Intrinsic Piezoelectric Response in Perovskite Alloys: PMN-PT versus PZT

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First-principles supercell calculations and the modern theory of polarization are used to compute the e_{33} piezoelectric coefficients of $\mathrm{Pb(Zr_{0.5}Ti_{0.5}O_3)}$ (PZT) and 0.60 $\mathrm{Pb(Mg_{1/3}Nb_{2/3})O_3}$ + 0.40 $\mathrm{PbTiO_3}$ (PMN-PT) alloys. A drastic enhancement by a factor of 2.7 is found for e_{33} when going from PZT to PMN-PT. The huge value of e_{33} in PMN-PT comes from the large response of the internal coordinates of Pb, Ti, Nb, and O atoms to a macroscopic strain. On the other hand, the Mg atoms contribute little to the piezoelectricity for dielectric and elastic reasons.

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Complex insulating perovskite $A(B'B'')\mathrm{O}_3$ and $A(B'B''B''')\mathrm{O}_3$ alloys are of great current interest for actual or potential uses based on their exceptional piezoelectric properties [1]. Examples include the $\mathrm{Pb(Zr_{1-x}Ti_x)O_3}$ (PZT) alloys that are currently used in piezoelectric transducers and actuators [2–4], and most recently, the class of $\mathrm{Pb(Mg_{1/3}Nb_{2/3})O_3}$-$\mathrm{PbTiO_3}$ (PMN-PT) and $\mathrm{Pb(Zn_{1/3}Nb_{2/3})O_3}$-$\mathrm{PbTiO_3}$ (PZN-PT) materials which, when synthesized in single-crystal form, exhibit remarkably large piezoelectric constants and maximum strain levels [5]. These latter materials thus promise dramatic improvements in the resolution and range of ultrasonic and sonar listening devices [6].

A recent *ab initio* study has concluded that the large piezoelectric response observed experimentally in PZT is not consistent with the calculated "intrinsic" response of a supercell realization of the alloy at zero temperature [7], and should instead be ascribed to an "extrinsic" source. Of course, care must be taken in making comparisons between a piezoelectric constant computed under such ideal conditions and one measured experimentally for a real material. Obviously, the piezoelectric response is generally temperature dependent, and may tend to diverge when approaching the Curie temperature [5]. Moreover, the piezoelectricity can depend sensitively on alloy concentration when close to the morphotropic phase boundary [8,9], so that comparisons should only be made at the same composition. Still, the intrinsic response of a supercell realization of a single-crystal material at given x and T may not be the whole story. The most obvious extrinsic contribution to the piezoelectric response is the motion of ferroelectric domain walls. However, several other factors, that could be regarded as extrinsic, may also play a role. The coexistence of tetragonal and rhombohedral phases in the vicinity of the morphotropic phase boundary is believed to enhance the piezoelectric response of PZT (see Ref. [10], and references therein). The partial compositional order is rather complicated in compounds such as PMN-PT: one finds some degree of short-range disorder, partial rocksalt-like order at intermediate length scales (~50 Å), and an absence of true long-range order [11]. The compositional fluctuations are likely to be coupled in some way to the "nanopolar domains" that are thought to be important for the strain response of PMN-PT-like compounds [12,13]. In the case where experiments are done on ceramic samples, the measured piezoelectric response is really some type of complicated orientational average of the microscopic single-crystal response. And finally, stoichiometric nonuniformities and defects of all types (point defects, dislocations, grain boundaries) may affect the piezoelectric response if present in the material.

The thrust of this paper is to investigate the contribution of *intrinsic* effects on the enhancement of the piezoelectric response when going from PZT to PMN-PT. We want both to quantify such effects and to identify their microscopic origins. Motivated to clarify these issues, we decided to calculate the e_{33} piezoelectric coefficient of *ordered* supercells of $\mathrm{Pb(Zr_{0.5}Ti_{0.5}O_3)}$ and 0.60 $\mathrm{Pb(Mg_{1/3}Nb_{2/3})O_3}$ + 0.40 $\mathrm{PbTiO_3}$ alloys at zero temperature. Such a calculation obviously leaves out any effects of finite temperature or compositional disorder (e.g., compositional fluctuations on the scale of the "nanopolar regions"). We also performed simulations on the common parent end member $\mathrm{PbTiO_3}$ (PT) to assess the intrinsic role of alloying on piezoelectricity. The Ti compositions of the alloys are chosen to be slightly *larger* than those at the morphotropic phase boundary—47% in PZT vs 35%-38% in PMN-PT [10,14]—in order that the ferroelectric ground states of the presently studied systems have experimentally the same tetragonal point group ($P4mm$) as their common parent compound $\mathrm{PbTiO_3}$.

