc3 ordered, (c) W2 ordered.
Fig. 4. Dielectric properties as a function of temperature measured at 100Hz, 1kHz, 10kHz, and 100kHz. (a) PMN, (b) La3 and La3 ordered.
Fig. 4. Dielectric properties as a function of temperature measured at 100Hz, 1kHz, 10kHz, and 100kHz. (c) Sc3 and Sc3 ordered, (d) W2 and W2 ordered.
Fig. 5. Dielectric constant $\varepsilon_r$ vs. temperature relationship at 1 kHz in all the prepared ceramics.
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Fig. 7. Polarization vs. electric field curves measured at 4 Hz at different temperatures. (a) La3 ordered, (b) Sc3 ordered, (c) W2 ordered.
Fig. 8. Ferroelectric properties of all the ceramics measured from the P~E hysteresis loops.

(a) Remanent polarization $P_r$, and (b) coercive field $E_c$. 
Table I. The structure and properties of La, Sc and W-doped PMN ceramics.

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<th>Ceramic</th>
<th>Density</th>
<th>Lattice parameter (Å)</th>
<th>Grain size (µm)</th>
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<th>$T_{C0}$ (°C)</th>
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<td>-18</td>
<td>45.1</td>
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5. Zr-modified Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) with Long Range Cation Order


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5.1 Abstract

The 1:1 structural order and B-site cation order in Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) ceramics was significantly enhanced by Zr\(^{4+}\) substituting Nb\(^{5+}\) according to the chemical formula Pb(Mg\(_{1/3}\)Zr\(_{2x/3}\)Nb\(_{2(1-x)/3}\))O\(_3-x/3\). The enhanced structural and cation order was revealed by both x-ray diffraction and transmission electron microscopy. The increased charge difference and the introduced oxygen vacancies were suggested to account for the observed long range cation order. Typical relaxor ferroelectric behavior was preserved even in the ceramics with a high degree of cation order.

*Keywords*: lead magnesium niobate, cation order, Zr-doping, oxygen vacancy

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5.2 Introduction

Lead magnesium niobate Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} (PMN) has been extensively investigated due to its unique relaxor ferroelectric behavior\textsuperscript{1,2}. The ferroelectric domains in PMN manifest themselves as polar nanoregions, which nucleate at the Burns temperature $T_B \approx 650K$.\textsuperscript{3} Upon cooling, the polar nanoregions begin to grow, reaching about 7nm at 10K, with the most significant growth taking place around the intrinsic Curie temperature $T_{C0} = 213K$.\textsuperscript{4} The structure of the polar regions is slightly distorted along the $<111>$ direction, yet the long-range structure preserves cubic symmetry without any phase transition down to liquid He temperature. The polar axis of these nanodomains is randomly fluctuating among the eight equivalent directions.\textsuperscript{3} The polar nanoregions can grow into micrometer-sized ferroelectric domains under external electric fields during cooling, which corresponds to a first order relaxor to normal ferroelectric phase transition.\textsuperscript{5-7}

It is believed that the relaxor ferroelectric behavior of PMN is associated with the nanometer scale 1:1 B-site cation order. In the ordered domains, every other $\{111\}$ plane of the B-site lattice is solely occupied by Nb\textsuperscript{5+} cations (referred to as the B\textsuperscript{″}-sublattice in literature), the other $\{111\}$ plane (referred to as the B\textsuperscript{′}-sublattice) is randomly occupied by Mg\textsuperscript{2+} and the rest Nb\textsuperscript{5+} cations. This “random site model”\textsuperscript{8} keeps the composition the same and preserves the charge neutrality between the ordered and disordered regions. The cation ordered domains, ranging from 2 to 5 nm in size, are embedded in the disordered matrix and do not grow upon thermal treatment. It was suggested that the growth of the cation ordered domains is constrained by the slow kinetics.\textsuperscript{9}

However, the thermally stable nanometer-scale cation order in PMN can be significantly enhanced via chemical modification with La\textsuperscript{3+}, Sc\textsuperscript{3+} or W\textsuperscript{6+}\textsuperscript{10-13}. The development of long range cation order in these modified PMN ceramics has been attributed to (1) the increased size/charge difference between cations on the B\textsuperscript{′}- and the B\textsuperscript{″}-sublattices,
and (2) the reduced mismatch in the charge/size of the cations on the random B′-sublattice. Large size tetravalent cation Zr\(^{4+}\) has also been incorporated into PMN by forming solid solutions with PbZrO\(_3\) (PZ) in order to coarsen the cation ordered domains.\(^{10}\) However, both slow cooling from high temperatures and thermal annealing at a fixed temperature in the range of 900°–1325°C failed to produce large cation ordered domains in a series of compositions in the (1-x)PMN–xPZ solid solution system.\(^{10}\) It should be noted that in the closely related (1-x)Pb(Mg\(_{1/3}\)Ta\(_{2/3}\))O\(_3\)–xPbZrO\(_3\) solid solution system, enhanced cation order has been confirmed.\(^8\)

In the (1-x)PMN–xPZ solid solution, Zr\(^{4+}\) presumably substitutes both Mg\(^{2+}\) and Nb\(^{5+}\). The long range 1:1 cation order is absent due to the ineffectiveness of this substitution in extending the stability range of the ordered phase to higher temperatures where extensive B-site cation diffusion is possible.\(^8\)–\(^{10}\) In the present work, we still use Zr\(^{4+}\) to modify PMN, but with a different scheme, to promote the 1:1 B-site cation order. Our ceramics were prepared according to the chemical formula Pb(Mg\(_{1/3}\)Zr\(_{x/3}\)Nb\(_{2(1-x)/3}\))O\(_3\)–x/3. Therefore, the compositions were so designed that Zr\(^{4+}\) only replaces Nb\(^{5+}\), but not Mg\(^{2+}\). To preserve charge neutrality, oxygen vacancies are expected to be introduced according to

\[
2\text{ZrO}_2 \rightarrow 2\text{Zr}_{\text{Nb}}^{\prime} + 4\text{O}_2^- + V_{\text{O}}^{**} \quad (1)
\]

The rational for following this new modification scheme includes: (1) The introduced oxygen vacancies may facilitate the diffusion of B-site cations, assisting the development of long range cation order. (2) Zr\(^{4+}\) (0.72Å) has an identical size as Mg\(^{2+}\) (0.72Å) on the B-site lattice.\(^{14}\) Therefore, it is anticipated that Zr\(^{4+}\) occupies the B′-sublattice with Mg\(^{2+}\), replacing only the Nb\(^{5+}\) (0.64Å) cations on this sublattice. As a consequence, the mismatch in the charge/size of the cations on the random B′-sublattice (Mg\(^{2+}\), Zr\(^{4+}\), Nb\(^{5+}\)) is reduced, the charge/size difference between the B′-cations and the B′′-cations (Nb\(^{5+}\)) is increased. These factors have been known to stabilize the ordered phase.\(^{15,16}\) (3) Reducing the fraction of Nb\(^{5+}\)
by Zr\textsuperscript{4+}-substitution can suppress the tendency of pyrochlore phase formation during processing.\textsuperscript{17} (4) PbZrO\textsubscript{3} is a typical antiferroelectric perovskite. The competition between the antiferroelectric dipole order and the nanoscale ferroelectric dipole order is of fundamental significance.\textsuperscript{18,19}

5.3 Experimental Procedure

Polycrystalline ceramic samples were synthesized using the columbite method\textsuperscript{17} according to the nominal chemical formula Pb(Mg\textsubscript{1/3}Zr\textsubscript{2/3}xNb\textsubscript{2(1-x)/3})O\textsubscript{3-x/3}. Compositions with a series of $x$ (0.03, 0.06, 0.09, 0.15, and 0.25) were prepared and referred to as OZ3, OZ6, OZ9, OZ15 and OZ25, respectively. OZ25 is a unique composition since the nominal chemical formula becomes Pb[(Mg\textsubscript{1/3}Zr\textsubscript{1/6})Nb\textsubscript{1/2}]O\textsubscript{2.92}, where the Nb\textsuperscript{5+} on the B’-sublattice is expected to be completely substituted by Zr\textsuperscript{4+} and the molar ratio of the larger (Mg\textsuperscript{2+} and Zr\textsuperscript{4+}) to smaller (Nb\textsuperscript{5+}) B-site cations reaches 1:1.

High purity (>99.9 wt.%) oxide powders of PbO, MgO, Nb\textsubscript{2}O\textsubscript{5} and ZrO\textsubscript{2} were used as the starting materials. The B-site oxides were baked prior to batching to ensure precise stoichiometry. These oxide powders were mixed and manually ground with agate mortar and pestle with ethanol for 2 hours in order to minimize contamination from mill media. The mixed B-site oxide powders were calcined at 1100°C for 4 hours in a platinum crucible. The calcined powders were then mixed with PbO powder (with 1 at.% excess), manually ground for 2 hours, and calcined in a platinum crucible at 900°C for 4 hours to form phase pure perovskite powders. The perovskite powders, with polyvinyl alcohol binder (2 wt.% aqueous solution) added, were used to form pellets by cold pressing at a uniaxial pressure of 150MPa. The pellets were buried in PMN protective powder, sintered at 1250°C for 3 hours, slowly cooled (5°C/hour) from 1200°C down to 1000°C, held at 900°C for 6 hours, and then cooled down to room temperature. A pellet of pure PMN without addition of Zr\textsuperscript{4+} was also prepared with the same procedure as a reference sample.
After the surface layer was removed, the density of these ceramics was measured by the Archimedes method and the grain size was examined by scanning electron microscopy (SEM). X-ray diffraction tests were performed on sintered pellets to check the phase purity and degree of cation order. The cation ordered domains were also directly imaged with dark field technique in a transmission electron microscope (TEM). Dielectric characterization was carried out with an LCR meter (HP-4284A, Hewlett-Packard, Santa Clara, CA) in conjunction with an environmental chamber (9023, Delta Design, Poway, CA). A heating/cooling rate of 2°C/min was used during the measurements. Electric field induced phase transition was evaluated by the thermal depolarization current with a picoammeter (Model 486, Keithley, Cleveland, OH).

