Ferroelectricity of Perovskites under Pressure

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(Received 9 August 2005; published 31 October 2005)

Ab initio simulations and experimental techniques are combined to reveal that, unlike what was commonly accepted for more than 30 years, perovskites and related materials *enhance* their ferroelectricity as hydrostatic pressure increases above a critical value. This unexpected high-pressure ferroelectricity is different in nature from conventional ferroelectricity because it is driven by an original electronic effect rather by long-range interactions.

DOI: 10.1103/PhysRevLett.95.196804 PACS numbers: 77.80.Bh, 62.50.+p, 77.84.Dy

$AB\mathrm{O}_3$ perovskites form one of the most important classes of materials because they can exhibit a broad range of properties, e.g., superconductivity, magnetism, ferroelectricity, and multiferroism. Such properties can be varied—and thus optimized to generate various devices with great performance and diverse functionalities—thanks to many factors. Examples of such factors are external magnetic and electrical fields, atomic substitution, chemical ordering, and pressure.

Indeed, a famous 30-year-old Letter [1] demonstrated that hydrostatic pressure P reduces, and even annihilates for high enough value, ferroelectricity (FE) in perovskites [2,3]. Such reduction can be understood when recalling that the occurrence of "conventional" FE results from a delicate balance between long-range Coulomb ionic interactions favoring ferroelectric distortions and short-range electronic effects preferring the undistorted paraelectric cubic structure [4,5]. This balance can be tipped towards FE by small covalent effects—especially, the hybridization between the d orbitals of the B transition metal and the O $2p$ states—that weaken short-range repulsions [6]. A simple and widely used theory indicates that short-range repulsions increase more rapidly than long-range attractions *as pressure increases*, leading to the reduction of FE [1].

The aims of this Letter are threefold. First of all, we discover, by combining theoretical and experimental techniques, that such reduction indeed occurs at low pressure *but does not hold at high pressure*, since the "classical" PbTiO_3 material is found to adopt a nonmonotonous behavior with pressure. As a result, an increase in P above a critical value *enhances* its ferroelectricity. The second aim of this Letter is to reveal that high-pressure FE is dramatically different from conventional FE (occurring at low P) since the former is electronically—rather than ionically—driven. Finally, we found that such high-pressure ferroelectricity is a general phenomenon since it exists in other perovskites, as well as other materials. Playing with pressure may thus lead to the design of devices with enhanced or new capabilities.

We conducted calculations at 0 K within the density functional theory and the pseudopotential method with the following electrons being treated as valence in PbTiO_3: Pb $5s$, Pb $5p$, Ti $3s$, Ti $3p$, Ti $3d$, Ti $4s$, O $2s$, and O $2p$. Our results are qualitatively independent on technical details such as the used exchange-correlation functional [7–9], pseudopotential types [10,11], kinetic energy cutoff (that was varied between 40 Ry and 120 Ry), or softwares [12–14]. We performed: (1) total energy calculations (with full relaxation) to determine the evolution of some phases as a function of P up to $\sim$120 GPa [3], and (2) phonon calculations of a specific structure [15].

On an experimental point of view, high-pressure Raman scattering and x-ray diffraction were carried out at room temperature in a gasketed diamond anvil cell on pure PbTiO_3 samples. Nitrogen or argon served as the pressure-transmitting medium which ensured a hydrostatic environment and the pressure was calibrated using the standard ruby fluorescence method. Depolarized Raman spectra up to 44 GPa of a powder sample were performed in backscattering geometry using a 514.53 nm-excitation line from an Ar^+ ion laser focused to a spot of 2–4 μm. The scattered light was analyzed using a T64000 Jobin-Yvon spectrometer and collected with a charge coupled device. The x-ray diffraction data collections up to 48 GPa were performed twice on two 20 μm-single crystals using the rotating crystal technique at ID30 high-pressure beam line at the European Synchrotron Radiation Facility [16]. More than 50 nonequivalent Bragg reflections ($2\theta > 24°$) were recorded on an image plate detector with a focused monochromatic wavelength of $\lambda = 0.3738$ Å. A silicon powder standard was used to determine precisely the wavelength, the sample-to-detector distance, and the inclination angles of the detector.

