Huge Enhancement of Electromechanical Responses in Compositionally Modulated $Pb(Zr_{1-x}Ti_x)O_3$

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Monte Carlo simulations based on a first-principles-derived Hamiltonian are conducted to study the properties of $Pb(Zr_{1-x}Ti_x)O_3$ alloys compositionally modulated along the [100] pseudocubic direction near the morphotropic phase boundary. It is shown that compositional modulation causes the polarization to continuously rotate away from the modulation direction, resulting in the unexpected triclinic and C-type monoclinic ground states and huge enhancement of electromechanical responses (the peak of piezoelectric coefficient is as high as 30 000 pC/N). The orientation dependence of dipole-dipole interaction in modulated structure is revealed as the microscopic mechanism to be responsible for these anomalies.

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Complex perovskite alloys have been studied for more than 50 years, which are of great importance not only because they have wildly technical applications for their large electromechanical responses [1], but also because they are fundamentally interesting for their anomalous properties and the relations to the microscopic structure. Recently, two breakthroughs were achieved in the research of complex perovskites. One is the observation of large enhancement of piezoelectric constants in single crystals [2,3]. The second is the discovery of a low-temperature monoclinic phase in $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) near the morphotropic phase boundary (MPB) [4,5]. Inspired by such progress, a considerable amount of work has been done to search larger electromechanical response and unobserved phases in complex perovskites. Particularly, an *ab initio* calculation on $Pb(Sc_{0.5}Nb_{0.5})O_3$ (PSN) revealed that atomic rearrangement would lead simultaneously to large electromechanical responses and unusual structural phases [6]. The difference between the valences of the B atoms (Sc^{3+} and Nb^{5+}) was pointed out to be the main reason for the existence of these anomalous properties and this mechanism is expected to be generally applicable in a given class of heterovalent perovskite alloys, which is likely to have large technological and fundamental implications. However, it is unclear whether there is any interesting effect in the modulated homovalent systems where the B atoms have the same valences.

In this Letter, we investigate the influences of compositional modulation on the homovalent PZT solid solutions near MPB. Remarkably, it is found that the atomic ordering along the [100] direction leads to the suppression of P_x (x component of the polarization). Unexpected new ground states of triclinic (Tri) and C-type monoclinic (M_C) phases appear with greatly enhanced piezoelectric coefficients. The orientation dependence of dipole-dipole interaction in modulated structure is revealed to be responsible for these anomalies. Such microscopic mechanism is expected to work in MPB region of any homovalent perovskite when the atomic ordering is produced.

We adopt the effective Hamiltonian of PZT alloys proposed by Bellaiche, Garcia, and Vanderbilt [7], which is derived from first-principles calculation, to predict the properties of compositionally modulated PZT structures by conducting Monte Carlo simulations. In this scheme, the total energy E is written as the sum of an average energy and a local energy as [7,8]

$$E(\{\mathbf{u}_i\}, \{\mathbf{v}_i\}, \eta_H, \{\sigma_j\}) = E_{\mathrm{ave}}(\{\mathbf{u}_i\}, \{\mathbf{v}_i\}, \eta_H) + E_{\mathrm{loc}}(\{\mathbf{u}_i\}, \{\mathbf{v}_i\}, \{\sigma_j\}), \qquad (1)$$

where $\mathbf{u}_i$ is the local soft mode in unit cell i, $\mathbf{v}_i$ is the dimensionless local displacement related to the inhomogeneous strain [9], η_H is the homogeneous strain tensors, and $\sigma_j = \pm 1$ represents the presence of a Zr or Ti atom, respectively, at lattice site j of the PZT alloy. All the parameters of Eq. (1) are derived from the first-principles calculation and are listed in Refs. [7,8]. The modulated structures under consideration are made of the sequences $Pb(Zr_{1-x+\nu}Ti_{x-\nu})O_3/Pb(Zr_{1-x-\nu}Ti_{x+\nu})O_3$ along the [100] direction with B atoms randomly distributing within each [100] plane. $10 \times 10 \times 10$ or $12 \times 12 \times 12$ supercells with periodic boundary conditions are used in

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Monte Carlo simulations to get well converged results. Equation (1) is based on the virtual crystal approximation (VCA) [10,11]. The parameters of Zr and Ti atoms are composition dependent, which reflects an average influence from surrounding atoms. Considering that the modulation length of our studied structures is small (only two monolayers) and a Zr or Ti atom will be influenced by atoms from planes with different compositions, we adopt the parameters corresponding to the overall composition x for all atoms in the modulated structures. Some detailed tests are also carried out, which show that the anomalous properties of the modulated structures revealed in this Letter are not sensitive to the choice of parameters.

