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First-principles study of piezoelectricity in tetragonal $PbTiO_3$ and $PbZr_{1/2}Ti_{1/2}O_3$

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The local orbital extension of the linearized augmented plane wave (LAPW+LO) method within the general gradient approximation was used to determine structural and ferroelectric properties of tetragonal $PbTiO_3$ (PT), and two chemically ordered $PbZr_{1/2}Ti_{1/2}O_3$ (PZT 50/50) phases, with B-site cations ordered along [001], and [111] directions. Stable ferroelectric ground states were found in all structures. Bulk spontaneous polarization, dynamical charges (Z^*), and piezoelectric stress tensor elements were determined from ground-state Berry's phase calculations. Ordering along the polar [001] direction was found to enhance the e_{33} piezoelectric stress modulus in PZT 50/50. While theoretical piezoelectric stress moduli of PT, $e_{15}=3.15\ \mathrm{C/m^2}$, $e_{31}=-0.93\ \mathrm{C/m^2}$, and $e_{33}=3.23\ \mathrm{C/m^2}$, agree well with single-crystal experimental data, computed proper moduli of bulk crystalline PZT, $e_{33}(P4\mathrm{mm})=4.81\ \mathrm{C/m^2}$ and $e_{33}(I4\mathrm{mm})=3.60\ \mathrm{C/m^2}$, differ significantly from low-temperature experimental moduli of polycrystalline samples. [S0163-1829(99)03319-6]

I. INTRODUCTION

Many of the technologically important ferroelectics are oxides with simple perovskite, or more complex perovskite related structures. $PbTiO_3$ (PT) is one of the simplest members of this class of materials. It has a clearly established phase transition with $T_c=766$ K from a paraelectric cubic to a ferroelectric tetragonal phase, and its electronic structure has been studied extensively.[1–4] Therefore, PT is an obvious starting point for understanding piezoelectricity in ferroelectrics. PT is also an end member for PZT, and the newly discovered relaxor-PT materials with very high-electromechanical coupling properties and low-dielectric loss. The latter materials, represented by $PbZn_{1/3}Nb_{2/3}O_3$-$PbTiO_3$ (PZN-PT) and $PbMg_{1/3}Nb_{2/3}O_3$-$PbTiO_3$ (PMN-PT),[5] may revolutionize acoustic sensors and transducers, with important applications in medical ultrasound and acoustic measurements. The other object of this study, lead zirconate titanate, is one of the best known ferroelectric materials, due to its excellent ferroelectric and piezoelectric properties in polycrystalline form. Ceramics based on lead titanate and lead zirconate titanate $PbZr_{1-x}Ti_xO_3$, either in pure or in doped form, are the materials of choice in a wide range of applications including actuators, ultrasonic transducers, piezoelectric transformers, and acoustic scanners.[6] In contrast to the newly discovered relaxor-PT materials, which are relatively insensitive to composition, near morphotropic boundary compositions are necessary in PZT-related materials to achieve high-piezoelectric coefficients. The growth of good quality single crystals has not been successful for a significant part of the PZT phase diagram,[7] while experimental single-crystal structural and piezoelectric data is readily available for PT. Due to the lack of single-crystal data for PZT, determination of bulk dielectric, piezoelectric, and elastic properties of this material usually involves indirect methods,[8] and low-temperature measurements to freeze out external domain wall and thermal effects.[9] Therefore, *ab initio* determination of piezoelectric properties can also provide us with an important estimate for the missing single-crystal data of PZT and related ferroelectric materials.