Figure 1(a) shows the predicted pressure dependency of the difference $\Delta H = H - H_{\text{cubic}}$ between the H_{cubic} enthalpy of the paraelectric cubic $Pm\bar{3}m$ state and the H enthalpy of three tetragonal phases: $P4mm$, that can only have ferroelectric distortions; $I4/mcm$, that is associated with antiferrodistortive rotation of the oxygen octahedra; and $I4cm$, that can exhibit both polar and antiferrodistortive degrees of freedom.

For the lowest P, only ferroelectric distortions exist in $I4cm$, which is thus identical to $P4mm$. This latter phase has the lowest ΔH, as consistent with the fact that it is the well-known ground state of PbTiO_3. When increasing P above ~3 GPa, significant antiferrodistortive deformations occur [as expected in perovskites [1,3]] in both $I4/mcm$ and $I4cm$, making these phases favorable over $P4mm$. On the other hand, Fig. 1(a) also indicates an unexpected result, namely, that *increasing pressure above a critical value enhances ferroelectricity*. Indeed, an increase in P from 0 to ~20 GPa leads to a ΔH becoming less negative in both $I4cm$ and $P4mm$—as consistent with the commonly believed pressure-induced reduction of FE [1–3], but the ΔH-versus-P curve of these two phases adopts an opposite behavior above $P_c \sim 30$ GPa—revealing that PbTiO_3 wants to become more and more ferroelectric after this critical pressure. These tendencies are emphasized by the pressure dependency of the calculated c/a axial ratio in $P4mm$ [see Fig. 1(b)]. It first strongly decreases with P until reaching a cubiclike value ~1 in the vicinity of P_c, and then it gradually increases as P further increases. Interestingly, high-pressure enhancement of FE is not limited to tetragonal states since we found that other ferroelectric phases have a turning point around 20 GPa and become more and more stable with respect to the paraelectric phase above 30 GPa [17]. This is emphasized in Fig. 2(a) by the first-principle-predicted pressure behav-

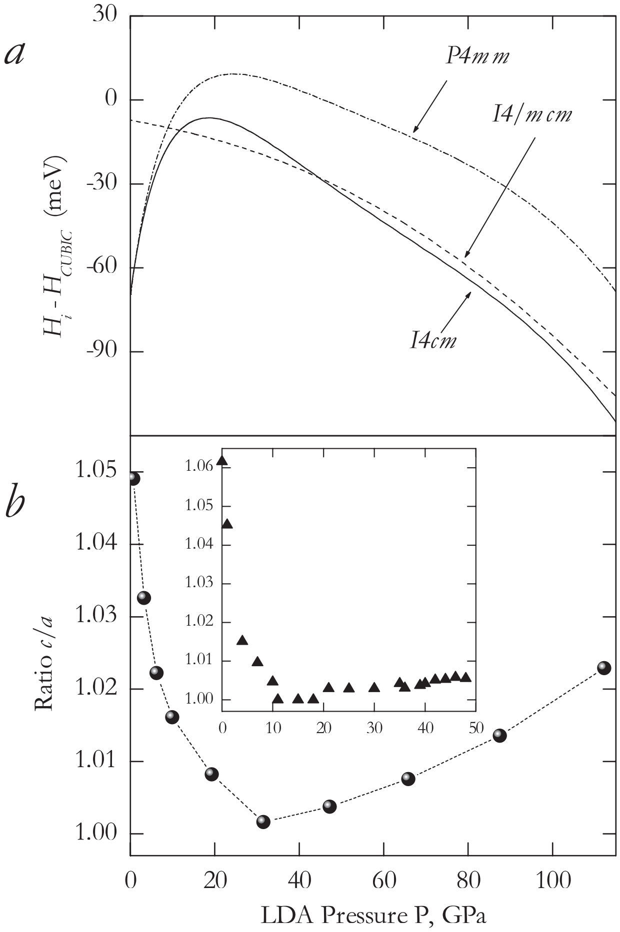

FIG. 1. Pressure dependency of some physical properties of PbTiO_3. Panel (a) shows the enthalpy differences ΔH between the indicated tetragonal phases and the paraelectric cubic phase, as calculated within the local density approximation (LDA). Panel (b) displays the predicted c/a distortion at 0 K, and the one measured at room temperature from x-ray diffraction with increasing pressure (see inset), for $P4mm$.

