Local Structure and Macroscopic Properties in
PbMg$_{1/3}$Nb$_{2/3}$O$_3$-PbTiO$_3$ and PbZn$_{1/3}$Nb$_{2/3}$O$_3$-PbTiO$_3$ solid solutions

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Abstract
We have examined the local structure of PbMg$_{1/3}$Nb$_{2/3}$O$_3$-PbTiO$_3$ (PMN-PT) and
PbZn$_{1/3}$Nb$_{2/3}$O$_3$-PbTiO$_3$ (PZN-PT) solid solutions using density functional theory. We find that
the directions and magnitudes of cation displacement can be explained by an interplay of cation-
nonlinear bonding, electrostatic dipole-dipole interactions and short-range direct and through oxygen
Pb-B-cation repulsive interactions. We find that the Zn ions off-center in the PZN-PT system,
which also enables larger Pb and Nb/Ti displacements. The off-centering behavior of Zn lessens
Pb-B-cation repulsion, leading to a relaxor to ferroelectric and a rhombohedral to tetragonal phase
transition at low PbTiO$_3$ content in the PZN-PT system. We also show that a simple quadratic
relationship exists between Pb and B-cation displacements and the temperature maximum of di-
electric constant, thus linking the enhanced displacements in PZN-PT systems with the higher
transition temperatures.
Heterovalent ferroelectric perovskite solid solutions have been intensively studied as they exhibit a range of interesting structural and dielectric properties which make them useful in device applications. Relating the macroscopic properties of these materials to the microscopic properties of the constituent atoms is an important scientific goal and is vital for the rational design of new materials with improved properties. The technologically important PbMg$_{1/3}$Nb$_{2/3}$O$_3$-PbTiO$_3$ (PMN-PT) and PbZn$_{1/3}$Nb$_{2/3}$O$_3$-PbTiO$_3$ (PZN-PT) solid solutions are good subjects for an investigation of structure-property correlations due to the availability of a wide range of experimental data and because the small difference between Mg and Zn ionic sizes cannot explain the differences in the characteristics of the two solid solutions such as a higher $T_c$ and dielectric constant observed for PZN.

Ab-initio Density Functional Theory (DFT) calculations were performed for the $(1-x)$PMN–$x$PT and $(1-x)$PZN–$x$PT systems using $2 \times 2 \times 2$ 40-atom or $3 \times 2 \times 2$ 60-atom supercells with periodic boundary conditions at experimental volume. The energy of the system was evaluated using a local density approximation exchange-correlation functional and was minimized with respect to the atomic coordinates by a quasi-Newton method with no symmetry imposed. A $2 \times 2 \times 2$ $k$-point sampling of the Brillouin zone was used. The calculations were done with designed non-local norm conserving pseudopotentials. We study four compositions with $x = 0$, 0.25, 0.625 and 1.0 For pure PMN and PZN we used a 60-atom supercell with B-cations arranged according to the random-site model. A B-cation arrangement consistent with the random-site model as well as two disordered B-cation arrangements were used to model the 0.25 composition and three disordered B-cation configurations were used for the 0.625 composition.

The excellent agreement between the pair distribution functions (PDF) obtained from our relaxed 60-atom structure for PMN and by neutron-scattering experiments (Figure 1) and similar agreement between DFT and experimental PDFs in previous studies of PbSc$_{2/3}$W$_{1/3}$O$_3$-PbTiO$_3$ (PSW-PT), PbSc$_{2/3}$W$_{1/3}$O$_3$-PbZrO$_3$ (PSW-PZ) and PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) solid solutions indicate that the size of our supercells is sufficient for capturing the local structure of these materials.

We find that at all compositions PZN-PT and PMN-PT local structure is governed by three main interactions. First, bonding interactions with oxygen favor large Pb and B-cation displacements (Table I) and creation of short Pb-O and B-O bonds. Second, short-range repulsive Pb-B-cation interactions create anisotropy in the potential energy surfaces felt by
the Pb cations, leading to a variation in the preferred local displacement direction for the Pb atoms (Table I, Figure 2). Third, electrostatic interactions favor dipole alignment and tend to minimize the scatter in displacement direction, eliminating displacements opposite to the overall polarization of the supercell (Figure 2). Breathing motion by the B-O\textsubscript{6} octahedra (to achieve preferred octahedral volume) and small octahedral rotations (0-5°) are also present.

Examination of the data in Table I shows that for both solid solutions Pb displacement magnitudes predicted by DFT are unchanged by the addition of PT, whereas the average magnitude of the B-cation displacements steadily increases with PT content. The cation displacements are larger in PZN-PT than in PMN-PT, with especially large difference for the B\textsuperscript{2+} cations. While Mg ions are only slightly displaced, the Zn ions exhibit significant distortions even in pure PZN and Ti-like 0.27 Å distortions in Ti-rich PZN-PT. As will be explained later, the large Zn distortions also account for the larger magnitude of Pb, Nb and Ti distortions in the PZN-PT system.

