Origin of morphotropic phase boundaries in ferroelectrics

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A piezoelectric material is one that generates a voltage in response to a mechanical strain (and vice versa). The most useful piezoelectric materials display a transition region in their composition phase diagrams, known as a morphotropic phase boundary1–4, where the crystal structure changes abruptly and the electromechanical properties are maximal. As a result, modern piezoelectric materials for technological applications are usually complex, engineered, solid solutions, which complicates their manufacture as well as introducing complexity in the study of the microscopic origins of their properties. Here we show that even a pure compound, in this case lead titanate, can display a morphotropic phase boundary under pressure. The results are consistent with first-principles theoretical predictions5, but show a richer phase diagram than anticipated; moreover, the predicted electromechanical coupling at the transition is larger than any known. Our results show that the high electromechanical coupling in solid solutions with lead titanate is due to tuning of the high-pressure morphotropic phase boundary in pure lead titanate to ambient pressure. We also find that complex microstructures or compositions are not necessary to obtain strong piezoelectricity. This opens the door to the possible discovery of high-performance, pure-compound electromechanical materials, which could greatly decrease costs and expand the utility of piezoelectric materials.

Originally the term ‘morphotropic’ referred to phase transitions due to changes in composition1–2, but it has come to be used mainly for the common ‘morphotropic phase boundaries’ (MPB) that separate regions of tetragonal symmetry from those of rhombohedral symmetry by varying the composition in ferroelectrics6. We use the term here also to describe the same phenomenon induced by pressure. It was recently understood that the apparent continuous-phase transitions through the MPB region from tetragonal to rhombohedral, which are not allowed by symmetry, are mediated by intermediate phases of monoclinic symmetry6, and that the high electromechanical response in this region is related to this phase transition6 because of symmetry-allowed polarization rotation8,9.

That the most useful ferroelectrics of this type are complex materials has complicated the discovery and development of even-higher-performance piezoelectrics. For example, relaxor single crystal ferroelectrics such as PMN-PT (PbMg1/3Nb2/3O3–PbTiO3) have electromechanical coupling ten times that of the currently used PZT (PbZrO3–PbTiO3) materials, and are revolutionizing applications ranging from medical ultrasound and sonar to energy harvesting. However, because the materials are complex solid solutions which melt incongruently, the melt-grown crystals are zoned, and must be selected for desired properties, a costly process that has delayed more widespread use of these promising materials and complicated the study of the physical origin of their behaviour. Such behaviour in a pure material could greatly advance the field. Here we show such behaviour in pure PbTiO3 under pressure.

PbTiO3 has long been considered a simple classic ferroelectric, with a single phase transition from the ferroelectric tetragonal structure to cubic perovskite at 776 K and ambient pressure6. A classic Raman study showed two soft modes, both vanishing at a pressure of 12 GPa at 300 K (room temperature)10. For the zero-temperature theoretical computations6,8 to be consistent with the room-temperature data requires low-temperature phase transitions, so we performed cryogenic high pressure in situ Raman and synchrotron powder X-ray diffraction experiments11,12 to explore the theoretical predictions of a series of phase transitions in PbTiO3.

Figure 1 shows representative diffraction patterns measured at 10 K, indicating pressure-induced structural transitions. Energy dispersive diffraction shows only intensity changes with changing pressure whereas the high-resolution diffraction data clearly display peak splittings that result from symmetry-lowering transitions (Fig. 1 inset). The two experiments are therefore complementary and allow us to choose limited angular ranges to scan in the high-resolution measurements while ensuring complete coverage of the diffraction pattern.

Figure 2a shows our low-frequency Raman spectra and their pressure dependences are shown in Fig. 2b. There are two soft modes: one hardens above 15 GPa and the other hardens above 20 GPa. Figure 2c displays the pressure dependence of the intensity of the Raman band (centred at 190 cm−1) and the inset shows the high-frequency Raman spectra. These results indicate that there are two successive phase transitions, at 15 and 20 GPa. The presence of the higher-frequency Raman modes indicates that the phase above 20 GPa is not cubic in symmetry. The appearance of a peak at 400 cm−1 above 20 GPa is consistent with the rotation of the TiO6 octahedra that results in a rhombohedral R3c structure predicted in our computations and observed in PZT13 (Supplementary Fig. 7).

