First-principles study of structural stability and elastic property of pre-perovskite $PbTiO_3$*

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The structural stability and the elastic properties of a novel structure of lead titanate, which is named pre-perovskite $PbTiO_3$ (PP-PTO) and is constructed with TiO_6 octahedral columns arranged in a one-dimensional manner, are investigated by using first-principles calculations. PP-PTO is energetically unstable compared with conventional perovskite phases, however it is mechanically stable. The equilibrium transition pressures for changing from pre-perovskite to cubic and tetragonal phases are −0.5 GPa and −1.4 GPa, respectively, with first-order characteristics. Further, the differences in elastic properties between pre-perovskite and conventional perovskite phases are discussed for the covalent bonding network, which shows a highly anisotropic character in PP-PTO. This study provides a crucial insight into the structural stabilities of PP-PTO and conventional perovskite.

Keywords: elastic properties, phase transition, density-functional theory, $PbTiO_3$

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1. Introduction

Lead titanate ($PbTiO_3$, PTO), which undergoes a single ferroelectric transition from tetragonal phase to cubic phase with the increase of temperature or pressure, has attracted much attention because of its applicability to fundamental research and practical applications, serving not only as a prototype ferroelectric but also as an end member of practical piezoelectrics.[1−4] Recently, Wu and Cohen[5] and Ahart *et al.*[6] identified a tetragonal–monoclinic–cubic phase transition in the PTO induced by high pressure in excess of 20 GPa, demonstrating that a pure compound can also display a morphotropic phase boundary, which plays a very important role in ferroelectrics. To the best of our knowledge, all reported PTO structures including cubic, tetragonal, and monoclinic phases, belong to the conventional perovskite, wherein the TiO_6 octahedrals share corners to form a three-dimensional (3D) network. Extensive investigations into the electronic structures indicate that the ferroelectricity in the ABO_3 perovskite is the result of a delicate balance between short-range (SR) repulsions, which favour a cubic structure, and long-range (LR) Coulomb interactions, which favour a tetragonal structure.[7,8] For instance, the cubic $PbTiO_3$ forms a 3D covalent bonding network, and the perovskite tetragonal $PbTiO_3$ forms a 2D structure comprised of TiO_5 pyramids, which are strongly constructed by the Pb–O covalent bond.[9]

Recently, a new phase was discovered in the PTO nanofiber,[10] which is called pre-perovskite phase PTO (PP-PTO) due to its transformation into the perovskite phase after being annealed at temperatures higher than 350 °C. In PP-PTO, each TiO_6 octahedron pair that shares an edge is stacked over adjacent pairs in an interlacing manner to form a one-dimensional (1D) column as shown in Fig. 1. In the present paper, we for the first time report this 1D-structured perovskite-like oxide with a formula ABO_3. The TiO_6 columns in the PP-PTO are constructed by Ti–O covalent bonds and linked by Pb–O covalent bonds to form a 3D covalent bonding network, which has been hypothesized as being the key to stabilize the 1D-stacking-manner structure in ambient conditions. This newly structured PTO has a great impact on the research of the functional material phase transition and metastablility.

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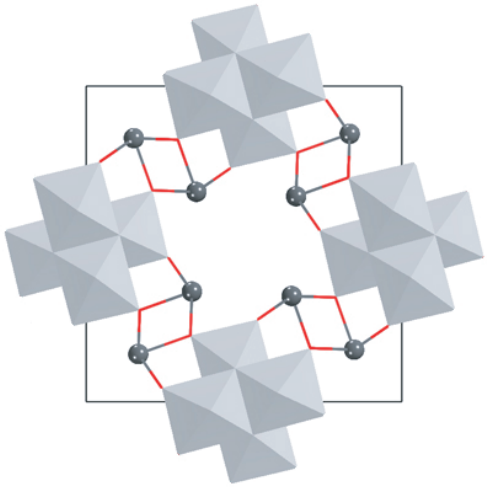


Fig. 1. (colour online) Schematic diagram of the newly structured $PbTiO_3$, where lead atoms are denoted as black solid circles.