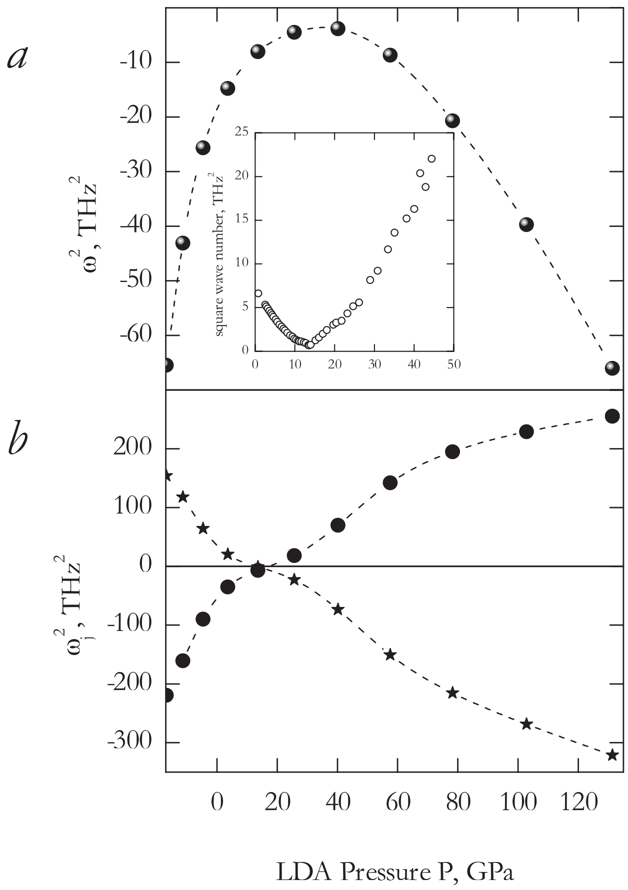

FIG. 2. Pressure behavior of phonons in paraelectric cubic PbTiO_3. Panel (a) displays the square of the zone-center TO phonon frequency in the cubic phase within LDA at 0 K. Panel (b) shows the contributions from the Coulomb interactions (dots) within the rigid ions model and non-Coulomb interactions (stars) to this square. Inset of panel (a) shows the squared frequency of the lowest E(1TO) Raman mode with increasing pressure at 300 K.

ior of the zone-center transverse optical (TO) mode frequency in the *paraelectric cubic Pm-3m* phase.

The square of such frequency is always negative, which indicates that $PbTiO_3$ has a ferroelectric instability and thus cannot be paraelectric cubic for any pressure at 0 K. More importantly, the magnitude of this square first decreases with P and then increases above P_c—confirming that $PbTiO_3$ has to become more and more ferroelectric above a critical pressure.

Let us now check if these predictions are confirmed by our 300 K measurements. Below 12 GPa, the observed diffraction patterns are consistent with the tetragonal $P4mm$ state, with c/a rapidly decreasing as P increases [see inset of Fig. 1(b)]. For 12 GPa $< P <$ 20 GPa, a and c cannot be distinguished, and the resulting structure is pseudocubic, rather than cubic, because Raman signal still persists in this range. Above 20 GPa, the diffraction patterns are consistent with a tetragonal ferroelectric $P4mm$ phase having a c/a increasing monotonically with pressure—until reaching a small but significant value of 1.006 for 48 GPa [18]. The prediction of a critical pressure above which FE is enhanced is thus indeed confirmed by our experimental x-ray data [19]. Moreover, the inset of Fig. 2(a) displays the pressure dependency of the wave number of the lowest-frequency E-symmetry TO zone-center phonon mode, as measured by Raman scattering. This mode softens when varying P from atmospheric conditions to 14 GPa, which agrees with both previous observations [2] and our simulations indicating that the first desire of $PbTiO_3$ under pressure is to reduce FE. On the other hand, above 20 GPa, the measured square of the wave number increases linearly and strongly when increasing P. This, and the observation of well-defined Raman spectra with sharp lines and new peaks, is once again consistent with the predictions of an enhancement of FE above a critical pressure.