5.4 Results

5.4.1 Crystal structure and chemical order

Density measurement showed that all ceramic samples were dense. The relative density is listed in Table I, all in the range of 94~98%. SEM examination confirmed the high relative density and revealed the grain size of the ceramics. Fig. 1 shows the SEM micrographs of the OZ3 and OZ9 ceramics, from which the grain size is determined to be 14.2μm for OZ3 and 8.5μm for OZ9. The grain size of all ceramics is listed in Table I, where it is evident that it decreases with increasing Zr concentration.

X-ray diffraction experiments indicate a pure perovskite phase for all compositions, as shown in Fig. 2. The spectra can be indexed as a cubic structure and the lattice parameter is listed in Table I. In general, the lattice parameter increases with Zr concentration, indicating that Zr$^{4+}$ was indeed incorporated into the lattice. In addition to the major diffraction peaks, (½ ½ ½)-type superlattice peaks are also seen, as marked in Fig. 2(a). The appearance of these superlattice peaks is an indication of the presence of long range 1:1
B-site cation order.\textsuperscript{8-13} Fig. 2(b) shows the diffraction spectra of the (½ ½ ½) peak ($2\theta \approx 19^\circ$) obtained at a slower scan rate. It is evident that the superlattice peak emerges in OZ6 and gets stronger in OZ9 and OZ15. However, the superlattice peak surprisingly disappears in OZ25, indicating a weakened cation order. Following the common procedure used in literature,\textsuperscript{8} the ordering parameter $\alpha$ is evaluated and listed in Table I, assuming that all Zr\textsuperscript{4+} occupies the B’-sublattice in ceramics with complete cation order. The results suggest that long range 1:1 B-site cation order can be developed in Zr-modified PMN, in contrast to previous studies.\textsuperscript{10} It appears that introduced oxygen vacancies have assisted the diffusion and facilitated the development of chemical order.

The enhanced cation order is further confirmed by TEM analysis, as shown in Fig. 3. These dark field micrographs were formed with the (½ ½ ½) superlattice spot in the <110>-zone axis electron diffraction pattern. The average cation ordered domain size is estimated to be 6nm for OZ6, 40nm for OZ9, 100nm for OZ15, and 6nm for OZ25. The TEM results are consistent with the x-ray diffraction experiments (Fig. 2 (b)). The chemical order is significantly enhanced by Zr$^{4+}$ incorporation up to OZ15 (10 at.% occupancy of Zr$^{4+}$ on B-site). Further increase in the content of Zr$^{4+}$ is actually detrimental to the development of the cation order. The absence of long range chemical order in OZ25 will be discussed in Section IV.

5.4.2 Dielectric properties

The dielectric constant, $\varepsilon_r$, of these ceramics as a function of temperature was measured at 100Hz, 1kHz, 10kHz, and 100kHz. The dielectric constant maxima, $\varepsilon_m$, at 1kHz and the temperature at the maxima, $T_m$, for all compositions are summarized in Table I. Fig. 4 presents the dielectric constant and loss tangent plots for the OZ6, OZ9, OZ15, and OZ25 ceramics, with the same scale on abscissa and ordinate for direct visual comparison. It is evident that all samples exhibit a broad dielectric constant peak with strong frequency
dispersion, indicating that the relaxor ferroelectric behavior is preserved even in samples with a long range cation order. The dielectric loss is relatively low and comparable to each other. With increasing Zr doping concentration, while \( \varepsilon_m \) fluctuates slightly, \( T_m \) consistently shifts to higher temperatures. This is likely due to the high Curie temperature of PbZrO\(_3\).

The diffuse phase transition in these relaxor ferroelectric oxides is further quantitatively evaluated with the diffuseness parameter \( \delta \) determined by fitting the data (1kHz) to the following equation in the temperature range above \( T_m \) where \( \varepsilon_m < 1.5 \varepsilon_r \) \(^{1,20}\):

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

The results are also listed in Table I. Surprisingly, a high diffuseness parameter \( \delta \) is found in ceramics with a high degree of cation order. This trend is valid even in the ceramic OZ25, where one sixth of the B-site is occupied by Zr\(^{4+}\) and long range cation order is absent.

5.4.3 Electric field-induced phase transition

PMN-based relaxor ferroelectrics can be stabilized in several ferroelectric states under different temperature/electric field conditions.\(^{5-7}\) One of the most important parameters that delineates these states is the thermal depolarization temperature \( T_{C0} \) under the “zero-field-heating after field-cooling” condition, which marks a real phase transition from the induced ferroelectric phase to the ergodic relaxor phase. \( T_{C0} \) has been considered as an intrinsic property of relaxor ferroelectric materials since it is independent from the applied field strength during the field-cooling.\(^{6}\) In the current study, \( T_{C0} \) is measured by monitoring the thermal depolarization current after the sample was cooled down to low temperatures under 10 kV/cm. The results are shown in Fig. 5, where sharp depolarization current peaks were recorded for pure PMN and OZ3 but broader peaks were seen for OZ6, OZ9, OZ15, and OZ25. This indicates that the induced ferroelectric phase transforms into the ergodic
relaxor phase within a very narrow temperature range (~1°C) for pure PMN and OZ3 while a wider range (~6°C) for others. $T_{C0}$ is read from Fig. 5 as the temperature at the current peaks and is also listed in Table I. Similar to the temperature $T_m$, $T_{C0}$ consistently shifts to higher temperatures with increasing Zr doping concentration.

The integration of the depolarization current curve with respect to time is a measure of the macroscopic polarization preserved in the sample during the zero-field-heating process. Such an integration process leads to the polarization vs. temperature curves shown in Fig. 6. Although different depolarization curves are observed, the macroscopic polarization developed during the field-cooling process is in the range of 27~37 μC/cm². The development of macroscopic polarization is a manifestation of the electric field-induced relaxor to normal ferroelectric phase transition.

The difference between $T_m$ and $T_{C0}$ of a relaxor ferroelectric material was suggested to be indicative of the degree of long range polar order. For a relaxor ferroelectric material where the polar order is short range, $T_{C0}$ is usually much lower than $T_m$. While for a normal ferroelectric material where a long range polar order is present, these two temperatures converge into the Curie point. The last column in Table I lists the difference between $T_m$ and $T_{C0}$ in all compositions. It is obvious that Zr doping reduces the gap between the two characteristic temperatures. This seems to suggest that Zr-modification enhances the long range polar order, irrespective to the cation order.

**5.5 Discussion**

**5.5.1 The cation order**

As evidenced by both x-ray diffraction and TEM analysis, long range 1:1 B-site cation order can be developed in Zr-modified PMN polycrystalline ceramics. The apparent difference between our Pb(Mg$_{1/3}$Zr$_{2/3}$)O$_3$ system and the previous (1-x)PMN–xPZ
system\textsuperscript{10} is the oxygen vacancy resulted from the selective substitution of Nb\textsuperscript{5+} with Zr\textsuperscript{4+}. The presence of long range cation order in Pb(Mg\textsubscript{1/3}Zr\textsubscript{2/3}Nb\textsubscript{2(1-x)/3})O\textsubscript{3-x/3} but not in (1-x)PMN–xPZ suggests that the oxygen vacancy has played a critical role assisting B-site cation diffusion. The ordering mechanism is proposed as follows. Considering the size of the three B-site cations,\textsuperscript{14} Mg\textsuperscript{2+} 0.72Å, Zr\textsuperscript{4+} 0.72Å, and Nb\textsuperscript{5+} 0.64Å, Zr\textsuperscript{4+} is expected to share the B′-sublattice with Mg\textsuperscript{2+} and Nb\textsuperscript{5+}, while the B″-sublattice is solely occupied by Nb\textsuperscript{5+}. The compound Pb(Mg\textsubscript{1/3}Zr\textsubscript{2/3}Nb\textsubscript{2(1-x)/3})O\textsubscript{3-x/3} can then be expressed as Pb[(Mg\textsubscript{2/3}Zr\textsubscript{4/3}Nb\textsubscript{(1-4x)/3})\textsubscript{1/2}(Nb)\textsubscript{1/2}]O\textsubscript{3-x/3} (0.0≤x≤0.25) to reflect the 1:1 B-site cation order. When x=0.0, the expression becomes Pb[(Mg\textsubscript{2/3}Nb\textsubscript{1/3})\textsubscript{1/2}(Nb)\textsubscript{1/2}]O\textsubscript{3}, which is the random site model for pure PMN.\textsuperscript{8,9} At x=0.25, the expression becomes Pb[(Mg\textsubscript{2/3}Zr\textsubscript{1/3})\textsubscript{1/2}(Nb)\textsubscript{1/2}]O\textsubscript{2.92}, which is the OZ25 composition in this study where the B′-sublattice is expected to be full with large cations of Mg\textsuperscript{2+} and Zr\textsuperscript{4+} and the B″-sublattice is expected to be full with smaller Nb\textsuperscript{5+}. Following the same arguments, the random site model would be Pb[(Mg(2-2x)/3Zr\textsubscript{2x}Zr\textsubscript{(1-4x)/3})\textsubscript{1/2}(Nb)\textsubscript{1/2}]O\textsubscript{3} (0.0≤x≤0.25) for the (1-x)PMN–xPZ solid solution.

