

Morphotropic phase boundary in pure perovskite lead titanate at room temperature



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ABSTRACT

For many decades, great efforts have been devoted to pursue a large piezoelectric response by an intelligent design of morphotropic phase boundaries (MPB) in solid solutions, where tetragonal (T) and rhombohedral (R) structures coexist. For example, classical $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ single crystals demonstrate a giant piezoelectric response near MPB. However, as the end member of these solids, perovskite-structured PbTiO_3 always adopts the T phase at room temperature. Here, we report a pathway to create room temperature MPB in a single-phase PbTiO_3 . The uniaxial stress along the c-axis drives a T-R phase transition bridged by a monoclinic (M) phase, which facilitates a polarization rotation in the monodomain PbTiO_3 . Meanwhile, we demonstrate that the coexistence of T and R phases at room temperature can be achieved via an extremely mismatched heterointerface system. The uniaxial pressure is proved as an efficient way to break the inherent symmetry and able to substantially tailor the phase transition temperature T_c . These findings provide new insights into MPB, offering the opportunity to explore the giant piezoelectric response in single-phase materials.

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1. Introduction

A morphotropic phase boundary (MPB) is a coexistent region of T and R structure in the phase diagram, which has been well established in $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ from the 1950s and subsequent relaxor $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ single crystals [1,2]. Near such regions, a large piezoelectric response is usually found [2–4]. To understand such response, a polarization rotation mechanism has been developed, where the energetically favorable rotation from a $[001]_T$ direction to a $[111]_R$ direction generates a pronounced strain by

costing a low electric field [3,5–7]. This mechanism can also be mediated via the creation of an M phase, as a structural bridge between the T and R phase [4,7,8]. These findings make the concept of MPB highly attractive for exploring high-performance piezoelectric materials from an experimental design [9–11]. However, the empirical tuning of the exact structure of the solid solutions remains very complex. The realization of MPB in a single-phase material would be of great interest for both the understanding of the fundamental mechanism of the electromechanical response and the design and optimization of the giant piezoelectric effect [11–13].

As a typical ferroelectric material with a simple perovskite structure, PbTiO_3 has been identified to adopt a T phase below the ferroelectric phase transition temperature ($\sim 490^\circ\text{C}$) [14,15]. Owing to its simple structure, PbTiO_3 is an ideal model to explore the origin of ferroelectricity [16–18] and therefore, it triggered many research efforts on exploring the existence of MPB and the large

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piezoelectricity near MPB [7,10,11,19]. Nevertheless, the existence of room temperature MPB for pure PbTiO_3 has not been achieved so far, neither theoretically nor experimentally. As anisotropic stress, the uniaxial pressure has been widely proved as a unique and efficient way to involve an inherent symmetry breaking [20,21], bypass the extreme and harsh conditions to achieve a phase transition, such as dramatically increasing the critical temperature T_c of superconductivity in Sr_2RuO_4 [22,23]. Meanwhile, the R phase has a pseudo-cubic structure with a smaller volume of the unit cell and c/a ratio than the T phase [6,11]. We performed first-principles density functional theory calculations and found that a uniaxial compressive strain applied along the c -axis can drive the T phase of PbTiO_3 to gradually transform into M-like and R-like phases (details in Fig. S1). These findings provided us with a possible clue for achieving MPB at room temperature. Herein, we report a facile uniaxial pressure is an efficient way to break inherent symmetry to drive a single-component ferroelectric to MPB at room temperatures, not necessitating the extreme and harsh conditions, such as low temperature and high pressure. Furthermore, we designed an extremely mismatched (010) $\text{SrTiO}_3/\text{PbTiO}_3$ heterostructure, in which we achieved a stable co-existence of T and R phases by inducing the interfacial c -axis compressive strain. Our findings pave a simple and facile way to obtain an MPB situation in pure phase perovskites; the triggering conditions that reach MPB are significantly reduced and confirmed the possibility of achieving the giant piezoelectric effect by an actual example of interface engineering, which certainly will trigger particular interest in designing MPB for a giant piezoelectric effect.