In the present work, we investigate the elastic property and the structural stability of the PP-PTO and predict the equilibrium transition pressures for the transitions from the pre-perovskite phase to cubic and tetragonal phases by using first-principles calculations. Although these calculations do not include the effects of temperature and surface, they provide valuable insights into both the new PTO and the conventional perovskite structures.

2. Details of calculations

The calculations in this study were carried out by using the density-functional theory (DFT) within the local density approximation (LDA) as implemented in the ABINIT package.[11] We used the plane waves and the extended norm-conserving pseudopotentials,[12] which include lead 5d, 6s, and 6p; titanium 3s, 3p, 3d, and 4s; and oxygen 2s and 2p as the valence states. To save computation time, a primitive cell of the PP-PTO was considered to contain 20 atoms ($4\times PbTiO_3$, 4 unit cells). The convergence on the PP-PTO was reached for a 55-hartree plane-wave kinetic energy cutoff and a Monkhorst–Pack's mesh with twelve special k points. All of these calculations were performed on a cluster Lenovo 1800. The detailed results for the cubic and the tetragonal perovskite PTOs, henceforth referred to as the CP-PTO and the TP-PTO, respectively, have already been published.[13] Therefore, we will just provide a brief summary in this article to establish the notation and to provide a baseline for comparison with TP-PTO and CP-PTO.

3. Results

The structural relaxation of the novel structure PTO with space group $I4/m$ (PP-PTO) is performed until the maximum residual force reaches less than 1×10^{-6} Hartree/Bohr ($\sim 5 \times 10^{-5}$ eV/Å). The equilibrium lattice parameters are compared with the experimental data obtained by the neutron powder diffraction, as listed in Table 1. The theoretically obtained structural parameters are in good agreement with the experimental ones, and have deviations less than 2%. Usually, the LDA underestimates the lattice parameters,[14,15] and therefore, the experimental lattice parameters correspond to a negative pressure of $P = -4.2$ GPa. The residual pressure with the fully relaxed structure is less than 8×10^{-5} GPa, which is adequate to perform the following calculations of the elastic properties.

Table 1. Optimized structural parameters of PP-PTO compared with the experimental results. The crystal has a tetragonal structure with space group $I/4m$.

	Neutron diffraction $a = b = 12.367$ Å $c = 3.808$ Å			Theory $a = b = 12.179$ Å $c = 3.745$ Å		
	x	y	z	x	y	z
Pb(8h)	0.165	0.151	0.5	0.164	0.149	0.5
Ti(8h)	0.471	0.142	0.5	0.468	0.143	0.5
O1(8h)	0.169	0.289	0	0.166	0.289	0
O2(8h)	0.543	0.260	0.5	0.550	0.262	0.5
O3(8h)	0.605	0.028	0.5	0.604	0.026	0.5

The calculated cohesive energy is shown as a function of volume in Fig. 2 for the PP-PTO, the CP-PTO, and the TP-PTO. The equilibrium energy of the PP-PTO is 88 meV/f.u. and 40 meV/f.u. higher than those of the TP-PTO and the CP-PTO, respectively, indicating that the ground state of the PTO is the TP-PTO and the PP-PTO is energetically unstable. The bulk modulus B obtained from Fig. 2 by using the Birch–Murnaghan equation of state are 210 GPa, 106 GPa, and 65 GPa for the CP-PTO, the TP- PTO,

and the PP-PTO, respectively. The LDA underestimates the lattice constants and the influence of temperature is not considered, which generally leads to the decrease of the bulk modulus. However, the predictions of B are found to be generally larger than the experimental results,[13] although the experimental value of the PP-PTO is not available. However, the comparison between the theoretical values within the identical formalism framework is meaningful. From the predicated bulk modulus, the PP-PTO is much more compressible than the CP-PTO and the TP-PTO, which can be explained by the larger spacing between the TiO_6 octahedral columns (Fig. 1).

