Zr-modified Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ with long range cation order

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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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I. 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$^{5+}$ cations (refereed to as the B"-sublattice in literature), the other {111} plane (refereed to as the B'-sublattice) is randomly occupied by Mg$^{2+}$ and the rest Nb$^{5+}$ 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$^{3+}$, Sc$^{3+}$ or W$^{6+}$.\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 $B'$- and the $B''$-sublattices, and (2) the reduced mismatch in the charge/size of the cations on the random $B'$-sublattice. Large size tetravalent cation $\text{Zr}^{4+}$ has also been incorporated into PMN by forming solid solutions with $\text{PbZrO}_3$ (PZ) in order to coarsen the cation ordered domains.\textsuperscript{10} However, both slow cooling from high temperatures and thermal annealing at a fixed temperature in the range of $900^\circ\text{C}–1325^\circ\text{C}$ failed to produce large cation ordered domains in a series of compositions in the $(1-x)\text{PMN}-x\text{PZ}$ solid solution system.\textsuperscript{10} It should be noted that in the closely related $(1-x)\text{Pb(Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3-x\text{PbZrO}_3$ solid solution system, enhanced cation order has been confirmed.\textsuperscript{8}

In the $(1-x)\text{PMN}-x\text{PZ}$ solid solution, $\text{Zr}^{4+}$ presumably substitutes both $\text{Mg}^{2+}$ and $\text{Nb}^{5+}$. 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.\textsuperscript{8,10} In the present work, we still use $\text{Zr}^{4+}$ 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 $\text{Pb(Mg}_{1/3}\text{Zr}_{2/3}\text{Nb}_{2(1-x)/3})\text{O}_3-x/3$. Therefore, the compositions were so designed that $\text{Zr}^{4+}$ only replaces $\text{Nb}^{5+}$, but not $\text{Mg}^{2+}$. To preserve charge neutrality, oxygen vacancies are expected to be introduced according to

$$2\text{ZrO}_2 \rightarrow 2\text{Zr}_{\text{Nb}} + 4\text{O}_o + V_{\text{o}}^{\text{\bullet\bullet}}$$  \hspace{1cm} (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) $\text{Zr}^{4+}$ (0.72Å) has an identical size as $\text{Mg}^{2+}$ (0.72Å) on the B-site lattice.\textsuperscript{14} Therefore, it is anticipated that $\text{Zr}^{4+}$ occupies the $B'$-sublattice with $\text{Mg}^{2+}$, replacing only the $\text{Nb}^{5+}$ (0.64Å) cations on this sublattice. As a consequence, the mismatch in the charge/size of the cations on the random $B'$-sublattice ($\text{Mg}^{2+}$, $\text{Zr}^{4+}$, $\text{Nb}^{5+}$) 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$^{4+}$-substitution can suppress the tendency of pyrochlore phase formation during processing.$^{17}$ (4) PbZrO$_3$ is a typical antiferroelectric perovskite. The competition between the antiferroelectric dipole order and the nanoscale ferroelectric dipole order is of fundamental significance.$^{18,19}$

II. Experimental Procedure

Polycrystalline ceramic samples were synthesized using the columbite method$^{17}$ according to the nominal chemical formula Pb(Mg$_{1/3}$Zr$_{2/3}$)O$_3$. 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$_{1/3}$Zr$_{1/6}$)O$_{2.92}$, where the Nb$^{5+}$ on the B′-sublattice is expected to be completely substituted by Zr$^{4+}$ and the molar ratio of the larger (Mg$^{2+}$ and Zr$^{4+}$) to smaller (Nb$^{5+}$) B-site cations reaches 1:1.

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 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 grinded 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^{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).

III. Results

(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, $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$-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.$^{8-13}$ Fig. 2(b) shows the diffraction spectra of the $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ peak ($2\theta\approx19^\circ$) 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,$^{8}$ the ordering parameter $\alpha$ is evaluated and listed in Table I, assuming that all Zr$^{4+}$ 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.$^{10}$ 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 $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ 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.

(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 $\varepsilon_m<1.5\varepsilon_r$:

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

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.