For PT, we adopt the ferroelectric tetragonal cell denoted "Theory II" in Ref. [15]. To facilitate comparison between the PZT and PMN-PT alloys, we choose supercells that are similar in the sense that they both exhibit atomic ordering along the [100] direction. For PZT, there are two different (100) B planes ($n = 2$) corresponding to an alternance of pure Zr planes with pure Ti planes, with a total of 10 atoms per cell. For PMN-PT, we use the minimal number of planes ($n = 5$) consistent with a Ti composition of 40%, yielding a 25-atom cell. We also choose a planar ordering sequence that respects M_x mirror symmetry, in order to be as close as possible to the experimental situation. This allows two choices, either Ti/Nb/Mg/Nb/Ti or Nb/Ti/Mg/Ti/Nb, for the alternation of the B planes along [100]. The first choice is adopted because it leads to a lower electrostatic energy among the differently charged species (Ti^{4+}, Mg^{2+}, and Nb^{5+}) [16]. For both the PZT and PMN-PT supercells, the spontaneous polarization direction is chosen along the [001] direction, i.e., perpendicular to the atomic ordering direction. Consequently, each (001) B plane is equivalent and exhibits the same overall atomic composition. This situation is intended to mimic atomic disordering along the tetragonal ferroelectric direction.

The ferroelectric ground state will thus belong to the orthorhombic $P2mm$ point group for both alloys. However, it should be regarded as "quasitetragonal $P4mm$," since we choose the lattice vectors to be $\mathbf{R}_1 = na_0[1,0,0]$, $\mathbf{R}_2 = a_0[0,1,0]$, and $\mathbf{R}_3 = c[0,0,1]$, where a_0 is the lattice parameter and c/a_0 is the "tetragonal" axial ratio. That is, we preserve the ideal 1:1 axial ratio between the two lattice spacings perpendicular to the ferroelectric (tetragonal) axis (more precisely, a 1:n ratio between the superlattice vectors in the compositionally unmodulated and modulated directions, respectively).

We perform local-density approximation (LDA) [17] calculations on the above supercells using the Vanderbilt ultrasoft-pseudopotential scheme [18]. The semicore shells of all of the metals are included in the valence, which leads to 44, 88, and 220 electrons per cell in PT, PZT, and PMN-PT, respectively. (6,6,6), (6,6,3), and (6,6,1) Monkhorst-Pack meshes [19] are used for the PT, PZT, and PMN-PT supercells, respectively, in order to provide good convergence of the results [20]. Other technical details of the calculation can be found in Refs. [20,21].

The lattice parameter a_0, the axial ratio c/a_0, and the atomic displacements consistent with the symmetries of our structures are fully optimized by minimizing the total energy and the Hellmann-Feynman forces, the latter being smaller than 0.05 eV/Å at convergence. We find that PZT and PMN-PT exhibit similar lattice constants (3.99 vs 3.96 Å), while differing considerably in their axial ratios. We find $c/a_0 = 1.0345$ for PZT, consistent with the experimental value of 1.02 obtained at room temperature for $Pb(Zr_{0.53}Ti_{0.47}O_3)$ [1]. On the other hand, we find a much smaller value $c/a_0 = 1.004$ in PMN-PT. The fact that this value is close to unity may be consistent with the "quasicubic" denomination sometimes given to the ferroelectric ground state of PMN-PT [14].

For a given structure, the modern theory of polarization [22,23] is used to calculate the spontaneous polarization $\mathbf{P}$ as a Berry phase of the Bloch states [22]. Then the piezoelectric coefficients can be computed as

$$e_{ij} = \frac{1}{2\pi\Omega} \sum_{\alpha} R_{\alpha,i} \frac{d}{d\eta_j} (\Omega \mathbf{G}_\alpha \cdot \mathbf{P}), \qquad (1)$$

where Ω is the cell volume and $\alpha = 1,2,3$ runs over the three real-space lattice vectors $\mathbf{R}_\alpha$ and reciprocal lattice vectors $\mathbf{G}_\alpha$, and η_j is the macroscopic strain. Equation (1) has recently been derived in order to make the piezoelectric coefficients independent of the choice of branch of the Berry phase [24]. At the same time, Eq. (1) automatically eliminates of the so-called "improper" terms [25] as required to correctly predict the piezoelectric coefficients [24]. Technically, Eq. (1) is evaluated by finite differences between two strain configurations: first, that of the ferroelectric ground state and, second, for an additional 1% strain relative to this ground state. In the second run, the relative atomic coordinates naturally have to be reoptimized in response to the applied strain.

