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First-principles investigation of ferroelectricity in epitaxially strained Pb_2TiO_4

Craig J. Fennie and Karin M. Rabe
Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854-8019, USA

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The structure and polarization of the as-yet hypothetical Ruddlesden–Popper compound Pb_2TiO_4 are investigated within density-functional theory. Zone center phonons of the high-symmetry K_2NiF_4-type reference structure, space group I4/mmm, were calculated. At the theoretical ground-state lattice constants, there is one unstable infrared-active phonon. This phonon freezes in to give the I2mm ferroelectric state. As a function of epitaxial strain, two additional ferroelectric phases are found, with space groups I4mm and F2mm at compressive and tensile strains, respectively.

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The occurrence of ferroelectricity in the ABO_3 perovskite structure has been known since the 1950's.[1] Recently, first-principles density-functional (DFT) methods have proved invaluable in elucidating the observed behavior of known perovskite oxide ferroelectrics, antiferroelectrics, and quantum paraelectrics.[2,3] Examples include the alkaline-earth titanates,[4–6] the alkali metal tantalates and niobates,[7,8] and the lead-based perovskites.[4,9] There is also a growing interest in applying these methods to the design of ferroelectrics based on the perovskite structure.[10,11]

Another path to new materials leads beyond the perovskite structure. The Ruddlesden–Popper (RP) family of compounds are closely related to the perovskites.[12] They can be viewed as a stacking of AO-terminated ABO_3 perovskite [001] slabs of thickness equal to n primitive lattice constants. Adjacent slabs are shifted relative to one another along [110] by $a/2$, giving the homologous series $A_{n+1}B_nO_{3n+1}$. The $n=1$ structure is shown in Fig. 1.

Given the structural similarity to the perovskites, it seems surprising that there have been no confirmed cases of ferroelectricity in the RP family of compounds.[13] Bulk phases of RP titanates have been reported only for some members of the $Sr_{n+1}Ti_nO_{3n+1}$ and $Ca_{n+1}Ti_nO_{3n+1}$ series.[14] It should not be surprising that neither the strontium nor the calcium RP series of compounds appear to display ferroelectricity given that the end members ($n=\infty$) are $SrTiO_3$ and $CaTiO_3$, respectively, neither of which themselves are ferroelectric. Still, the fact that only a few RP titanates have so far been synthesized in bulk does not preclude the possibility that a metastable RP ferroelectric phase could be produced by an appropriate synthetic process. In order to identify such a system, it is convenient to use first-principles DFT methods, for example, to investigate an as-yet hypothetical first member of a RP series (where the effects of the structural modification would be most severe) whose end member is a perovskite ferroelectric.

In this paper, we show that Pb_2TiO_4, an $n=1$ RP compound based on ferroelectric endmember $PbTiO_3$, is a promising candidate for a high-polarization ferroelectric. Regarding the presence of Pb_2TiO_4 (or higher n compounds) in the bulk phase diagram, reports are conflicting and no structural information is available.[15–17] However, as discussed above, it may be possible to produce a metastable form using modern epitaxial growth techniques. Using first-principles DFT calculations, we compute the ground-state structure and polarization, finding that Pb_2TiO_4 is a ferroelectric with a polarization comparable to $PbTiO_3$. Furthermore, the direction of the polarization can be changed by an applied epitaxial strain.

First-principles DFT calculations were performed within the local density approximation as implemented in the Vienna *ab initio* Simulations Package (VASP).[18] A plane-wave basis set and projector-augmented wave potentials were employed.[19] The electronic wave functions were expanded in plane waves up to a kinetic energy cutoff of 500 eV. Integrals over the Brillouin zone were approximated by sums on a $6\times6\times6$ Γ-centered mesh of k points. Polarization was calculated using the modern theory of polarization as implemented in VASP.[20]

We approach the problem of searching for possible ferroelectric states by first calculating the properties of the RP high-symmetry reference structure, space group: I4/mmm, the structure one expects for the paraelectric phase. We performed full optimization of the lattice parameters ($a=3.857$ Å, $c=12.70$ Å) and internal coordinates ($z_{Pb}=0.3507$, $z_{O_{II}}=0.1562$). The residual Hellmann–Feynman forces were less than 2 meV/Å. Next, we calculated the zone-center phonons of this reference system by computing the dynamical matrix at $q=0$ using the direct method in which each ion was moved by approximately 0.01 Å. A similar approach could be used to identify possible zone-boundary instabilities, not considered here. We then froze in the real-space eigendisplacements of selected unstable modes and performed full relaxations in the space group determined by the symmetry breaking mode. Finally, we compute the polarization.