2. Experiment section

2.1. Materials

Single-crystal and monodomain PbTiO_3 bulk samples were synthesized by a two-step hydrothermal method as follows: $\text{Pb}(\text{NO}_3)_2$ and tetrabutyl titanate were used as starting materials. Potassium hydroxide was used as a mineralizer. Potassium hydroxide was first dissolved in deionized water, tetrabutyl titanate was then added in the aqueous solution, and $\text{Pb}(\text{NO}_3)_2$ solution was finally dropwise added under vigorous stirring. The resultant products were washed with water and ethanol several times and subsequently dried at 60 °C in air for 12 h. PbTiO_3 nanoplates were first prepared under hydrothermal condition [24]. $\text{SrTiO}_3/\text{PbTiO}_3$ heterostructures were synthesized by a facile hydrothermal method as follows: Mixing tetrabutyl titanate and strontiumnitrate in aqueous solution as precursor, and sodium hydroxide was used as crystallographic controlling agent. PbTiO_3 nanoplates were added in the solution after stirring. The reaction was performed in an autoclave at 200 °C for 10 min to 24 h.

2.2. Characterizations

Transmission electron microscope (TEM) samples are prepared using a focus ion beam (Quanta 3D FEG, FEI). High-angle annular dark field-scanning transmission electron microscope (HAADF-STEM) experiments were performed on an aberration-corrected TEM (FEI Titan G2 80–200 Chemi STEM). The integrated differential phase contrast (iDPC-STEM) was conducted on an aberration-corrected TEM (FEI Titan Themis). The in-situ loading experiment was performed on a TEM (FEI Tecnai G2 F20 S-TWIN) with a nanoindentation system (Hysitron PI95). The synchrotron X-ray diffraction was carried out at the beamline 15U1, Shanghai Synchrotron Radiation Facility, China. The X-ray wavelength was 0.6199 Å. The monodomain structure of PbTiO_3 was characterized by the piezoelectric force microscope (BRUKER DIMENSION ICON).

3. Results and discussions

To verify the suggestion that a simple uniaxial stress might break the inherent symmetry and reach an MPB at room temperature, an in-situ experiment of uniaxial pressure is loaded on a single-crystal and monodomain PbTiO_3 at room temperature (characterization in Fig. S2). As shown in Fig. 1a, a pillar of T phase PbTiO_3 with a size of 1 μm was prepared for in-situ pressure loading analysis [16]. The electron diffraction patterns of the initial state and the compressed state are shown in Fig. 1b. As the pressure increases, the intensity of the 001 spot significantly decreases, and the shift of the 002 spot implies a dramatic reduction of c value (Fig. 1c). This variation of the c parameter is consistent with the phase transition from T to R. This transition is reversible, and spots recover to their initial state when the pressure is unloaded.

To further clarify the dynamical aspect of the phase transition, the evolution of the lattice parameters and diffraction patterns was monitored as a function of time (Fig. 1c–g). In the initial stage, there is elastic deformation (red background); the c value gradually decreases while a increases. When the compressive stress reaches 1.63 ± 0.30 GPa, the evolution of both lattice parameters and c/a reaches a platform (gray background), corresponding to a c/a of 1.030; this can be interpreted as an intermediary region in the phase transition sequence. With the pressure further increasing, the c value abruptly drops to about 0.385 Å, and the c/a ratio also changes abruptly from ~ 1.030 to ~ 0.98 . After transforming into the R phase, the lattice parameters and c/a ratio reach another platform (blue background). When the compressive pressure is gradually unloaded, the abrupt change and the platform are similar to the loading process. This confirms that the two platforms, in loading and unloading, are related to the existence of an intermediate phase in the phase transition sequence.

Based on the above results, it is reasonable to conclude that the T to R phase transformation in PbTiO_3 can be realized at room temperature through the application of a uniaxial pressure. Previous reports [4,7,8] also mention that there may exist a low symmetry phase connecting T and R phases. Ahart reported [11] that pure PbTiO_3 goes through a $\text{T} \rightarrow \text{M} \rightarrow \text{R}$ phase transition under a huge hydrostatic pressure (20 GPa) at ultra-low temperature (10 K). The emergence of the M phase is accompanied by an abrupt change in the β angle of the unit cell in the vicinity of the T-M transition. With this in mind, we analyzed the evolution of the β -90° angle to verify the existence of this T-M phase transition (Fig. 1f). These measurements show that in the initial T phase, R phase, and recovery stage, the deviation from 90° remains stable at $(0.0 \pm 0.43)^\circ$, whereas at the onset of the transition stage, there is a jump in both the loading and the unloading directions. The β -90° angle approaches 1.2° at both transition stages, indicating the existence of a monoclinic (M) phase. Moreover, we further compared experimental and simulated diffraction patterns; both the position and the intensity ratio of diffraction spots show an excellent agreement for all three phases (Fig. 1g and Fig. S3). This provides proof for the existence of a T-M-R phase transition sequence induced by the application of an in-situ uniaxial stress along $[001]_T$.

