The occurrence of ferroelectricity in the $ABO_3$ perovskite structure has been known since the 1950's. Recently, first-principles density functional methods have proved invaluable in elucidating the observed behavior of known perovskite oxide ferroelectrics, anti-ferroelectrics, and quantum paraelectrics. Examples include the alkaline-earth titanates, the alkali metal tantalates and niobates, and the lead-based perovskites. There is also a growing interest in applying these methods to the design of new ferroelectrics based on the perovskite structure.

Another path to new materials leads beyond the perovskite structure. The Ruddlesden-Popper (RP) family of compounds are closely related to the perovskites. They can be viewed as a stacking 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. Bulk phases of RP titanates have been reported only for some members of the $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ and $\text{Ca}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ series. 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 many RP titanates are not thermodynamically stable 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 density functional (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$_2$TiO$_4$, an $n=1$ RP compound based on ferroelectric end-member PbTiO$_3$, is a promising candidate for a high-polarization ferroelectric. Regarding the presence of Pb$_2$TiO$_4$ (or higher $n$ compounds) in the bulk phase diagram, reports are conflicting and no structural information is available. 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$_2$TiO$_4$ 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). A plane wave basis set and projector-augmented wave potentials were employed. The electronic wavefunctions 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 $6 \times 6 \times 6$ Γ-centered mesh of $k$-points. Polarization was calculated using the modern theory of polarization as implemented in VASP.

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 ($a=3.857\,\text{Å}, c=12.70\,\text{Å}$) and internal coordinates ($z_{Pb}=0.3507, z_{O_1}=-0.1562$). The residual Hellmann-Feynman forces were less than 2 meV/Å. Next we calculated the zone-center phonons of this reference system.

Fig. 1. (color online) Crystal structure of Ruddlesden-Popper compound Pb$_2$TiO$_4$, Space group $I4/mmm$. 

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by computing the dynamical matrix at \( q = 0 \) using the direct method where each ion was moved by approximately 0.01 Å. 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 \( \text{Pb}_2\text{TiO}_4 \) in the \( I4/mmm \) high-symmetry reference structure, there are three infrared-active (i.r.) modes that transform according to the reducible representation \( A_{2u} \) and four i.r. modes that transform according to \( E_u \). The one-dimensional (1-d) \( A_{2u} \) modes involve atomic distortions along [001] while in the 2-d \( E_u \) modes, atoms move in the plane perpendicular to [001]. Our calculations reveal that at the ground-state structural parameters, \( I4/mmm \) \( \text{Pb}_2\text{TiO}_4 \) has one phonon with an imaginary frequency (\( \omega = 96i \text{ cm}^{-1} \)), indicative of an instability. This unstable phonon is infrared-active of \( E_u \) symmetry type. Therefore, \( \text{Pb}_2\text{TiO}_4 \) in the \( \text{RP} \) structure does indeed display a ferroelectric instability. The real-space eigendisplacements of this unstable ferroelectric mode consists of \( \text{Pb} \) and \( \text{Ti} \) atoms moving against a non-rigid oxygen octahedra (with larger displacements of the apical oxygens in the \( \text{Pb}_2 \text{O} \) layer). As for \( \text{PbTiO}_3 \), the character of the ferroelectric instability in \( \text{Pb}_2\text{TiO}_4 \) involves significant \( \text{Pb} \) displacements moving against oxygen in the \( \text{Pb}-\text{O} \) planes. This involvement of the \( \text{Pb} \) site in both \( \text{PbTiO}_3 \) and \( \text{Pb}_2\text{TiO}_4 \) differs from non-\( \text{Pb} \) based compounds (e.g. \( \text{BaTiO}_3 \)) and has been attributed to the \( \text{Pb}^{2+} \) lone-pair. It is in fact this lone-pair that stabilizes \( \text{PbTiO}_3 \) in the tetragonal phase, and may have a role in facilitating the ferroelectric distortion in \( \text{Pb}_2\text{TiO}_4 \).