For Pb_2TiO_4 in the I4/mmm high-symmetry reference structure, there are three infrared (IR)-active modes that transform according to the irreducible representation A_{2u} and four IR modes that transform according to E_u. The one-dimensional A_{2u} modes involve atomic distortions along [001] while in the two-dimensional E_u modes, atoms move in the plane perpendicular to [001]. Our calculations reveal that at the ground-state structural parameters, I4/mmm Pb_2TiO_4 has one phonon with an imaginary frequency ($\omega=96i$ cm^{-1}), indicative of an instability. This unstable phonon is IR active of E_u symmetry type. Therefore, *Pb_2TiO_4 in the RP structure does indeed display a ferroelectric instability*. The real-space eigendisplacements of this unstable ferro-

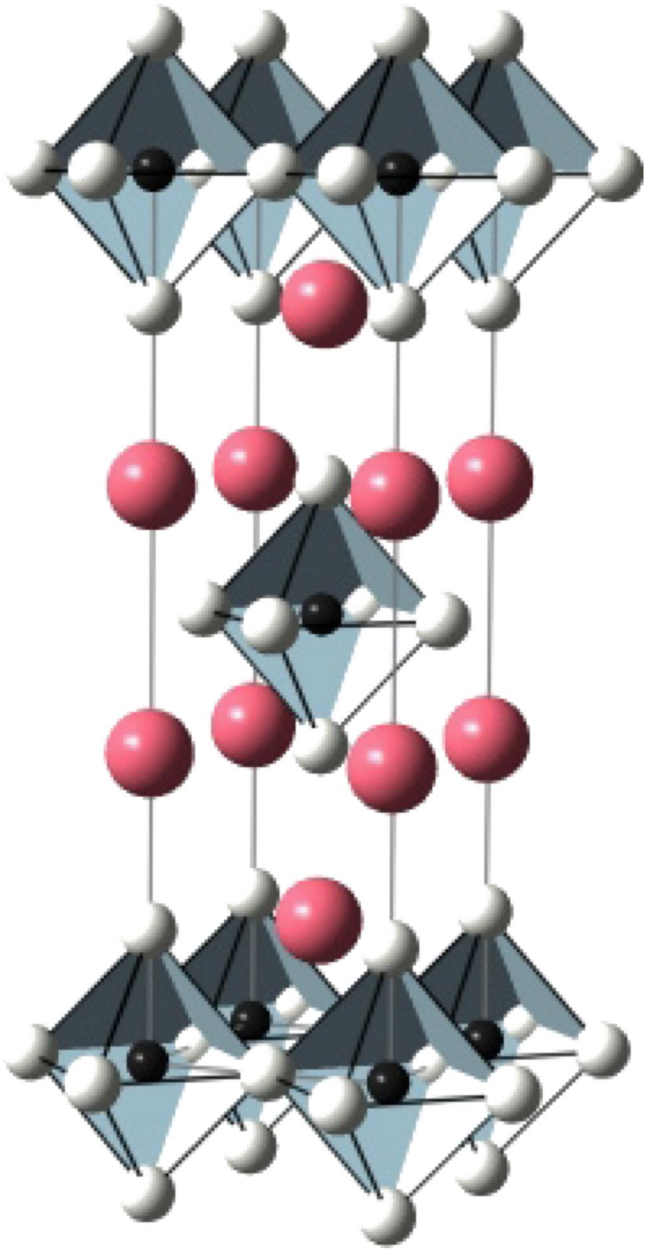

FIG. 1. (Color online) Crystal structure of RP compound Pb_2TiO_4, space group I4/mmm.

electric mode consists of Pb and Ti atoms moving against a nonrigid oxygen octahedron (with larger displacements of the apical oxygens in the PbO layer). As for $PbTiO_3$,[2] the character of the ferroelectric instability in Pb_2TiO_4 involves significant Pb displacements moving against oxygen in the Pb–O planes. This involvement of the *A*-site cation in both $PbTiO_3$ and Pb_2TiO_4 differs from non-Pb-based compounds (e.g., $BaTiO_3$) and has been attributed to the Pb^{2+} $6s^2$ lone pair. It is in fact this lone-pair physics that stabilizes $PbTiO_3$ in the tetragonal phase[4] and may have a role in facilitating the ferroelectric distortion in Pb_2TiO_4.[21]

