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# Isostructural phase transitions of tetragonal perovskite titanates under negative hydrostatic pressure

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## Abstract

Phase transitions within the tetragonal space group  $P4mm$  associated with anomalous enhancement of tetragonality in  $PbTiO_3$  and  $BaTiO_3$  under negative hydrostatic pressure were theoretically predicted by Tinte *et al* (2003 *Phys. Rev. B* **68** 144105). In the present study, with special interest in the origin of the phase transition, we made a series of analogous calculations for six perovskite titanates ( $ATiO_3$ , where  $A = Ca, Sr, Cd, Ba, Eu$  or  $Pb$ ). All six compounds are found to undergo similar phase transitions. One of the Ti–O bonds is virtually broken at the transition. The transition pressures for  $CaTiO_3$ ,  $CdTiO_3$  and  $PbTiO_3$  are near  $-4$  GPa, which is significantly different from the case for those of  $BaTiO_3$ ,  $EuTiO_3$  and  $SrTiO_3$ : they are near  $-10$  GPa. The transition pressure and volume change at the transition cannot be correlated with the A cation radius. Instead, they depend on the tetragonality of the original crystal, which is influenced by the relative stability of the cubic structures under zero pressure.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

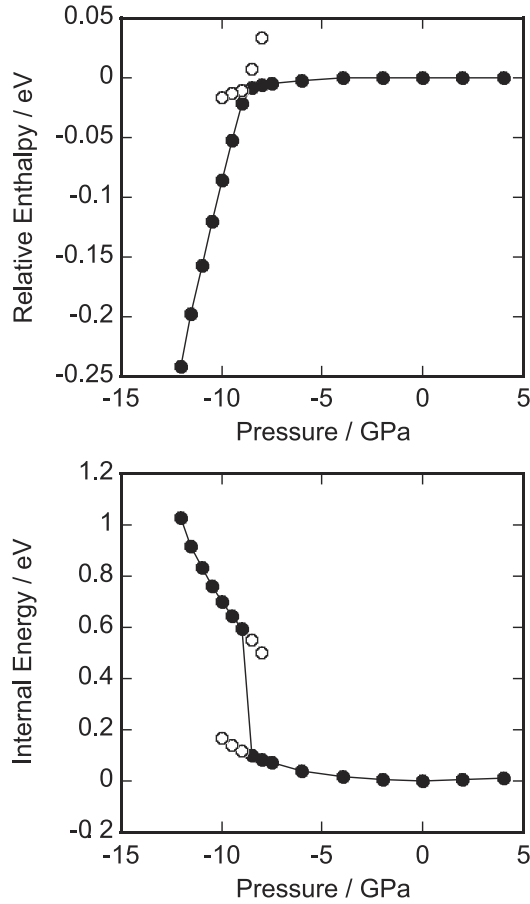
Besides their technological importance as ferroelectrics and piezoelectrics, perovskite titanates have been extensively studied to gain fundamental insight into their phase transition behaviour. Many perovskite titanates exhibit cubic structures with  $Pm\bar{3}m$  symmetry at high temperatures under ambient pressure. At low temperatures the cubic structures are known to be dynamically unstable, eventually undergoing phase transitions to lower symmetry structures such as in space groups  $P4mm$ ,  $I4/mcm$ ,  $R3m$  and  $Pnma$ . Ferroelectricity appears only in non-centrosymmetric structures, e.g.  $P4mm$  or  $R3m$  symmetry. Among the six perovskite titanates,  $CaTiO_3$ ,  $SrTiO_3$ ,  $CdTiO_3$ ,  $BaTiO_3$ ,  $EuTiO_3$  and  $PbTiO_3$ , only  $BaTiO_3$  and  $PbTiO_3$  have been reported to form a tetragonal phase with  $P4mm$  symmetry.