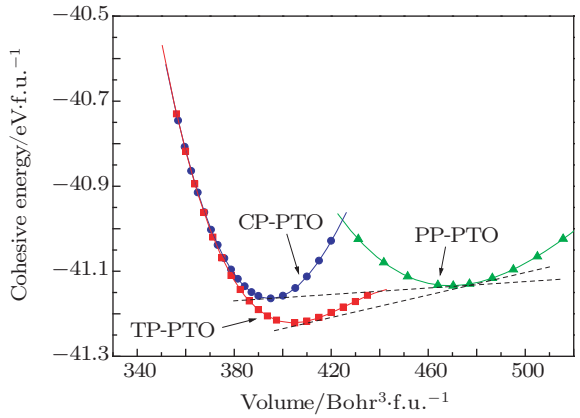


Fig. 2. (colour online) Cohesive energies of CP-PTO, TP-PTO, and PP-PTO each as a function of volume.

The volume compressions each as a function of pressure are plotted in Fig. 3, showing that the PP-PTO is the softest. The pressure P is obtained from $P = -\mathrm{d}E/\mathrm{d}V$, where E and V are the cohesive energy and the volume of the unit cell, respectively. The volume of the unit cell for the fully optimized structure is denoted as V_0. The V/V_0 ratios of the CP-PTO, the TP-PTO, and the PP-PTO decrease nonlinearly with the increase of pressure, indicating that their bulk moduli are not constant. According to the definition of the bulk modulus, $B = -PV_0/\Delta V$ with $\Delta V = V - V_0$, the bulk modulus can be calculated as a function of pressure (see the insert in Fig. 3). The bulk moduli of the CP-PTO, the TP-PTO, and the PP-PTO increase with the increase of the pressure, which reveals that the materials generally become harder and harder under pressure.

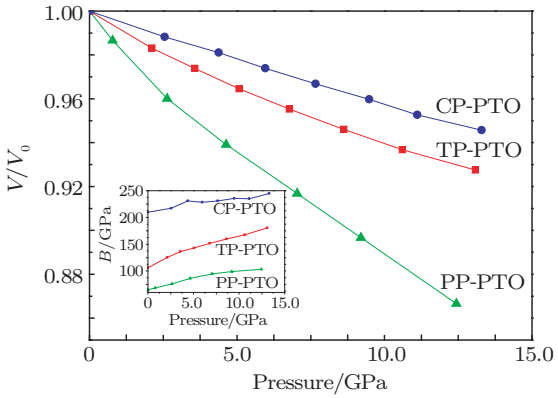


Fig. 3. (colour online) Volume compressions of CP-PTO, TP-PTO, and PP-PTO each as a function of pressure. The insert shows pressure dependences of bulk moduli for CP-PTO, TP-PTO, and PP-PTO.

To further investigate the elastic property of the material, it is necessary to study the elastic stiffness constants (c_{ij}). Other elastic constants, such as the compliance tensors (s_{ij}), the shear moduli, and the Poisson's ratio, can be gained from the elastic stiffness constants.[16] Thus, we mainly pay attention to the elastic stiffness constants in this work. Because of its tetragonal structure with a mirror symmetry perpendicular to the four-fold axis ($4/m$), there are seven independent elastic stiffness constants (c_{ij}) in the Voigt matrix notation for the PP-PTO, which are c_{11}, c_{33}, c_{44}, c_{66}, c_{12}, c_{13}, and c_{16}. The elastic tensors are calculated based on the density-functional perturbation theory (DFPT),[17,18] and are shown in Table 2. The elastic constants are obtained as the difference between the clamped-ion part corresponding to the purely electronic property and the internal-strain part corresponding to the relative displacement of the sublattices

$$c_{ij} = c_{ij}^{\mathrm{clamped-ion}} - c_{ij}^{\mathrm{internal-strain}}. \qquad (1)$$

Therefore, elastic constants c_{ij} are also referred to as the relaxed-ion elastic constants.[15] The corresponding Young's moduli are found to be 70.2 GPa for $E[100]$ and 198.3 GPa for $E[001]$.