First, we consider the properties of modulated PZT as a function of composition x by setting parameter ν to its maximum value ($\nu = x$). Figure 1(a) shows the Cartesian coordinates (u_x, u_y, u_z) of the supercell average of the local mode vectors at $T = 50$ K. (Because of the difference between the theoretical and experimental temperatures [7], it corresponds to an "experimental" temperature around 30 K.) In the nonmodulated case, it was demonstrated that disordered $\mathrm{Pb(Zr_{1-x}Ti_x)O_3}$ has a pseudocubic [111] direction polarized ($u_x = u_y = u_z > 0$) rhombohedral phase (R) for $x < 0.475$, a [001] direction polarized ($u_x = u_y = 0 < u_z$) tetragonal phase (T) for $x > 0.49$, and an A-type monoclinic phase (M_A) with $0 < u_x = u_y < u_z$ for $0.475 < x < 0.49$ [7,8]. In the modulated case, for compositions outside MPB, the local mode vectors are slightly affected as shown in Fig. 1(a). However, the precise symmetry has been changed by the atomic ordering, and the phases are recognized as B-type monoclinic (M_B) and orthorhombic (O). The interesting phenomena appear within the MPB region. For $0.480 < x < 0.485$, u_x decreases drastically, which results in a triclinic (Tri) phase with $u_x \neq u_y \neq u_z$. When x is larger than 0.485, u_x vanishes and an unexpected ground state appears in the modulated systems: a C-type monoclinic (M_C) phase with $0 = u_x < u_y < u_z$. Figure 1(a) thus depicts a polarization rotation in modulated PZT structures following the sequence of M_B-Tri-M_C-O as the Ti composition increases. Although Tri and M_C phases in PZT were first demonstrated in the simulation of electric-field induced transformation in disordered rhombohedral PZT by Bellaiche *et al.* [12], it has not been observed experimentally yet because the predicted electric field required to induce the Tri and M_C phases is too high (~ 500 kV/cm for composition close to MPB) compared with what experiments can provide. Thus the present study demonstrates an alternative routine to observe such phases with fewer experimental obstacles.