The stability of the 1:1 order in the random site structure depends on (1) the average valence difference of cations occupying the B′- and the B″-sublattices, (2) the average size difference of cations occupying the two sublattices, and (3) the mismatch in the size and charge of the cations occupying the random B′-sublattice.\textsuperscript{15,16} Now we compare these three factors between our Pb(Mg\textsubscript{1/3}Zr\textsubscript{2x}Nb\textsubscript{2(1-x)/3})O\textsubscript{3-x/3} system and the previous (1-x)PMN–xPZ system. For (1-x)PMN–xPZ, the charge difference between the B′- and the B″-sublattices does not change with x and remains +2 for x up to 0.25. For our OZ series, the charge difference is

\[ 5 - \left( 2 \times \frac{2}{3} + 4 \times \frac{4x}{3} + 5 \times \frac{1-4x}{3} \right) = 2 + \frac{4x}{3} \]  

which increases with x and reaches +2.33 in OZ25. For the size difference between B′ and B″, it is increased to the same degree with composition x in both systems because of the
identical size of Mg\(^{2+}\) and Zr\(^{4+}\). In terms of the charge/size mismatch on the random B'-sublattice, it is reduced in a similar way with \(x\) in both systems. The size mismatch is zero at \(x=0.25\) for both systems. Therefore, the larger charge difference is the key factor to account for the presence of the 1:1 cation order in \(\text{Pb(Mg}_{1/3}\text{Zr}_{2x/3}\text{Nb}_{2(1-x)/3})\text{O}_{3-x/3}\). It is believed that the increased charge difference expands the thermodynamically stable region of the ordered phase in our OZ system to higher temperatures where significant B-site cation diffusion can occur. At the same time, the introduced oxygen vacancy further facilitates such diffusion process, leading to the development of long range 1:1 order.

The above arguments predict a strong 1:1 cation order in OZ25 where the differences in size and charge between B'-cations and B''-cations reach maximum and the size mismatch on B'-site is zero. However, the diminishing cation order in OZ25 shown in Fig. 2 and 3 indicates that additional factors also play a role here. We believe that the introduced oxygen vacancy is one of the significant “additional factors”. As stated in the Introduction section, the purpose of introducing oxygen vacancies is to facilitate the diffusion of B-site cations. It should be noted that the perovskite structure of \(\text{Pb(Mg}_{1/3}\text{Zr}_{2x/3}\text{Nb}_{2(1-x)/3})\text{O}_{3-x/3}\) may be able to accommodate only a limited number of oxygen vacancies. Both TEM and SEM examination of these ceramics indicated that MgO particles are found in OZ25 (Fig. 7), but not in other compositions. These MgO particles in OZ25 were not picked up by x-ray diffraction (Fig. 2). It appears that the concentration of oxygen vacancy in OZ25 is too high to preserve the perovskite structure. As a result, Mg\(^{2+}\) is pushed out of the lattice, forming MgO particles. This implies that Zr\(^{4+}\) not only replaces the Nb\(^{5+}\), but also the Mg\(^{2+}\) on the B'-sublattice in OZ25. When this happens, the differences in size and charge between B'-cations and B''-cations in OZ25 are much less than expected, leading to a much weaker chemical order.

The oxygen vacancy in the OZ series deserves further consideration. Oxygen in perovskite forms an oxygen octahedron network. The B-site cations (Mg\(^{2+}\), Zr\(^{4+}\), Nb\(^{5+}\)) are sitting in the center of oxygen octahedra. When an oxygen vacancy is introduced, the
coordination number of the two neighboring octahedral cations will be reduced from 6 to 5. Among Mg$^{2+}$, Zr$^{4+}$, and Nb$^{5+}$, only Nb$^{5+}$ is stable with lower coordination. So we suggest that the oxygen vacancies in our OZ system are associated with Nb$^{5+}$ cations. However, in the ordered structure the association of an oxygen vacancy with a Nb$^{5+}$ cation on the B''-sublattice must also reduce the coordination number of the neighboring B' cation. If the neighboring B' cation is Mg$^{2+}$ or Zr$^{4+}$, the stability of the ordered structure will be severely reduced. Therefore, a stable 1:1 order requires that each and every oxygen vacancy form the Nb$^{5+}$(B')-$V_0$-Nb$^{5+}$(B'') configuration. From the random site model of the OZ system, Pb[(Mg$_{2/3}$Zr$_{4/3}$Nb$_{(1-4x)/3}$)$_{1/2}$(Nb)$_{1/2}$]O$_3$, the amount of oxygen vacancy is $x/3$, while the amount of Nb$^{5+}$ on the B'-sublattice is $(1-4x)/3$ ($0 \leq x \leq 0.25$). These two quantities are plotted in Fig. 8 as a function of composition $x$. It is evident that the amount of oxygen vacancies equals to the amount of the Nb$^{5+}$ cations on the B'-sublattice when $x=0.20$. Therefore, for $x \leq 0.2$ it is possible for every oxygen vacancy to be coordinated by one Nb$^{5+}$ cation on the B'-sublattice and one Nb$^{5+}$ cation on the B''-sublattice. But for higher values of $x$, the amount of oxygen vacancy exceeds the amount of Nb$^{5+}$ on B'. At $x=0.25$, there is no Nb$^{5+}$ on the B'-sublattice and the oxygen vacancies can no longer be accommodated by the 1:1 ordered perovskite structure. This resulted in the loss of the 1:1 order and the presence of second phase MgO in OZ25. To further verify this hypothesis, a new composition of OZ20 was prepared and examined by x-ray diffraction. The OZ20 ceramic is phase pure perovskite with a strong 1:1 cation order. The ordering parameter $\alpha$ is calculated to be 0.6. The ordering parameter $\alpha$ for all the OZ ceramics is plotted in Fig. 8. Obviously, the 1:1 order is lost quite dramatically right after $x=0.20$. The complex balance among these conditions makes OZ15, the ceramic with an intermediate amount of Zr$^{4+}$, the highly ordered composition.

Furthermore, the stable Nb$^{5+}$(B')-$V_0$-Nb$^{5+}$(B'') configuration elegantly explains the loss tangent data shown in Fig. 4. Since all oxygen vacancies are fixed with the Nb$^{5+}$(B')-Nb$^{5+}$(B'') pairs, they would not contribute to the dielectric loss. As a consequence,
the loss tangent does not increase significantly with oxygen vacancies as Zr content increases.

The suggested Nb$^{5+}$-V$^{O^-}$-Nb$^{5+}$ model can be further extended to disordered Pb(Mg$_{1/3}$Zr$_{2/3}$)O$_3$-$x$ compounds where Mg$^{2+}$, Zr$^{4+}$, and Nb$^{5+}$ randomly occupy the B-site lattice (there is no B’ and B” anymore). If on average, each oxygen vacancy needs two Nb$^{5+}$ cations to stabilize, the composition of $x=0.50$ would be a unique composition where the amount of Nb$^{5+}$ (1/3) is twice the amount of oxygen vacancy (1/6). To be conservative, we prepared another new composition OZ45 with a slightly lower composition $x=0.45$. Three pellets were sintered at 1250°C for 3 hours but cooled with different rates. The first pellet was slowly cooled at 5°C/hour, the second pellet was cooled at ~500°C/hour (furnace cool), and the third one was quenched in air right after sintering. As expected, x-ray diffraction revealed the presence of MgO second phase (Fig. 9). It is interesting to notice that the MgO peak intensity gets weaker as the cooling rate increases, indicating that more oxygen vacancies can be accommodated in a more disordered structure. The destabilized perovskite structure even in OZ45 (with a lower amount of oxygen vacancy than OZ50) suggests that small clusters of Nb$^{5+}$ (embryos for the 1:1 cation order) may be present in these disordered pellets. The Nb$^{5+}$-V$^{O^-}$-Nb$^{5+}$ configuration for a stable perovskite OZ45 or OZ50 requires discrete and isolated Nb$^{5+}$-Nb$^{5+}$ pairs.

It should be noted that the ceramic specimens in this study have been exposed to high temperatures ($\geq$900°C) for a prolonged period (~50 hours). Even though precautions (1at.% excess PbO, plenty protective powder, double crucible configuration, etc.) were taken during processing, lead evaporation loss may still be a concern. Therefore, lead loss could be another “additional factor” influencing cation order in these ceramics. Since the surface of the ceramic presumably experiences more severe lead loss than the center during sintering, the thickness variation of lattice parameter, ordering parameter, and phase purity of OZ9 and OZ15 has been monitored with x-ray diffraction. The original thickness of both sintered
pellets was 1.6mm and the surface layer was successively removed by mechanical grinding. The results are listed in Table II. For OZ15, 100% perovskite phase is seen from the surface to the center while for OZ9, slight amount of pyrochlore phase was observed on the surface. This confirms that higher Zr content inhibits the pyrochlore structure. More interesting results in Table II are the change in the lattice parameter and the ordering parameter along the pellet thickness. The lattice parameter increases slightly from the surface to the center, supporting the argument that the lead evaporation loss is more severe at the surface. The ordering parameter also increases from the surface to the center, indicating that lead loss is detrimental to the development of long range B-site cation order and any contribution of lead loss to the strong cation order observed in OZ15 can be ruled out.