First-principles calculations of perovskite titanates have been reported by a number of groups [1–8]. In particular, Tinte *et al* [8] reported that an abrupt change in lattice parameters and volume take place in  $PbTiO_3$  and  $BaTiO_3$  when *negative* hydrostatic pressure is applied; tetragonal  $P4mm$  symmetry is

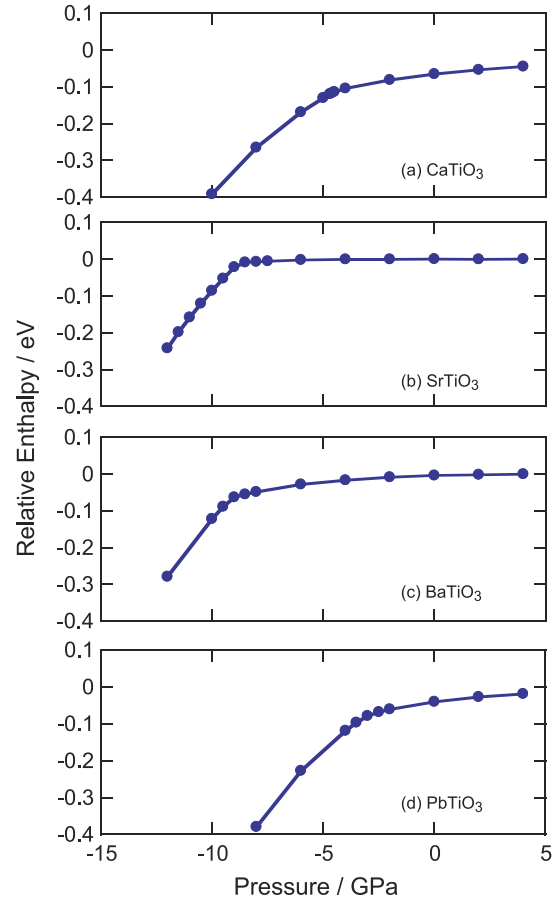
retained. The transition invokes anomalous enhancement of the tetragonality and therefore the ferroelectric polarization. Tinte *et al* [8] developed a phenomenological model to describe the transition. However, no other reports have appeared on this subject. It is not known whether a similar transition takes place in other perovskite titanates. Furthermore, no information is available about the factors that determine the transition pressure and the volume change at the transition. Since the phase transition is expected to take place under negative hydrostatic pressure, experiments to confirm the existence of the transition are difficult. We have therefore carried out first-principles calculations to further explore this phenomenon. Lattice parameters, lattice volume, internal energy, enthalpy as well as the bond lengths are reported as a function of pressure. The transition behaviours of the six titanates are discussed comparatively.

## 2. Computational procedures

All calculations were performed within the local density approximation (LDA) [9, 10] to density functional theory



**Figure 1.** Top: relative enthalpy,  $\Delta H$ , of the  $P4mm$  structure to the  $Pm\bar{3}m$  structure as a function of external hydrostatic pressure for  $\text{SrTiO}_3$ . Bottom: internal energy of the  $P4mm$  structure of  $\text{SrTiO}_3$  relative to the value at zero pressure. Open circles correspond to metastable structures.



**Figure 2.** Relative enthalpy, of the  $P4mm$  structure and the  $Pm\bar{3}m$  structure, as a function of external hydrostatic pressure for (a)  $\text{CaTiO}_3$ , (b)  $\text{SrTiO}_3$ , (c)  $\text{BaTiO}_3$ , and (d)  $\text{PbTiO}_3$ .

(DFT) using the plane-wave basis pseudopotential method as implemented in the CASTEP code [11]. Ultrasoft pseudopotentials of the Vanderbilt type [12] were used. Using this method, we can obtain the theoretical structure through precise calculations of forces and stresses, not only at zero pressure but also at a given pressure. Atomic orbitals explicitly treated as valence electrons were 2s, 2p for O; 3s, 3p, 3d and 4s for Ti; 3s, 3p and 4s for Ca; 4s, 4p and 5s for Sr; 4d and 5s for Cd; 5s, 5p and 6s for Ba; 4f, 5s, 5p and 6s for Eu; and 5d, 6s and 6p for Pb. Spin polarization was taken into account only for  $\text{EuTiO}_3$ , in which the magnetic structure was assumed to be ferromagnetic for simplicity. The plane-wave cut-off energy was 600 eV. Within the constraints of  $P4mm$  symmetry, lattice constants and internal atomic positions were optimized until the residual Hellmann–Feynman (HF) forces were less than  $5 \times 10^{-4} \text{ eV \AA}^{-1}$  and the residual stresses were smaller than  $10^{-3} \text{ GPa}$ . The structure was examined as a function of external hydrostatic pressure ranging from +4 to  $-12 \text{ GPa}$ . A  $k$ -point spacing of  $0.04 \text{ \AA}^{-1}$  was used. The overall energy convergence was better than  $1 \text{ meV/f.u.}$  Some calculations were also made within the constraints of  $Pm\bar{3}m$  symmetry. In this study, all calculations are made for the ground state ( $T = 0 \text{ K}$ ) and no temperature dependence is considered.