(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 ($\sim 1^\circ$C) for pure PMN and OZ3 while a wider range ($\sim 6^\circ$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\(\mu\)C/cm\(^2\). 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.$^{12}$ For a relaxor ferroelectric material where the polar order is short range, $T_{C0}$ is usually much lower than $T_m$.\(^6,^{12}\) 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.

IV. Discussion

(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$_{x/3}$Nb$_{2(1-x)/3}$)O$_{3-x/3}$ system and the previous (1-x)PMN–xPZ system$^{10}$ is the oxygen vacancy resulted from the selective substitution of Nb$^{5+}$ with Zr$^{4+}$. The presence of long range cation order in Pb(Mg$_{1/3}$Zr$_{x/3}$Nb$_{2(1-x)/3}$)O$_{3-x/3}$ 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, $^{14}$ Mg$^{2+}$ 0.72Å, Zr$^{4+}$ 0.72Å, and Nb$^{5+}$ 0.64Å, Zr$^{4+}$ is expected to share the B’-sublattice with Mg$^{2+}$ and Nb$^{5+}$, while the B’’-sublattice is solely occupied by Nb$^{5+}$. The compound Pb(Mg$_{1/3}$Zr$_{x/3}$Nb$_{2(1-x)/3}$)O$_{3-x/3}$ can then be expressed as Pb[(Mg$_{2/3}$Zr$_{x/3}$Nb$_{1(1-x)/3}$)$_{1/2}$(Nb)$_{1/2}$]O$_{3-x/3}$ (0.0≤x≤0.25) to reflect the 1:1 B-site cation order. When x=0.0, the expression becomes Pb[(Mg$_{2/3}$Nb$_{1/3}$)$_{1/2}$(Nb)$_{1/2}$]O$_3$, which is the random site model for pure PMN.$^{8,9}$ At x=0.25, the expression becomes Pb[(Mg$_{2/3}$Zr$_{1/3}$)$_{1/2}$(Nb)$_{1/2}$]O$_{2.92}$, which is the OZ25 composition in this study where the B’-sublattice is expected to be full with large cations of Mg$^{2+}$ and Zr$^{4+}$ and the B’’-sublattice is expected to be full with smaller Nb$^{5+}$. Following the same arguments, the random site model would be Pb[(Mg$_{(2-2x)/3}$Zr$_{2x}$Nb$_{(1-x)/3}$)$_{1/2}$(Nb)$_{1/2}$]O$_3$ (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_{1/3}Zr_{2/3}Nb_{2(1-x)/3})O_{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\textsuperscript{2+} and Zr\textsuperscript{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 Pb(Mg_{1/3}Zr_{2/3}Nb_{2(1-x)/3})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 Pb\(_{1/3}\)Zr\(_{2x/3}\)Nb\(_{2(1-x)/3}\)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\(_{4x/3}\)Nb\(_{1(1-4x)/3}\))_{1/2}(Nb)_{1/2}]O_{3-x/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$_O^-$(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$_{2/3}$)Nb$_2$(1-$x$)O$_{3-x/3}$ 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 (≥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.