Similar to PT, there is only one high-temperature cubic paraelectric phase in the experimental phase diagram of PZT.[10] At low temperatures, however, the phase diagram of PZT is far more complex, and it contains regions corresponding to several phase transitions. Compositions for $x>0.52$ in $PbZr_{1-x}Ti_xO_3$, including pure PT, show only one low-temperature tetragonal phase, which belongs to the $P4$mm symmetry group. The high Zr content region of the diagram is considerably more complicated. Pure $PbZrO_3$ (PZ) at low temperatures occurs in a complex antiferroelectric orthorhombic structure. Pulsed-neutron scattering experiments show that atoms in PZ are significantly displaced locally from the average sites determined by crystallographic analysis.[11] Near the ferroelectric-paraelectric transition temperature of the high Zr-content PZT, the structure of the material is less established. Transmission-electron spectroscopy studies[12] revealed an intermediate ferroelectric (FE) phase with rhombohedral symmetry. Other investigations showed an AFE tetragonal phase of $PbZr_{1-x}Ti_xO_3$ for compositions with $x<0.03$.[13] This AFE phase disappears with increasing Ti content, at $x>0.07$. Solid solutions of rhombohedral $PbZr_{1-x}Ti_xO_3$ for $0.07<x<0.35$ show an R3m to R3c phase transition. The rhombohedral region can be further partitioned based on the type and ordering of the oxygen octahedra rotations.[14]

The phase diagram of the PZT solid solution shows a nearly temperature-independent morphotropic phase transition for compositions near $PbZr_{0.45}Ti_{0.55}O_3$. The most widely applied piezoelectric ceramic is PZT with compositions near this morphotropic boundary. At this concentration, the piezoelectric moduli, the remnant polarization, and the material's dielectric susceptibility have their maxima. Chemically ordered $PbZr_{1/2}Ti_{1/2}O_3$ phases investigated in this study are the

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computationally simplest systems with stoichiometry close to that of the morphotropic-phase boundary.

The 1:1 ordering pattern chosen in this study can be found experimentally in ferroelectrics, and is very common along the [111] direction in Pb containing perovskites with the formula of $Pb(B'B'')O_3$. Nevertheless, chemical ordering has not been considered as a possibly important feature of PZT, mainly because long-range chemical ordering has not been observed experimentally in pure PZT.[15] Ignoring covalency, the degree of order is determined by the size and charge differences between the two B-site ions; the larger the difference the more favored the ordered state is. The energy difference between ordered and disordered PZT phases is expected to be small, since the charges of the B site cations are equal, neither is there a large difference between their sizes. The available experimental data (x-ray and TEM) show no long-range order in microcrystalline PZT, and they predict a shorter than 2-nm coherence length. We have chosen to study ordered materials because of their relative computational simplicity. When drawing conclusions, however, one has to keep in mind that chemical order can have a subtle effect on many properties of $A(B'B'')O_3$ type ferroelectric perovskites.[16] Long-range B-site cation order with short coherence length can result in relaxor-type behavior, whereas both local-atomic disorder and long-coherence lengths can lead to normal ferroelectric or antiferroelectric properties.[17] We consider a ferroelectric material a normal ferroelectric, if it can be characterized by a sharp first- or second-order change in permittivity about their Curie temperature, weak frequency dependence of permittivity, and strong anisotropy of light scattering, while relaxor ferroelectrics have broad, strong frequency-dependent maxima with weak remnant polarization. Relaxors also show very weak anisotropy to light scattering and no x-ray line splitting due to their pseudocubic structure.

Highly oriented PZT films can be prepared by using layer-by-layer deposition techniques.[18–20] These low-temperature methods can create films oriented along various axes depending on the substrate used in the deposition process. The structure of these films could provide a unique example to compare with theoretical results of ordered infinite crystals. So far, however, not even these layered materials showed experimental evidence for long-range chemical order.

Since the ferroelectric instability results from a delicate balance between short-range repulsions favoring the occupance of high-symmetry sites, and long-range dipolar forces favoring symmetry lowering ferroelectric distortion; usually highly sophisticated first-principles computational methods are required to adequately describe the properties of ferroelectric materials.[21] Simpler, ionic models can fail to reproduce ferroelectric properties, since they are less capable of describing covalent bonding between oxygens and the cations, considered by many as the major driving force behind ferroelectricity. Covalent bonding decreases short-range repulsive forces, and very frequently lowers the symmetry of local environments, therefore is crucial in creating the ferroelectric distortion. Bonding promotes the displacement of potential surface minima from high symmetry, sites.