Table 2. Elastic tensors of PP-PTO in the unit of GPa.

	c_{11}	c_{12}	c_{13}	c_{16}	c_{33}	c_{44}	c_{66}
c of clamped-ion	253.1	131.9	107.0	–17.1	364.2	89.6	112.1
c of internal-strain	154.3	88.7	27.2	–22.0	76.4	28.2	55.3
Total	98.8	43.2	79.8	4.9	287.8	61.4	56.8

The entire set of c_{ij} satisfies the Born criteria,[19] i.e., $c_{66} > 0$, $c_{44} > 0$, $c_{33} > 0$, $c_{33} \times c_{11} - c_{13}^2 > 0$, and $(c_{11} \times c_{66} - c_{12} \times c_{66} - c_{16}^2) \times (c_{12} \times c_{33} - 2 \times c_{13}^2 + c_{33} \times c_{11}) > 0$, which indicates that the PP-PTO is mechanically stable. The theoretical value of c_{11} describing the stress along the a axis induced by the strain in the a axis is 98.9 GPa. The value of c_{33} describing the stress along the c axis induced by the strain in the c axis is 287.8 GPa, which is approximately 3 times that of c_{11}. This finding suggests that the PP-PTO is strongly anisotropic with regard to the elasticity. The clamped-ion part of the PP-PTO along the a axis ($c_{11}^{\mathrm{clamped-ion}} = 253.1$ GPa) is much lower than its counterpart $c_{33}^{\mathrm{clamped-ion}}$ along the c axis, which is 364.2 GPa. This can be attributed to the fact that in the a–b plane, the TiO_6 columns are linked by the Pb–O bonding but are not fully constructed by the Ti–O bonding, which is shown in Fig. 1. This tendency implies that the TiO_6 octahedral network is much stiffer than the Pb–O bonding. The calculated values[13] of $c_{11}^{\mathrm{clamped-ion}}$ in the CP-PTO and the TP-PTO are 383.7 GPa and 326.9 GPa, respectively, which are much higher than the value of $c_{11}^{\mathrm{clamped-ion}}$ in the PP-PTO and are close to the value of $c_{33}^{\mathrm{clamped-ion}}$ in the PP-PTO. The fact that the bonding networks in the CP-PTO and the TP-PTO along the a axis both consist of the Ti-O bonding further supports the assumption.

There is only one independent structural parameter in the CP-PTO: lattice length a. Therefore, no relative displacement between the sublattices is allowed, and the internal-strain parts are zero. However, in the TP-PTO, there are three independent internal coordinates, which allow the sublattices to displace along the c axis and yield a large value of $c_{33}^{\mathrm{internal-strain}}$, 260.4 GPa. For the PP-PTO, the relative displacements between the sublattices are allowed in the a–b plane because of its symmetry, and this also yields a large value of $c_{11}^{\mathrm{internal-strain}}$, 154.3 GPa, which is lower than $c_{33}^{\mathrm{internal-strain}}$ of the TP-PTO. These results indicate that the displacement of the sublattice of the TP-PTO along the c axis is easier than that of the PP-PTO in the a–b plane, which can be attributed to the stiff character of the 3D covalent bonding network.

The enthalpy at $T = 0$ K is written as $H = E + PV$.[20] Therefore, the PP-to-CP and the PP-to-TP phase transition pressures can be predicated from Fig. 2 by using the enthalpy difference defined as

$$\Delta H_{\mathrm{PP-CP(TP)}} = \Delta E_{\mathrm{PP-CP(TP)}} + \Delta V_{\mathrm{PP-CP(TP)}} \times P. \quad (2)$$

To avoid the numerical errors in fitting the E–V curves, the convergence of the order of the polynomial is tested. As shown in Fig. 4, the order of the polynomial does not influence the results significantly. The 3rd-order polynomial is considered to have adequate convergence to obtain reliable results. This behaviour reflects the large enthalpy difference between the PP-PTO and the CP(TP)-PTO. The PP-to-CP and the PP-to-TP phase-transition pressures are approximately −0.5 GPa and −1.4 GPa, respectively, which confirms that the PP-PTO is an energetically unstable phase compared with the CP-PTO and the TP-PTO in ambient conditions. The pressure dependence of the volume in the vicinity of the phase transition is shown in Fig. 5. The curves each shows a sudden jump (the vertical lines in Fig. 5), implying the first-order character of the phase transitions. In contrast, the pressure-induced TP-to-CP phase transition in $PbTiO_3$ has a non-pure second-order character.[21] All calculations ignore the influence of temperature