To understand the pressure behavior of $PbTiO_3$ and find which interactions stabilize FE at low and high pressures, we divide its total dynamical matrix—as calculated in the cubic paraelectric phase within our first-principles technique and yielding the results shown in Fig. 2(a)—into two parts. The first part consists of the Coulomb interactions computed within the rigid ions model from the determination of the Born effective charges and dielectric tensors [20]. The second part is deduced by subtracting the first part from the total dynamical matrix, and thus differentiates the real $PbTiO_3$ material from its rigid ions picture. This second part therefore gathers the nonclassical short-range interactions. Figure 2(b) shows the calculated contribution of these two parts to the zone-center soft TO phonon frequency in the cubic phase, as a function of P. Below P_c and as commonly expected [1], the Coulomb interactions favor FE while short-range interactions tend to annihilate it—since they have a negative and positive frequency square, respectively—and the decrease of FE when increasing P is driven by the cost of nonclassical short-range interactions becoming predominant over the gain associated with Coulomb interactions. Figure 2(b) also reveals that FE above P_c dramatically differs from the low-pressure "normal" ferroelectricity because of the reverse sign of Coulomb and short-range parts: it is now nonclassical short-range effects (which are electronic in nature) that favor FE at high pressure while Coulomb interactions (that involve ions "dressed by electrons") prefer paraelectricity. To determine which electrons are responsible for FE at high pressure, Figs. 3(a)–3(c) display some partial electronic density of states (PDOS) for cubic $PbTiO_3$ under different pressures.

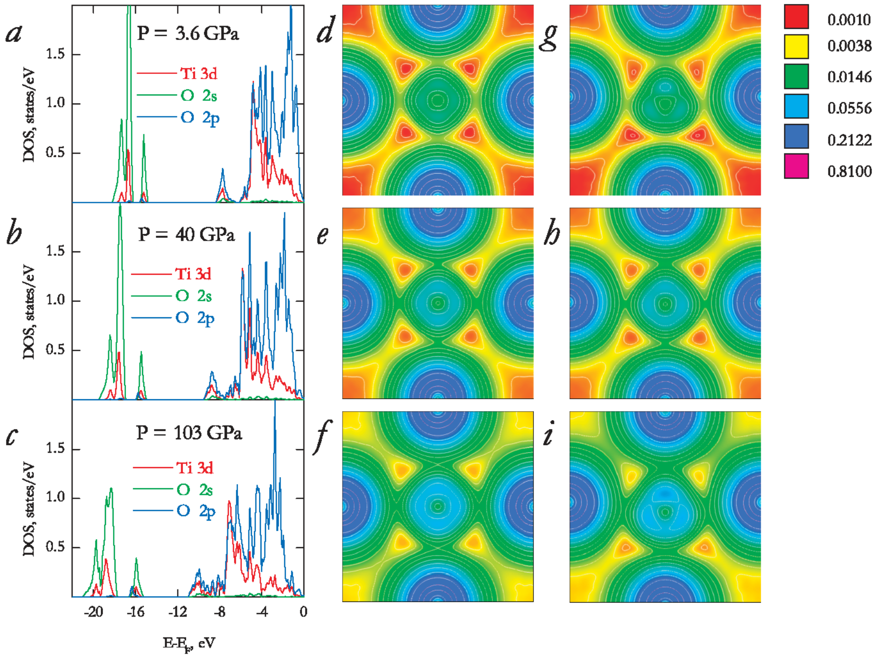

FIG. 3 (color). Electronic-related properties of $PbTiO_3$ under pressure. Panels (a), (b), and (c) display the partial electronic density of occupied states (PDOS) in the cubic phase at 3.6, 40, and 103 GPa, respectively, for the O $2s$, O $2p$, and Ti $3d$ orbitals. The zero in energy is chosen at the top of the valence band. Panels (d), (e), and (f) show the electronic charge density of the valence bands located between -22 and -15 eV in the vertical (100) plane passing through Ti (center), $O_{\|}$ (top and bottom sides), and $O_{\perp}$ (left and right sides) atoms for the cubic state at 3.6, 40, and 103 GPa, respectively. Panels (g)–(i) display the same information as panels (d)–(f), respectively, but for the $P4mm$ equilibrium—for which Ti moves towards the bottom oxygen atom.