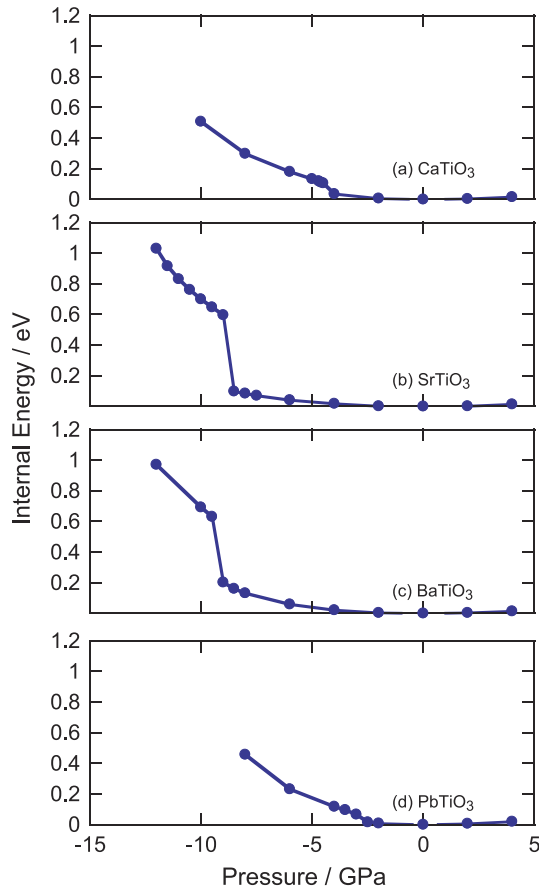
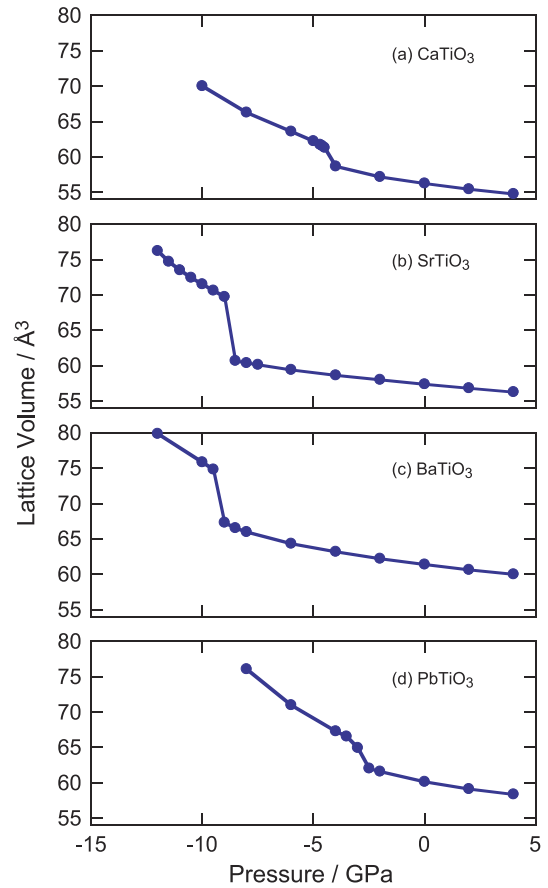
### 3. Results and discussion

The calculated lattice parameters of the six titanates are shown in table 1. Experimental data for the  $P4mm$  phase are known only for  $\text{BaTiO}_3$  [13] and  $\text{PbTiO}_3$  [14]. The calculated results underestimate these experimental values, with a maximum deviation of  $-3.0\%$  for the  $c$  parameter of  $\text{PbTiO}_3$ , which is still within typical LDA errors.

