

## Pressure induced phase transitions in $\text{PbTiO}_3$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2009 J. Phys.: Condens. Matter 21 064225

(<http://iopscience.iop.org/0953-8984/21/6/064225>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 17:47

Please note that [terms and conditions apply](#).

# Pressure induced phase transitions in $\text{PbTiO}_3$

P Ganesh and R E Cohen

Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road, Washington, DC 20015, USA

Received 30 June 2008, in final form 17 October 2008

Published 20 January 2009

Online at [stacks.iop.org/JPhysCM/21/064225](http://stacks.iop.org/JPhysCM/21/064225)

## Abstract

Recent theoretical simulations using density functional theory (DFT) and novel low temperature high energy x-ray diffraction experiments clearly show the existence of a high pressure morphotropic phase boundary (MPB) in pure  $\text{PbTiO}_3$ . The experiments show a richer phase diagram than the simulations, with multiple monoclinic phases ( $Pm$  and  $Cm$ ) in the MPB region. In this paper we examine the MPB region in more detail using high precision DFT calculations within the local-density approximation (LDA) and the Wu–Cohen generalized gradient approximation. Our results support the polarization rotation theory and open up fresh possibilities for applying chemical pressure to engineer novel electromechanical materials. We also explain why the zone-boundary mode is more likely to be stable only at higher pressures above  $\sim 25$  GPa and not at moderate pressures of  $\sim 10$  GPa, using the LDA.

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

## 1. Introduction

Piezoelectric single crystals such as PMN-PT ( $\text{PbMg}_{2/3}\text{Nb}_{1/3}\text{O}_3\text{-PbTiO}_3$ ) [1] with huge electromechanical coupling have great potential as a new generation of transducer materials. They are complex solid solutions that do not melt congruently, so that crystal boules generally have a compositional range due to fractional crystallization and therefore increases the cost of producing single phase materials. Understanding these systems fundamentally is not only an interesting problem in materials and solid state physics, but can lead to the development of new materials with improved properties. Optimally, we would like to have pure compounds that melt congruently, or piezoelectric materials that work well as thin films. The newer families of piezoelectric single crystals have strains and electromechanical coupling up to ten times that of the most commonly used piezoelectric ceramic PZT ( $\text{PbZrO}_3\text{-PbTiO}_3$ ). Although PZT is very inexpensive and very well characterized, there are many critical applications such as medical ultrasound where the improved properties of PMN-PT allow much higher resolution imaging and acoustic surgery, etc.

The best piezoelectric materials are ferroelectric solid solutions, characterized by a morphotropic phase boundary (MPB) separating tetragonal (T) and rhombohedral (R) regions. In PZT the electromechanical properties peak at the MPB, but in single crystals a wide range of compositions

on the rhombohedral side of the boundary have strong coupling. The boundary region is actually not a single phase transition, but contains one or more monoclinic (M) and possibly orthorhombic (O) phases, varying among different materials [2–5].

Perovskites have a high symmetry simple cubic high temperature parent structure, so that Slater considered the perovskite ferroelectrics to be materials that could be well understood even in 1950 [6]. However, the very simplicity and flexibility of the perovskite structure leads to a wide range of sensitive properties that have been intensely studied for five decades. At a fundamental level, the ferroelectric perovskites are known to have competing interactions. Long-range Ewald forces drive off-centering of the atoms from their high symmetry, centrosymmetric sites in cubic perovskite, whereas short-range forces stabilize the high symmetry structure. Hybridization between O 2p- and B-cation d-states such as Ti 3d, and the lone-pair interactions and hybridization between Pb and O, soften the repulsions and allow off-centering and ferroelectric behavior. It is the delicate balance between long-range and short-range forces that leads to the extreme sensitivity of these materials [7, 8]. The high electromechanical coupling in single crystal piezoelectrics and the presence of monoclinic phases in the MPB regions has been explained as being due to polarization rotation, where the polarization is rotated away from the [111] direction from an obliquely applied electric field, or in the phase transition

region [2, 7]. There are also competing zone-boundary instabilities, which are particularly important in  $\text{PbTiO}_3$  [9].

First-principles calculations [10] and cryogenic high pressure *in situ* Raman and synchrotron powder x-ray diffraction experiments [11] show formation of an MPB in pure  $\text{PbTiO}_3$  (PT) with pressure, with electromechanical coupling greater than any known material. This suggests that all of the high-coupling materials, including PZT, can be considered to be engineered PT with a transition under ambient conditions. Presence of the MPB region allows for polarization rotation from the tetragonal to the rhombohedral phase resulting in huge electromechanical coupling [2–5]. Complex solid solutions with  $\text{PbTiO}_3$  as one of the end members only tune the MPB region to ambient pressures by applying chemical pressure, and do not have an intrinsic role in the high coupling.

Phenomenological models based on Landau type expansion of the free energy [12, 13] in terms of the ferroelectric order parameter (i.e. polarization) up to 12th order predict a second-order transition from the tetragonal to one of two monoclinic phases ( $Cm$  (or  $M_A$ ) with  $\mathbf{P}$  along  $[xxz]$  and  $Pm$  (or  $M_C$ ) with  $\mathbf{P}$  along  $[x0z]$  along the pseudocubic axis), allowing a continuous rotation of the polarization from the ‘T’ phase along [1] to the ‘M’ phase. The  $Cm$  phase is further shown to be separated from the rhombohedral phase by a line of first-order phase transition, across which there is a discontinuous jump in the polarization from the (110) plane to the rhombohedral [111] direction. Under applied field along [001] the polarization can rotate continuously, followed by weak first-order phase transitions to monoclinic and ultimately tetragonal phases [14].