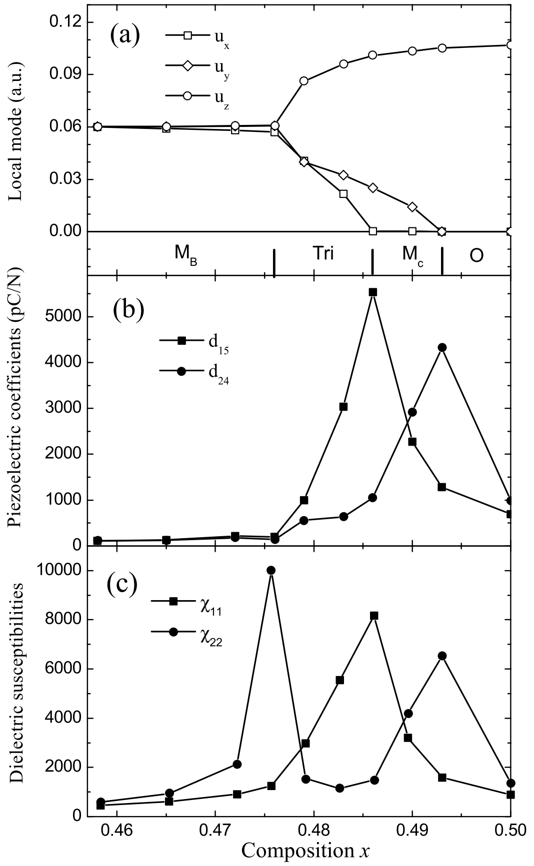

FIG. 1. (a) Average Cartesian coordinates of the local mode vectors; (b) piezoelectric coefficients d_{15} and d_{24}; (c) dielectric susceptibilities χ_{11} and χ_{22} as functions of composition x in atomic-ordered PZT alloys made of the $\mathrm{Pb(Zr_{1-x+\nu}Ti_{x-\nu})O_3/Pb(Zr_{1-x-\nu}Ti_{x+\nu})O_3}$ sequences. ν is set to its maximal value as $\nu = x$. The temperature in simulation is 50 K.

Figure 1(b) shows the corresponding piezoelectric coefficients and Fig. 1(c) the dielectric susceptibilities which are calculated in the correlation-function approach [13]. It shows that d_{15} reaches its maximum near the Tri to M_C transition and remains a remarkably large value above 1000 pC/N in the MPB region, while d_{24} achieves values above 1000 pC/N in M_C phase and reaches its maximum near the M_C to O transition. Another important piezoelectric coefficient, d_{33}, is not shown here because the modulations scarcely affect u_z and have little effect on d_{33}. The existences of the M_B-Tri, Tri-M_C, and M_C-O transitions also result in the peaks of dielectric responses, as shown in Fig. 1(c).

We also investigate the effects of the modulation parameter ν, the fluctuation amplitude, on the structural and piezoelectric properties of the modulated structures which have overall composition $x = 0.485$. Figure 2(a) shows the average local modes as a function of ν at 50 K. The structure of $\nu = 0$ (in the case of disordered PZT alloy) has $u_x = u_y < u_z$ characterizing the M_A structure with polarization lying between [111] and [001] directions. When ν becomes larger than 0.155, u_x begins to decrease. With increasing ν, u_x decreases gradually whereas u_y and u_z increase very slowly. This behavior corresponds to the phase with a Tri symmetry. When ν becomes larger than 0.45, u_x becomes null, while u_y and u_z remain unequal, indicating a M_C symmetry with a polarization between [011] and [001] directions.

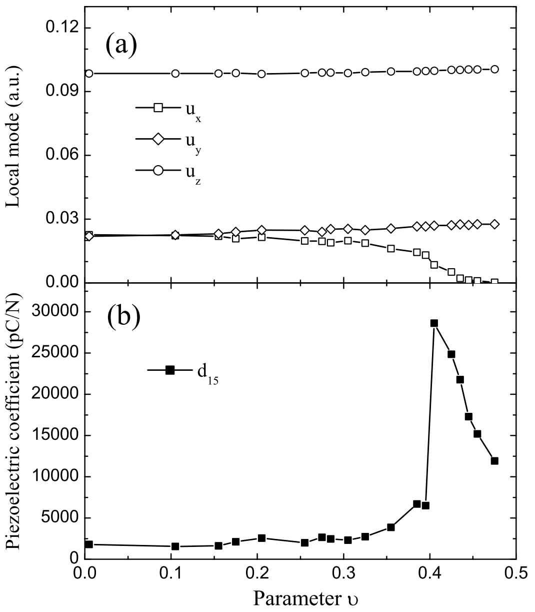

FIG. 2. (a) Average Cartesian coordinates of the local mode, and (b) piezoelectric coefficient d_{15}, as functions of the parameter ν in modulated PZT structures with $x = 0.485$ at 50 K.

Summarily, increasing the parameter ν leads to a continuous rotation of the polarization and transformation between different ground states which are driven by the annihilation of u_x—the polarization component along the direction of compositional modulation.