The contrast between the absence of Mg off-centering and the large Zn displacements is due to the different electronic structure of the two ions. While Mg is a simple metal and Mg\textsuperscript{2+}-O bonding is essentially ionic, the imperfect screening of the nuclear charge by the d-electrons and the presence of low-lying p orbitals make Zn more polarizable and enable covalent bonding with oxygen atoms [? ? ?].

As in other Pb containing ferroelectric perovskite solutions, Pb displacements are the determining factor for the average structure of our solid solutions [? ? ?]. Inspection of Figure 2 shows that the location of Mg atoms is the primary influence on the direction of Pb distortions. In all cases Pb atoms avoid cube faces with three Nb atoms and one Mg atom and move toward cube faces with two Mg and two Nb atoms. The avoidance of Nb-rich faces is due to the presence of oxygen atoms with two Nb neighbors. Such oxygen atoms have higher B-O bond order than the oxygen atoms in PbTiO\textsubscript{3} due to the higher valence of Nb. Since the total bond order of cation-oxygen bonds is conserved at 2, this prohibits the formation of short Pb-O bonds of high bond order and creates a strong effective Pb-Nb repulsive interaction. On the other hand, the oxygen atoms with Mg and Nb neighbors have a lower total B-O bond order than the oxygen atoms in PbTiO\textsubscript{3}, necessitating a formation of more short Pb-O bonds to compensate for B-O bond depletion [? ? ? ] and leading to a weaker effective Pb-Mg repulsion.

The larger Pb and B-cation displacements in the PZN-PT system are due to the coupling
between Zn and Pb and Nb off-center displacements through the Pb-B-cation repulsive interactions. The ionic size of Mg and Zn atoms is essentially the same [? ], which leads to very similar shortest allowed Pb-Mg and Pb-Zn distances. The greater ability of Zn atoms to off-center allows Pb atoms in PZN-PT solution to preserve the required Pb-B-cation distances for larger Pb displacements than in the PMN-PT system. The larger Pb displacements in turn cause larger Nb and Ti distortions to prevent high Pb-B-cation repulsion at short Pb-Nb and Pb-Ti distances.

The electrostatic dipole-dipole interactions favor alignment of cation displacements and prevent cation displacements in the \(^{(\bar{1}00)}\) direction in direct opposition to the overall polarization along [100] in Figure 2. The local direction of Pb displacement is determined by a balance between the need to align with other cation displacements and the need to minimize direct and through-oxygen Pb-B-cation repulsion [? ? ].

At high Ti content, collinear \([100]\) Pb atom distortions create short Pb-O bonds, maximize dipole alignment and minimize local Pb-B-cation repulsion by avoiding the Ti cations located along the \([111]\) direction. As Ti content decreases, the Pb local environments become anisotropic due to the presence of the overbonded and underbonded oxygen atoms which block Pb distortions toward some \([100]\) perovskite cube faces. This leads to a transition to a rhombohedral phase, where Pb cations move in a variety of low symmetry directions around the overall \([111]\) polarization direction toward the available low-repulsion cube faces. With the onset of random-site B-cation ordering, the high anisotropy created by a large amount of faces blocked by the presence of overbonded oxygen atoms forbids the formation of a long-range ferroelectric state even in the \([111]\) direction and leads to a relaxor phase. A similar explanation, albeit focused on the B-cation size difference, for the relaxor to ferroelectric transition in the ordered PMN-PSN system, was proposed by Farber and Davies [? ].

While exact Pb-environment population analysis in PMN-PT and PZN-PT is currently not possible due to the complex and unknown nature of the short-range B-cation ordering in these systems [? ? ], the above framework coupled with the differences in Zn and Mg distortion behavior explains why in the PZN-PT system the tetragonal phase is present at lower PT content (10%) than in the PMN-PT system (35%), as well as the recent discovery of ferroelectric phases even in pure PZN itself [? ]. A large Zn distortion softens Pb-Zn repulsion, making perovskite faces with Zn atoms more friendly toward a Pb distortion than the corresponding perovskite faces with Mg atoms in PMN. This increases the population of
the local environments favorable to tetragonal distortion, moving the relaxor to ferroelectric transition and the morphotropic phase boundary (MPB) to lower Ti concentrations.

