Electric-field induced polarization paths in $Pb(Zr_{1-x}Ti_x)O_3$ alloys

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Properties of $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) for compositions x near the morphotropic phase boundary and under an electric field are simulated using an *ab-initio* based approach. Applying an electric field of [111] orientation to tetragonal PZT (e.g., x=0.50) leads to the expected sequence of tetragonal, A-type monoclinic, and rhombohedral structures. However, the application of a field of orientation [001] to rhombohedral PZT (e.g., x=0.47) does not simply reverse this sequence. Instead, the system follows a complicated path involving also triclinic and C-type monoclinic structures. These latter phases are found to exhibit huge shear piezoelectric coefficients.

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The existence of a morphotropic phase boundary (MPB) is an important feature of the phase diagram of many technologically interesting perovskite alloys, such as $[Pb(Zn_{1/3}Nb_{2/3})O_3]_{(1-x)}[PbTiO_3]_x$ (PZN-PT), $[Pb(Sc_{1/2}Nb_{1/2})O_3]_{(1-x)}[PbTiO_3]_x$ (PSN-PT), and $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) [1]. In these materials, the MPB is the boundary in the temperature-composition plane separating the rhombohedral phase, in which the electric polarization is along the [111] direction, from the tetragonal structure, in which the polarization lies along the [001] direction. Applying an electric field to these alloys near the MPB generates an anomalously large change of strain. Very recent theoretical [2] and experimental [3] studies strongly suggest that such large piezoelectric response is driven by the electric-field induced *rotation* of the electrical polarization $\mathbf{P}$, rather than an electric-field induced change of magnitude of this polarization.

Despite these recent advances, many features related to the effects of electric fields on structural and piezoelectric properties of perovskite alloys near the MPB remain puzzling. For instance, based on calculations performed on the simple $BaTiO_3$ system, Ref. [2] proposed that applying an electric-field along the pseudo-cubic [001] direction in rhombohedral PZN-PT induces a rotation of the polarization occurring along the rhombohedral–tetragonal path (i.e., $\mathbf{P}$ continuously rotates from the [111] to [001] direction). On the other hand, Ref. [3] suggests a more complex mechanism in the same PZN-PT system in which the polarization first follows the rhombohedral–tetragonal path for small electric field, and then jumps to a new path connecting an orthorhombic to the tetragonal structure. However, due to experimental restrictions, the authors of Ref. [3] were only able to observe the second (and new) polarization path. As a result, the following questions are currently unanswered: If there is indeed a new polarization path at higher electric-field, what is the transitional mechanism allowing such a change of polarization path? Is this transitional mechanism sudden or does it happen over a broad range of electric field? Another aspect that is poorly understood is the striking difference between the electric-field behavior on opposite sides of the MPB: applying an electric field to a tetragonal alloy leads to a much smaller change of strain than is observed for a rhombohedral composition [1]. Furthermore, most studies investigating piezoelectricity in perovskite materials focused on the d_{33} piezoelectric coefficient. As a result, other coefficients that may exhibit even larger values could have been overlooked. On may also wonder what is the consequence of the polarization paths proposed in Ref. [3] on piezoelectricity.

In this Letter we address the problems summarized above by investigating the effect of an electric field on the structural and piezoelectric properties of PZT alloys near the MPB. Starting with a composition that is tetragonal at zero field, we find that applying an electric field along the [111] pseudo-cubic direction leads to a polarization that simply rotates in the $(\bar{1}10)$ plane from [001] to [111], i.e., from the tetragonal (T) to the rhombohedral (R) structure, via an intermediate A-type monoclinic (M_A) structure [4]. The resulting d_{33} piezoelectric coefficient is only large very close to the M_A–R transition. On the other hand, starting with a rhombohedral PZT composition, we find that applying an electric field along the [001] pseudo-cubic direction does *not* simply generate the reverse transition sequence R–M_A–T. Instead, the polarization begins to follow this $(\bar{1}10)$-plane R–M_A–T path at low fields, but before reaching the T phase, the polarization crosses over to join the (100)-plane O–M_C–T path connecting the orthorhombic (O) to the tetragonal structure via an intermediate C-type monoclinic (M_C) structure (as hinted for PZN-PT in Ref. [3]). (The notation for monoclinic phases is that of Ref. [5], with M_A and M_C phases having polarization lying in the $(\bar{1}10)$ and (100) planes, respectively.) The crossing from the M_A