Both experimentally, and theoretically, spontaneous strain and volume effects were found to play an important role in ferroelectric phase transitions and properties related to ferroelectric instabilities. Unfortunately, strain and volume can be a relatively strong function of applied computational methods, requiring an even more careful analysis of the final theoretical results. First-principle density-functional theory (DFT) methods have been used effectively to contribute to the microscopic understanding of the basic principles underlying ferroelectricity. Since the local-density approximation (LDA) usually gives volumes that are too small by several percent, in some cases the ferroelectric instability was found to be suppressed at LDA optimized volumes. Results of LDA calculations were found to be in best agreement with experimental observables when properties are obtained at experimental lattice parameters. Calculations within the general gradient approximation (GGA) (Ref. 22) yield ferroelectric parameters very similar to those of the LDA calculations, but the GGA parameters were found to be closer to the experimental results, and thus the well depths are more accurate at optimized theoretical volumes. Former theoretical papers have demonstrated that sufficiently high-quality DFT results can account for the overall nature of the potential surface in a ferroelectric material, including depth, and shape of soft-mode displacement wells together with hybridization effects.

II. METHOD

A. Electronic structure method

We reported recently optimized structural properties, piezoelectric response, and dynamical charge-tensor elements of PT.[23] In this paper, we present additional internal structural details of this material, as well as the structural and piezoelectric properties of a closely related, technologically one of the most important ferroelectric materials, PZT 50/50. All properties presented formerly and in this paper were computed within the general gradient approximation using the full-potential *ab initio* LAPW method with local-orbital (LO) extension.[24] The LAPW+LO method includes local orbitals in addition to the normal LAPW basis to allow treatment of all the valence bands in a single-energy window and greater variational freedom. Local orbitals used to include the semicore Zr $4s$, $4p$ and Ti $3s$, $3p$ states with the valence bands as well as to help the relaxation of the linearization of the Pb $5d$, Zr $4d$, Ti $3d$, and O $2s$, $2p$ states. There is no pseudopotential approximation, core states of atoms were calculated self-consistently in the crystal potential and were treated fully relativistically, while valence states were treated semirelativistically. The Perdew-Burke-Ernzerhof 1996 (PBE96) (Ref. 22) exchange-correlation parametrization was used in the calculations. The value of RK_{max} was set to 8.3, LAPW sphere radii of 2.0, 1.7, 1.7, and 1.6 a.u. were used for Pb, Zr, Ti, and O, respectively. Pb $5d$, $6s$, $6p$, Zr $4s$, $4p$, $4d$, $5s$, Ti $3s$, $3p$, $3d$, $4s$, and O $2s$ and $2p$ orbitals were treated as valence orbitals. The special-points method[25] was applied for Brillouin-zone samplings with a $4\times4\times4$ **k**-point mesh in PT, and a $6\times6\times4$ and $4\times4\times4$ **k**-point mesh for the [001] and the [111] ordered PZT structures, respectively. The **k**-space integrations in the Berry's phase calculations were made on a uniform $4\times4\times20$ **k**-point mesh in PT, and on a $4\times4\times15$ **k**-point mesh in PZT. Results were checked for convergence with respect to the number of **k** points and $\mathrm{RK}_{\max}$. Analytical forces were calculated using the formulation of Yu *et al.*[26]

B. First-principles determination of macroscopic polarization

The total closed-circuit (zero-field) macroscopic polarization of a strained sample $\vec{P}^T$ can be expressed as $P_i^T=P_i^s+e_{i\nu}^T\epsilon_\nu$, where P_i^s is the spontaneous polarization of the unstrained sample, ϵ_ν is the strain-tensor element, and $\mathrm{e}_{i\nu}^T$ defines the piezoelectric response.[27] At low temperatures PT and PZT 50/50 are tetragonal and belong to crystal class 4mm. The three independent piezoelectric tensor components of this class are $e_{31}=e_{32}$ and e_{33}, which describe the zero-field polarization induced along the z axis when the crystal is uniformly strained in the basal xy plane and along the z axis, respectively, and $e_{15}=e_{24}$, which measures the change of polarization perpendicular to the z axis induced by shear strain. This latter component is related to the induced polarization by $\Delta P_1=e_{15}^T\epsilon_5$ and $\Delta P_2=e_{15}^T\epsilon_4$. The total induced polarization along the crystallographic c axis can be expressed as $\Delta P_3=e_{33}^T\epsilon_3+e_{31}^T(\epsilon_1+\epsilon_2)$, where $\epsilon_1=(a-a_0)/a_0$, $\epsilon_2=(b-b_0)/b_0$ and $\epsilon_3=(c-c_0)/c_0$ are strains along the a, b, and c axis, respectively, and a_0, b_0, and c_0 are lattice parameters of an unstrained reference structure. The change in total macroscopic polarization, containing both electronic and rigid ionic-core contributions, is a well-defined bulk property at zero electric field. Therefore, the total piezoelectric constant can be calculated from finite differences of polarizations between crystals of different shapes and volumes.