5.5.2 The polar order

Although the grain size of the ceramics varies with thermal treatment and Zr content, it should be pointed out that previous investigations in PMN suggested the grain size has negligible effects on dielectric properties. Therefore, we attribute the changes in the observed dielectric behavior to Zr doping and the development of B site cation order in the following discussion.

The ceramics under investigation are Zr-modified PMN, therefore their crystal structure contains PbZrO$_3$ primary cells. PbZrO$_3$ is a typical anti-ferroelectric material with Curie point around 230°C. Therefore, $T_m$ in the Pb(Mg$_{1/3}$Zr$_{2x/3}$Nb$_{2(1-x)/3})$O$_3$ system shifts to higher temperatures as Zr$^{4+}$ concentration increases (see Table I).

Also evident in Table I are the reducing temperature gap between $T_m$ and $T_{C0}$ and the fluctuating diffuseness parameter $\delta$ as Zr$^{4+}$ content increases. This implies that the degree of long range polar order is enhanced but the diffuseness of the phase transition is not suppressed. The diffuseness parameter $\delta$ appears to be correlated to the cation ordering parameter $\alpha$ in an opposite way: a higher $\delta$ is found in ceramics with a lower $\alpha$. In addition,
the parameter $\delta$ seems to be decoupled from the broadness of the thermal depolarization current peak. This is in sharp contrast to the previously reported $\text{Pb}(\text{B}^{3+}_{1/2}\text{B}^{5+}_{1/2})\text{O}_3$ system, such as $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$ (PST), where the structural order is accompanied by chemical order due to 1:1 stoichiometric ratio of $\text{Sc}^{3+}$ and $\text{Ta}^{5+}$. In PST, the polar order changes from relaxor ferroelectric to normal ferroelectric as the 1:1 order is strengthened. It is suggested that when the ferroelectrically inactive larger cation $\text{Sc}^{3+}$ in $B'$ is next to a ferroelectrically active smaller cation $\text{Ta}^{5+}$ in $B''$, the intermediate oxygen anion shifts towards the active cation and displace the $\text{Pb}^{2+}$ cations towards the $B'$ site along <111>. Thus, the presence of 1:1 stoichiometric chemical order leads to long-range polar order, resulting in normal ferroelectric behavior.

However, in the present $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$-based system, the nonstoichiometric 1:1 structural order is not coupled with the chemical order. The presence of an active cation in the $B'$-sublattice frustrates the long-range dipole order, preserving the relaxor ferroelectric behavior even in 1:1 structurally ordered ceramics. Specifically, there are two primary types of electrical dipoles in $\text{Pb}(\text{Mg}_{1/3}\text{Zr}_{2x/3}\text{Nb}_{2(1-x)/3})\text{O}_{3-x/3}$. The first type is due to the rhombohedral distortion of the unit cell and the displacement of $B$-site cations along the <111> directions. It has been shown previously that incorporating $\text{Zr}^{4+}$ into PMN enhances the rhombohedral distortion in the polar nanoregions and eventually leads to a rhombohedral symmetry with long range dipole order. Therefore, it appears that the reduced temperature gap between $T_m$ and $T_{C0}$ is primarily caused by the enhanced rhombohedral distortion due to $\text{Zr}^{4+}$ incorporation. In other words, the primary contribution to the observed enhanced polar order comes from the first type of electrical dipoles within individual unit cells.

The other type of electrical dipoles forms between adjacent unit cells containing different $B$-cations and/or oxygen vacancies. Since the A-site cation is $\text{Pb}^{2+}$, a 4+ cation is needed at the $B$-site to balance the charge within a unit cell of $\text{ABO}_3$. Therefore, each and
every unit cell containing a Mg\(^{2+}\) is a substitutional point defect carrying effective two negative charges. Similarly, each and every unit cell containing a Nb\(^{5+}\) carries effective one positive charge. As revealed by Eq. (1), every two Zr\(^{4+}\) cations require one oxygen vacancy to maintain charge neutrality. All these point defects form the inter-unit-cell level electrical dipoles and these dipoles do not order in a long range even if a long range 1:1 B-site cation order exists. For compositions with 0<x<0.25 in Pb(Mg\(_{1/3}\)Zr\(_{2x/3}\)Nb\(_{2(1-x)/3}\))O\(_{3-x/3}\), the B'-sublattice is randomly occupied by Mg\(^{2+}\), Zr\(^{4+}\), and Nb\(^{5+}\) in cation ordered domains. Clusters of these cations may well be present. We believe the disorder of these inter-unit-cell level dipoles and the associated chemical fluctuation are primarily responsible for the diffuseness of the dielectric phase transition. As for OZ25, since Zr\(^{4+}\) substitutes both Mg\(^{2+}\) and Nb\(^{5+}\) at the B'-sublattice, much less oxygen vacancies than expected are resulted. At the same time, the large amount of Zr\(^{4+}\) enhanced the rhombohedral distortion of the unit cell significantly, which favors a rhombohedral structure with long range dipole order and low diffuseness. The disorder of the inter-unit-cell dipoles is hence overwhelmed by the strong long range order of the first type dipoles, leading to a much reduced diffuseness parameter in OZ25.

5.6 Conclusions

Long range 1:1 structural and cation order can be developed in Pb(Mg\(_{1/3}\)Zr\(_{2x/3}\)Nb\(_{2(1-x)/3}\))O\(_{3-x/3}\) ceramics where Zr\(^{4+}\) is designed to replace Nb\(^{5+}\) only. Compared to the (1-x)PMN-xPZ system, the presence of long range 1:1 order in the Pb(Mg\(_{1/3}\)Zr\(_{2x/3}\)Nb\(_{2(1-x)/3}\))O\(_{3-x/3}\) ceramics is due to the increased charge differences between the B'-cations (Mg\(^{2+}\), Zr\(^{4+}\), Nb\(^{5+}\)) and the B''-cations, resulting in an extended thermodynamically stable region for the ordered phase. The introduced oxygen vacancy has further assisted the B-site cation diffusion, leading to the development of 1:1 cation order.

The oxygen vacancy is believed to be associated with Nb\(^{5+}\)(B')-Nb\(^{5+}\)(B'') pairs,
forming a stable $\text{Nb}^{5+}$-$V_0$-$\text{Nb}^{5+}$ configuration in the ordered structure of the $\text{Pb(Mg}_{1/3}\text{Zr}_{2x/3}\text{Nb}_{2(1-x)/3})\text{O}_{3-x/3}$ ceramics. As a consequence, the amount of the oxygen vacancy (in turn, the amount of the $\text{Zr}^{4+}$ substitution) that can be accommodated in the ordered structure is limited by the availability of $\text{Nb}^{5+}(\text{B}')$-$\text{Nb}^{5+}(\text{B}'')$ pairs.

The dielectric and ferroelectric behavior suggests that long range order of the electrical dipoles due to unit cell rhombohedral distortion is strengthened by incorporating $\text{Zr}^{4+}$. The diffuseness of the dielectric phase transition can be primarily attributed to the disorder of the dipoles formed between adjacent unit cells. The competition between the two types of electrical dipoles results in the complicated dielectric behavior in the $\text{Pb(Mg}_{1/3}\text{Zr}_{2x/3}\text{Nb}_{2(1-x)/3})\text{O}_{3-x/3}$ ceramics. In contrast to other complex perovskites such as $\text{Pb(Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$ where coupled structural and chemical order leads to a normal ferroelectric behavior, the relaxor ferroelectric behavior is preserved in the Zr-modified PMN ceramics with long range 1:1 order due to the chemical randomness on the B’-sublattice.
5.7 Figure list

Fig. 1. SEM micrographs of the fracture surfaces of the OZ3 and OZ9 ceramics. (a) OZ3, (b) OZ9.

Fig. 2. X-ray diffraction spectra of the Pb(Mg\(^{1/3}\)Zr\(^{2/3}\)x\(^{1/3}\)Nb\(^{2(1-x)/3}\)O\(^{3-x/3}\) ceramics. (a) whole pattern to show phase purity, (b) slow scan between 18° and 20° to shown the (½ ½ ½) superlattice peak. Strong 1:1 cation order is revealed by x-ray in the OZ9 and OZ15 ceramics.

Fig. 3. TEM dark field imaging with the (½ ½ ½) superlattice spot in the <110>-zone axis electron diffraction pattern of the Pb(Mg\(^{1/3}\)Zr\(^{2/3}\)x\(^{1/3}\)Nb\(^{2(1-x)/3}\)O\(^{3-x/3}\) ceramics. (a) OZ6, (b) OZ9, (c) OZ15, (d) OZ25.

Fig. 4. Dielectric properties as a function of temperature of the Pb(Mg\(^{1/3}\)Zr\(^{2/3}\)x\(^{1/3}\)Nb\(^{2(1-x)/3}\)O\(^{3-x/3}\) ceramics measured at 100Hz, 1kHz, 10kHz, and 100kHz. (a) OZ6, (b) OZ9, (c) OZ15, (d) OZ25.

Fig. 5. Thermal depolarization current measurement under zero-field heating after field-cooling at 10kV/cm in the Pb(Mg\(^{1/3}\)Zr\(^{2/3}\)x\(^{1/3}\)Nb\(^{2(1-x)/3}\)O\(^{3-x/3}\) ceramics.

Fig. 6. Polarization integrated from the thermal depolarization current as a function of temperature in the Pb(Mg\(^{1/3}\)Zr\(^{2/3}\)x\(^{1/3}\)Nb\(^{2(1-x)/3}\)O\(^{3-x/3}\) ceramics.