The most striking effect is that Ti 3*d* orbitals (and more precisely their e_g parts) dramatically increase their mixing with the O 2*s* orbitals above P_c [21]. Such effects can be seen in Figs. 3(d)–3(f) that display the contribution of the *low-lying* valence bands ranging between -22 and -15 eV (that solely originate from the O 2*s* orbitals in an ionic picture) to the total electronic charge density of the cubic phase in a vertical (100) plane. Note, in particular, the pressure-induced increase of the charge density around Ti and the noticeable charge distribution at the middle of the Ti-O bonds. Moreover, Figs. 3(g)–3(i)—that show the same information than Figs. 3(d)–3(f) but for *P*4*mm* having ferroelectric distortions along the [001] direction—reveal that $PbTiO_3$ enhances its FE at high pressure to reduce the energetically costly overlap [22] between Ti $3d(e_g)$ and O 2*s* orbitals. This is clearly indicated by the fact that, for $P = 103$ GPa, *each* of the three maxima in the partial electronic charge density around Ti avoids to point along the O atom towards which Ti is moving.

In summary, we found that, unlike commonly thought, $PbTiO_3$ becomes more ferroelectric as P increases above a critical value, in order to reduce the overlap between the B $d(e_g)$ and O 2*s* orbitals (such overlap exists because pressure naturally brings B and O atoms closer to each other). Such pressure-induced phenomenon should occur in any insulating perovskite as well as other structures involving a transition metal surrounded by oxygen. As a matter of fact, we indeed found—by performing additional *ab initio* calculations (not shown here)—that $BaTiO_3$, $BaZrO_3$, $Pb(Zr, Ti)O_3$, and WO_3 *all* exhibit an enhancement of ferroelectricity at high pressure. Depending on the energetic difference between ferroelectric and paraelectric phases at atmospheric pressure, such phenomenon can lead to various overlooked or original effects, e.g., (i) the disappearance and then reentrance of ferroelectricity under pressure; (ii) the occurrence of FE at high pressure in a nominally paraelectric compound; and (iii) the existence of FE at any pressure. We thus hope that this Letter will stimulate the investigation of novel effects in "smart" materials under pressure.

This work is supported by the Office of Naval Research, National Science Foundation, and the Department of Energy. We thank Huaxiang Fu and Ivan Naumov for useful discussions, Mohamed Mezouar and Wilson Crichton from ID30 beamline (ESRF) for their technical support.

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[17] Rhombohedral, monoclinic, and tetragonal phases have been theoretically investigated. We found that rhombohedral states are the most stable ones at high pressure and at 0 K.

[18] Note that such $c/a \sim 1.006$ is close to that of the well-known tetragonal ferroelectric phase of $BaTiO_3$ at 300 K and at atmospheric pressure.

[19] Unlike the calculations reported in Fig. 1(a), our measured diffraction data are not consistent with the activation of antiferrodistortive motions at high pressure, up to 48 GPa. This discrepancy is simply due to the fact that experiments are conducted at 300 K while simulations are performed at 0 K, and that it is easier to activate antiferrodistortive motions at lower temperature.

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[21] Note that the contribution of Pb orbitals is not shown because our first-principles calculations reveal that Pb is relatively ferroelectric inactive at high pressure. On the other hand, our simulations also confirmed that Pb is ferroelectric active at low pressure, as consistent with previous work [5]. This indicates that the atomic characteristics of the soft-mode dramatically change with pressure in $PbTiO_3$. Note that our first-principles calculations also predict that the topmost group of valence bands exhibits the well-known hybridization between O 2*p* and Ti 3*d* orbitals [4,5]. The integrated PDOS of this group have a smooth and small pressure dependency, thus ruling out that high-pressure FE is caused by this *p*-*d* hybridization.

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