to the M_C structure occurs via an intermediate triclinic (Tri) structure that is stable over a substantial electric-field range. The overall transition sequence is thus R–M_A–Tri–M_C–T. We find that both the triclinic and M_C phases exhibit huge shear d_{15} piezoelectric coefficients.

We use the numerical scheme proposed in Ref. [6], which involves the construction of an alloy effective Hamiltonian ($H_{\rm eff}$) [7] from first-principles calculations [8–10] and its use in Monte-Carlo simulations to compute finite-temperature properties of PZT alloys. The effect of an external static electric field $\mathbf{E}$ on physical properties is included by adding a $-\mathbf{P}\cdot\mathbf{E}$ term in $H_{\rm eff}$ (see Ref. [11]). In the present study, the temperature is kept fixed at 50 K, and well-converged results are obtained with $10\times10\times10$ simulation boxes (5000 atoms) [12]. We use atomic configurations mimicking maximal compositional disorder, consistent with experimental conditions [13]. Data from the simulations on the local mode vectors $\mathbf{u}$ (directly proportional to the electric polarization) and the homogeneous strain tensor are used within the correlation-function approach of Refs [11,14] to obtain the piezoelectric response. Up to 2×10^5 Monte-Carlo sweeps are first performed to equilibrate the system, and then 2×10^5 sweeps are used to get the various statistical averages.

Previous studies [6,12,15] have demonstrated that our effective Hamiltonian approach gives a very good account of experimental and direct first-principles findings in perovskite alloys. In particular, it successfully predicts the existence of three low-temperature ferroelectric phases for $Pb(Zr_{1-x}Ti_x)O_3$ solid solutions near its MPB [6]: a tetragonal (T) phase for larger x compositions ($x > 49\%$ at 50 K), a rhombohedral (R) phase for smaller x compositions ($x < 47.5\%$ at 50 K), and the recently discovered monoclinic (M_A) phase [4] in between. The polarization is parallel to the pseudo-cubic [001], [111], or $[vv1]$ ($0<v<1$) direction for the T, R, or M_A phase, respectively. The electrical polarization can thus be viewed as rotating in a $(\bar{1}10)$ plane from [001] to [111] as the Ti composition decreases in the monoclinic phase [6]. (In the following, we adopt the convention that the x, y and z axes are chosen along the pseudo-cubic [100], [010] and [001] directions, respectively, and the piezoelectric tensor is represented in the orthonormal basis formed by $\mathbf{a}_1 = [100]$, $\mathbf{a}_2 = [010]$ and $\mathbf{a}_3 = [001]$.)

We first consider a tetragonal PZT composition, x=0.5, under an electric field applied along the [111] direction. The polarization of this alloy is initially along $\hat{z}$ when no electric field is applied. Figure 1(a) displays the cartesian components (u_x, u_y and u_z) of the supercell average of the local mode vectors in this solid solution as a function of the magnitude of the electric field. It demonstrates that applying a small electric field along the [111] direction in $Pb(Zr_{0.50}Ti_{0.50})O_3$ perturbs the system in the expected way: the polarization rotates away from the [001] direction, as evidenced by the fact that u_x and u_y become non-zero. The strain tensor given by our simulations indicates that the resulting structure