We find that there is also a strong relationship between the low-temperature cation displacements as found by our DFT calculations and the experimentally obtained temperature position of the dielectric constant maximum $T_{\varepsilon,\text{max}}$. A qualitative relationship between average lattice displacement and ferroelectric to paraelectric phase transition temperature $T_c$, which is closely linked to $T_{\varepsilon,\text{max}}$, was found by Abrahams, Kurtz and Jamieson (AKJ) in 1968 [?]. However, examination of the original AKJ paper shows that the largest discrepancies between predicted and experimental $T_c$ are for the Pb containing perovskites PbFe$_{1/2}$Nb$_{1/2}$O$_3$ and PT. We find that $T_{\varepsilon,\text{max}}$ at 1 MHz for PMN-PT, PZN-PT, PZT, PbSc$_{1/2}$Nb$_{1/2}$O$_3$ (PSN), PSW-PT and PSW-PZ solid solutions is predicted by

$$T_{\varepsilon,\text{max}} = ad_{\text{Pb}}^2 + bd_{B'}^2 f_{B'},$$

where $d_{\text{Pb}}$ is the average magnitude of the Pb distortions, $d_{B'}$ is the average magnitude of the distortions, $f_{B'}$ is the fraction of the ferroelectrically active B-cations in solution and $a$ and $b$ are constants (1739 and 5961 respectively) in units of K/Å$^2$.

The dependence of $T_{\varepsilon,\text{max}}$ on local structure presented in Equation 1 can be further simplified by transforming cation and oxygen displacements $u_i$ into 0 K local dipole moments $P_{0i}$ via their Born effective charge tensors $Z^*_i$ [2]. This leads to

$$T_{\varepsilon,\text{max}} = \gamma|P_{0i}|^2 = \gamma \left( \sum_i |P_{0i}| \right)^2 = \gamma \left( \sum_i \frac{|Z^*_i \cdot u_i|}{NV_0} \right)^2$$

or

$$T_{\varepsilon,\text{max}} = \gamma P_0^2 = \gamma \left( \sum_i \frac{P_{0i}}{N} \right)^2 = \gamma \left( \sum_i \frac{Z^*_i \cdot u_i}{NV_0} \right)^2$$

where $\gamma$ is a constant, $N$ is the number of primitive unit cells and $V_0$ is the volume of a primitive unit cell and $|P_{0i}|$ and $P_0$ are the 0 K average magnitude of the local dipole moment and the overall polarization respectively. Figure 3 shows the correlation between the $T_{\varepsilon,\text{max}}$ predicted by Eqns. 1-3 and experimental $T_{\varepsilon,\text{max}}$ data [?]. The clustering of the data around the $y=x$ line indicates that Eqns. 1-3 accurately and quantitatively capture the trends in
Comparing the data for PMN-PT and PZN-PT systems in Table I, we see that the higher $T_{\epsilon, \text{max}}$ for PZN-PT system is directly related to larger $P_0$ and $|P_{0i}|$ values due to off-centering behavior on the B$^{2+}$ site.

The correlations presented in Figure 3 can be explained based on fourth-order Landau theory for ferroelectric crystals. The equilibrium polarization is given by

$$dG/dP = 0 = 2\alpha(T - T_0)P + 4\beta P^3 \tag{4}$$

where $\alpha$ and $\beta$ are constants, $T_0$ is the Curie-Weiss temperature at which the dielectric constant $\epsilon$ diverges and $P$ is polarization. Substituting $T=0$ used in our DFT calculations and solving for $T_0$, we obtain $T_0 = 2\beta P_0^2/\alpha$, thus relating the $T_0$ to the square of computed 0 K polarization. The high quality of the fit in Figure 2 means that for the Pb-based perovskites examined here the ratio $\beta/\alpha$ is nearly constant.

The nearly constant dependence of $T_{\epsilon, \text{max}}$ on $P_0^2$ and $|P_{0i}|$ can be interpreted as follows. Experimental results have shown that ferroelectric to paraelectric phase transitions in Pb based perovskites such as PMN and PZT are of order-disorder character [? ? ], with Pb displacements at $T_0$ of up to 70% of the low temperature value. The parameter governing the temperature of such an order-disorder transition is the coupling strength between the Pb and B-cation displacements in neighboring unit cells (corresponding to the $J$ parameter in spin models). The coupling is due to electrostatic effects favoring dipole alignment and covalent chemical bonding effects disfavoring under- and over-bonded oxygen atoms. Dipole alignment strengths depend only on polarization strengths and gives rise to the overall
dependence of $T_0$ on $P_0^2$ or $|P_{bi}|^2$, with the variation in through-oxygen coupling accounting for the differences between experimental and predicted $T_{\epsilon,\text{max}}$ values in Figure 3. While predicted $T_{\epsilon,\text{max}}$ values are of the same quality for Eqn. 1 and Eqn. 2, the correlation between $P_0$ and $T_{\epsilon,\text{max}}$ is somewhat worse. This suggests that the freezing in of large distortions enhances stability of ferroelectricity, giving rise to higher $T_{\epsilon,\text{max}}$. Even though some of the distortions frozen in are not parallel, they still contribute to the coupling of dipoles in neighboring unit cells due to through-oxygen interactions.