Our experimental results are further confirmed by calculations with the phenomenological thermodynamic theory and recalculated the low-temperature hydrostatic pressure results in Ahart's work [11] to verify the accuracy and feasibility of the calculation (Fig. S4). The stress and temperature phase diagram of bulk PbTiO_3 under uniaxial c -axis compressive stress is shown in Fig. 1h (Methods). Both experiments and calculations reflect a fact that a facile uniaxial pressure is an efficient way to drive the T-M-R phase transition at room temperature, not necessarily the extreme and harsh conditions. All conditions for this approach can be realized in practical applications, such as interface engineering.

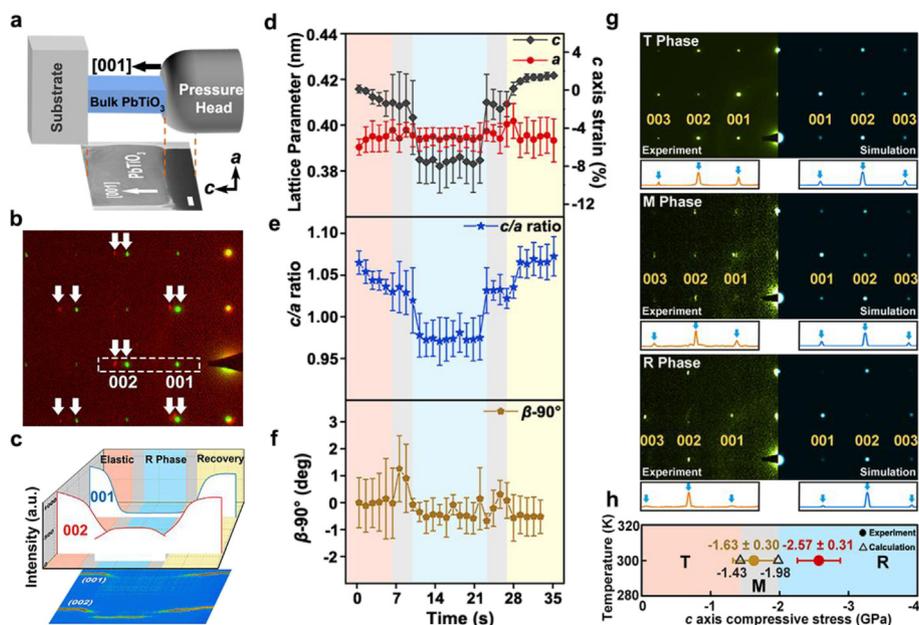


Fig. 1. In-situ pressure loading analysis results of single-crystal and monodomain PbTiO_3 when applying a uniaxial stress along [001]. (a) Schematic of the experimental setup. Scale bar 200 nm. (b) [010] zone axis selected area diffraction pattern of the initial state (green) and compressed state (red). (c) Evolution of the 001 and 002 diffraction spot intensity versus time. (d–f) Evolution profiles of lattice parameters, c -axis strain, c/a ratio, and $\beta-90^\circ$ angle of the unit cell in PbTiO_3 . (g) Evolution of experimental and simulated diffraction patterns of the T, M, and R phases. (h) Phase diagram of bulk PbTiO_3 under uniaxial stress along the c -axis. Circles and triangles indicate experimental and calculated phase transition points at 300 K, respectively.

To realize the uniaxial strain needed for room-temperature MPB in PbTiO_3 , we designed a (001) SrTiO_3 /(100) PbTiO_3 epitaxial heterostructure, where various stress can be introduced by a huge lattice mismatch (a mismatch of up to 6.4% can theoretically introduce a maximum tensile and compressive stress of +12.6 GPa and -5.25 GPa). Such heterointerface is an ideal platform to further explore whether the R phase can stably exist in pure PbTiO_3 at room temperature, and what c -axis pressure can drive the T-R phase transition at room temperature [25]. Taking advantage of the electrostatic force-driven oxide heteroepitaxy [24,26], (010) SrTiO_3 / PbTiO_3 heterostructures have been prepared (Methods). Fig. 2a shows a HAADF-STEM image of the (010) SrTiO_3 / PbTiO_3 interface.