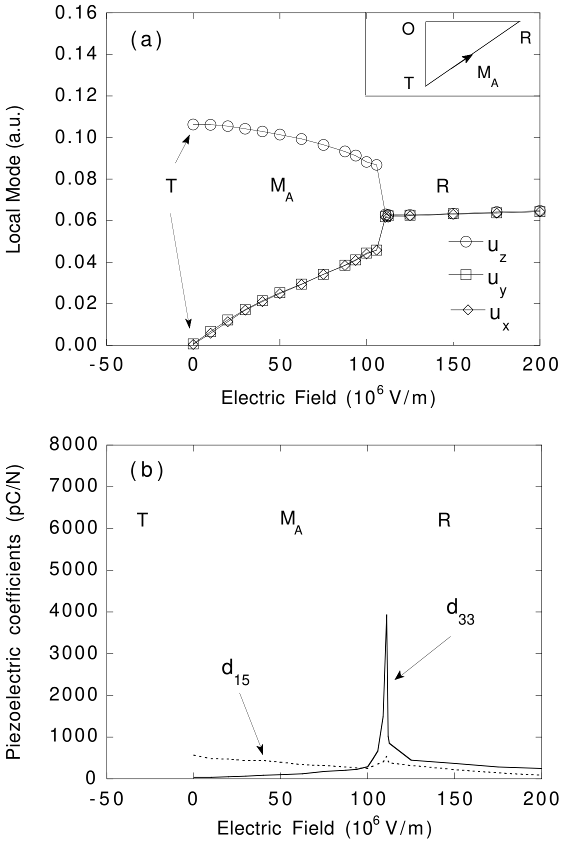

FIG. 1. (a) Cartesian components u_x, u_y and u_z of the local-mode vector, and (b) d_{33} and d_{15} piezoelectric coefficients, as a function of the magnitude of the electric field applied along the pseudo-cubic [111] direction in disordered single crystals of $Pb(Zr_{0.50}Ti_{0.50})O_3$ at T=50 K. Insert illustrates the path followed by the polarization.

is the monoclinic M_A structure. As the magnitude of the electric field along the [111] direction increases, u_z decreases, while u_x and u_y increase and remain equal. The polarization in this M_A structure thus rotates towards the [111] direction within the $(\bar{1}10)$ plane. For a sufficiently large electric field ($\sim 110\times10^6$ V/m), u_z becomes equal to u_x and u_y, signaling a phase transition to a rhombohedral structure [16] with the polarization aligned along the [111] direction. The path followed by the polarization in going from the T via the M_A to the R structure with increasing field is illustrated in the insert of Fig. 1(a).

Figure 1(b) shows the resulting behavior of the d_{33} and d_{15} piezoelectric coefficients. We decided to focus on these two coefficients because we numerically found that they are the largest ones among all the 18 piezoelectric constants. One can note that d_{15} is larger than d_{33} in the T structure (and in most of the range of stability of the M_A structure). This is consistent with recent measurements revealing that the piezoelectric elongation of the tetragonal unit cell of PZT does not occur along the polar [001] direction [17]. The large value of d_{15} also explains the strong (averaged) piezoelectric response observed in ceramic tetragonal samples [6]. One can also see that d_{33} is predicted to be larger in the R phase than in the T and M_A structures. This prediction is consistent with the findings of Refs. [1,18] that the d_{33} coefficient of rhombohedral materials can be very large along the [001] direction when the polar direction is oriented along the pseudo-cubic [111] direction. Figure 1(b) also reveals that d_{33} adopts values larger than 1,000 pC/N in a narrow electric-field range centered around the M_A–to–R transition. Note that d_{15} is also enhanced in this region, but has much smaller values than d_{33}.

We now investigate the effect of an electric field applied along the [001] direction to a rhombohedral PZT composition, $Pb(Zr_{0.53}Ti_{0.47})O_3$. The polarization of this alloy starts along the pseudo-cubic [111] direction (i.e, $u_x = u_y = u_z$) when no external electric field is present. Figure 2(a) reveals an unusual behavior of the polarization and a resulting rich phase diagram. As expected, applying a small electric field along the [001] direction of $Pb(Zr_{0.53}Ti_{0.47})O_3$ perturbs the R structure to the M_A structure, for which $0 < u_x = u_y < u_z$. As the magnitude of the electric field increases, the polarization rotates towards the [001] direction, with u_z increasing while u_x and u_y are decreasing. However, as shown in Fig. 2(a), $Pb(Zr_{0.53}Ti_{0.47})O_3$ then adopts two behaviors that do not occur in the $Pb(Zr_{0.50}Ti_{0.50})O_3$ alloy. First, for an electric field ranging between 50 and 88×10^6 V/m, u_x, u_y and u_z are all non-zero and different from each other, and the strain tensor identifies this as a *triclinic* (Tri) phase. Second, for an electric field ranging between 88 and 110×10^6 V/m, u_x vanishes while u_y and u_z remain zero and different from each other. This characterizes a second type of monoclinic phase denoted M_C [5,19,20]. At larger electric field, $Pb(Zr_{0.53}Ti_{0.47})O_3$ finally transforms from this monoclinic (M_C) phase into the tetragonal (T) phase, for which the polarization is along the [001] direction (u_z is then the only nonzero component).