(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.\textsuperscript{21,22} 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\textsubscript{3} primary cells. PbZrO\textsubscript{3} is a typical anti-ferroelectric material with Curie point around 230°C.\textsuperscript{23} Therefore, $T_m$ in the Pb(Mg\textsubscript{1/3}Zr\textsubscript{2/3}x/3Nb\textsubscript{2(1-x)/3})O\textsubscript{3-x/3} system shifts to higher temperatures as Zr\textsuperscript{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\textsuperscript{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 Pb(B\textsuperscript{3+/1/2}B\textsuperscript{5+/1/2})O\textsubscript{3} system, such as Pb(Sc\textsubscript{1/2}Ta\textsubscript{1/2})O\textsubscript{3} (PST), where the structural order is accompanied by chemical order due to 1:1 stoichiometric ratio of Sc\textsuperscript{3+} and Ta\textsuperscript{5+}. In PST, the polar order changes from relaxor ferroelectric to normal ferroelectric
as the 1:1 order is strengthened.\textsuperscript{24} It is suggested that when the ferroelectrically inactive larger cation Sc\textsuperscript{3+} in B’ is next to a ferroelectrically active smaller cation Ta\textsuperscript{5+} in B’’, the intermediate oxygen anion shifts towards the active cation and displace the Pb\textsuperscript{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 Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{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.\textsuperscript{15,16,25,26} Specifically, there are two primary types of electrical dipoles in Pb(Mg\textsubscript{1/3}Zr\textsubscript{2/3}Nb\textsubscript{2/3(1-x)/3})O\textsubscript{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 Zr\textsuperscript{4+} into PMN enhances the rhombohedral distortion in the polar nanoregions and eventually leads to a rhombohedral symmetry with long range dipole order.\textsuperscript{16,17,27} Therefore, it appears that the reduced temperature gap between \(T_m\) and \(T_{CO}\) is primarily caused by the enhanced rhombohedral distortion due to Zr\textsuperscript{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 Pb\textsuperscript{2+}, a 4+ cation is needed at the B-site to balance the charge within a unit cell of ABO\textsubscript{3}. Therefore, each and every unit cell containing a Mg\textsuperscript{2+} is a substitutional point defect carrying effective two negative charges. Similarly, each and every unit cell containing a Nb\textsuperscript{5+} carries effective one positive charge. As revealed by Eq. (1), every two Zr\textsuperscript{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$_{2/3}$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.

V. Conclusions

Long range 1:1 structural and cation order can be developed in Pb(Mg$_{1/3}$Zr$_{2/3}$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$_{2/3}$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 Nb$^{5+}$-V$_{O}$-Nb$^{5+}$ configuration in the ordered structure of the Pb(Mg$_{1/3}$Zr$_{2/3}$Nb$_{2(1-x)/3}$)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 \( \text{Zr}-\text{modified PMN} \) ceramics with long range 1:1 order due to the chemical randomness on the \( \text{B}' \)-sublattice.
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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\(_{2/3}\)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\(_{2/3}\)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\(_{2/3}\)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\(_{2/3}\)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\(_{2/3}\)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\(_{2/3}\)Nb\(_{2(1-x)/3}\))O\(_{3-x/3}\) ceramics according to the random site model Pb[(Mg\(_{2/3}\)Zr\(_{4/3}\)Nb\(_{1-4x/3}\))\(_{1/2}\)(Nb\(_{1/2}\))O\(_{3-x/3}\) \((0.0\leq x\leq0.25)\). 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-x/3} ceramics.

<table>
<thead>
<tr>
<th>Ceramic</th>
<th>Relative density</th>
<th>Lattice parameter (Å)</th>
<th>Grain size (µm)</th>
<th>Ordering parameter α</th>
<th>ε_{m} @ 1kHz (°C)</th>
<th>T_{m} @ 1kHz (°C)</th>
<th>δ (°C)</th>
<th>T_{CO} (°C)</th>
<th>T_{m}-T_{CO} (°C)</th>
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<td>PMN</td>
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<td>4.0481</td>
<td>14.3</td>
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<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>
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<td>17690</td>
<td>-2</td>
<td>35.6</td>
<td>-55</td>
<td>53</td>
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<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>
</tr>
<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>
<td>-50</td>
<td>50</td>
</tr>
<tr>
<td>OZ15</td>
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<td>0.8</td>
<td>18160</td>
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<td>42.2</td>
<td>-40</td>
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<tr>
<td>OZ25</td>
<td>94%</td>
<td>4.0873</td>
<td>6.3</td>
<td>0</td>
<td>18900</td>
<td>96</td>
<td>33.8</td>
<td>83</td>
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</table>
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 α</th>
<th>Perovskite phase purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>OZ9</td>
<td>0</td>
<td>4.0478</td>
<td>0.20</td>
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<td></td>
<td>0.80</td>
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<td>OZ15</td>
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<td>4.0561</td>
<td>0.73</td>
<td>100%</td>
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<td></td>
<td>0.47</td>
<td>4.0567</td>
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<td>100%</td>
</tr>
<tr>
<td></td>
<td>0.82</td>
<td>4.0575</td>
<td>0.82</td>
<td>100%</td>
</tr>
</tbody>
</table>
Fig. 2
Fig. 4
Fig. 5

Fig. 6
Fig. 7
Fig. 8

Fig. 9