According to the results of a geometric phase analysis for Fig. 2b and c, nearby each dislocation core in PbTiO_3 , there is a particular region that shows the c -axis compressive strain is around -2.3%, and the a -axis tensile strain is around +0.7% (Fig. S5), leading to a decrease in the c/a ratio approaching 1, which is favorable for the formation of the R phase.

We further recorded iDPC-STEM images [27] to determine the polarization distribution near the interface (Fig. 2d). The polarization direction, far from the dislocation, is along [001], corresponding to the T phase (Fig. 2e). In the region where the c/a ratio is approaching 1, the polarization direction rotates from horizontal [001] to 45° anticlockwise, which matches the projection of the [111] polarization in the R phase (Fig. 2f). Meanwhile, as shown in

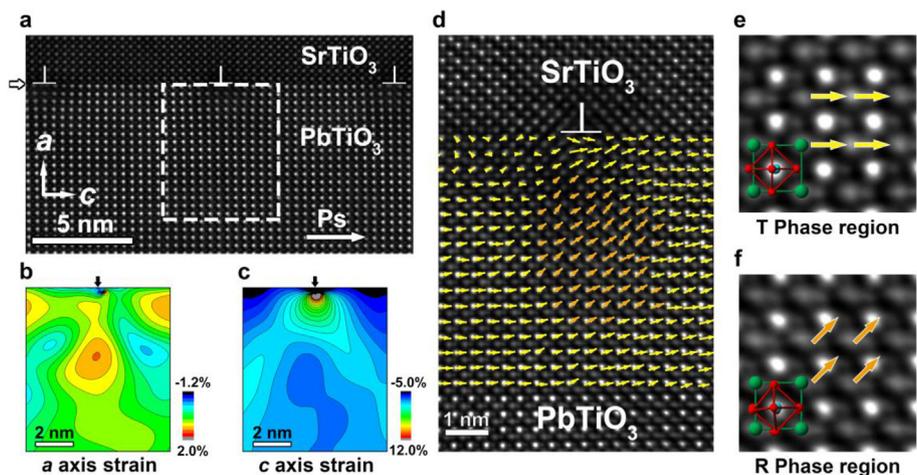


Fig. 2. Atomic-level STEM characterization of the (010) SrTiO_3 / PbTiO_3 heterointerface. (a) Cross section of HAADF-STEM image along the [010] zone axis. (b–c) GPA results for a -axis and c -axis strain contour mapping of a dislocation region, indicated in (a) by a white-dashed square. (d) iDPC-STEM image superimposed with the corresponding polarization direction of each unit cell in PbTiO_3 . (e–f) Magnified iDPC images of ordinary and rotated polarization regions.

Fig. 3a and b, we calculated the unit-cell c/a ratio around a single dislocation region. These data reveal that beneath the dislocation core, the c/a ratio reaches about 1.03, whereas away from the dislocation, the ratio is 1.065 ± 0.003 , matching well with that of the T phase (Fig. S8b). By statistically evaluating the lattice parameters and displacement of Ti atoms, we can confirm the existence of an M phase in PbTiO_3 as a bridge between T and R phases, and the R phase symmetry is confirmed as $R3c$ (Figs. S6–7 and Table S1). It can therefore be concluded that a uniaxial compressive strain along the c -axis is favorable to reduce the c/a ratio and to induce a stable R phase.

To investigate the 'phase boundary' (or MPB), we quantitatively analyzed the statistical strain distribution of the T and R regions (Fig. 3c–e). Both in the a -axis and c -axis strain projection planes, there is an obvious boundary or overlap region between R and T phases (Fig. 3c). According to the results in Fig. 3d and e, the maximum of the frequency locates at the R region with negative c -axis strain and positive a -axis strain, and the corresponding values are $\sim -1.4\%$ and $+0.5\%$, respectively, whereas both the c -axis and a -axis strains of the T phase are almost zero. Moreover, the average values for the c/a ratio and cell volume of the T and R regions have been determined (Fig. S8). All the above results are consistent with the existence of the R phase. However, in ferroelectrics, a polarization rotation may also originate from a flexoelectric effect, which is a coupling effect between a strain gradient and an electric polarization [28,29]. The strain gradient distribution along the c -axis is calculated; it is obvious that the gradient value is close to zero, implying that a flexoelectric effect is negligible (Fig. S9). Therefore, the boundary of T and R phases can be reasonably confirmed, based on the statistical data in Fig. S10a. Meanwhile, the phase diagram of the biaxial strain of c and a for bulk PbTiO_3 was calculated and shown in Fig. S10b, matching well with the experimental phase diagram in Fig. S10a.