The insert of Fig. 2(b) summarizes the path followed by the polarization in $Pb(Zr_{0.53}Ti_{0.47})O_3$: **P** first rotates in the $(\bar{1}10)$ plane from [111] to [vv1] (R to M_A), then switches via [wv1] (Tri) to the (100) plane, where it finishes by rotating from [0v1] (M_C) to [001] (T). That is, the polarization starts along the R–M_A–T path and then switches to the O–M_C–T path to complete the transformation to the T phase.

The electric-field induced R–M_A–T transformation path has been observed experimentally in nominally rhombohedral PZT alloys [17], but the unavailability of single-crystal PZT complicates the experimental determination of the polarization paths depicted in Fig. 2(a). Furthermore, we find that the change of path occurs at electric fields that are high compared to those that can be used experimentally (our calculations predict that an electric field of $\sim 100 \times 10^6$ V/m is needed to see the transitions to the Tri and M_C phases, while the highest field applied experimentally in Ref. [3] is 2×10^6 V/m).

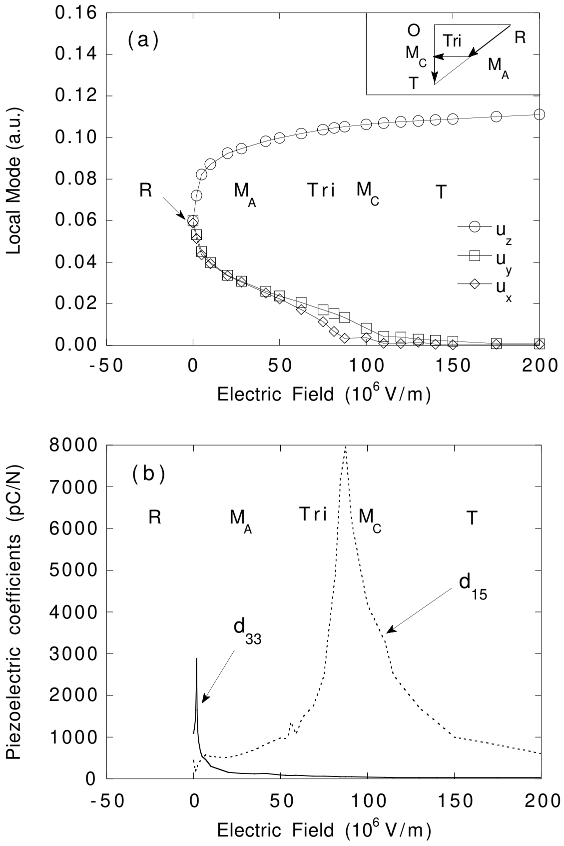

FIG. 2. (a) Cartesian components u_x, u_y and u_z of the local-mode vector, and (b) d_{33} and d_{15} piezoelectric coefficients, as a function of the magnitude of the electric field applied along the pseudo-cubic [001] direction in disordered single crystals of $Pb(Zr_{0.53}Ti_{0.47})O_3$ at T=50 K. Insert illustrates the path followed by the polarization.