Theoretical and experimental studies have suggested that polarization rotation is essential for the large piezoelectric response in the perovskite alloys [14,15]. Such an effect is clearly demonstrated in Fig. 2(b) where the piezoelectric coefficient d_{15} is depicted. With decreasing u_x, d_{15} increases from 2000 pC/N to 8000 pC/N gradually in the Tri phase for $0.2 < \nu < 0.4$. Then d_{15} reaches a very steep peak about 30 000 pC/N at $\nu \simeq 0.4$ where the polarization most easily rotates [see also Fig. 2(a)]. After that, d_{15} decreases slowly but still remains large values even in M_c phase. As one can see in Fig. 2(b), d_{15} is larger than 10 000 pC/N for a broad range of $\nu > 0.4$. To our best knowledge, such a huge enhancement of the piezoelectric coefficient has never been reported in any perovskite material before.

Temperature properties of the material are important for its application performances. Here we investigate the influence of temperature on a structure with $x = 0.485$ and $\nu = 0.305$, which adopts a Tri ground state in Fig. 2(a). The resulting piezoelectric properties are depicted in Fig. 3. A huge d_{24} piezoelectric coefficient peak appears near the O to M_C transition (the information of average local mode is not shown here), around which d_{24} remains larger than 5000 pC/N for a broad range of temperature. The simulations also predict the d_{15} peak consistent with the transition from M_C to Tri phase. In addition, it is found that with increasing ν, the M_C-Tri transition temperature decreases, and consequently, the temperature of d_{15} peak is dependent on the value of the modulation parameter ν. This dependence brings great convenience to developing piezoelectric devices for application at different temperatures.

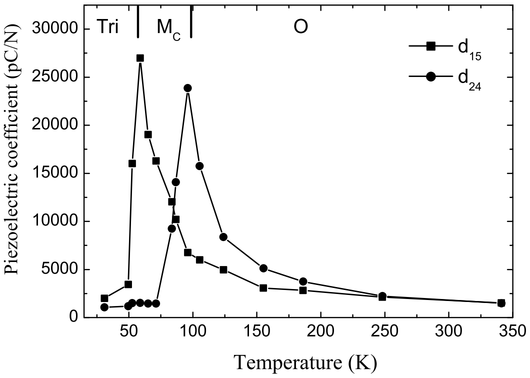

FIG. 3. Piezoelectric coefficients in modulated PZT structure with $x = 0.485$ and $\nu = 0.305$ as functions of temperature.

The above intriguing results can be understood by considering the orientation dependence of dipole-dipole interaction in modulated structures.

Although $PbZrO_3$ and $PbTiO_3$ are similar enough to form $Pb(Zr_{1-x}Ti_x)O_3$ solid solutions at any composition x, their intrinsic polarization properties are different to some extent. As a result, the magnitude of polarization vibrates with varying local composition that is caused by the structural modulation. In our calculation, the Ti-rich planes have larger average local mode, while Ti-poor planes have smaller values of local mode.

In the homovalent alloys such as PZT, the long-range polarization interactions are described in dipole-dipole interaction energy [8,9]:

$$E_{\text{dipole}} = \frac{Z^{*2}}{\epsilon_\infty}\sum_{i<j}\frac{\mathbf{u}_i\cdot\mathbf{u}_j - 3(\hat{\mathbf{R}}_{ij}\cdot\mathbf{u}_i)(\hat{\mathbf{R}}_{ij}\cdot\mathbf{u}_j)}{R_{ij}^3}, \qquad (2)$$

where Z^* is the Born effective charge and ϵ_∞ the optical dielectric constant of the material. When the dipole is uniform ($\mathbf{u}_i \equiv \langle\mathbf{u}\rangle$), E_{dipole} is isotropic, i.e., E_{dipole} is independent of the direction of the polarization. However, when the magnitude of the dipole fluctuates due to the structural modulation, the situation differs. E_{dipole} becomes dependent on the angle between the directions of modulation and polarization [see Fig. 4(a)]: when the polarization is parallel to the modulation, the dipoles are aligned shoulder to shoulder and the energy is higher; when the polarization is perpendicular to the modulation, the dipoles are aligned end to end so that the energy is lower. To further clarify this point, we present a simple numerical analysis here. The local modes in a [100] plane are assumed to fluctuate as

$$\mathbf{u}_i = \langle\mathbf{u}\rangle[1 + \xi K_i], \qquad (3)$$

where ξ is the fluctuation amplitude, and K_i is equal to $+1$ or -1 depending on which [100] plane the dipole