The upper panel of figure 1 shows the relative enthalpy of the  $P4mm$  phase as a function of pressure for  $\text{SrTiO}_3$ . The enthalpy,  $H$ , was calculated as  $H = U + pV$ , where  $U$ ,  $p$  and  $V$  are the internal energy, the external pressure and lattice volume, respectively. Both  $U$  and  $V$  were obtained from LDA calculations. In order to magnify the change near the transition, the relative value of the enthalpy, between  $P4mm$  and cubic  $Pm\bar{3}m$  structures under the given pressure, i.e.,  $\Delta H(p) = H(p, P4mm) - H(p, Pm\bar{3}m)$ , is shown. The lower panel of figure 1 shows the internal energy of the  $P4mm$  phase relative to the value at zero pressure. The transition pressure,  $p_t$ , is taken as the pressure at which the jump in internal energy occurs. It also corresponds to change in gradient in the enthalpy plot. The pressure dependence of the enthalpy is found to differ markedly between before and after the transition, although the space group remains unchanged. Near the transition pressure, some metastable structures can

**Table 1.** Calculated lattice parameters ( $a$ ,  $c$  and  $c/a$ ), transition pressure ( $\Delta p_t$ ), volume change ( $\Delta V_t$ ) and internal energy change ( $\Delta U_t$ ) at the transition point, along with the A site cation radius and difference in total energy.

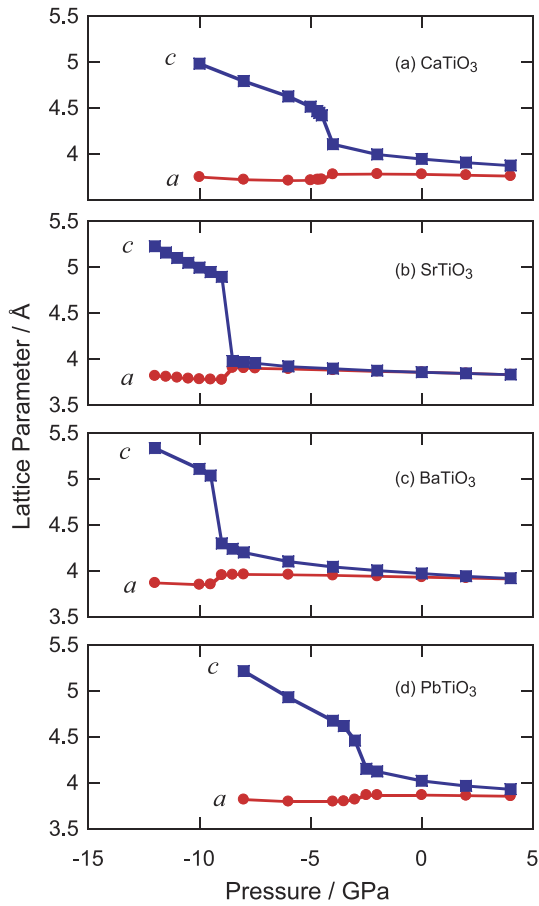
Space group		CaTiO <sub>3</sub>	SrTiO <sub>3</sub>	CdTiO <sub>3</sub>	BaTiO <sub>3</sub>	EuTiO <sub>3</sub>	PbTiO <sub>3</sub>
$P4mm$	$a$ (Å)	3.777	3.856	3.780	3.932	3.854	3.869
	$c$ (Å)	3.945	3.857	3.989	3.972	3.854	4.020
	$c/a$	1.044	1.000	1.055	1.010	1.000	1.039
	$p_t$ (GPa)	-4.2	-8.8	-3.3	-9.3	-9.3	-2.9
	$\Delta V_t$ (Å <sup>3</sup> )	2.5	9.2	2.5	7.5	9.8	3.0
$Pm\bar{3}m$	$\Delta U_t$ (eV)	0.08	0.50	0.05	0.42	0.57	0.04
	$a$ (Å)	3.807	3.856	3.806	3.939	3.854	3.891
	A site cation radius (Å)	1.43	1.47	1.43	1.53	1.47	1.49
	Difference in total energy (meV/f.u.)	-65	0	-118	-3	0	-40