The key role of \( \text{Pb} \) is further emphasized by comparison with \( \text{Ba}_2\text{TiO}_4 \). A compound at this composition, barium orthotitanate, has been identified in the bulk phase diagram. It crystallizes not in the \( \text{RP} \) structure but rather in the monoclinic distorted-\( \text{K}_2\text{SO}_4 \) structure (space group: \( P2_1/n \)). A calculation for the structure and zone-center phonons of \( I4/mmm \) \( \text{Ba}_2\text{TiO}_4 \) in the hypothetical RP structure, exactly analogous to that for \( \text{Pb}_2\text{TiO}_4 \), shows no evidence for any ferroelectric instability, even for varying epitaxial strain.

Returning to \( \text{Pb}_2\text{TiO}_4 \), 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 \( \text{Pb}_2\text{TiO}_4 \) in this orthorhombic space group are displayed in Table I. We imposed the convention, \( \sum_i \Delta x_i = 0 \), where \( \Delta x_i \) 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 \( \text{Pb} \) and \( \text{Ti} \) ions moving against the non-rigid 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 \( P_s = 68 \mu \text{C/cm}^2 \), along [100] as required by symmetry. Therefore \( \text{Pb}_2\text{TiO}_4 \) in the \( \text{RP} \) structure is a ferroelectric with a spontaneous polarization comparable to that of \( \text{PbTiO}_3 \).

Epitaxy plays a dual role in our thinking about the \( \text{Pb}_2\text{TiO}_4 \) system. As will be discussed shortly, one possible route to synthesize thin films of \( \text{Pb}_2\text{TiO}_4 \) in the RP structure is through the use of epitaxial stabilization. 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, \( I4/mmm \) \( \text{RP} \) structure and explore the effect of epitaxial strain on the low-frequency infrared-active modes. We impose epitaxial strain by constraining the two basal primitive vectors of the \( \text{bct} \) lattice to an angle of 90 degrees 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 \( \text{PbTiO}_3 \) as the reference strain (i.e. for 0% strain we fixed the in-plane lattice constant of \( \text{Pb}_2\text{TiO}_4 \) to that of ferroelectric \( \text{PbTiO}_3 \)). For each value of fixed strain we again perform relaxation of the ions and c-axis.

Referred to tetragonal \( \text{PbTiO}_3 \), the ground-state \( I4/mmm \) structure has an in-plane strain of approximately -0.3%. For small compressive strains the phonon instabilities of epitaxial \( \text{Pb}_2\text{TiO}_4 \) are expected to be similar to those in the unconstrained structure. This corre-

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**Table I: Crystal structure of ferroelectric \( \text{Pb}_2\text{TiO}_4 \), Space Group: \( I2mm \), \( a=3.985 \text{ Å} \), \( b=3.826 \text{ Å} \), \( c=12.70 \text{ Å} \).**

| Atom | Wyckoff | Coordinates |
|------|---------|-------------|
| \( \text{Pb} \) | (4c) | \( m \) | 0.0616 | 0.3508 |
| \( \text{Ti} \) | (2a) | \( 2mm \) | 0.0256 | 0 |
| \( \text{O} \) | (2a) | \( 2mm \) | -0.0190+0.5 | 0 | 0 |
| \( \text{O} \) | (2b) | \( 2mm \) | -0.0307 | 0.5 | 0 |
| \( \text{O} \) | (4c) | \( m \) | -0.0496 | 0 | 0.1538 |
sponds 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. Fig. 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. 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.

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$_2$TiO$_4$ undergoes a series of structural transitions with epitaxial strain. Over the range of slightly tensile to compressive strains, Pb$_2$TiO$_4$ forms in the $I2mm$ space group. Following the convention appearing in the literature 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 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. 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.

Compounds unstable in the RP structure at atmospheric pressures have been synthesized under high-
Recently a new series of centrosymmetric Ruddlesden-Popper phases, \( \text{KLnTiO}_{3n+1} \) series where bulk phases are known to be unstable.\(^{32}\) Another example has been the low pressure synthesis of \( \text{Ba}_2\text{RuO}_4 \) in the RP structure.\(^{32}\) The growth of thin films of \( \text{Pb}_2\text{TiO}_4 \) would provide a means to realize the interesting behavior of this material with epitaxial strain.

Initially, we asked the question whether \( \text{Pb}_2\text{TiO}_4 \) in the Ruddlesden-Popper 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 \( \text{Pb}_2\text{TiO}_4 \) could be made in the RP structure (bulk or thin films) it would undergo a ferroelectric structural transition to the orthorhombic \( \alpha \)-phase with a spontaneous polarization comparable to that of bulk \( \text{PbTiO}_3 \).