The electronic part of the polarization was determined using the Berry's phase approach.[28] The details of this approach as applied to the LAPW+LO method are described in one of our former papers.[23] In summary, one can calculate the polarization difference between two states of the same solid, under the necessary condition that the crystal remains an insulator along the path that transforms two states into each other through an adiabatic variation of a crystal Hamiltonian parameter (λ). Expressing electronic polarization in terms of a dynamic current[29] instead of static-charge separation provides well-defined bulk quantities at the adiabatic limit. The magnitude of the electronic polarization of a system in state (λ) is defined only modulo eR/Ω, where **R** is the shortest real-space lattice vector and Ω is the volume of the cell. In practice the eR/Ω factor can be eliminated by careful inspection, if the changes in polarization are such that $|\Delta\mathbf{P}|\ll|e\mathbf{R}/\Omega|$. The electronic polarization difference between two crystal states can be then expressed as $P^{el}=P^{el}(\lambda_2)-P^{el}(\lambda_1)$. Common origins to determine electronic and core parts can be arbitrarily assigned along the crystallographic axes. The individual terms in the polarization sum do depend on the choice; however, the final results are independent of origin.

Elements of the macroscopic piezoelectric tensor can be further separated into two parts: a clamped-ion or homogeneous strain contribution evaluated at vanishing internal strain,[30] and a term that is due to an internal microscopic strain, i.e., the relative displacements of differently charged sublattices. *Proper* macroscopic polarization changes (P_i^P) that do not include terms from the rotation or dilation of the spontaneous polarization (P_i^s) of a ferroelectric are given by $P_i^P=P_i^T-\Sigma_j(\epsilon_{ij}P_j^s-\epsilon_{jj}P_i^s)$. The difference between proper and total polarizations is due only to the homogeneous part, and it should be noted that the homogeneous part appears as a pure electronic term only in the expression for the *proper* piezoelectric modulus. It is also evident, that the proper and total piezoelectric constants differ only in materials with nonzero polarization in the unstrained crystal (i.e., pyroelectrics). For some constants, such as e_{33}, proper and improper terms are identical.

Homogeneous strain contributions to the piezoelectric modulus can be evaluated from polarization differences as a function of strain, with the internal parameters kept fixed at their values corresponding to zero strain. Terms that arise from internal microscopic relaxation,[31,32] can be calculated after determining the elements of the dynamical transverse-charge tensors and variations of internal coordinates as a function of strain. Transverse charges in general are the mixed second derivatives of a suitable thermodynamic potential with respect to atomic displacements and electric field. They measure the change in polarization induced by unit displacement of a given atom at zero electric field to linear order. In a polar insulator transverse charges indicate the extent of polarization change induced by relative sublattice displacements. While many ionic oxides have Born effective charges close to their static values,[33] ferroelectric perovskites display anomalously large dynamical charges.[34,35,23]

III. RESULTS

A. Internal structures

The smallest-ordered PZT unit cells, with B site cations ordered along the [001] or [111] directions, contain two formula units. LAPW total energies of the [001] ordered PZT structure were determined within $P4$mm symmetry, and the [111] ordered tetragonal structure within the $I4$mm symmetry, both at the experimental lattice parameters of the microcrystalline PZT 50/50 phase. We did not consider other than tetragonal ordered structures in this study. Table I contains optimized theoretical internal parameters of the ten atom unit cells. These optimized internal configurations served as reference states in polarization calculations. Conditions under which internal structural parameters and polarization related properties of $\mathrm{PbTiO_3}$ were determined have been described in details in our former paper.[23]