Fig. 7. MgO particles observed in the OZ25 ceramic. (a) SEM micrograph of the fracture surface. The area marked by the dark circle is analyzed with an x-ray energy dispersive spectrometer (XEDS). (b) the XEDS data confirm the composition of Mg and O.

Fig. 8. The amount of Nb\(^{5+}\) on the B’-sublattice and oxygen vacancy as a function of composition \(x\) in the (Mg\(^{1/3}\)Zr\(^{2/3}\)x\(^{1/3}\)Nb\(^{2(1-x)/3}\)O\(^{3-x/3}\) ceramics according to the random site model \(\text{Pb}[(\text{Mg}^{2/3}\text{Zr}^{4/3}\text{Nb}^{(1-4x)/3})_{1/2}\text{(Nb)}_{1/2}]\text{O}^{3-x/3}\) (0.0≤\(x\)≤0.25). The measured ordering parameter \(\alpha\) in the ceramics is reduced significantly right after \(x=0.20\).
Fig. 9. The MgO second phase x-ray diffraction peak in the OZ45 ceramic.
Fig. 1. SEM micrographs of the fracture surfaces of the OZ3 and OZ9 ceramics. (a) OZ3, (b) OZ9.
Fig. 2. X-ray diffraction spectra of the Pb(Mg$_{1/3}$Zr$_{2x/3}$Nb$_{2(1-x)/3}$)O$_3$–x/3 ceramics. (a) whole pattern to show phase purity, (b) slow scan between 18° and 20° to shown the (½ ½ ½) superlattice peak. Strong 1:1 cation order is revealed by x-ray in the OZ9 and OZ15 ceramics.
Fig. 3. TEM dark field imaging with the \((\frac{1}{2} \frac{1}{2} \frac{1}{2})\) superlattice spot in the \(<110>\)-zone axis electron diffraction pattern of the \(\text{Pb(Mg}_{1/3}\text{Zr}_{2/3}\text{Nb}_{2(1-x)/3})\text{O}_{3-x/3}\) ceramics. (a) OZ6, (b) OZ9, (c) OZ15, (d) OZ25.
Fig. 4. Dielectric properties as a function of temperature of the Pb(Mg$\frac{1}{3}$Zr$\frac{2}{3}$)O$_3$ ceramics measured at 100Hz, 1kHz, 10kHz, and 100kHz.  (a) OZ6, (b) OZ9, (c) OZ15, (d) OZ25.
Fig. 5. Thermal depolarization current measurement under zero-field heating after field-cooling at 10kV/cm in the Pb(Mg$_{1/3}$Zr$_{2/3}$)O$_3$ ceramics.
Fig. 6. Polarization integrated from the thermal depolarization current as a function of temperature in the Pb(Mg_{1/3}Zr_{2/3}Nb_{2(1-x)/3})O_{3-x/3} ceramics.
Fig. 7. MgO particles observed in the OZ25 ceramic. (a) SEM micrograph of the fracture surface. The area marked by the dark circle is analyzed with an x-ray energy dispersive spectrometer (XEDS). (b) the XEDS data confirm the composition of Mg and O.
Fig. 8. The amount of Nb$^{5+}$ on the B'-sublattice and oxygen vacancy as a function of composition $x$ in the $(\text{Mg}_{1/3}\text{Zr}_{2x/3}\text{Nb}_{2(1-x)/3})\text{O}_{3-x/3}$ ceramics according to the random site model $\text{Pb}[(\text{Mg}_{2/3}\text{Zr}_{4x/3}\text{Nb}_{(1-4x)/3})_{1/2}(\text{Nb})_{1/2}]\text{O}_{3-x/3}$ ($0.0 \leq x \leq 0.25$). The measured ordering parameter $\alpha$ in the ceramics is reduced significantly right after $x=0.20$. 
Fig. 9. The MgO second phase x-ray diffraction peak in the OZ45 ceramic.
Table I. The structure and properties of the Pb(Mg$_{1/3}$Zr$_{2/3}$)O$_3$ ceramics.

<table>
<thead>
<tr>
<th>Ceramic</th>
<th>Relative density</th>
<th>Lattice parameter (Å)</th>
<th>Grain size (m)</th>
<th>Ordering parameter $\alpha$</th>
<th>$\varepsilon_m$ @ 1kHz</th>
<th>$T_m$ @ 1kHz (°C)</th>
<th>$\delta$ (°C)</th>
<th>$T_{C0}$ (°C)</th>
<th>$T_m-T_{C0}$ (°C)</th>
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<td>PMN</td>
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<td>14.3</td>
<td>0</td>
<td>17390</td>
<td>-9</td>
<td>38.6</td>
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<tr>
<td>OZ3</td>
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<td>4.0450</td>
<td>14.2</td>
<td>0</td>
<td>17690</td>
<td>-2</td>
<td>35.6</td>
<td>-55</td>
<td>53</td>
</tr>
<tr>
<td>OZ6</td>
<td>96%</td>
<td>4.0527</td>
<td>9.9</td>
<td>0.2</td>
<td>18900</td>
<td>0</td>
<td>37.8</td>
<td>-52</td>
<td>52</td>
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<tr>
<td>OZ9</td>
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<td>8.5</td>
<td>0.5</td>
<td>16850</td>
<td>0</td>
<td>42.8</td>
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<td>50</td>
</tr>
<tr>
<td>OZ15</td>
<td>98%</td>
<td>4.0575</td>
<td>7.6</td>
<td>0.8</td>
<td>18160</td>
<td>4</td>
<td>42.2</td>
<td>-40</td>
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<td>OZ25</td>
<td>94%</td>
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<td>6.3</td>
<td>0</td>
<td>18900</td>
<td>96</td>
<td>33.8</td>
<td>83</td>
<td>13</td>
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Table II. Thickness variation of crystal structure of the OZ9 and OZ15 ceramics. The thickness of as-sintered pellets is 1.6mm.

<table>
<thead>
<tr>
<th>Ceramic</th>
<th>Distance from surface (mm)</th>
<th>Lattice parameter (Å)</th>
<th>Ordering parameter $\alpha$</th>
<th>Perovskite phase purity</th>
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<td>OZ9</td>
<td>0</td>
<td>4.0478</td>
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<td>OZ15</td>
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<td>4.0561</td>
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<td></td>
<td>0.47</td>
<td>4.0567</td>
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<td></td>
<td>0.82</td>
<td>4.0575</td>
<td>0.82</td>
<td>100%</td>
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</table>
5.8 References


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6. Dielectric and Ferroelectric Properties of (1-\(x\))Pb(Mg\(\frac{1}{3}\)Nb\(\frac{2}{3}\))O\(_3\)–\(x\)PbZrO\(_3\) Ceramics with Cation Order

A paper to be submitted to *Journal of Physics: Condensed Matter*

Xiaohui Zhao and Xiaoli Tan¶

6.1 Abstract

Electrical properties and the B-site cation order were investigated in the (1-x)Pb(Mg\(\frac{1}{3}\)Nb\(\frac{2}{3}\))O\(_3\)–xPbZrO\(_3\) (0 \(\leq\) \(x\) \(\leq\) 0.25) solid solution ceramics. It was found that long range 1:1 B-site cation order can be developed through slow cooling during sintering in the solid solution with compositions around \(x=0.10\). The observed long range cation order is in sharp contrast to previous studies where a disordered structure was invariably resulted in the (1-x)Pb(Mg\(\frac{1}{3}\)Nb\(\frac{2}{3}\))O\(_3\)–xPbZrO\(_3\) solid solution. The ceramics with cation order display dielectric and ferroelectric properties similar to those disordered ceramics reported in literature. The dielectric properties were also compared in detail to our previous Pb(Mg\(\frac{1}{3}\)Zr\(\frac{2}{3}\)Nb\(\frac{1-x}{3}\))O\(_3\)\(-x/3\) ceramics where Zr\(^{4+}\) is designed to substitute Nb\(^{5+}\) only. The results were discussed on the basis of the relationships between cation order and electric dipole order.

*Keywords*: lead magnesium niobate, cation order, lead zirconate, ferroelectric properties

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6.2 Introduction

Due to its unique dielectric and relaxor ferroelectric behavior, lead magnesium niobate Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN) has been extensively investigated for several decades.$^{1,2}$ The ferroelectric domains in PMN manifest themselves as polar nanoregions, which nucleate at the Burns temperature $T_B \approx 650$K.$^3$ While the structure of the polar regions is slightly distorted along the $<111>$ direction, the long-range structure preserves cubic symmetry without any phase transition down to liquid He temperature. The polar axis of these nanodomains is randomly fluctuating among the eight equivalent $<111>$ directions.$^2$ External electric fields can strengthen the dipole order by growing polar nanoregions into micrometer-sized ferroelectric domains within a narrow temperature range, which corresponds to a first order relaxor to normal ferroelectric phase transition.$^{4-6}$

It is believed that the relaxor ferroelectric behavior of PMN has its origin in the nanometer scale 1:1 B-site cation order. According to the widely accepted “random site model”,$^7$ in the cation ordered domains, every other $\{111\}$ plane of the B-site lattice is solely occupied by Nb$^{5+}$ cations (referred to as the B″-sublattice in literature), the other $\{111\}$ plane (referred to as the B′-sublattice) is randomly occupied by Mg$^{2+}$ and the rest Nb$^{5+}$. This model implies that there is no composition difference and charge imbalance between the ordered and disordered regions. The cation ordered domains, around 2 to 5 nm in size, are embedded in the disordered matrix and highly stable against extended thermal annealing. It was suggested that the growth of the cation ordered domains is constrained by the slow kinetics.$^8$