The X-ray and Raman data are consistent with monoclinic symmetry between 10 and 20 GPa. Monoclinic phases, identified by similar splitting of tetragonal diffraction peaks, were also found at the morphotropic phase boundaries in PZT, PMN-PT and PZN-PT14–16. Two monoclinic phases are possible depending on the direction of the polarization. For polarizations along [xxz] the space group is Cm (designated Mx), and for polarizations along [xz] the space group is Pm (designated M0)17. The tetragonal (110)–(101) doublet would split into a quadruplet in both Pm and Cm monoclinic phases and revert to a doublet in the rhombohedral phase. These changes would be accompanied by a splitting of the tetragonal (111) singlet into a doublet in the monoclinic Pm phase as well as
in the rhombohedral $R3c$ phase, and a triplet in the monoclinic $Cm$ phase. Our high-resolution angle-dispersive experiment performed at 115 keV (0.1077 Å) was capable of resolving a splitting of the tetragonal doublet, which points to a lowering of symmetry. We can clearly identify the tetragonal–monoclinic transition at 11.4 GPa from the splitting of the (110)–(011) doublet. The monoclinic phase persists up to 20 GPa. The persistence of the overall monoclinic symmetry is clear in the high-resolution X-ray data, although all of the peaks are not resolved clearly, owing to the resolution of the angle-dispersive experiment at the low angles accessible in the diamond anvil cell (DAC) in the cryostat. We also attribute the changes observed in the Raman spectra at 15 GPa to the $Pm–Cm$ transition at this pressure.

We fitted our high-resolution diffraction data while fixing the peak profiles using the Au pressure standard as reference. This allowed us to model broadening due to non-hydrostatic stresses (we found no signs of stress-induced peak broadening in the pressure–temperature range of these experiments). The fits are superposed on the observed data in Fig. 1. The same fits allowed us to obtain cell parameters to a high degree of precision using a small subset of the diffraction peaks obtained from high-resolution X-ray diffraction experiments. Using these cell parameters, we calculated two lattice strains. The longitudinal strain is related to the axial ratio $c/a$ and the shear strain to the angle $\beta = \pi/2$. The parameter $\Delta a$ shows weak discontinuities across the phase transitions at 11.4 and 15 GPa, whereas the shear strain assumes a non-zero value above 11.4 GPa and monotonically decreases to zero above 20 GPa (Fig. 3). The discontinuity in cell parameters is consistent with a weak first-order transition from $Pm$ to $Cm$, and is hard to explain in any other way that is consistent with our Raman data.

Using density functional theory within the local density approximation, Wu and Cohen$^7$ theoretically predicted a series of phase transitions in PbTiO$_3$ between tetragonal and cubic (24 GPa) as a function of pressure at 0 K. They found that the tetragonal phase is stable below 10 GPa with the lowest free energy, the monoclinic phase has the lowest free energy between 10 and 12 GPa, and the zone-centre rhombohedral phase is the stable phase above 12 GPa. Additional calculations we performed show zone-boundary transitions

**Figure 1** | Pressure dependence of energy dispersive and high-resolution angle-dispersive X-ray diffraction spectra at selected pressures at 10 K. The single asterisk represents the ghost peak and the double asterisks mark the superposition of the ghost peak and the real peak. The major reflection lines were indexed with a pseudocubic symmetry (pc). For instance, the pseudocubic (110) reflection splits into a doublet in the monoclinic phase and a quadruplet in the monoclinic phase. The inset shows high-resolution diffraction data at different pressures: the left panels show the pseudocubic (100) reflection at 8.4 GPa (tetragonal phase), at 13.2 GPa (monoclinic phase, the (100) reflection is missing) and at 22 GPa (rhombohedral phase); the right panels show the pseudocubic (110) reflection at 8.4 GPa (tetragonal phase), at 13.2 GPa (monoclinic phase, the (101) reflection is missing), and at 22 GPa (rhombohedral phase).