Generally, the $\mathrm{BO_6}$ octahedron is regarded as the building block of the perovskite structure. Besides the two most important internal elements of PT and PZT, namely the $\mathrm{ZrO_6}$, and $\mathrm{TiO_6}$ octahedra, we also investigate the distribution of Pb-O and O-O bond distances, and compare them to experimental data and bond lengths calculated from effective ionic radii.[36] Based on the latter values, the sum of Zr-O ionic radii is 2.12 Å in an ideal $\mathrm{ZrO_6}$ octahedron, whereas in $\mathrm{TiO_6}$ the sum of Ti-O ionic radii equals to 2.00 Å. The ideal O-O distances therefore in the undistorted octahedra would be 3.00 Å for $\mathrm{ZrO_6}$ and 2.83 Å for $\mathrm{TiO_6}$.

We find a slightly distorted $\mathrm{O_6}$ octahedron around the central Ti atom in the optimized $\mathrm{PbTiO_3}$ structure, with edge lengths of 2.75, 2.84, and 2.87 Å. These distances are very similar to Glazer and Mabud's[37] low-temperature data, refined by the Rietveld neutron profile method. The Ti atom is strongly displaced from the center of the octahedron by

TABLE I. Structural parameters and Z^*_{33} values of tetragonal PZT 50/50. Internal coordinates (u) are given in terms of the lattice constants of the $P4$mm unit cell.

	PZT $P4$mm				PZT $I4$mm			
Atom	x	y	z	Z^*	x	y	z	Z^*
u_{Pb}	0	0	0	3.46	0	0	0	3.23
u_{Pb}	0	0	0.5300	2.83				
u_{Zr}	0.5000	0.5000	0.2435	6.06	0.5000	0.5000	0.2268	5.96
u_{Ti}	0.5000	0.5000	0.7410	5.35	0.5000	0.5000	0.2255	5.69
u_{O}	0.5000	0.5000	0.9555	-4.44	0.5000	0.5000	0.9452	-4.55
u_{O}	0.5000	0.5000	0.4813	-4.79	0.5000	0.5000	0.4613	-4.95
u_{O}	0.5000	0	0.1938	-2.33	0.5000	0.0142	0.1922	-2.16
u_{O}	0.5000	0	0.7152	-1.91				

0.31 Å, resulting in 1.78, 1.97, and 2.39 Å Ti-O interatomic distances, in good agreement with Glazer and Mabud's nearly temperature-independent values of 1.75, 1.98, and 2.42 Å.

A highly strained oxygen octahedron was found around the Zr atom in tetragonal PZT with $P4$mm symmetry. Calculated oxygen-oxygen distances are 2.82, 2.85, and 3.13 Å, all of which are very far from the ideal 3.00 Å. The Zr atom is displaced from the center of the octahedron, and the calculated Zr-O distances range from 1.97 to 2.39 Å. Similarly, to the Zr atom, the environment around the Ti atom is highly unsymmetric, with Ti-O interatomic distances varying from 1.78 to 2.16 Å. However, oxygen-oxygen distances around the Ti atom are very close to the values determined from ionic effective radii and are in the range of 2.80–2.85 Å. In tetragonal PZT with $I4$mm symmetry, similarly to that computed for the $P4$mm structure, we found strongly displaced central B-site cations. Optimized Zr-O distances are in the range of 1.95 to 2.34 Å, while the calculated Ti-O distances are 1.83, 1.97, and 2.19 Å. All interatomic distance distributions are very similar in the two ordered PZT structures, and in PT, with one exception; the oxygen octahedron around the Zr is significantly more distorted in the $P4$mm structure. Apart from this, O-O distances in PZT $I4$mm, PZT $P4$mm, and PT were found to be very close to those determined from crystallographic experiments and effective ionic radii.

In the ideal, cubic perovskite structure the Pb atoms are surrounded by twelve oxygen atoms at equal distances. For twelve coordinated Pb the Pb-O radius sum is 2.89 Å, and is very close to the O-O distances. Tetragonal strain, distortion, and relative displacement of oxygen octahedra can lower this symmetry. In PT, the Pb atom is displaced in the same direction as the Ti atom by 0.43 Å. Because of the Pb atom's displacement relative to the O octahedron, the Pb environment loses its high symmetry, with Pb-O computed bond lengths ranging from 2.53, and 2.78 to 3.20 Å. Glazer and Mabud's[37] PT data based on the rigid octahedron model gives very similar 2.51, 2.83, and 3.24 Å values. Pb-O atomic distances range from 2.53 to 3.44 Å in the optimized $P4$mm PZT structure, and one also finds similar 2.57, 2.86, and 3.25 Å Pb-O bond lengths in the $I4$mm tetragonal PZT structure.