In summary, we have examined structure-property correlations for PMN-PT and PZN-PT solid solutions. We find that the local direction of Pb displacements in these systems is governed by an interplay between the electrostatic dipole-dipole alignment interactions and Pb-B repulsive interactions, as was previously found for PZT. We find that Zn ions off-center; this reduces Pb-B repulsions resulting in smaller Ti content at MPB and allowing larger displacements by the Pb, Nb and Ti ions. A strong relationship exists between the cation displacements or $P_0$ and $T_{\epsilon,\text{max}}$, which can be explained in the Landau theory framework by the constant ratio of $\alpha$ and $\beta$ parameters and is a natural consequence of the order-disorder nature of phase transitions in Pb-based ferroelectrics. The link between $\alpha$ and $\beta$ also explains the opposite trends in $\Delta E_{\text{FE}}$ and $T_c$ found in the PZT, PSW-PT and CPT systems. Fundamentally, we have shown that behavior of individual ions in heterovalent perovskite ferroelectric solid solutions can be directly linked to changes in local structure and macroscopic collective properties.

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TABLE I: Results of DFT calculations for PMN-PT and PZN-PT systems. Pb displacement magnitudes in PMN predicted by DFT are in agreement with recent experimental data [?] and \( P \) magnitudes for PMN and PT are in good agreement with previous theoretical calculations [?]. Predicted cation displacements from center of oxygen cage in Å, Pb displacement angle scatter \( \theta_{Pb} \) in °, average and local polarization in C/m² and experimental \( T_{c,max} \) [?] in K.

|        | Pb B²⁺ Nb/Ti | \( \theta_{Pb} \) | \( P_0 \) | \( T_{c,max} \) |
|--------|--------------|--------------------|----------|-----------------|
| PMN    | 0.398 0.056  | 0.168              | 65       | 0.38, 0.67      | 276             |
| PMN-0.25PT | 0.389 0.080 | 0.181              | 33       | 0.55, 0.68      | 397             |
| PMN-0.625PT | 0.387 0.099 | 0.216              | 28       | 0.66, 0.74      | 583             |
| PT     | 0.440        | 0.280              | 0        | 0.88, 0.88      | 765             |
| PZN    | 0.444 0.148  | 0.189              | 67       | 0.43, 0.73      | 424             |
| PZN-0.25PT | 0.461 0.258 | 0.205              | 35       | 0.66, 0.79      | 547             |
| PZN-0.625PT | 0.424 0.270 | 0.237              | 27       | 0.74, 0.80      | 643             |
| PT     | 0.440        | 0.280              | 0        | 0.88, 0.88      | 765             |
FIG. 1: Comparison of PDFs obtained from relaxed structure of 60-atom supercell of PMN (solid) and by neutron-scattering (dashed) \[?\]. Similar agreement is obtained for other systems \[? ? \].

[1] Ionized +2 reference configurations were used for Pb, Mg, and Zn, ionized +4 and +5 were used for Ti and Nb and a neutral reference configuration was used for O. Energy cutoff of 50 Ry were used for all elements except for Zn for which 56 Ry was used. Real space cutoffs were 2.0, 1.83, 1.95, 1.70, 1.75 and 1.5 for Pb, Mg, Zn, Ti, Nb and O respectively.

[2] Following approach of Ref. 26, we used approximate $Z^*$ values of 3.6, 2.6, 2.6, 7.4, 4.0, 12.0, 6.4 and 6.4 for Pb, Mg, Zn, Nb, Sc, W, Ti and Zr respectively. Oxygen $Z^*$ were $\approx -5.0$ and $\approx -2.5$ for the parallel and perpendicular elements of the tensor respectively, varied slightly to satisfy the electrostatic sum rule for each composition.
FIG. 2: Relaxed structure of 60-atom supercell of PMN obtained by DFT calculations. Cation displacements from high-symmetry positions are shown by arrows scaled up by a factor of 4. Pb atoms displace away from Nb-rich faces. Blue, pink, red and gray represent Pb, Nb, Mg and O atoms respectively.
FIG. 3: Correlations between experimental $T_{\varepsilon, \text{max}}$ and predicted $T_{\varepsilon, \text{max}}$ for PZN, PZN-PT, PMN, PMN-PT, PSW, PSW-PT, PSW-PZ, PSN and PZT systems. Values for predicted $T_{\varepsilon, \text{max}}$ are obtained by Eqn. 1 (squares) with $a=1739$ and $b=5961$, Eqn. 2 using local polarization with $\gamma=942$ (stars) and Eqn. 2 using overall polarization with $\gamma=1189$ (circles).