**Figure 3.** Internal energy of the  $P4mm$  structure relative to the value at the zero pressure as a function of the external hydrostatic pressure for (a) CaTiO<sub>3</sub>, (b) SrTiO<sub>3</sub>, (c) BaTiO<sub>3</sub>, and (d) PbTiO<sub>3</sub>.**Figure 4.** Lattice volume of the  $P4mm$  structure as a function of the external hydrostatic pressure for (a) CaTiO<sub>3</sub>, (b) SrTiO<sub>3</sub>, (c) BaTiO<sub>3</sub>, and (d) PbTiO<sub>3</sub>.

be obtained as local minima of the enthalpy during structure optimization, as represented by the open circles in figure 1. These enthalpies lie on curves extrapolated smoothly from points on the other side of the transition.

Similar calculations were made for the other titanates. Relative enthalpies, internal energies, lattice volumes and lattice constants are shown in figures 2, 3, 4 and 5, respectively, for CaTiO<sub>3</sub>, SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, and PbTiO<sub>3</sub>. The other two titanates (CdTiO<sub>3</sub> and EuTiO<sub>3</sub>) exhibit analogous behaviours. At first glance, the four titanates appear to present similar pressure dependences of the relative enthalpy (figure 2) with

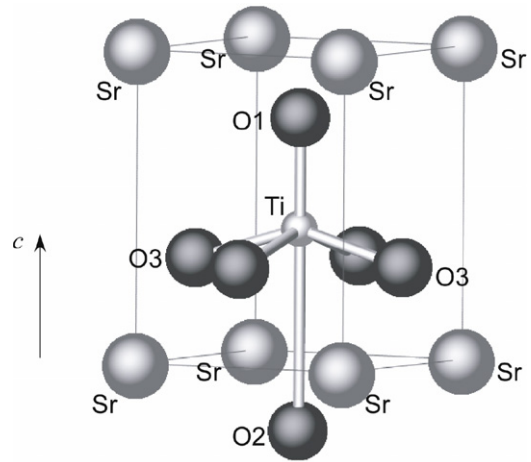
small variation in the transition pressure. However, the magnitudes of the changes of internal energy,  $\Delta U_t$ , and volume,  $\Delta V_t$ , at the transition clearly differ among the four titanates.  $\Delta U_t$  and  $\Delta V_t$  obtained from figures 3 and 4 are listed in table 1. As can be seen in figure 3, the dependence of internal energy on pressure for CaTiO<sub>3</sub> and PbTiO<sub>3</sub> differs from that for SrTiO<sub>3</sub> and BaTiO<sub>3</sub>. SrTiO<sub>3</sub> and BaTiO<sub>3</sub> have much lower  $p_t$  than the others. It is interesting that they exhibit larger  $\Delta U_t$  and  $\Delta V_t$ . In the work by Tinte *et al* [8] similar calculations were made only for BaTiO<sub>3</sub> and PbTiO<sub>3</sub>. But they did not report  $\Delta U_t$ . Their calculated  $p_t$  for PbTiO<sub>3</sub> and BaTiO<sub>3</sub> were  $-4.8$



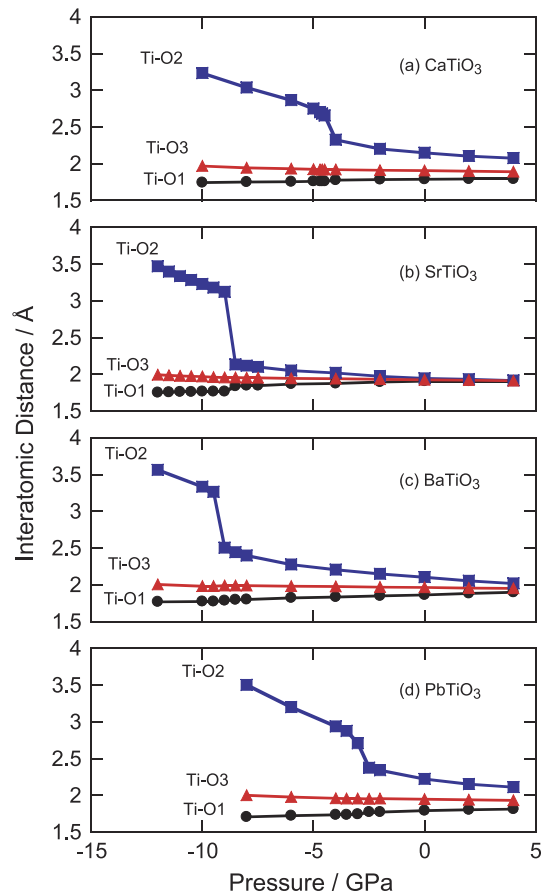
**Figure 5.** Lattice parameters of the  $P4mm$  structure,  $c$  and  $a$ , as a function of the external hydrostatic pressure for (a)  $\text{CaTiO}_3$ , (b)  $\text{SrTiO}_3$ , (c)  $\text{BaTiO}_3$ , and (d)  $\text{PbTiO}_3$ .