The key role of Pb is further emphasized by comparison with Ba_2TiO_4. A compound at this composition, barium orthotitanate, has been identified in the bulk phase diagram. It crystallizes not in the RP structure but rather in the monoclinic distorted-K_2SO_4 structure (space group: $P2_1/n$).[22] A calculation for the structure and zone-center phonons of I4/mmm Ba_2TiO_4 in the hypothetical RP structure, exactly analogous to that for Pb_2TiO_4, shows no evidence for any ferroelectric instability, even for varying epitaxial strain.

TABLE I. Crystal structure of ferroelectric Pb_2TiO_4, space group: I2mm, $a=3.985$ Å, $b=3.826$ Å, $c=12.70$ Å.

Atom	Wyckoff	Coordinates		
Pb	(4c) m	0.0616	0	0.3508
Ti	(2a) 2mm	0.0256	0	0
O_{Ix}	(2a) 2mm	$-0.0190+\frac{1}{2}$	0	0
O_{Iy}	(2b) 2mm	-0.0307	$\frac{1}{2}$	0
O_{II}	(4c) m	-0.0496	0	0.1538

Returning to Pb_2TiO_4, we search for the ferroelectric ground state by freezing-in the real-space eigendisplacement pattern of the unstable E_u mode, and performing full relaxations of all ions and lattice constants consistent with the resultant space group. Since this E_u mode is doubly degenerate, any linear combination of the degenerate modes polarized along [100] and [010] is an equivalent eigendisplacement. We considered two linear combinations; one polarized along [100], a second polarized along [110]. Freezing-in the E_u mode polarized along [100] results in a body-centered orthorhombic space group, I2mm. For the distortion along [110], the resulting space group is face-centered orthorhombic F2mm. Since this F2mm structure is slightly higher in energy (20 meV/formula unit) than the I2mm structure, we now consider only the latter (we will revisit F2mm below when discussing the effect of epitaxial strain). Our calculated structural parameters of Pb_2TiO_4 in this orthorhombic space group are displayed in Table I. We imposed the convention, $\Sigma_i \Delta x_i = 0$, where Δx_i is the deviation along [100] from the centrosymmetric position of ion *i*. It can be seen that the relaxed structure can in fact be related to the high-symmetry RP structure by small displacements of Pb and Ti ions moving against the nonrigid oxygen octahedra, consistent with the freezing-in of the E_u phonon instability of the high-symmetry structure as proposed. Finally, we calculate the spontaneous polarization P_s. We find that $P_s = 68\ \mu C/cm^2$, along [100] as required by symmetry. Therefore *Pb_2TiO_4 in the RP structure is a ferroelectric with a spontaneous polarization comparable to that of $PbTiO_3$*.[23]

Epitaxy plays a dual role in our thinking about the Pb_2TiO_4 system. As will be discussed shortly, one possible route to synthesize thin films of Pb_2TiO_4 in the RP structure is through the use of epitaxial stabilization.[24,25] In addition, it is becoming increasingly possible to grow oxide thin films coherently on substrates with a relatively wide range of lattice constants (1–2% lattice mismatch is currently the norm). This provides an additional parameter to "tune" the properties of the material to desired values by applying an in-plane (or epitaxial) strain to the thin film compared to bulk.

With this in mind we consider again the high-symmetry, I4/mmm RP structure and explore the effect of epitaxial strain on the low-frequency IR-active modes. We impose epitaxial strain by constraining the two basal primitive vectors

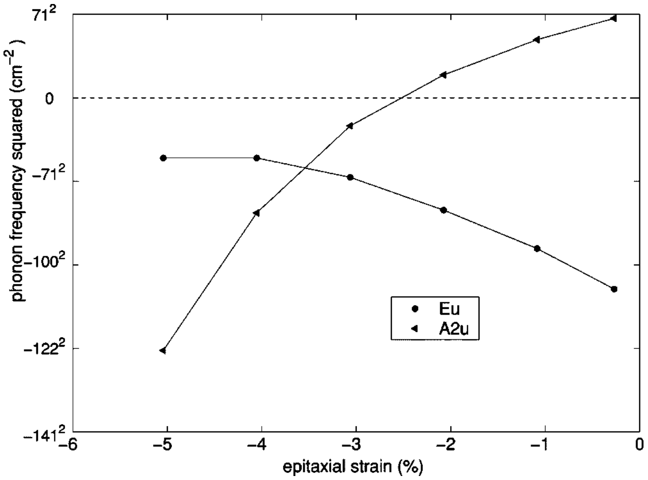

FIG. 2. Soft IR-active phonon frequencies as a function of in-plane compressive strain for the lowest-frequency E_u phonon and lowest-frequency A_{2u} phonon of the high-symmetry paraelectric I4/mmm reference structure.