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1. M.E. Lines and A.M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon Press, Oxford, 1977).
2. Ph. Ghosez, E. Cockayne, U.V. Waghmare, and K.M. Rabe, Phys. Rev. B 60, 836 (1999).
3. R.E. Cohen, J. Phys. Chem. Solids 61, 139 (2000).
4. R.E. Cohen, Nature 358, 136 (1992).
5. C. LaSota, C.-Z. Wang, R. Yu, and H. Krakauer, Ferroelectrics 194, 109 (1997).
6. E. Cockayne and B. P. Burton, Phys. Rev. B 62, 3735 (2000).
7. D.J. Singh, Phys. Rev. B 53, 176 (1996).
8. I. Inbar and R.E. Cohen, Phys. Rev. B 53, 1193 (1996).
9. D.J. Singh, Phys. Rev. B 52, 12 559 (1995).
10. N.A. Spaldin and W.E. Pickett, J. Solid State Chem. 176, 615 (2003).
11. S.V. Halilov, M. Fornari, and D.J. Singh, Appl. Phys. Lett. 81, 3443 (2002).
12. S.N. Ruddlesden and P. Popper, Acta Crystallogr. 10, 538 (1957); 11, 54 (1958).
13. The \( n=2 \) RP \( \text{Ca}_2\text{Ti}_2\text{O}_7 \) crystallizes in a polar space group although ferroelectricity has not been reported.
14. Recently a new series of centrosymmetric Ruddlesden-Popper phases, \( \text{KLnTiO}_{3n+1} \) \( n = 1 \) \((\text{Ln} = \text{La, Nd, Sm, Eu, Gd, Dy})\), has been reported (see Ref. 13).
15. I.N. Belyaev, Russian J. Inorg. Chem. 15 148 (1970).
16. M.A. Eisa, M.F. Abadir, and A.M. Gadalla, Trans. J. Brit. Ceram. Soc. 79 100 (1980).
17. J.-R. Soh, H.M. Lee, and H.-S. Kwon, Calphad 18 237 (1994).
18. G. Kresse and J. Furthmuller, Phys. Rev. B 47, R558 (1993); G. Kresse and J. Furthmuller, ibid. 54, 11169 (1996).
19. P. Blöchl, Phys. Rev. B 50, 17953 (1994); G. Kresse and D. Joubert, ibid. 59, 1758 (1999).
20. D. King-Smith and D. Vanderbilt, Phys. Rev. B 47, 1651 (1993).
21. R. Seshadri and N. A. Hill, Chem. Mater. 13, 2892 (2001).
22. J.A. Bland, Acta Cryst. 14, 875 (1961).
23. For tetragonal \( \text{PbTiO}_3 \), a 6x6x6 k-point grid and an energy cutoff of 500 eV, \( a = 3.867\AA \) and \( P_s = 65\mu C/cm^2 \).
24. D.G. Schlom, et al., Mater. Sci. Eng. B 87, 282 (2001).
25. O. Yu. Gorbenko, S.V. Samoilenkov, I.E. Graboy, and A.R. Kaul, Chem. Mater. 14, 4026 (2002).
26. Epitaxial strain (\%) \( \equiv 100\left(a-a_{\text{PbTiO}_3}\right)/a_{\text{PbTiO}_3} \).
27. Ph. Ghosez, X. Gonze, and J.-P. Michenaud, Europhys. Lett. 33, 713 (1996).
28. N.A. Pertsev, A.G. Zembilgotov, and A.K. Tagantsev, Phys. Rev. Lett., 1988 (1998).
29. To definitively say whether the \( \text{Cm} \) structure can be realized the monoclinic angle would have to be allowed to vary independently of the \( c \)-axis during cell relaxations, which was not done here for computational simplicity.
30. J.A. Kafalas and J.M. Longo, J. Solid State Chem. 4, 55 (1972).
31. J.H. Haeni, et al., Appl. Phys. Lett. 78, 3292 (2001).
32. Y. Jia, et al., Appl. Phys. Lett. 74, 3830 (1999).
33. R.E. Schaak and T.E. Mallouk, J. Solid State Chem. 161, 225 (2001).