Pulsed neutron-scattering studies of local structures in PZ and PZT concluded that local atomic structures in PZ and PZT can deviate significantly from crystallographic long-range structural parameters.[38] In addition, the pulsed neutron atomic pair-distribution function studies indicate that local atomic structures are very similar along a wide range of composition in PZT. In particular, the environment of Pb was found nearly independent of composition, with a strongly off-centered Pb atom in the PbO_{12} unit. Our studies also support a model in which the local Pb-O environment is relatively independent of chemical and long-range structural parameters. The local environment of Zr and Pb are relatively well known from studies of PZ and high Zr content PZT. The first crystallographic model of PZ based on x-ray and neutron-diffraction studies was proposed by Jona *et al.*[39] Fujishita and Hoshino[40] found very similar cation positions in their study. However, they assigned the centrosymmetric *Pbam* spacegroup to PZ, due to the lack of unbalanced oxygen shifts. This also resulted in a smaller deformation of the O octahedra around the Zr atoms than in Jona's study. Our model, which is based on an ideal, infinite-periodic solid, produces structures that are very similar to those determined by crystallographic models. Atomic-distance distributions are in good agreement with Glazer and Mabud's, and Fujishita and Hoshino's[40] results. Our studies, however, do not support the model with very short O-O distances found by Jona *et al.*

B. Polarization and piezoelectricity

Born effective charges were obtained from changes of macroscopic polarization induced by small displacements of atomic sublattices (Table I). Comparing PZT and formerly published PT results,[23] we found that ordering and chemical environment have little effect on the magnitude of Born effective charges in these structures. Similar to other perovskite-type ferroelectric oxides, these charges were found significantly larger than their nominal ionic values. Our results satisfy the acoustic sum rule $\Sigma_j Z^*_{j,ii} = 0$ showing that the computations are sufficiently converged with respect to computational conditions.

A theoretical spontaneous polarization value of 0.70 C/m^2 was computed in the [111]-ordered PZT structure, compared to a value of 0.74 C/m^2 in the [001] structure. These values are in good agreement with low-temperature experimental data,[41,42] and are somewhat smaller than the value of 0.88 C/m^2 computed for single-

TABLE II. e_{33} piezoelectric stress tensor elements (C/m^2) of tetragonal $PbTiO_3$ and ordered PZT 50/50.

	$PbTiO_3$	PZT 50/50 ($P4$mm)	PZT 50/50 ($I4$mm)
Homogeneous	-0.88	-0.65	-0.65
Proper Homogeneous	-0.88	-0.65	-0.65
Internal Strain	4.11	5.46	4.25
Total	3.23	4.81	3.60
Experiment	3.35 [a]	27.0 [d]	
	6.50 [b]	11.9 [e]	
	5.0/4.1 [c]		

[a] Reference 45.

[b] Reference 46.

[c] Reference 47, two sets of velocity RMS deviations.

[d] Reference 43, RT data.

[e] Reference 9, low T data.

crystal PT.[23] Polarization values were carefully checked with respect to the mesh density used in **k**-space integrations of the Berry's phase method. **k**-point meshes less dense than $4\times4\times15$ were found to be insufficient. However, polarization differences obtained on denser meshes differ by less than one percent from values computed on the $4\times4\times15$ mesh.

Piezoelectric constants were determined by using both direct and indirect methods. In the direct approach, absolute macroscopic polarization values were computed at a reference structure P^{ref} and at several strained structures P^{ϵ}, with equilibrium internal parameters determined at each strain value. Applied strain values were typically in the $\pm1\%$ range. The slope of the $(P^{\epsilon}-P^{ref})$ vs strain curve in the linear regime yielded directly the piezoelectric constants. Clamped-ion contributions to the piezoelectric moduli were determined from slopes of polarization vs strain curves. During this set of calculations, internal parameters were kept fixed at their values optimized in the unstrained reference structure. When combined with the effective charges and our displacement-strain derivatives we find no significant difference (less than 0.5%) between moduli calculated by direct and indirect methods, indicating that the linear approximation used to describe the piezoelectric response of PT and PZT 50/50 is valid for the applied magnitude of strains. Using this method, we formerly reported piezoelectric stress moduli of PT, $e_{15}=3.15$ c/m^2, $e_{31}=-0.93$ c/m^2, $e_{33}=3.23$ c/m^2, which agreed well with single-crystal experimental data.