and  $-10.6$  GPa, respectively, whereas those of  $p_t$  in the present study are  $1\text{--}2$  GPa smaller at  $-2.9$  and  $-9.3$  GPa. A small discrepancy can also be seen in  $\Delta V_t$ . In order to determine the cause of this, we performed some further calculations using the PAW method [15]. These calculations have produced the same  $p_t$  as the present study. Therefore we believe our calculated values to be reliable.

As can be seen in figure 5, lattice parameters  $c$  and  $a$  change in different ways at the transition. In other words, the tetragonality as defined by  $c/a$  changes significantly at the transition. The origin of the change in the tetragonality can be found by detailed examination of the interatomic distances between Ti and O. The atomic structure of  $\text{SrTiO}_3$  below the transition pressure ( $p = -10$  GPa) is shown in figure 6. At zero pressure, Ti forms almost perfect octahedra together with its surrounding six oxygen atoms. Below the transition pressure, one of the two Ti–O bonds along the  $c$  axis becomes greatly distorted, while the others become shorter. This can be seen clearly in figure 7, in which the interatomic distances of the three different Ti–O bonds are shown as a function of pressure. At the transition pressure, only the Ti–O2 bond distance exhibits a discrete jump. The coordination number (CN) of Ti effectively decreases from 6 to 5; the breaking of this bond can be considered to be the cause of the change in the tetragonality at the transition.