**Figure 2** | Raman spectra. **a**, Raman spectra at selected pressures. **b**, Pressure dependences of the squares of soft-modes frequencies. Points are data and lines are guides to the eyes. The symbol size represents the size of the error bars (±50 cm$^{-1}$). Above 20 GPa, the Raman band becomes broad; the vertical lines represent the Raman linewidth. **c**, Pressure dependence of the integrated intensity of the Raman band centred at 190 cm$^{-1}$ (standard error ±0.04; the largest error is ±0.125 at 20 GPa); the inset shows Raman spectra at 12.4 GPa at 20 K. The changes in soft-modes and intensity of the Raman band at 15 and 20 GPa reflect the monoclinic $M_2$ to monoclinic $M_3$, and the monoclinic $M_3$ to rhombohedral phase transitions. These results indicate that the monoclinic phase transitions are real phase transitions, and are not due to nanotwinning or microstructure changes.
from R3m to R3c at 18 GPa, R3c to R3c at 20 GPa, and R3c to R3c at 60 GPa.

Our experimental results suggest a phase transition sequence from tetragonal to monoclinic at 10 GPa, monoclinic M$_c$ to monoclinic M$_c$ at 15 GPa, and monoclinic to rhombohedral at 20 GPa. The high-pressure rhombohedral phase is due to a zone-boundary instability as is seen theoretically (ref. 18 and our theoretical calculations). There may be a narrow wedge of the five-atom-per-cell R3m structure between the monoclinic and zone boundary R point phases, which we could not resolve in our experiments. Conventional X-ray diffraction is centrosymmetric and therefore cannot differentiate whether the zone-boundary phase is R3c or R3c. Figure 4 shows our proposed phase diagram. The precise details of the phase diagram may also be sensitive to non-hydrostatic stresses. The details of the phase diagram are less important than the fundamental result—that there exists a morphotropic phase boundary region under pressure at cryogenic temperatures in PbTiO$_3$.

First-principles calculations show that the soft-mode potential surface has two absolute minima along the [00±1] directions at ambient pressure owing to the large lattice strain of about 6% (ref. 19). If it were not for the lattice strain, the global minima would be along the [111] directions, as in BaTiO$_3$, and there would be a rhombohedral ground state$^{20}$. As pressure increases, theory and experiment show decreasing lattice strain, with a ground state eventually along [111] in the predicted and observed rhombohedral phases.

monoclinic phase between the rhombohedral and tetragonal phases simply arises from higher-order terms in a Taylor expansion of the energy$^{27}$, corresponding to a rotation of the polarization direction. The ease of rotating the polarization is responsible for the predicted huge electromechanical coupling in the transition region$^{17}$. The high-temperature transition additionally has an order–disorder contribution, where the four (±1±1) directions are occupied in the tetragonal phase and eight (±1±1±1) directions are occupied in the cubic phase. This allows for the direct tetragonal to cubic transition observed at room temperature. The competition with octahedral rotations, common in these materials$^{25,26}$, adds complexity to the problem.

Thus we find that a MPB phase boundary region can arise in a pure material under pressure at low temperature and consequently the polarization can easily rotate between different symmetries. Our results show clearly that the classic MPB that gives rise to large electromechanical coupling does not require random fields, compositional heterogeneity, polar nanoregions, mesostructural heterogeneity, or nanodomains. The latter are effects of the soft rotational dynamics rather than the cause of high coupling. Our results demonstrate rather that the high coupling materials such as PMN-PT and PZN-PT simply compositionally tune the inherent transition observed in PbTiO$_3$ to ambient pressure. We show the possibility of finding a pure compound with a large coupling MPB-like behaviour at room pressure, which would lead to great advances in ultrasound and other electromechanical applications.

Our results also provide strong evidence against the nanotwin theory for the monoclinic phases at MPBs, which asserts that observed monoclinic phases$^2$ are actually nanotwinned rhombohedral and tetragonal nanodomains$^{34-35}$. Our first-principles calculations clearly show the ground state to be monoclinic, and we see clear evidence of tetragonal to monoclinic, monoclinic to monoclinic, and monoclinic to rhombohedral phase transitions in our micro-Raman data (Fig. 2 and Supplementary Fig. 9), which would not be present if instead there was a progressive change in microstructure with pressure. It is true that nanodomains could give apparent monoclinic diffraction, and it is true that materials at MPBs contain complex domain microtextures, but it does not logically follow that such microtextures are evidence against monoclinic symmetry. In fact, we would expect more complex microstructures for the monoclinic phase, because there are 24 possible domain orientations, compared to six for tetragonal, for example. The complex microstructures do complicate interpretation of dynamical properties, and will give extrinsic contributions to the electromechanical coupling$^{26}$.