Berlincourt *et al.*[43] measured the room-temperature values of elastic compliances s_{ij}^{E} and piezoelectric strain constants d_{ij} for a number of poled-ceramic PZT compositions using standard-resonance methods. In tetragonal PZT, the piezoelectric stress constant e_{ij} is related to the piezoelectric strain constants by

$$e_{33}=2d_{31}C_{13}^{E}+d_{33}C_{33}^{E}, \tag{1}$$

$$C_{13}^{E}=-s_{13}^{E}/s, C_{33}^{E}=(s_{11}^{E}+s_{12}^{E})/s, s=s_{33}^{E}(s_{11}^{E}+s_{12}^{E})-2(s_{13}^{E})^2. \tag{2}$$

Their measurements give the value of $e_{33}=27.0$ C/m^2 in the ceramic material.

Our theoretical values of 3.60 C/m^2 ($I4$mm) and 4.81 C/m^2 ($P4$mm) (Table II) differ significantly from these values. However, room-temperature measurements do include external contributions to the piezoelectric modulus, such as domain-wall and thermal-defect motions. At very low temperatures these contributions can be eliminated from the measurements of d_{ij} piezoelectric strain coefficients.[9] Using the low-temperature data of standard piezoelectric resonance measurements obtained for poled, pure, ceramic PZT 50/50, the measured value of $e_{33}=11.9$ C/m^2 is still more than twice as big as the theoretical value.

Further investigation of various contributions to the e_{33} modulus of PZT 50/50 reveals several important details about the nature of piezoelectric response in PZT 50/50. Homogeneous contributions (-0.65 C/m^2) are independent of ordering and are slightly smaller in magnitude than the contribution found in tetragonal $PbTiO_3$(-0.88 C/m^2).[23] However, ordering along the polarized [001] direction slightly enhances the internal strain part of the e_{33} modulus, resulting in somewhat larger piezoelectric response for the $P4$mm structure.

IV. CONCLUSIONS

We have investigated the structural and electronic properties of tetragonal PT and two chemically ordered tetragonal PZT 50/50 phases. Internal atomic-distance distributions in these materials were found very similar to those obtained by experimental neutron-diffraction studies. Computed local-atomic structures are also very similar in PT and in the two ordered tetragonal PZT phases. Despite the periodic method used in this study, the model produced highly polarized, distorted PbO_{12} units in these materials, almost identical to local clusters found by Teslic and co-workers in PZ and PZT.[38,44]

We have used the Berry's phase approach within the all-electron LAPW+LO formalism to compute polarization-related properties of PT and chemically ordered PZT 50/50 single-crystal materials. Chemical B-site ordering along the [001] direction couples better with [001] strain, which results in larger e_{33} piezoelectric stress modulus in the $P4$mm PZT structure than in the [111]-ordered material. Theoretical intrinsic piezoelectric moduli in ordered PZT 50/50 were found to be somewhat larger, but relatively close to the e_{33}

modulus of single-crystal $PbTiO_3$. This indicates, similarly to local structures, that at the atomic level, no significant difference was found between PZT 50/50 and PT. Spontaneous polarization, dynamical charges, and piezoelectric moduli all support this similarity. Based on our computations, PZT with compositions close to the morphotropic boundary should behave very similarly to PT, which lacks the excellent piezoelectric properties of PZT. Since the computed piezoelectric moduli in both ordered PZT phases differ significantly from experimental data, even after experimentally ‘‘freezing out’’ certain extrinsic contributions, we conclude that the large piezoelectric response in PZT 50/50, unlike in PT, either cannot be described in simple terms of conventional single-crystal piezoelectric response, or that B-site cation disorder significantly enhances piezoelectric properties in this material.

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