However, we find that the transformations displayed in Fig. 2(a) all occur at smaller electric fields in PZT alloys for which the Ti composition x is closer to the MPB: increasing the Ti composition in PZT from 46% to 47% leads to a considerable decrease of the critical electric field, giving rise to the Tri phase at ~ 50 instead of 150×10^6 V/m, and to the M_C phase at ~ 88 instead of 237×10^6 V/m. Thus a practical observation of the change of polarization path depicted in Fig. 2(a) would probably require the use of a single-crystal PZT alloy with a composition lying as close as possible to the MPB.

While the R–M_A–T path of the polarization has recently been predicted to occur in (zero-field rhombohedral) $BaTiO_3$ when applying an [001]-oriented electric field, no change of path has been predicted to occur in this material even at very high field [2,11]. Similarly, the O–M_C–T path has recently been observed in (zero-field rhombohedral) 92%–$PbZn_{1/3}Nb_{2/3}O_3$ 8%–$PbTiO_3$ under an [001]-oriented electric field [3]. However, because of some experimental limitations, the R–M_A–T path and the transitional triclinic phase, that probably both occur at small fields, have yet to be observed in this material. To our knowledge, the present study is thus the first demonstrating the existence of these two different polarization paths, and the transitional phase connecting them, in a cubic perovskite system under electric field [21].

Furthermore, Fig. 2(b) clearly shows that these unusual polarization paths have a drastic effect on the d_{33} and d_{15} piezoelectric coefficients of $Pb(Zr_{0.53}Ti_{0.47})O_3$. For instance, Fig. 2(b) reveals that the d_{33} coefficient suddenly peaks at a small field, when $Pb(Zr_{0.53}Ti_{0.47})O_3$ adopts the M_A structure. This peak corresponds to a sudden increase of the strain η_3. d_{33} then decreases with a further increase of the magnitude of the electric field, implying that the strain η_3 then adopts a flatter strain-*vs.*-field slope. Interestingly, both the sudden increase and the flatter behavior of the strain have been observed in rhombohedral PZN-PT [1] and were predicted to occur in rhombohedral $BaTiO_3$ [2] when applying an [001]-oriented electric field.

The most striking result of Fig. 2(b) is the huge enhancement of the shear d_{15} piezoelectric coefficient associated with the change of polarization path: d_{15} increases from 1,000 to 8,000 pC/N with increasing electric field within the transitional Tri phase. Once the polarization is along the O-M_C-T path (i.e., when the system has transformed to the M_C phase), d_{15} decreases with a further increase of the electric field [19]. However, d_{15} remains large, even in the tetragonal phase under very high electric field. As a result, d_{15} is larger than 2,000 pC/N for a wide range of electric fields, e.g., $\sim 50 \times 10^6$ V/m.

In summary, we have used the first-principles derived computational scheme proposed in Ref. [6] to study the structural and piezoelectric properties of disordered $Pb(Zr_{1-x}Ti_x)O_3$ solid solutions near the MPB under an electric field. Our main results are: (1) the response of the polarization to an electric field is qualitatively different in the tetragonal and rhombohedral phases; (2) specifically, rhombohedral alloys near the MPB exhibit an unusual switching of the polarization path under applied field; (3) a large piezoelectric response can result from such a path switch; and (4) the shear piezoelectric coefficients (e.g., d_{15}) could be exploited to achieve a drastic improvement in response in piezoelectric devices.

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[19] Note that a close inspection of the symmetry of the piezoelectric tensor confirms the identification of the Tri and M_C phases.
[20] The case $u_z > u_y > u_x$ is equivalent by symmetry to the case $u_z > u_x > u_y$ for both the triclinic (Tri) and monoclinic (M_C) phases. Our simulation led to the first case by "accident," i.e., it could also have generated the second situation. Note that the piezoelectric coefficient d_{15} shown in Fig. 2(b) is consistent with the first case, i.e. the '1' index corresponds to an electric field applied along the x-axis – which has the smallest cartesian component of the local mode – while '5' refers to the shear η_{xz} strain – i.e., coupling the axes exhibiting the smallest and largest cartesian components of the local mode.
[21] It should be noted that we find that the polarization takes the same complex path, in reverse, upon the progressive release of the field. This reversibility might be intrinsic to a defect-free system and has not been observed experimentally [3].