The results for e_{33} of PT, PZT, and PMN-PT are shown in Table I. One can first notice that PT exhibits a piezoelectric constant of 3.8 C/m^2 that compares well with the recent *ab initio* result of 3.2 C/m^2 [25]. Our calculated value is also consistent with the experimental room-temperature findings ranging between 4.1 and 5.0 C/m^2 [26], since e_{33} is expected to increase with temperature. Second, alloying $PbTiO_3$ with $PbZrO_3$ does not provide any enhancement of piezoelectricity with respect to PT. A similar conclusion was also reached in Ref. [7], where values of e_{33} equal to 3.6 and 4.8 C/m^2 have been predicted for two ordered $Pb(Zr_{0.5}Ti_{0.5}O_3)$ supercells. These calculated values compare rather well with our finding of 3.4 C/m^2 obtained using a different ordered supercell. Our result confirms the conclusion of Ref. [7], i.e., that the large e_{33} piezoelectric coefficient experimentally observed in $Pb(Zr_{0.5}Ti_{0.5})O_3$—estimated to be of the order of 12 C/m^2 in ceramic samples at very low temperature [27]—does not mainly come from intrinsic contributions. However, calculations including "true" atomic disordering are needed to definitively check this assumption since lowering the symmetry of a supercell has been shown to increase the piezoelectric response [28]. Finally and most importantly, we find that PMN-PT exhibits a dramatically larger intrinsic piezoelectric response than either PT or PZT. As can be seen from Table I, e_{33} is predicted to be larger in PMN-PT than in PZT by a factor of about 2.7 at $T = 0$. To our knowledge, this e_{33} for PMN-PT is the largest intrinsic piezoelectric coefficient ever predicted for a material using *ab initio* density-functional methods (the previous largest being 5.1 C/m^2 for a low-symmetry supercell of Pb_3GeTe_4 [28]). Direct low-temperature

TABLE I. Piezoelectric coefficients of $PbTiO_3$ (PT), $Pb(Zr_{0.5}Ti_{0.5}O_3)$ (PZT), and 0.60 $Pb(Mg_{1/3}Nb_{2/3})O_3$ + 0.40 $PbTiO_3$ (PMN-PT), in C/m^2. Values in parentheses are those calculated in Ref. [25].

	PT		PZT	PMN-PT
e_{33}	3.8	(3.2)	3.4	9.1
$e_{33,c}$	−1.0	(−0.9)	−0.8	−0.6
$e_{33,i}$	4.8	(4.1)	4.2	9.7

measurements of e_{33} in tetragonal PMN-PT are needed to provide a fair comparison with our prediction.

In order to obtain further insight into the differences between PZT and PMN-PT, the piezoelectric coefficients can be decomposed into "clamped-ion" and "internal-strain" contributions

$$e_{33} = e_{33,c} + e_{33,i} \tag{2}$$

following Refs. [25,29]. The "clamped-ion" or "homogeneous-strain" contribution $e_{33,c}$ is given by Eq. (1) for the case $i = j = 3$ and *evaluated at vanishing internal strain* (that is, *without* allowing the additional relaxation of the relative atomic coordinates that would be induced by the strain). The internal strain part $e_{33,i}$ measures just those contributions to the piezoelectric response coming from these internal distortions, and is simply calculated as the difference between e_{33} and $e_{33,c}$.

Table I gives the decomposition of the piezoelectric coefficients. First, note that the main contribution to e_{33} comes from $e_{33,i}$, while $e_{33,c}$ decreases the magnitude of e_{33} by its negative sign. Such features were also found and pointed out in Refs. [7,25] for PT and ordered PZT. Second, both $e_{33,c}$ and $e_{33,i}$ have similar values in PT and PZT, which leads to a comparable e_{33} as reported above. The most valuable information indicated in Table I is that the enhancement of piezoelectricity found when going from PZT to PMN-PT is due mainly to a drastic change of $e_{33,i}$. In other words, PMN-PT has a much larger piezoelectric response than PZT because of the internal microscopic strain, while the two alloys have similar clamped-ion coefficients.

As indicated in Refs. [25,29], $e_{33,i}$ is simply related to the effective charge tensor Z^* and to the response $du_3/d\eta_3$ of the internal atomic coordinates to a macroscopic strain,

$$e_{33,i} = \sum_k \frac{ec}{\Omega} Z^*_{33}(k) \frac{du_3(k)}{d\eta_3}, \tag{3}$$

where k runs over all of the atoms in the cell, e is the magnitude of the electron charge, and c and Ω are the lattice constant along the z direction and the volume of the cell, respectively. Equation (3) indicates that the large value of $e_{33,i}$ in PMN-PT could arise either from (i) a dielectric effect, namely, a large value of the effective charges; or (ii) an elastic effect, namely, a large response of the internal coordinates to a macroscopic strain. Equation (3) also shows that $e_{33,i}$ can be decomposed into specific atomic contributions by gathering all of the k indices running over the same type of atom.