of the body-centered-tetragonal lattice to an angle of 90° and to a fixed equal length (i.e., corresponding to that of an implicit coherently matched square-lattice substrate). In Fig. 2, we show how the phonon frequencies for the lowest-frequency E_u and A_{2u} phonons vary as a function of compressive epitaxial strain. We use the computed a parameter of tetragonal ferroelectric $PbTiO_3$ (Ref. 23) as the reference strain (i.e., for 0% strain, we fixed the in-plane lattice constant of Pb_2TiO_4 to that of ferroelectric $PbTiO_3$).[26] For each value of fixed strain, we again perform relaxation of the ions and c axis.

Referred to tetragonal $PbTiO_3$, the ground-state I4/mmm structure has an in-plane strain of approximately −0.3%. For small compressive strains, the phonon instabilities of epitaxial Pb_2TiO_4 are expected to be similar to those in the unconstrained structure. This corresponds to the far right of the Fig. 2. It is evident that the lattice dynamics in this region of zero or small epitaxial strains are dominated by the largely unstable E_u mode, as previously discussed. If we now increase the compressive epitaxial strain (i.e., from right to left) the E_u mode stiffens while the A_{2u} mode softens considerably and becomes unstable at $\approx -2.5\%$ strain. Figure 2 shows that for large compressive strains (-4 to -5%), the highly unstable A_{2u} should dominate the lattice dynamics while for intermediate strain values, both an A_{2u} mode and an E_u mode are unstable and comparable in value. This behavior with strain can be simply understood as arising from volume effects. As we increase the in-plane compressive strain, the effective volume in which the E_u mode (polarized in-plane, perpendicular to the c axis) vibrates decreases. This increases the short-range repulsive forces, thereby stiffening the force constant.[27] In contrast, the effective volume of the A_{2u} mode (polarized parallel to the c axis) increases with increasing compressive strain leading to a softening of the force constant.

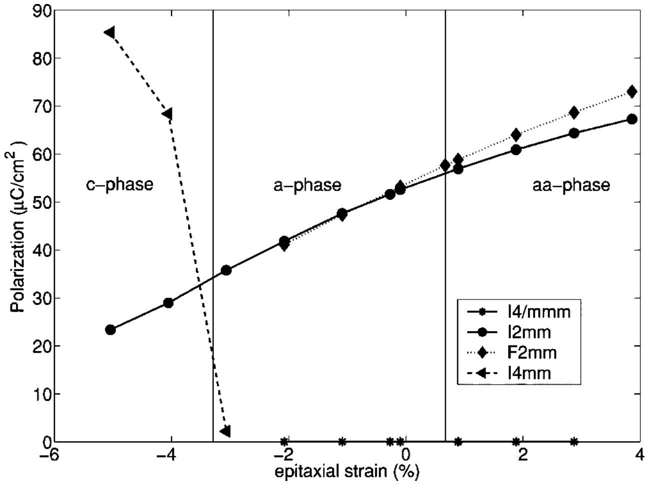

FIG. 3. Polarization along [001] (I4mm), [100] (I2mm), and [110] (F2mm) as a function of epitaxial strain.

Next, we use these phonon instabilities (Fig. 2) as a guide to search for additional epitaxially stabilized ferroelectric structures. At each value of strain, we first freeze-in separately the real space eigendisplacement pattern corresponding to the A_{2u} mode (I4mm), the E_u [100] mode (I2mm), the E_u [110] mode (F2mm), and both the A_{2u} and the E_u [100] modes (Cm). Then, we relax all ions and the c-axis lattice parameter while keeping the in-plane lattice parameters fixed. Finally, we calculate the total energy, Fig. 4, and the polarization, Fig. 3, of the resultant structures as a function of epitaxial strain.