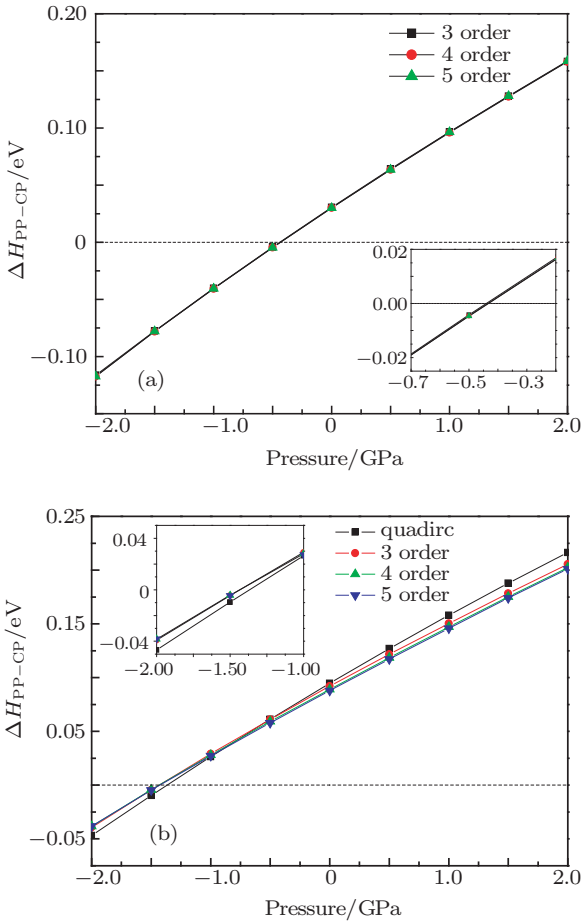


Fig. 4. (colour online) Differences in enthalpy (a) between PP-PTO and CP-PTO and (b) between PP-PTO and TP-PTO. The inserts show the corresponding plots around the transitions.

and have been performed at 0 K. The increase of temperature usually leads to the decrease of the transition pressure. Therefore, a more negative transition pressure is expected at room temperature, and the PP-PTO should be even less stable in ambient conditions. However, after the PP-PTO been annealed at 300 °C for 24 h, no distinguishable phase transition is observed. This unexpected stability can be attributed to the fact that in order to allow an actual transformation occur, the driving force of the phase transition must overcome the dynamic barrier of the transformation rather than the enthalpy difference between the ending and the starting phases. Thus, there appears to be a non-thermodynamic driving force, which dominates the PP-to-CP and the PP-to-TP phase transitions, as expected.

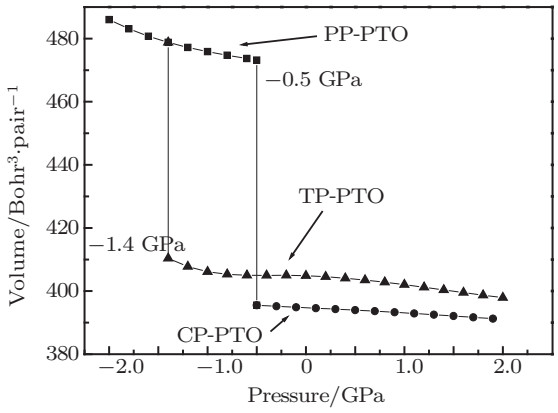


Fig. 5. Volumes each as a function of pressure in the vicinity of the phase transition.

4. Conclusion

An in-depth investigation of the mechanical properties and the structural stabilities of the PP-PTO has been carried out using first-principles calculations. The PP-PTO is found to be energetically less stable than the CP-PTO and the TP-PTO; however, it is mechanically stable. The calculated bulk modulus of the PP-PTO is 65 GPa, which is significantly lower than that of the CP-PTO or the TP-PTO. The PP-PTO exhibits highly anisotropic elastic properties, c_{33} of 287.8 GPa is approximately 3 times that of c_{11} of 98.8 GPa, which originates from its 3D covalent bonding network. The equilibrium transition pressures at 0 K of the PP-to-CP and the PP-to-TP transitions are determined to be −0.5 GPa and −1.4 GPa, respectively, with a first-order character. These results provide a crucial insight into the phase transition and the structural instability of the PP-PTO with respect to the elastic properties. The present study has paved the way for further stress analysis and strain energy estimation of the PP-PTO.

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