However, the thermally stable nanometer-scale cation order in PMN can be significantly enhanced via chemical modification with La$^{3+}$, Sc$^{3+}$ or W$^{6+}$. $^{9-12}$ Zr$^{4+}$ has also been incorporated into PMN by forming solid solutions with PbZrO$_3$ (PZ) in order to coarsen the cation ordered domains.$^9$ It was reported that, in the (1-$x$)PMN–$x$PZ solid solution system, both slow cooling from high temperatures and thermal annealing at a fixed temperature failed
to produce large cation ordered domains in a series of compositions. Viewing this difficulty, we previously took a different approach to incorporate Zr$^{4+}$ into PMN for long range cation order.$^{13}$ Zr$^{4+}$ was designed to substitute Nb$^{5+}$ only according to the chemical formula $\text{Pb} \left( \frac{\text{Mg}}{3} \frac{\text{Zr}}{3} \frac{\text{Nb}}{3} (1-x) \frac{\text{O}}{3} \right)$ (0$\leq$$x$$\leq$0.25, referred to as the OZ series). As described in detail in our previous publication, long range cation order was successfully developed in the ceramics of the OZ series.$^{13}$ The OZ series composition can actually be viewed as a solid solution of $(1-x)\text{Pb} \left( \frac{\text{Mg}}{3} \frac{\text{Nb}}{3} \right) \text{O}_3$–$x\text{Pb} \left( \frac{\text{Mg}}{3} \frac{\text{Zr}}{3} \right) \text{O}_{8/3}$, where oxygen vacancies need to be introduced to preserve charge neutrality. Therefore, the OZ series is chemically different from the $(1-x)\text{PMN}$–$x\text{PZ}$ system.

The present study was originally designed to confirm the claim in Ref. 9 that long range cation order cannot be developed in the $(1-x)\text{PMN}$–$x\text{PZ}$ system and to demonstrate the need of oxygen vacancies for cation order in the OZ series. Unexpectedly, long range 1:1 B-site cation order was seen in the $(1-x)\text{PMN}$–$x\text{PZ}$ system in the present study. The observed cation order is interpreted in terms of charge/size differences of cations on B$'-$ and B$''$-sublattices.$^{14,15}$ The dielectric and ferroelectric properties of the $(1-x)\text{PMN}$–$x\text{PZ}$ ceramics with long range cation order are compared with ordered OZ series$^{13}$ and disordered $(1-x)\text{PMN}$–$x\text{PZ}$ ceramics.$^{16,17}$

6.3 Experimental Procedure

Following the columbite method,$^{18}$ polycrystalline ceramic samples of $(1-x)\text{Pb} \left( \frac{\text{Mg}}{3} \frac{\text{Nb}}{2} \frac{\text{Zr}}{3} \right) \text{O}_3$–$x\text{PbZrO}_3$ were synthesized. Compositions with $x=0.06$, 0.15, and 0.25 were prepared and hereafter are referred to as PZ6, PZ15 and PZ25, respectively. High purity (>99.9 wt.%) oxide powders of PbO, MgO, Nb$_2$O$_5$ and ZrO$_2$ were used as the starting materials. The B-site oxides were baked prior to batching to ensure precise stoichiometry. These oxide powders were mixed and manually grinded for 2 hours, then calcined at 1100°C for 4 hours in a platinum crucible. The calcined powders were then mixed with PbO powder
(with 1 at.% excess), manually ground for 2 hours, and calcined at 900°C for 4 hours to form phase pure perovskite powders. Pellets were formed by uniaxial pressing with binder. Sintering was carried out at 1250°C for 3 hours followed by slow cooling (3.3°C/hour) from 1200°C down to 1100°C. To minimize the Pb loss during processing, pellets were buried in protective powders and a double crucible configuration was used.

The density of the sintered ceramics was measured with the Archimedes method after the surface layer was removed by mechanical grinding. X-ray diffraction tests were performed on sintered pellets to determine phase purity and degree of cation order. Dielectric characterization was carried out with an LCR meter (HP-4284A, Hewlett-Packard, Santa Clara, CA) in conjunction with an environmental chamber (9023, Delta Design, Poway, CA). A heating/cooling rate of 2°C/min was applied during the measurements. Electric field induced phase transition was evaluated by the thermal depolarization current with a picoammeter (Model 486, Keithley, Cleveland, OH). The polarization hysteresis was measured with a standardized ferroelectric test system (RT-66A, Radiant technologies, Albuquerque, NM).

6.4 Results

6.4.1 Crystal structure and cation order

The relative density of all sintered ceramics, listed in Table I, are in the range of 90~98%. X-ray diffraction experiments indicate a pure perovskite phase for all compositions, as shown in Fig. I(a). The spectra can be indexed as a cubic structure and the lattice parameter is listed in Table I, together with lattice parameters for selected OZ series ceramics. The observed cubic structure and the measured lattice constants agree well with results in literature on
disordered (1-x)PMN-xPZ ceramics.\textsuperscript{16,17,19} In addition to the major diffraction peaks, ($\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$)-type superlattice peaks are also seen, as marked in Fig. 1(a). The appearance of these superlattice peaks is an indication of the presence of long range 1:1 B-site cation order.\textsuperscript{7-13} Fig. 1(b) shows the diffraction spectra of the ($\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$) peak ($2\theta \approx 19^\circ$) obtained at a slower scan rate. The superlattice peak is evident in PZ6 and PZ10 but weak in PZ25. The ordering parameter $\alpha$ is evaluated following the common procedure used in literature\textsuperscript{7} and listed in Table I, assuming that all Zr$^{4+}$ occupies the B$'$-sublattice in ceramics with complete cation order. The results demonstrated that long range 1:1 B-site cation order can be developed in the (1-x)PMN-xPZ solid solution system, in contrast to the results reported in Ref. 9.

6.4.2 Dielectric properties

The dielectric constant, $\varepsilon_r$, and loss tangent, of the PZ6, PZ10, and PZ25 ceramics as a function of temperature was measured at 100Hz, 1kHz, 10kHz, and 100kHz, and are plotted in Fig. 2. The same scale on abscissa and ordinate is used for the plots for direct visual comparison. The dielectric constant maxima, $\varepsilon_m$, at 1kHz and the temperature at the maxima, $T_m$, for these compositions are summarized in Table I. It is evident that all samples exhibit a broad dielectric constant peak with strong frequency dispersion, indicating that the relaxor ferroelectric behavior is preserved even in samples with a long range cation order. The loss tangent is relatively low and comparable to each other. Due to the high curie temperature of PbZrO$_3$, $T_m$ of the (1-x)PMN-xPZ solid solution ceramics shifts to higher temperatures consistently with increasing $x$.

The diffuse phase transition in these relaxor ferroelectric oxides is further quantitatively evaluated with the diffuseness parameter $\delta$ determined by fitting the data (1kHz) to the following equation in the temperature range above $T_m$ where $\varepsilon_m \leq 1.5 \varepsilon_r$:\textsuperscript{120}

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

(1)
The results are also listed in Table I. For the solid solution \((1-x)\)PMN–\(x\)PZ, the diffuseness parameter \(\delta\) first increases, then decreases with composition \(x\), reaching a maximum in PZ6.

**6.4.3 Electric field-induced phase transition**

PMN-based relaxor ferroelectrics can be stabilized in several ferroelectric states under different temperature/electric field conditions.\(^4\,^6\) One of the most important parameters that delineates these states is the thermal depolarization temperature \(T_{C0}\) under the “zero-field-heating after field-cooling” condition, which marks a real phase transition from the induced ferroelectric phase to the ergodic relaxor phase. \(T_{C0}\) has been considered as an intrinsic property of relaxor ferroelectric materials since it is independent from the applied field strength during the field-cooling.\(^5\) In the current study, \(T_{C0}\) is measured by monitoring the thermal depolarization current after the sample was cooled down to low temperatures under 10 kV/cm. The results are shown in Fig. 3, where sharp depolarization current peaks were recorded for all of the samples. \(T_{C0}\) is read from Fig. 3 as the temperature at the current peaks and is also listed in Table I. It is clear that \(T_{C0}\) consistently shifts to higher temperatures with increasing PbZrO\(_3\) content.

The difference between \(T_m\) and \(T_{C0}\) of a relaxor ferroelectric material was suggested to be indicative of the degree of long range polar order.\(^1\)\(^1\) For a normal ferroelectric material where a long range polar order is present, these two temperatures converge into the Curie point. In the last column in Table I the difference between \(T_m\) and \(T_{C0}\) for all compositions is listed. It is obvious that increase in PbZrO\(_3\) content in the solid solution reduces the gap between the two characteristic temperatures, indicating that incorporation of PbZrO\(_3\) enhances the long range polar order.

The electric field-induced relaxor to normal ferroelectric phase transition was further characterized by the polarization hysteresis measurement at temperatures below \(T_m\). The
measurements recorded well-defined hysteresis loops at low temperatures for all three compositions, as shown in Fig. 4. The remnant polarization $P_r$ and the coercive field $E_c$ were read from the hysteresis loops and are plotted as a function of temperature in Fig. 5. The square hysteresis loops and the large $P_r$ values confirm the formation of a normal ferroelectric phase under electric fields below the temperature $T_{C0}$. The coercive field $E_c$ has been considered as the critical field for the relaxor-to-ferroelectric phase transition. Fig. 5(b) indicates that as temperature decreases, the critical field needed for the phase transition increases dramatically. It should be also pointed out that the electric field-induced relaxor to normal ferroelectric phase transition persists in $(1-x)\text{PMN}-x\text{PZ}$ ceramics with long range cation order.