Based on the above results, it is reasonable to speculate that uniaxial pressure along the c -axis is able to significantly reduce trigger conditions of the T-M-R phase transition. As reported theoretically, the superior piezoelectricity near MPB is mainly

attributed to the large shear piezoelectric response [30–32]. In this work, a new pathway to the superior piezoelectricity was explored. The profile of piezoelectric coefficient d_{33} to the c -axis stress was calculated by involving the modified coefficients of the Landau potential. Interestingly, an abrupt increase of d_{33} at the T-M phase boundary at 300 K has been found (Fig. S11), suggesting the existence of optimum piezoelectric efficiency near the MPB.

4. Conclusion

In summary, a combination of in-situ experimental investigations, verification in the interface system, and theoretical calculations revealed that a facile uniaxial pressure is an efficient way to break inherent symmetry to drive a single-component ferroelectric to MPB at room temperatures, not necessitating the extreme and harsh conditions, such as low temperature and high pressure. This phase is crucial for exploring and understanding the high piezoelectric response in this simple perovskite at room temperature. Furthermore, we designed an extremely mismatched (010) $\text{SrTiO}_3/\text{PbTiO}_3$ heterostructure, in which we achieved a stable coexistence of T and R phases by inducing the interfacial c -axis compressive strain. Our findings pave a simple and facile way to obtain an MPB situation in pure phase perovskites. Complex solid solutions or under extremely critical conditions are no longer the only path to MPB.

Credit author statement

The project was conceived and designed by H.T. and Ze Zhang; Z.R. and G.H. prepared the single-phase PbTiO_3 and (010) $\text{SrTiO}_3/\text{PbTiO}_3$ heterostructure samples; Z.Z. and C.X. performed TEM experiments; Y.H., J.H., and S.L. did first-principles calculations; X.M. and H.H. did phase-field simulations; Z.Z. and C.X. wrote the manuscript. All authors were involved in the analysis of the results and contributed to writing the paper.

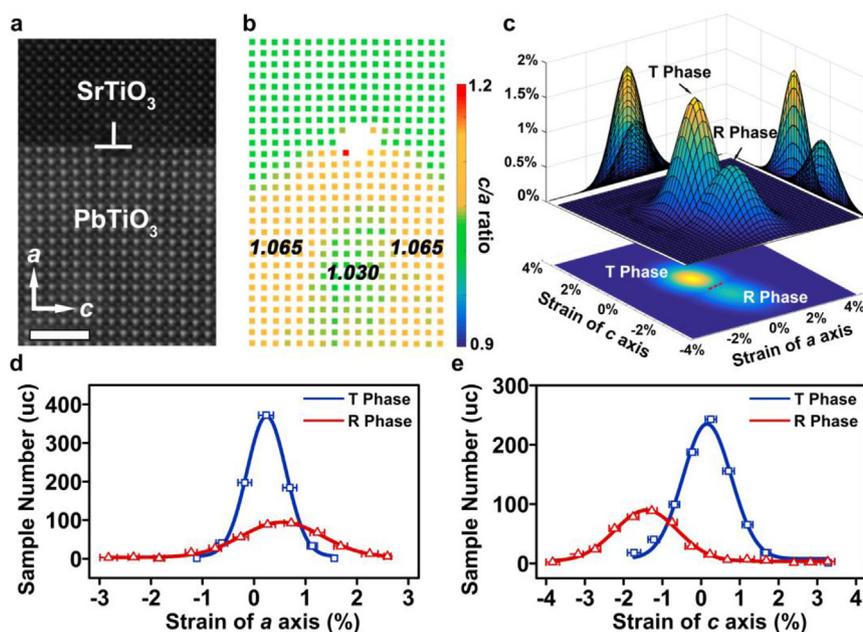


Fig. 3. Unit cell by unit cell strain analyses of the highly strained region. (a) HAADF-STEM image of a single dislocation region. Scale bar 2 nm. (b) Unit-cell mapping of the c/a ratio in the region of (a). (c) Statistical histogram of c -axis and a -axis strain of R and T phase regions, the height represents the frequency of the strain values. (d–e) Statistical profiles of a -axis and c -axis strain of the R and T phase regions.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mtnano.2022.100275>.

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