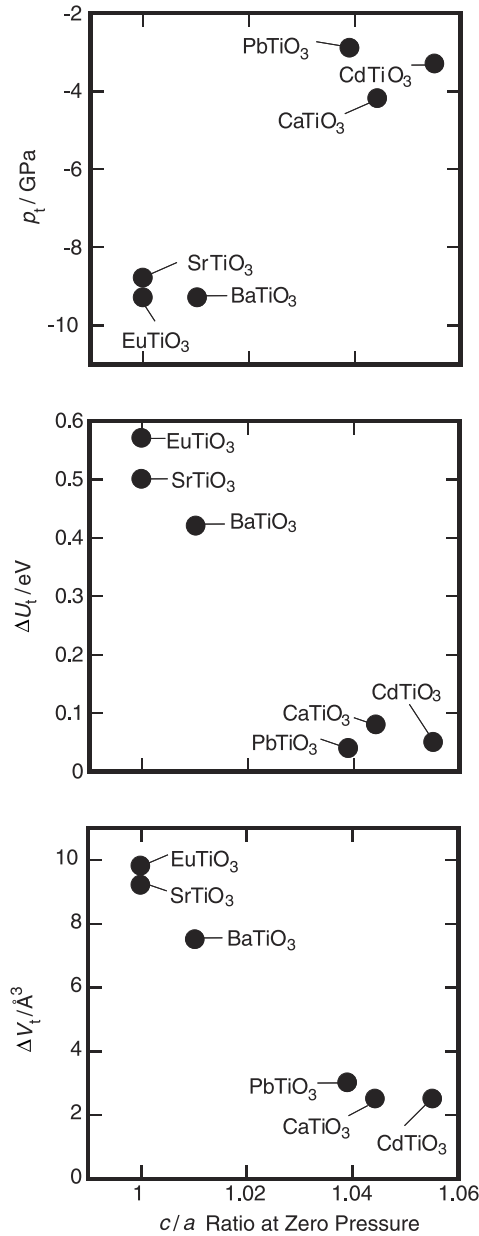


**Figure 6.** Atomic structure of  $\text{SrTiO}_3$  obtained below the transition pressure ( $p = -10$  GPa).



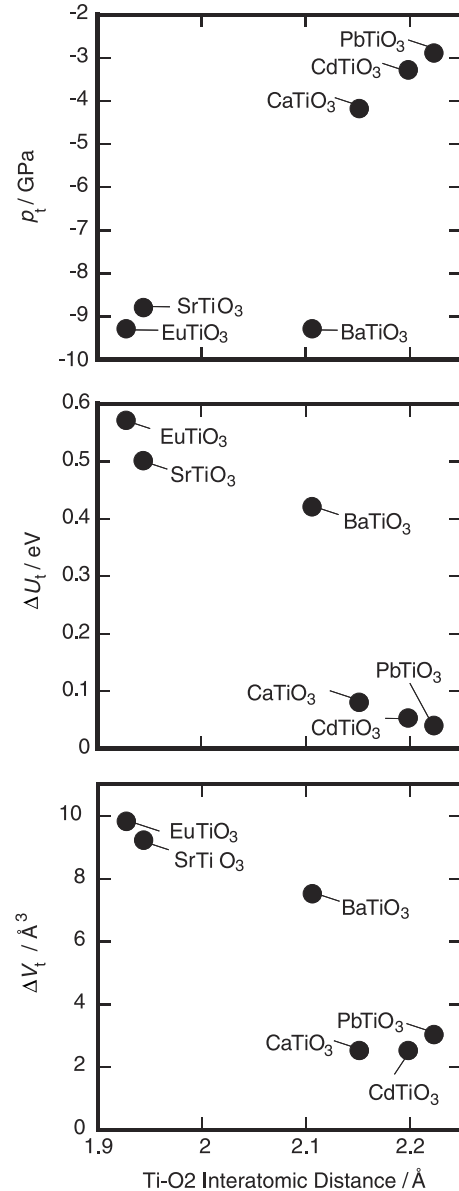
**Figure 7.** Theoretical interatomic distance between Ti and O in the  $P4mm$  structure as a function of external hydrostatic pressure for (a)  $\text{CaTiO}_3$ , (b)  $\text{SrTiO}_3$ , (c)  $\text{BaTiO}_3$ , and (d)  $\text{PbTiO}_3$ . O1 to O3 denote oxygen atoms in different environments as shown in figure 6.

The structures and phase transition of perovskite oxides are often discussed in terms of cation radii. Although ionic radius is an empirical parameter which cannot be determined uniquely, it is possible to compare the differences in cation radii calculated from theoretical lattice parameters of a cubic



**Figure 8.** Relationship between transition pressure ( $p_t$ ), change in internal energy ( $\Delta U_t$ ) and volume change ( $\Delta V_t$ ) at the transition, and  $c/a$  ratio at zero pressure.

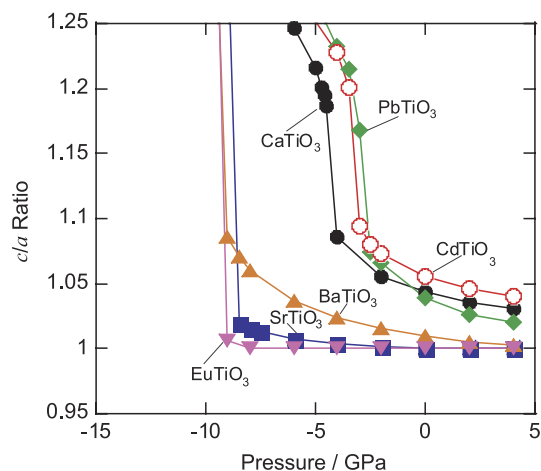
perovskite structure without ambiguity. Assuming that the ionic radius of  $O^{2-}$  is 1.26 Å [16], the ionic radii of  $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Ba^{2+}$  and  $Pb^{2+}$  can be calculated to be 1.43, 1.47, 1.53, 1.49 Å, respectively (table 1). Although these values are larger than the empirical ionic radii given in the literature [16], they may be used for qualitative comparison. According to the present calculations,  $SrTiO_3$  and  $BaTiO_3$  show much lower  $p_t$  than the other two titanates. They also exhibit much larger  $\Delta U_t$  and  $\Delta V_t$ . No simple correlation can be seen between the transition behaviour and the cation radii obtained from the cubic structures. Instead of the averaged cation radii from the idealized cubic structures, the anisotropy of the tetragonal structures needs to be taken into consideration. Figure 8 shows  $p_t$ ,  $\Delta U_t$  and  $\Delta V_t$  as a function of the theoretical  $c/a$  at zero