### 6.5 Discussion

#### 6.5.1 The cation order

The results in the present study demonstrated that long range 1:1 B-site cation order can be developed in selected compositions in the $(1-x)\text{PMN}-x\text{PZ}$ solid solution system under proper heat treatment. The observations are in contrast to a previous study\(^9\) where attempts to grow cation ordered domains in $(1-x)\text{PMN}-x\text{PZ}$ were failed. However, neither detailed heat treatment conditions nor specific ceramic compositions were described in Ref. 9. In the following, explanations are offered for the observed long range cation order in $(1-x)\text{PMN}-x\text{PZ}$ (0≤$x$≤0.25) ceramics.

There are three factors that facilitate a long range 1:1 B-site cation order in $\text{A(}_{1/2}\text{B'}_{1/2}\text{B''})_3$ perovskite oxides:\(^{14,15}\) (1) a large difference in the charge of cations occupying the $\text{B'}$- and the $\text{B''}$-sublattices ($\Delta q$), (2) a large difference in the size of cations occupying the two sublattices ($\Delta r$), and (3) a small mismatch in the charge/size of the cations on the random $\text{B'}$-sublattice. The mismatch is evaluated by the standard deviation of charges
(\sigma_q) and sizes (\sigma_r) of cations on the random site.

In the (1-x)PMN–xPZ solid solution system, the B-site cation radii are \(r_{\text{Mg}^{2+}}=0.72\text{Å},\ r_{\text{Nb}^{5+}}=0.64\text{Å},\) and \(r_{\text{Zr}^{4+}}=0.72\text{Å}\). Presumably the 1:1 B-site cation order can be expressed as Pb[(Mg(2-2x)/3Zr2xNb(1-4x)/3)1/2(Nb)1/2]O3 (0.0\(\leq x\leq 0.25\), where the random B′-sublattice is shared by \(\text{Mg}^{2+}\), \(\text{Zr}^{4+}\), and \(\text{Nb}^{5+}\). At \(x=0.25\), the expression becomes Pb[(Mg1/2Zr1/2)1/2(Nb)1/2]O3 where the random B′-sublattice is full with large cations of \(\text{Mg}^{2+}\) and \(\text{Zr}^{4+}\) while the B′-sublattice is solely filled with small cations of \(\text{Nb}^{5+}\). This is the PZ25 composition in this study.

According the random site model Pb[(Mg(2-2x)/3Zr2xNb(1-4x)/3)1/2(Nb)1/2]O3 (0.0\(\leq x\leq 0.25\), the charge difference \(\Delta q\), the size difference \(\Delta r\), and the mismatch on the random B′-sublattice are plotted as a function of composition \(x\) in Fig. 6. The charge difference remains 2e within the composition range while the size difference linearly increases. On the random sites of the B′-sublattice, both the mismatch of charge, \(\sigma_q\), and the mismatch of size, \(\sigma_r\), monotonically decrease with increasing \(x\). Therefore, Fig.6 indicates that long range 1:1 B-site cation order should be facilitated by forming the (1-x)PMN–xPZ solid solution. This is what was observed in this study.

The above arguments predict a strong 1:1 cation order in PZ25 where \(\Delta r\) reaches maximum, \(\sigma_q\) reaches minimum, and \(\sigma_r\) equals to zero. However, only a very weak cation order was seen in PZ25 in this study. To explain this discrepancy, the configurational entropy on the random B′-sublattice needs to be considered. The random distribution of \(\text{Mg}^{2+},\ \text{Zr}^{4+},\) and \(\text{Nb}^{5+}\) on the B′-sublattice introduces a significant configurational entropic contribution to the free energy of the random site structure, which can introduce large changes in the stability of the ordered structure. The complex and delicate balance among these conditions makes PZ10, the ceramic with an intermediate amount of PbZrO3 in the composition range 0\(\leq x\leq 0.25\), the highly ordered composition.
6.5.2 The polar order

Previous investigations in PMN suggested that the grain size has negligible effects on dielectric properties.\textsuperscript{22,23} Therefore, we attribute the features in the observed dielectric behavior to the incorporation of PbZrO\textsubscript{3} and the development of B-site cation order in the following discussion. PbZrO\textsubscript{3} is a typical antiferroelectric oxide with long range dipole order and its Curie point (230°C) is much higher than the \( T_m \) of PMN.\textsuperscript{24} Therefore, \( T_m \) and \( T_{CO} \) in the (1-\( x \))PMN–\( x \)PZ system shift to higher temperatures as composition \( x \) increases (see Table I). It should be noted that \( T_m \) of PZ10 and PZ25 measured in the present study is lower than the reported values of the same composition without cation order in the literature.\textsuperscript{16,17} This suggests that cation order shifts \( T_m \) to lower temperatures, which is consistent with our previous studies on the PMN ceramics with other dopants.\textsuperscript{11,12} It is also evident that the temperature gap between \( T_m \) and \( T_{CO} \) is reduced as PbZrO\textsubscript{3} content increases, implying that the degree of long range polar order is enhanced. It has been shown previously that incorporating Zr\textsuperscript{4+} into PMN enhances the rhombohedral distortion in the polar nanoregions and eventually leads to a rhombohedral symmetry with long range polar order.\textsuperscript{16,17,19} Therefore, it appears that the reduced temperature gap between \( T_m \) and \( T_{CO} \) is primarily caused by the enhanced rhombohedral lattice distortion.

The change in \( \varepsilon_m \) is more dramatic when compared with reported data of disordered (1-\( x \))PMN–\( x \)PZ ceramics in literature.\textsuperscript{16,17} The \( \varepsilon_m \) of PZ10 and PZ25 measured in the present study is about twice as that reported in Ref. 16 and 17 in the same composition without cation order. Therefore, long range 1:1 B-site cation order seems to significantly enhance dielectric permittivity. The persistence of the typical relaxor ferroelectric behavior in PZ6, PZ10, and PZ25 ceramics with long range cation order is believed to be due to the cations on the B’-sublattice.\textsuperscript{15} The random distribution of Mg\textsuperscript{2+}, Zr\textsuperscript{4+}, and Nb\textsuperscript{5+} on the B’-sublattice and the pertinent random local fields randomize the displacements of Pb\textsuperscript{2+} cations and disrupt the long range polar order. As a result, a typical relaxor behavior is still seen even in PZ10, the
ceramic with the strongest 1:1 cation order in this study.

It is worthwhile to compare the dielectric properties of the (1-x)PMN–xPZ ceramics with the (1-x)Pb(Mg_{1/3}Nb_{2/3})O_3–xPb(Mg_{1/3}Zr_{2/3})O_{8/3} (denoted as OZ100x) ceramics.\textsuperscript{13} For this purpose, the dielectric properties of OZ9 and OZ15 are also included in Table I. According to the chemical formula, PZ6 and PZ10 have the same Zr\textsuperscript{4+} content as, but less Mg\textsuperscript{2+} content than OZ9 and OZ15, respectively. Comparisons between PZ6 and OZ9, PZ10 and OZ15 indicate that the PZ compositions show a lower \( T_m \) and \( T_C0 \), a smaller \( \varepsilon_m \) and \( \delta \), and a greater (\( T_m-T_C0 \)) than their OZ counterparts. The observed difference is likely due to the different chemical compositions and the cation ordering mechanism. The larger amount of Mg\textsuperscript{2+} on the B\textsuperscript{'}-sublattice in OZ9 and OZ15 makes their lattice constants bigger than PZ6 and PZ10, respectively (see Table I). Therefore, there is more open space for the ferroelectrically active Nb\textsuperscript{5+} to shuffle in response to external fields.\textsuperscript{25} Moreover, oxygen vacancies in OZ ceramics are believed to be associated with Nb\textsuperscript{5+}(B')-Nb\textsuperscript{5+}(B'') pairs.\textsuperscript{13} This will provide further room for Nb\textsuperscript{5+} in the lattice of OZ ceramics. As a consequence, the ferroelectricity is enhanced to a higher degree in OZ ceramics than in PZ ceramics at the same Zr\textsuperscript{4+} content. The stronger ferroelectricity in OZ ceramics manifests itself as higher \( T_m \) and \( T_C0 \), larger \( \varepsilon_m \) and smaller gap between \( T_m \) and \( T_C0 \). It is expected that the oxygen vacancy introduced in the lattice of OZ ceramics further randomizes the electric dipoles and local fields, which leads to a greater diffuseness parameter \( \delta \) in the OZ ceramics as seen in Table I. It is quite intriguing to notice that in the OZ ceramics both ferroelectricity and diffuseness can be enhanced simultaneously when Zr\textsuperscript{4+} replaces only Nb\textsuperscript{5+} in Pb(Mg_{1/3}Nb_{2/3})O_3.

6.6 Conclusions

Long range 1:1 B-site cation order has been successfully developed in the (1-x)PMN–xPZ (0\( \leq \)x\( \leq \)0.25) solid solution system. The increased size difference between the B' and B''-sublattices and the reduced charge/size mismatch on the random B'-sublattice are
primarily responsible for the development of cation order. Typical relaxor ferroelectric behavior is preserved in (1-x)PMN–xPZ (0≤x≤0.25) ceramics even with long range cation order. Compared to the disordered ceramics, cation ordered (1-x)PMN–xPZ ceramics show a significant higher dielectric constant maximum ε_m and a slightly lower T_m. The comparison with the cation ordered Pb(Mg_{1/3}Zr_{2/3}Nb_{2(1−x)/3})O_3−x/3 (0≤x≤0.25) ceramics reveals that, at the same Zr^{4+} content, ordered (1-x)PMN–xPZ ceramics displays a weaker ferroelectricity and less diffuseness.
6.7 Figure list

Fig. 1. X-ray diffraction spectra of the PZ6, PZ10, and PZ25 ceramics. The 1:1 B-site cation order is observed in all three ceramics. (a) Full scan, and (b) slow scan of the (½ ½ ½) superlattice peak.