Table II shows the effective charge Z^*_{33} for each type of atom, for the three compounds studied, as calculated by the Berry-phase approach [22]. The oxygen atoms are grouped into two types: those denoted O_3, located between two B atoms along the polarization direction; those denoted O_1, located between two B atoms in the perpendicular direction [15,25]. One can see trends already noticed in Refs. [7,25,30]: Z^*_{33} is about 3.5, −2.15, and −4.5 for Pb, O_1, and O_3 atoms, respectively, while the effective charge of both Ti and Zr atoms ranges between +5 and +6. One can also notice that PMN-PT differs from both PT and PZT in that it has B atoms, specifically Nb atoms, with a much larger effective charge. The value of +7.4 found for the Nb effective charge is comparable to the corresponding one for $PbZn_{1/3}Nb_{2/3}O_3$ (PZN), computed to range between +6.5 and +7.8 [21]. On the other hand, the Mg atom in PMN-PT has a much smaller effective charge than those of Ti and Zr in PT and PZT; Z^*(Mg) is very close to its ionic value of +2, exactly as found for Zn in PZN [21]. This is due to the lack of unoccupied d electrons [21].

TABLE II. Dynamical effective charge Z^*, derivative $du_3/d\eta_3$ of the internal atomic displacements with respect to a macroscopic strain for the different types of atoms in $PbTiO_3$ (PT), $Pb(Zr_{0.5}Ti_{0.5}O_3)$ (PZT), and 0.60 $Pb(Mg_{1/3}Nb_{2/3})O_3$ + 0.40 $PbTiO_3$ (PMN-PT). We use the convention that $\sum_k du_3(k)/d\eta_3 = 0$. The internal atomic displacements $u_3(k)$ of the ferroelectric ground state are also given for reference. Values in parentheses are those calculated in Ref. [25].

Z^*_{33}	PT		PZT	PMN-PT
Pb	3.5	(3.5)	3.0	3.6
Ti	5.5	(5.2)	5.3	5.8
Zr	···	···	6.0	···
Nb	···	···	···	7.4
Mg	···	···	···	1.9
O_1	−2.2	(−2.2)	−2.1	−2.1
O_3	−4.6	(−4.4)	−4.6	−5.1
η_3	PT		PZT	PMN-PT
Pb	0.37	(0.36)	0.36	0.94
Ti	0.20	(0.22)	0.17	0.40
Zr	···	···	0.24	···
Nb	···	···	···	0.39
Mg	···	···	···	0.06
O_1	−0.11	(−0.13)	−0.15	−0.40
O_3	−0.35	(−0.31)	−0.26	−0.47
u_3	PT		PZT	PMN-PT
Pb	0.500	(0.500)	0.452	0.452
Ti	0.037	(0.030)	−0.003	−0.031
Zr	···	···	0.016	···
Nb	···	···	···	−0.024
Mg	···	···	···	−0.006
O_1	0.111	(0.110)	0.083	0.021
O_3	0.600	(0.605)	0.555	0.508

Overall, PZT and PMN-PT have a very similar B-averaged effective charge equal to +5.7. Consequently, one can rule out the hypothesis that the enhancement of the intrinsic piezoelectricity found when going from PZT to PMN-PT is due to increased Z^* values. Table II shows that this enhancement rather arises from an elastic effect, namely, the large response of the internal atomic coordinates of PMN-PT to a macroscopic strain. More specifically, the Pb, Ti, and O atoms have a microscopic response about 2–3 times larger in PMN-PT than in PZT and PT. The Nb atoms also contribute to the enhancement of the piezoelectric response of PMN-PT, since the Nb displacements are about twice as large as those of Ti and Zr in PT and PZT. On the other hand, the Mg atom (the only B atom that is not a transition-metal atom) does not contribute to the large value of e_{33} in PMN-PT because of its almost-vanishing microscopic reaction to a macroscopic strain and its small Z^* value.

In summary, we performed ordered-supercell LDA calculations to investigate the intrinsic e_{33} piezoelectric coefficients of PT, PZT, and PMN-PT at zero temperature. We found that e_{33} has a comparable value in PZT and PT. This strongly confirms the hypothesis of Ref. [7] that the enhancement of piezoelectricity experimentally found when going from the parent compound (PT) to the alloy (PZT) is entirely due to extrinsic contributions, such as the motion of ferroelectric domain walls, or effects associated with the ceramic microstructure of the experimental material, or the coexistence of different crystallographic phases in the vicinity of the morphotropic phase boundary [10]. Our most important result is that PMN-PT exhibits a much larger value of e_{33} (9.1 $\mathrm{C/m^2}$, about 2.5 times larger) than in PT or PZT. To our knowledge, this e_{33} is the largest piezoelectric coefficient ever predicted using first-principles electronic-structure methods. While extrinsic factors undoubtedly play a role in amplifying the piezoelectric response in the real material, the enhancement of the intrinsic response is surely an essential part of the story. This enhancement is found to be caused by the very large response of the internal coordinates of Pb, Ti, Nb, and O atoms to a macroscopic strain.

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