Figure 3 | Lattice strain and monoclinic angle. a, Representation of the monoclinic unit cell with respect to the tetragonal unit cell. The polarization in Cm (monoclinic M$_c$) lies in the $a_{Cm}$ moment monoclinic plane (polarization $P = [xxz]$ in cubic cartesian coordinates) and is shown as $d_x$; the polarization in Pm (monoclinic M$_c$) lies in the $a_{Cm}'c_{Cm}'$ plane (polarization $P = [xz]$) and is shown as $d_x'$. Solid circles represent the pressure dependence of the $c/a$ ratio (standard error ±0.005). The parameter $c/a$ shows weak discontinuities across the phase transitions at 11.4 and 15 GPa. Open circles represent the monoclinic distortion angles of $\beta-90^\circ$ as a function of pressure, which corresponds to the shear strain (standard error ±0.1%). The shear strain assumes a non-zero value above 11.4 GPa and monotonically decreases to zero above 20 GPa. The phase transition point of the tetragonal T and M$_c$ phases is slightly different in Raman and X-ray diffraction experiments. It could be that the M$_c$ phase develops at a local scale at 10 GPa but only becomes long-range, and thus visible by X-ray diffraction, at higher pressure.

Figure 4 | Phase diagram for lead titanate. Open circles are obtained from refs 10 and 28; solid circles are experimental results from this work. Open squares are from ref. 3 (theoretical calculations), which give tetragonal symmetry below 11 GPa, monoclinic symmetry between 11 and 12 GPa, and rhombohedral symmetry above 12 GPa. The solid and dashed lines are guides for the eye and indicate the possible boundary of different phases at low temperature. Experimental results suggest that PbTiO$_3$ undergoes successive phase transitions, from tetragonal to monoclinic at 10 GPa, monoclinic M$_c$ to monoclinic M$_c$ at 16 GPa, and monoclinic to rhombohedral at 20 GPa. There could also be an R3m phase between the M$_c$ and R3c phases.
How can we use this information to develop new high-performance electromechanical compounds? We have shown that pressure induces large piezoelectric effects in PbTiO$_3$ in a phase transition region. The compression in the lattice constant $c$ from 0 to 10 GPa is about 5%. We could apply chemical pressure by substituting a smaller atom with similar polarizability for Pb in the A site. Sn$^{2+}$ has an ionic radius 6% smaller than Pb$^{2+}$, but tin is also less polarizable than lead. We desire an ordered compound, so we consider Pb$_{1-x}$Sn$_x$TiO$_3$ with Pb and Sn ordered in planes along 001. Local density approximation computations indeed show this to be a very promising material, with an orthorhombic ground state of symmetry $Pmm2_1$. (polarization along $[001]$, $c/a = 0.91$) with an energy difference of 12 meV per atom between $Pmm2_1$ and the next state $Cm$ (polarization along $[xxx]$, $c/a = 0.98$) followed by tetragonal $P4mm$ (polarization along $[001]$, $c/a = 1.12$) with a $\Delta E$ of 3 meV per atom. We predict strain differences $\varepsilon_{13} - \varepsilon_{11} = -0.10$, $-0.02$ and 0.11 in the three phases, respectively. Our results suggest easy of polarization rotation and large electromechanical strain. The properties of this compound are currently under investigation. We could design other possible materials as well from the simple idea of chemical pressure, now that we have shown the presence and origin of large electromechanical coupling under pressure in pure PbTiO$_3$.

