Pressure-Induced Anomalous Phase Transitions and Colossal Enhancement of Piezoelectricity in PbTiO$_3$

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We find an unexpected tetragonal-to-monoclinic-to-rhombohedral-to-cubic phase transition sequence induced by pressure, and a morphotropic phase boundary in a pure compound using first-principles calculations. Huge dielectric and piezoelectric coupling constants occur in the transition regions, comparable to those observed in the new complex single-crystal solid-solution piezoelectrics such as Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$-PbTiO$_3$, which are expected to revolutionize electromechanical applications. Our results show that morphotropic phase boundaries and giant piezoelectric effects do not require intrinsic disorder, and open the possibility of studying this effect in simple systems.

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The classic ferroelectric PbTiO$_3$ has been known to have a single ferroelectric tetragonal (T) to paraelectric cubic phase transition with increased temperature [1] or pressure [2] since its discovery [3] in 1950. It seemed unlikely to discover any new ferroelectric transitions in PbTiO$_3$, but we predict new ferroelectric phases under pressure. Piezoelectrics convert electric energy to mechanical energy, and vice versa. They are widely used in medical imaging, acoustic sensors and transducers, actuators, etc. PbTiO$_3$ has been extensively studied [1-2, 6, 7, 8, 9, 10, 11] to understand the electronic origin of ferroelectricity. The Pb-O and Ti-O hybridization has been known to weaken the short-range repulsions and gives rise to the ferroelectric distortion [7]. It has been found that pressure suppresses ferroelectricity since compression favours short-range repulsion, but there has been no previous work on the effect of pressure on piezoelectricity.

PbTiO$_3$ has a high c-axis strain of 6.5% (7.1%) at room (low) temperature. Under ambient pressure it undergoes a first-order phase transition at $T_c = 763$ K, and this transition is regarded as a typical displacive transition, which is associated with soft-modes [1]. The displacive phase transition temperature $T_c$ decreases under hydrostatic pressure. A Raman study of PbTiO$_3$ shows that $T_c$ reduces to 300 K and the phase transition becomes second-order at $P = 12.1$ GPa [2]. It indicates a tricritical point in the phase diagram, where the first-order phase transition changes to second-order, and it has been identified at $P = 1.75$ GPa, $T = 649$ K [12]. Increasing pressure further reduces $T_c$.

PbTiO$_3$ is an end member of Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$-PbTiO$_3$ (PMN-PT) and Pb(Zn$_{1/3}$Nb$_{2/3}$)$_3$O$_3$-PbTiO$_3$ (PZN-PT), which have piezoelectric coefficients an order of magnitude larger than those of conventional ferroelectrics [1]. The displacive transition is regarded as a typical displacive transition, which is associated with soft-modes [1]. The giant piezoelectric effects always do not occur along the spontaneous polarization direction [14, 15]. At ambient pressure PbTiO$_3$ has no such MPB because it has a rather stiff energy surface near the T phase and it has no R phase. Under high pressures the energy (enthalpy) surface is expected to be softer, and an MPB could arise.

In this Letter we address both issues of phase transitions and piezoelectricity of PbTiO$_3$ under hydrostatic pressures. We perform total energy as well as linear response computations, which have been proved to be highly reliable for ground state properties. We find anomalous phase transitions and giant enhancement of dielectricity and piezoelectricity near the phase transition regions induced by pressure.

We have carried out zero temperature ab initio computations based on density functional theory (DFT) within the local density approximation (LDA). We used the pseudopotential plane wave method implemented in the ABINIT package [21]. The plane wave energy cutoff is 60 Hartree, and the k-point mesh for Brillouin Zone integration is of $6 \times 6 \times 6$. We used the OPIUM program [22] to generate norm-conserving pseudopotentials, which were rigorously tested against the full-potential linearized augmented plane wave (LAPW) method [23]. We included semi-core states of Pb 5d$^{10}$, Ti 3s$^2$3p$^6$4d$^2$, and O 2s$^2$ in valence states. We chose the LDA instead of the generalized gradient approximation (GGA) because the GGA catastrophically overestimates both equilibrium volume and strain for tetragonal PbTiO$_3$ [24]. On the other
corresponds to a negative pressure $P_C$, macroscopic strain and electric field. Tensors $\epsilon_{\mu\nu}$ and piezoelectric stress constants $e_{\mu\nu}$ (Here Latin indexes run from 1 to 3, and Greek indexes from 1 to 6), we used the density functional perturbation theory (DFPT) \cite{25} of the linear response of strain type per-

Table I: Elastic ($c_{\mu\nu}$) and piezoelectric ($e_{\mu\nu}$) constants of tetragonal $P4mm$ PbTiO$_3$ with lattice constants $a = 3.902$ Å, $c = 4.155$ Å. $c_{\mu\nu}$ and $e_{\mu\nu}$ are in GPa and C/m$^2$, respectively. Here FS refers to the finite strain method.

| Methods | $c_{11}$ | $c_{12}$ | $c_{13}$ | $c_{33}$ | $c_{44}$ | $c_{66}$ | $c_{31}$ | $c_{33}$ | $c_{15}$ |
|---------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| DFPT    | 230      | 96.2     | 65.2     | 41.9     | 46.6     | 98.8     | 2.06     | 4.41     | 6.63     |
| FS      | 229      | 95.6     | 64.3     | 41.2     | 47.2     | 98.6     | 2.07     | 4.48     | 6.66     |

hand, the LDA moderately underestimates the volume (60.38 Å$^3$) and strain (4.6%), and the experimental $V_0$ corresponds to a negative pressure $P_0 = -2.2$ GPa.