As shown in Fig. 3, RP Pb_2TiO_4 undergoes a series of structural transitions with epitaxial strain. Over the range of slightly tensile to compressive strains, Pb_2TiO_4 forms in the I2mm space group. Following the convention appearing in the literature,[28] we refer to this phase as the a phase. The polarization in this phase varies from 34 $\mu C/cm^2$ at −3.3% strain to 56 $\mu C/cm^2$ at +0.7% strain. The minimum energy structure in the a phase occurs at a tensile strain of +0.55%, corresponding to the ground-state structure discussed above. As the compressive strain increases, the energy of the I2mm structure approaches that of the paraelectric I4/mmm structure, as shown in Fig. 4, while remaining about 3 meV lower

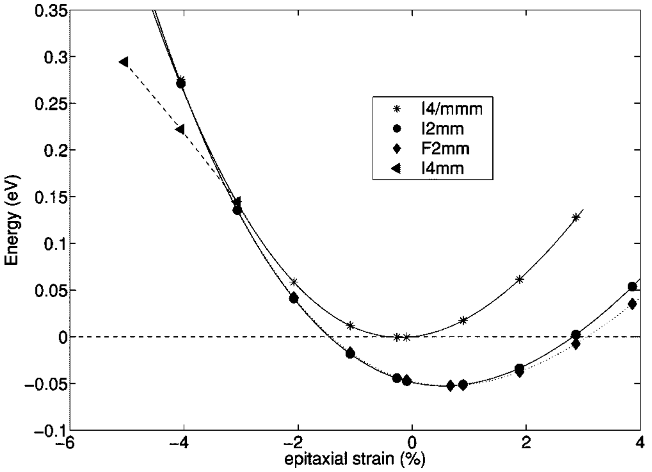

FIG. 4. Energy (per formula unit) as a function of epitaxial strain for space groups I4/mmm (paraelectric), I2mm (a phase), F2mm (aa phase), and I4mm (c phase).

for the values of strain that we considered. This is consistent with the leveling off of the E_u phonon as shown in Fig. 2 and explains why the polarization of the I2mm structure remains nonzero for large compressive strains. A transition from the *a* phase, with the polarization in plane, to a phase with the polarization along the *c* axis, i.e., from I2mm to I4mm, occurs for large compressive strains as anticipated from the phonon instabilities of the I4/mmm structure. This occurs at $\approx$-3.3% strain. We refer to this I4mm phase as the *c* phase. The polarization in the *c* phase approaches 70 $\mu C/cm^2$ at −4.0% strain and continues to increase. In the range where the two unstable mode frequencies cross, we considered the possibility that coupling between the two modes could lead to additional ferroelectric structures. However, relaxing the structures in the low-symmetry space group Cm always yielded one of the two higher-symmetry structures (*a* or *c* phase, depending on the value of the misfit strain). Thus, the transition from *a* to *c* with increasingly compressive in-plane strain appears to be first order.[29] Finally, for large enough tensile strains (greater than $\approx$0.7%) the F2mm structure becomes lower in energy than that of the I2mm structure. The polarization of this *aa*-phase is comparable to that of the *a* phase while the minimum energy structure occurs at a slightly more positive strain of +0.7% strain. The point at which the energy curves for the *a* and *aa* phases cross is of particular interest, as the in-plane polarization is nearly isotropic. The free rotation of the polarization might result in some unexpected interesting physical properties.

High-pressure techniques have been successful in the synthesis of RP structures, e.g., polycrystalline Ba_2RuO_4.[30] This route seems promising to synthesize bulk RP Pb_2TiO_4. Further, we suggest synthesis of nonbulk phases of this material through the use of epitaxial stabilization.[24,25] In fact, this method has proven quite successful for stabilizing a variety of oxide thin films in the RP structure. One example is that of the $Sr_{n+1}Ti_nO_{3n+1}$ series.[31] Another example has been the low-pressure synthesis of Ba_2RuO_4 in the RP structure.[32] The growth of thin films of Pb_2TiO_4 would provide a means to realize the interesting behavior of this material with epitaxial strain.

Initially, we asked the question whether Pb_2TiO_4 in the RP structure would be a ferroelectric. Using first-principles DFT calculations, we have seen that indeed it does display a ferroelectric instability. We have argued that if Pb_2TiO_4 could be made in the RP structure (bulk or thin films) it would undergo a ferroelectric structural transition to the orthorhombic *a* phase with a spontaneous polarization comparable to that of bulk $PbTiO_3$.

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