**METHODS SUMMARY**

Low-temperature, high-pressure X-ray diffraction measurements on powder samples of PbTiO$_3$ were performed at synchrotron X-ray sources. Liquid He was used in flow-type cryostats to achieve low temperatures, while the samples were pressurized using the DAC. Energy dispersive X-ray diffraction experiments$^{13}$ were performed at beamline 16-BM-D of HPCAT at the Advanced Photon Source. Additional high-energy, high-resolution angular dispersive diffraction experiments$^{13}$ were performed at beamline 11-ID-C at the Advanced Photon Source. We also conducted low-temperature, high-pressure Raman scattering on the (001)-orientated single crystals of PbTiO$_3$. First-principles density functional computations were performed within the local density approximation using the ABINIT package$^{37}$. 

**Full Methods** and any associated references are available in the online version of the paper at www.nature.com/nature.

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METHODS
X-ray diffraction. Single crystals of PbTiO$_3$ were grown by the flux method. Fine-grained powders of these crystals were loaded into stainless steel gaskets in a DAC with neon as the pressure medium. In addition, small ruby chips and Au powder were loaded together with the samples for pressure determination. The DACs were loaded into a He flow-type cryostat for low-temperature measurements at 10 K. We carried out the energy dispersive X-ray diffraction experiments at beamline 16-BM-D of HPCAT at the Advanced Photon Source. Additional experimental details about beamline 16-BM can be found in the Supplementary Information and ref. 11.

We performed high-energy, high-resolution angular dispersive diffraction (HEHRXD) experiments at beamline 11-ID-C at the Advanced Photon Source. Data were collected from the powder samples in DACs in symmetric flat-plate reflection geometry using 2$\theta$ scans over selected angular regions in the pressure range from 5 to 21 GPa at 10 K. This beamline provides a monochromatic incident beam with a wavelength close to 0.1077 Å (115 keV). Additional experimental details about beamline 11-ID-C can be found in the Supplementary Information and ref. 12.

The fits to the data were made by constraining the peak widths using the Au diffraction peak linewidths$^{29}$. The narrow width of the peaks (0.005$^\circ$) demonstrates the excellent quality of the sample and the nearly hydrostatic sample environment at high pressures. These conditions allowed us clearly to distinguish the specific characteristics of each phase on the basis of the splitting of the diffraction peaks. In particular, the monoclinic phase exhibits unique diffraction patterns that cannot be accounted for by either the tetragonal or the rhombohedral symmetries.

Assuming an error in Bragg angle of 0.0005$^\circ$ and a maximum wavelength error of 0.004 Å, we estimate an error in determining $d$ spacing of $\Delta d = 0.002 \text{Å}$ for $d = 3.969 \text{Å}$.

Raman scattering. We used two different experimental set-ups for Raman spectroscopy. The first was an XY Dilor triple grating system with a charge-coupled device (CCD) for measurements from 500 down to 10 cm$^{-1}$. The second was a Jobin Yvon HR-460 single grating system with double notch filters with higher throughput for measurements above a low-frequency cut-off of 80 cm$^{-1}$. The unpoled single-crystal sample, a 30 µm plate cut parallel to [001], was loaded into a DAC with Ne as the pressure medium. An Ar-ion laser was used as the light source, operated at the 514.5 nm wavelength with the averaged power less than 100 mW. To avoid the excessive elastic scattering from the diamonds, we used the 135$^\circ$ backscattering geometry. Additional experimental details are described in ref. 30.

Theoretical methods. Plane-wave pseudopotential computations were performed within the local density approximation using the ABINIT package$^{27}$. The PbTiO$_3$ computations used a converged plane-wave energy cut-off of 60 Hartrees, with $6 \times 6 \times 6$ converged Monkhost-Pack $k$-point meshes. The norm-conserving pseudopotentials include Pb 5$d$6$s$, Ti 3$d$3$p$3$d$, and O 2$s$ as band states generated with the code OPIUM (see http://opium.sourceforge.net for an open-source pseudopotential interface and unification module). The (Pb, Sn)TiO$_3$ computations used an energy cut-off of 130 Hartrees, with $4 \times 4 \times 4$ and $6 \times 6 \times 6$ $k$-point meshes in the ten-atom unit cell, and pseudopotentials generated using the OPIUM3.05_beta version. For Sn, 5$s$5$p$5$d$ were taken to be band states.