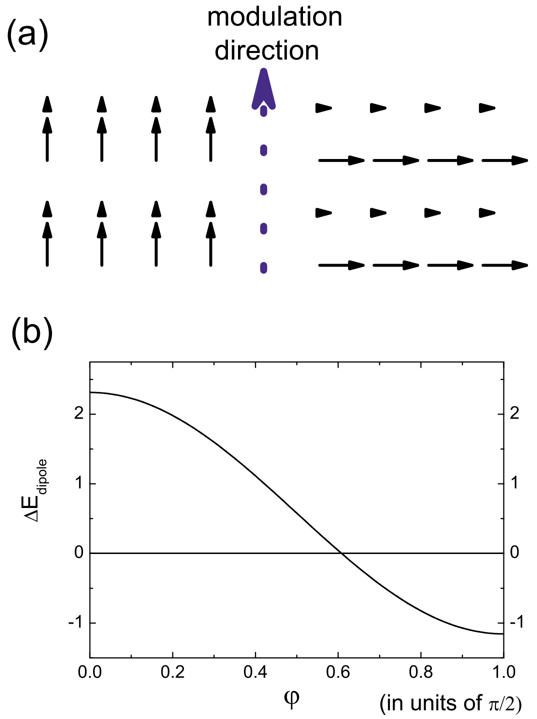

FIG. 4 (color online). (a) Schematic graphics of dipole alignment in modulated structure: dipole aligned parallel to modulation direction with higher energy (the left), and alignment perpendicular to modulation with lower energy (the right). (b) Variation of dipole-dipole interaction $\Delta E_{\mathrm{dipole}}$ [see Eq. (4)], as a function of φ (the angle between the polarization and the modulation direction). $\Delta E_{\mathrm{dipole}}$ is measured in units of E^0_{dipole}, while φ in units of $\pi/2$.

locates. It is easy to show that the dipole-dipole interaction energy can be rewritten as

$$E_{\mathrm{dipole}} = E^0_{\mathrm{dipole}} + \xi^2 \Delta E_{\mathrm{dipole}}. \tag{4}$$

$\Delta E_{\mathrm{dipole}}$ reflects the variation of dipole energy caused by the structural modulation and relies on the angle between the polarization and the modulation directions (denoted as φ). In Fig. 4(b), we plot $\Delta E_{\mathrm{dipole}}$ as a function of φ with polarization rotating from [100] to [010] direction. It shows that $\Delta E_{\mathrm{dipole}}$ has its maximum when the polarization is parallel to the modulation direction. When the direction of polarization deviates from that of modulation, $\Delta E_{\mathrm{dipole}}$ continuously decreases, and reaches the minimum with polarization perpendicular to the modulation direction. Accordingly, compositional modulation will cause the polarization to rotate away from the modulation direction, which results in unusual structure transitions and induces huge enhancement of piezoelectric coefficient, as revealed in the above case of PZT. In perovskite ultrathin films, the polarization is restricted in the normal direction by the strain from matrix, so the dipole-dipole interaction increases and violates the ferroelectricity below a critical thickness [16].

It is noted that the structures outside the MPB region are not sensitive to the atomic ordering. The main reason is that the dipole-dipole interaction is not the only part to determine the Hamiltonian. When the rotation occurs, the other parts of the Hamiltonian may increase and cause an energy barrier. MPB is a region where different phases have close free energy, which means that the energy barrier of polarization rotation is small. So the dipole-dipole energy dominates in this region and produces the anomalies. When the composition deviates from MPB, such energy barrier increases and the polarization rotation is prevented.

On the basis of the general microscopic mechanism discussed here, it is expected that solid solution made of homovalent perovskite ferroelectrics with a MPB should have the similar structural and piezoelectric anomalies as those of PZT when the atomic ordering is arranged. Besides, compared with heterovalent alloys such as PSN, experimental modifications to the atomic ordering of homovalent alloys such as PZT is more practicable because $\mathrm{Pb(Zr_{1-x}Ti_x)O_3}$ is stoichimetric at any x value.

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