Fig. 2. Dielectric properties of the (1-x)PMN–xPZ ceramics measured at 100Hz, 1kHz, 10kHz, and 100kHz. (a) PZ6, (b) PZ10, and (c) PZ25.

Fig. 3. Depolarization current measurement under zero-field heating of the (1-x)PMN–xPZ ceramics after field-cooling under 10kV/cm.

Fig. 4. Polarization vs. electric field hysteresis loops measured at 4 Hz at a series of temperatures in the (1-x)PMN–xPZ ceramics. (a) PZ6, (b) PZ10, (c) PZ25.

Fig. 5. Ferroelectric properties of the (1-x)PMN–xPZ ceramics read from the P~E hysteresis loops shown in Fig. 4. (a) Remanent polarization $P_r$, and (b) coercive field $E_c$.

Fig. 6. Factors controlling the 1:1 B-site cation order in the (1-x)PMN–xPZ (0≤x≤0.25) system. The cation order is assumed to be described by Pb[(Mg(2-2x)/3Zr2xNb(1-4x)/3)1/2(Nb)1/2]O3 (0.0≤x≤0.25), where the random B'-sublattice is shared by Mg2+, Zr4+, and Nb5+ and the B''-sublattice is solely occupied by Nb5+. (a) The charge difference $Δq$ and the size difference $Δr$ between the B'- and the B''-sublattices, (b) the standard deviation of charge $σ_q$ and size $σ_r$ of cations on the random B'-sublattice.
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Table I. The structure and properties of the (1-x)Pb(Mg_{1/3}Nb_{2/3})O_{3-x}PbZrO_{3} ceramics. The properties of selected Pb(Mg_{1/3}Zr_{2x/3}Nb_{2(1-x)/3})O_{3-x/3} ceramics (OZ9: x=0.09, OZ15: x=0.15) are also included for comparison.

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<th>Ordering parameter α</th>
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<th>T_{m} @ 1kHz (°C)</th>
<th>δ (°C)</th>
<th>T_{C0} (°C)</th>
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<td>-40</td>
<td>44</td>
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6.8 References


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7 General Conclusions

The unique dielectric and ferroelectric properties of PMN-based relaxor ferroelectrics have led to extensive investigations of their synthesis, processing, properties and structure. Although some advances have been made in optimizing these systems for various applications, several fundamental aspects of their behavior, in particular the nature of the cation ordering on the octahedral positions (B-site) and its impact on the dielectric and ferroelectric properties, remained poorly defined. Meanwhile, the information about the electric field-induced phase transition in these systems is quite limited. The main objective of the work presented in this dissertation was to develop long range cation order in PMN-based ceramics, and to investigate its impact on the electric dipole order. This research aims to better understand the correlation between cation order and electric dipole order in PMN. The secondary goal was to investigate the electric field-induced phase transitions in PMN single crystals and PMN-based ceramics.

The electric field-induced phase transitions were investigated in Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} single crystals with field applied along the \textlangle 111\rangle, \textlangle 110\rangle, and \textlangle 100\rangle directions. A ferroelectric state with reversible polarization exists within a U-shaped region in the E~T phase diagram for all three directions. Both the Curie temperature \(T_C\) and the freezing temperature \(T_f\) shifts to lower temperatures in the crystal under field directions in the sequence of \textlangle 111\rangle, \textlangle 110\rangle, and \textlangle 100\rangle. The ferroelectric state with reversible polarization can be triggered by electric fields greater than 3kV/cm in the (110) platelet, and 5kV/cm in the (100) platelet. In the temperature range defined by \(T_f\) and \(T_C\), electric fields along the \textlangle 111\rangle direction trigger only the relaxor cubic to ferroelectric rhombohedral phase transition. An additional ferroelectric rhombohedral to ferroelectric orthorhombic phase transition occurs in the (110) platelet at high electric fields (~20kV/cm). An E~T phase diagram was proposed for Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} crystals with different orientations.

The long range B-site cation order was successfully developed in PMN-based
ceramics when only \( \leq 3 \) at. % of La, Sc, or W was incorporated separately. Both X-ray diffraction and TEM observation have confirmed the long range cation order development. The increased size and charge difference between two B-site sublattices, together with the reduced mismatch on the B'-sublattice are believed to be the driving forces for the cation ordering development. However, the ordering mechanisms are different for different dopants. La substitutes Pb on the A-site and increases the molar fraction of larger Mg on the B'-site, leading to the increase of size and charge difference between two B-site sublattices. Sc substitutes Mg and Nb with a 1:2 ratio on the B'-sublattice, the introduction of larger Sc\(^{3+}\) cations favors the B-site cation order by increasing the size difference between two B-sublattices and reducing the charge mismatch at the B'-sublattice. W substitutes Nb at B'' sublattices, the charge and size difference between two B-site sublattices are both increased as a result of the smaller size and higher valence of W\(^{6+}\) (0.60 Å, 6+ vs. 0.64 Å, 5+ of Nb\(^{5+}\)).

Due to the different chemistries and ordering mechanisms, the enhanced cation ordering showed different impacts on the dielectric and ferroelectric properties in these perovskite materials.

In La doped PMN ceramics, the smaller La\(^{3+}\) leads to a more compact unit cell which in turn leads to a higher resistance for the shuffling of the ferroelectric active Nb\(^{5+}\) in response to external fields, and the increased Mg/Nb ratio also contributes to the weak ferroelectric response since Mg is ferroelectric inactive. Therefore, the dielectric behavior is significantly suppressed. In contrast, the introduction of larger Sc\(^{3+}\) cations to the B-site sublattice leads to more open space for Nb\(^{5+}\) to shuffle in response to external electric fields and Sc is ferroelectrically more active than Mg. As a result, the electrical dipole order is strengthened in Sc-doped PMN. Pb(Mg\(_{1/2}\)W\(_{1/2}\))O\(_3\) is an antiferroelectric perovskite with a complete B site cation order, and the dielectric behavior of W doped PMN ceramic is dictated by the competition between the relaxor and the antiferroelectric polar order. The dielectric permittivity is improved with the significant decrease in the diffuseness parameter when
cation order is developed. The electric field-temperature phase diagram is also proposed for specific compositions based on the results of the electric field-induced phase transition.

Long range cation order in Zr doped PMN was successfully achieved with two different approaches for the first time.

- **OZ series**: The composition was designed that Zr only replaces Nb at B' sublattice and oxygen vacancy is introduced.
- **PZ series**: The solid solution system between PMN and PbZrO₃.

In the OZ series, the increased charge differences between the B’-cations (Mg²⁺, Zr⁴⁺, Nb⁵⁺) and the B''-cations results in an extended thermodynamically stable region for the cation ordered phase. The introduced oxygen vacancy has further assisted the B-site cation diffusion, leading to the development of 1:1 cation order. In PZ series, the increased size difference between the B’- and B''-sublattices and the reduced charge/size mismatch on the random B’-sublattice are primarily responsible for the development of cation order. Compared with the OZ series, at the same Zr⁴⁺ content, ordered (1-x)PMN–xPZ ceramics displays a weaker ferroelectricity and less diffuseness. The difference of the dielectric behavior between these two systems is caused by the composition difference and different cation ordering mechanism.
8 Recommendations for Further Study

The current work has revealed that long range cation order can be developed in PMN-based ceramics by composition modification combined with a slow cooling procedure. Future study is suggested to focus on neutron diffraction analysis, which is much more sensitive than X-ray diffraction to detect the position of lighter atoms when there are heavy atoms (such as Pb) in the lattice. And the more detailed information about the real configuration of B-site cations in PMN-based ceramics could be detected. Based on the results, the cation ordered structure of PMN-based ceramics can be further confirmed. For example, the model for the cation order in the OZ series where Zr only occupies the B'-sublattice can be directly validated.

The polarization current measurements with different electrical and/or thermal histories need to be carried out. For example, the measurements under field cooling conditions need to be performed, and the phase boundary between the induced ferroelectric phase and the high temperature ergodic relaxor phase need to be determined experimentally from the measurement results. In addition, low frequency dielectric constant measurements are needed to determine the parameters of the Vogel-Fulcher law and then the relaxation process of PMN-based relaxor ceramics could be investigated. By comparing the fitting parameters in ceramics with and without cation order, the impact of cation order on the relaxation process can be determined.

At the same time, the most intriguing properties of relaxor ferroelectrics are their temperature- and frequency-dependent dielectric response. The quantitative relationship between the local structure and relaxor properties is still needed. A physics model should be sought to better define the diffuseness parameter of the ceramics with a clear picture of atomic structures.
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Appendix: Publication list

1. X. Zhao, W. Qu and X. Tan, “Doped Pb(Mg_{1/3}Nb_{2/3})O_3 Ceramics with Long Range Cation Order,” *Physical Review B*, to be submitted.

2. X. Zhao and X. Tan, “Dielectric and Ferroelectric Properties of (1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-xPbZrO_3 Ceramics with Cation Order,” *Journal of Physics: Condensed Matter*, submitted.


4. X. Zhao, W. Qu and X. Tan, “Zr-modified Pb(Mg_{1/3}Nb_{2/3})O_3 with Long Range Cation Order,” *Journal of the American Ceramic Society*, 91(9), 3031-3038 (2008).

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