To calculate the dielectric susceptibility $\chi_{ij}$, elastic constants $\epsilon_{\mu\nu}$, and piezoelectric stress constants $e_{\mu\nu}$ (Here Latin indexes run from 1 to 3, and Greek indexes from 1 to 6), we used the density functional perturbation theory (DFPT) \cite{25} of the linear response of strain type pertur-

Because the enthalpy differences among these phases are very small, the above calculated pressure-induced phase transition sequence needs to be examined by di-

FIG. 1: Stability of various phases as a function of pressure. (a) Enthalpy difference with respect to the C phase for the T and R phases. (b) Enthalpy difference with respect to the T phase for the M and R phases. (c) Enthalpy difference with respect to the T phase for the C phase. When the T-R phase transition occurs at high temperature and ambient pressure \cite{1} or high pressure and room temperature \cite{2}, both the $E(1TO)$ and $A_1(1TO)$ modes soften simultaneously. However, at 0 K we find that pressure induces condensation only of the $E(1TO)$ mode around $P = 10$ GPa [Fig. 1(c)]. A linear combination of the doubly degenerate $E(1TO)$ modes gives rise to the transition to the M phase. For the R phase, the $E(1TO)$ and $A_1(1TO)$

Table II: Elastic constants $c_{\mu\nu}$ and piezoelectric stress constants $e_{\mu\nu}$ of tetragonal $P4mm$ PbTiO$_3$ in GPa and C/m$^2$, respectively.

| $\mu\nu$ | $c_{\mu\nu}$ (GPa) | $e_{\mu\nu}$ (C/m$^2$) |
|----------|-------------------|-----------------------|
| $11$     | 53                | 0                     |
| $12$     | 97                | 0                     |
| $13$     | 53                | 0                     |
| $33$     | 59                | 0                     |
| $44$     | 53                | 0                     |
| $66$     | 53                | 0                     |
| $31$     | 53                | 0                     |
| $33$     | 59                | 0                     |

elasticity, phonon frequencies, and dielectricity. The pressure dependence of elastic constants $c_{44}$ in the T phase and $c_{11} - c_{12}$ in the R phase is shown in Fig. 1(c). Note that the cubic coordinate system is used for all cases, and elastic constants $c_{11} = c_{22} = c_{33}$ and $c_{12} = c_{13} = c_{23}$ in the R phase. We find that both $c_{44}$ and $c_{11} - c_{12}$ approach zero around 9 and 11.5 GPa, respectively. Negative $c_{44}$ and $c_{11} - c_{12}$ mean that the T and R phases are unstable respectively against shear and tetragonal shear strain, indicating phase transitions. The estimated phase transition pressures from elasticity anomalies agree well with the total energy results.

In tetragonal $P4mm$ PbTiO$_3$, the $E(1TO)$ and $A_1(1TO)$ modes originate from the triply degenerate $F_{1u}(1TO)$ mode in the C phase. When the T-C phase transition occurs at high temperature and ambient pressure \cite{1} or high pressure and room temperature \cite{2}, both the $E(1TO)$ and $A_1(1TO)$ modes soften simultaneously. However, at 0 K we find that pressure induces condensation only of the $E(1TO)$ mode around $P = 10$ GPa [Fig. 1(c)]. A linear combination of the doubly degenerate $E(1TO)$ modes gives rise to the transition to the M phase. For the R phase, the $E(1TO)$ and $A_1(1TO)$

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modes soften simultaneously at \( P \approx 22 \) GPa, going to the \( F_{1u}(1TO) \) mode in the C phase. This gives rise to the R-to-C phase transition. The linearity of the square of mode frequency \( \omega^2 \) vs. pressure close to phase transition indicates a Curie-Weiss pressure law. Fig. 1(d) shows that the static dielectric susceptibility \( \chi_{111} \) has a maximum around 9.5 GPa, indicating a first-order transition; while it diverges at \( P \approx 22 \) GPa, indicating a second-order transition, as can be understood from the Lyddane-Sachs-Teller (LST) relation. For the T phase near transition pressure, \( \chi_{111} = \chi_{22} \propto 1/\omega^2 |E(1TO)| \) and \( \chi_{333} \propto 1/\omega^2 |A(1TO)| \). Thus \( \chi_{111} \) increases rapidly around 9.5 GPa, whereas \( \chi_{333} \) does not. The same analysis can be applied to the R and C phases. The phase transition pressures obtained from phonon frequencies and dielectric constants also are consistent with the total energy results, and it shows that the computed small energy differences between phases are reliable. Our first-principles calculations neglect quantum fluctuations, which could reduce the phase transition pressures \( 27 \).