**Figure 9.** Relationship between transition pressure ( $p_t$ ), change in internal energy ( $\Delta U_t$ ) and volume change ( $\Delta V_t$ ) at the transition, and interatomic distance of Ti and O2 at zero pressure.

pressure. Both  $SrTiO_3$  and  $BaTiO_3$  show little tetragonality, whereas  $c/a \approx 1.04$  for  $CaTiO_3$  and  $PbTiO_3$ . The other two titanates,  $CdTiO_3$  ( $c/a = 1.055$ ) and  $EuTiO_3$  ( $c/a = 1.000$ ), are found to follow the same trend.

The tetragonal distortion of the lattice can be ascribed to the distortion of the  $TiO_6$  octahedron. As can be seen from the atomic structure in figure 6, the tetragonal distortion is due to the elongation of the Ti–O2 distance. Figure 9 shows  $p_t$ ,  $\Delta U_t$  and  $\Delta V_t$  as a function of the bond length of Ti–O2 under zero pressure. The same trends as in figure 8 can be seen. This suggests that  $p_t$ ,  $\Delta U_t$  and  $\Delta V_t$  are determined by the relative stability of the cubic perovskite structure or the regular  $TiO_6$  octahedron under zero pressure. In other words, they are influenced not only by the cation radii but also by the chemical bonding in the titanates.



**Figure 10.** Tetragonality,  $c/a$  ratio, as a function of external hydrostatic pressure for all six compounds.

Zone centre lattice instabilities of some perovskite titanates in the absence of external pressure were examined by carrying out first-principles phonon calculations.  $\text{CaTiO}_3$ ,  $\text{BaTiO}_3$  and  $\text{PbTiO}_3$  have been reported to exhibit imaginary frequencies at the  $\Gamma$  point [17, 18], whereas no imaginary modes can be found for  $\text{SrTiO}_3$  at the  $\Gamma$  point [19]. The energy difference between  $Pm\bar{3}m$  and  $P4mm$  structures according to the present calculations (table 1) is consistent with the trend in the phonon instability. For  $\text{CaTiO}_3$ ,  $\text{CdTiO}_3$  and  $\text{PbTiO}_3$  the tetragonal structure ( $P4mm$ ) is favoured by 40–118 meV/f.u., whereas for  $\text{BaTiO}_3$  the tetragonal  $P4mm$  structure is favoured by only 3 meV. On the other hand, for  $\text{SrTiO}_3$  and  $\text{EuTiO}_3$  the tetragonal  $P4mm$  structure is not favoured and they retain the cubic  $Pm\bar{3}m$  structure at zero pressure. Under negative hydrostatic pressures, these materials remain cubic in structure down to the proximity of the transition pressure, as shown in figure 10. In contrast, the tetragonality increases as pressure decreases for the other four titanates even below the transition pressure. It is natural that the stability of the cubic  $Pm\bar{3}m$  structure against the negative hydrostatic pressure is determined by the energy difference between  $Pm\bar{3}m$  and  $P4mm$  structures under zero pressure.

In summary, changes in structures and energies associated with the isostructural phase transitions of six perovskite

titanates ( $\text{ATiO}_3$ , where  $A = \text{Ca, Sr, Cd, Ba, Eu}$  or  $\text{Pb}$ ) under negative hydrostatic pressure have been revealed in detail using the plane-wave pseudopotentials method. The transition pressure and volume change at the transition cannot be correlated with the  $A$  cation radii. Instead, they are dependent on the tetragonality of the original crystal, which is determined by the relative stability of the cubic structure under zero pressure.

## Acknowledgments

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