We have predicted the pressure-induce phase transitions of PbTiO\(_3\) at 0 K. Combining our results with experimental finite temperature data, we propose a schematic \((P, T)\) phase diagram (Fig. 2), in which the intermediate M phase separates the T phase at low pressures and the R phase at higher pressures. This phase diagram bears remarkable resemblance to the \((x, T)\) phase diagram of PZT \( 18 \), where \( x \) is the PbTiO\(_3\) composition. The narrow M area is the MPB of PbTiO\(_3\), and it serves as a structure bridging the T and R phases in that its spontaneous polarization is located in the \((110)\) plane and between the pseudocubic [001] and [111] directions, which is very similar to that in PZT.

Pressure suppresses spontaneous polarization \( P^s \) [Fig. 3(a)] and the c-axis strain. Although the magnitude of \( P^s \) changes continuously at the T-M transition pressure, \( P_1' \) is discontinuous, indicating a first-order phase transition, consistent with the conclusion drawn from dielectric constants. We emphasize that when the T-M phase transition occurs, \( P^s \) retains about half of the magnitude under zero pressure and \( c/a = 1.012 \). These values are comparable to those of PMN-PT \( 19 \), PZN-PT \( 20 \), and PZT \( 28 \) in the T phase close to MPB.

Fig. 3(b) and 3(c) summarize the pressure effect on piezoelectricity of PbTiO\(_3\). For the T phase, \( e_{333} \) increases, whereas the piezoelectric strain coefficient \( d_{333} \) decreases with pressure. The relatively large \( d_{333} \) at \( P = -2.2 \) GPa is due to the LDA overestimation of strain at the experimental volume. Both \( e_{115} \) and \( d_{115} \) increase with pressure, and they rise dramatically for \( P > 4 \) GPa when \( c_{144} \) begins to drop quickly [Fig. 1(c)]. The T phase has \( d_{15} = e_{15}/c_{44} \), so that \( d_{15} \) increases even faster than \( e_{15} \). The pressure-induced large enhancements of \( e_{15} \) and \( d_{15} \) are a result of the sharp reduction of the enthalpy difference between the T and R phases, and both \( e_{15} \) and \( d_{15} \) diverge at the T-to-M phase transition pressure. For

![FIG. 2: Proposed \((P, T)\) phase diagram. It combines theoretical results (solid circles) at 0 K with experimental data (solid squares) at finite temperatures. In this figure we rescaled the theoretical pressure for the experimental volume to be zero by shifting. The open circles are our guess for these two tricritical points, and an \textit{ab initio} molecular dynamics simulation is needed to predict them accurately.](image)

![FIG. 3: Pressure dependence on piezoelectricity. (a) Spontaneous polarization \( P^s \). (b) Piezoelectric stress coefficients \( e_{115} \) and \( e_{333} \). (c) Piezoelectric strain coefficients \( d_{115} \) and \( d_{333} \).](image)
the R phase, both $e_{15}$ and $d_{15}$ are rather small, and $e_{33}$ jumps to over 30 C/m², increasing with pressure. $d_{33}$ has large values near the M phase and remains larger than 1500 pN/C for a broad range of pressure. The R phase under high pressure has $d_{33} \approx e_{33}/(c_{11} - c_{12})$, and the increase of $c_{11} - c_{12}$ with pressure [Fig. 1(c)] causes $d_{33}$ to decrease with pressure, even though $e_{33}$ rises. Note that $d_{33}$ at 12 GPa is smaller that at 13 GPa, and it could be due to numerical uncertainties, since small variations of elastic constants $c_{14}$ and $c_{15}$ change elastic compliance $s$ dramatically when $c_{11} - c_{12}$ is small. It is evident that the predicted giant piezoelectric effect of PbTiO$_3$ comes from non-collinear polarization rotation since the enhancement of $d_{15}$ in the T phase and $d_{33}$ in the R phase do not occur along the spontaneous polarization directions, and the M phase acts as a structural bridge between the T and R phases as indicated by pressure inducing polarization rotation from [001] to [111] directions.

We have demonstrated that pressure can induce an MPB in a simple compound PbTiO$_3$, which is very similar to the composition-induced MPB in complex solid-solutions, such as PZT [18], PMN-PT [19], and PZN-PT [20]. It is critical that these ferroelectric systems near MPB have distinct phases (different patterns of atomic displacements) with very close free energies. Each local MPB have distinct phases (different patterns of atomic displacements) with very close free energies. Each local

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