One can drive a phase transition either by changing composition or applying external pressure or electric field. This alters the energy surface allowing easy rotation of polarization. Depending on how the anisotropy of the energy surface changes with external field, one can either continuously rotate polarization from T to R via an intermediate low symmetry monoclinic phase leading to a MPB region or go discontinuously across the T–R or the T–O phase transition line [12, 13].

Polarization rotation has been shown to cause large electromechanical coupling in the vicinity of an MPB region in  $\text{PbTiO}_3$  [10] under pressure and in PZT with composition [15, 16]. Especially in the vicinity of the T–M boundary one observes a large  $d_{15}$  and in the R side a large  $d_{33}$  is observed. (Note that we use the cubic coordinate system throughout, so that ‘3’ is along the cubic  $z$ -axis, and not necessarily along either the polarization or field directions.) Polarization rotation has been experimentally observed in 52/48 PZT [17, 18] and thin film  $\text{PbTiO}_3$  under stress [19].

Here we investigate in more detail the pressure induced phase transitions in  $\text{PbTiO}_3$  using first-principles computations. We restrict our calculations to the following symmetries:  $P4mm$ ,  $Cm$ , and  $Pm$ ,  $R3m$ ,  $R3c$  and  $R\bar{3}c$ . The polar phases arise from the freezing in of the zone-center phonon in cubic  $\text{PbTiO}_3$  [9]. In addition to the polar distortions, cubic  $\text{PbTiO}_3$  is also unstable to zone-boundary distortions due to oxygen octahedral rotations ( $R_{25}$  mode). Pure oxygen rotations give rise to the  $R\bar{3}c$  phase, while

additions of polar distortions give rise to  $R3c$ . The unit cell is doubled for the zone-boundary phases.

## 2. Theoretical methods

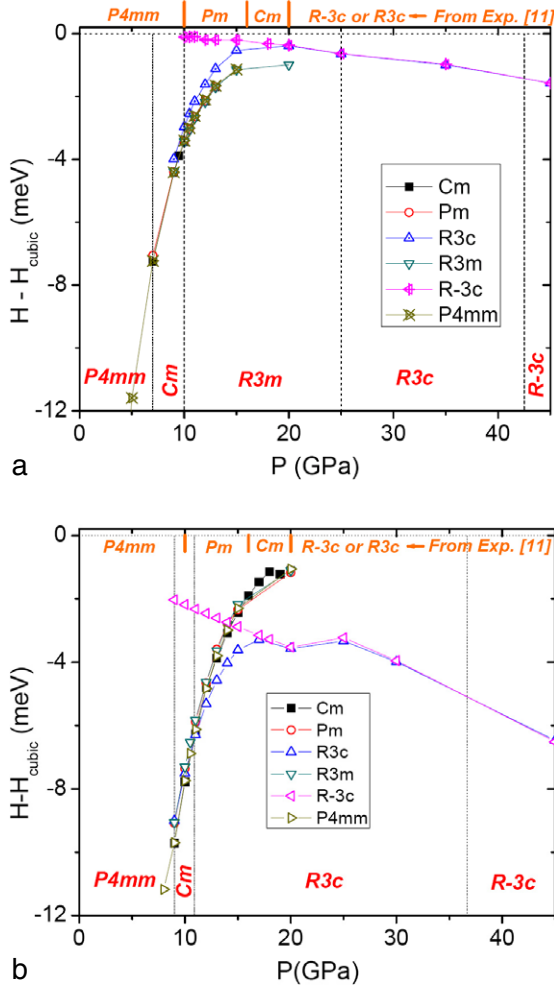
We used the pseudopotential plane-wave method within density functional theory (DFT) as implemented in the ABINIT package [20]. For the local exchange–correlation functional we use both the local-density approximation (LDA) and the Wu–Cohen GGA (WC-GGA), which gives better predictions of volume and strain for  $\text{PbTiO}_3$  [21] and many other solids [22]. We used an effective plane-wave energy cutoff of 78 Ha for structural optimization. A  $6 \times 6 \times 6$   $\mathbf{k}$ -point grid was used for all the phases. Forces were converged up to  $10^{-8}$  Hartrees/(bohr)<sup>3</sup>. For computations of polarization using the Berry’s phase method, higher mesh sizes were used. Norm conserving pseudo-potentials were generated using the OPIUM package [23] and they were tested rigorously against full-potential LAPW calculations [24]. We included semi-core states of Pb  $5d^{10}$ , Ti  $3s^23p^64d^2$  and O  $2s^2$  in the valence state. All of our calculations are for a static lattice (temperature is 0 K).

## 3. Results

We show the enthalpy differences with respect to the cubic phase ( $Pm\bar{3}m$ ) as functions of pressure in figure 1. Results using LDA are shown in figure 1(a). At low pressures, the stable phase is tetragonal, as it is well known. As pressure increases, around  $P \sim 7$  GPa, we find a transition to the monoclinic phase. The nature of the monoclinic phase appears to be  $Cm$  with polarization along  $[xxz]$ , but the  $Pm$  phase with polarization along  $[x0z]$  lies very close in energy to the  $Cm$  phase, only  $\sim 0.01$  meV above  $Cm$  at pressures around 9 GPa. It is quite possible for  $Pm$  to be stabilized by zero-point energy to be consistent with the experimental observation of a  $Pm$  phase before  $Cm$  [11].

The zone-boundary polar mode,  $R3c$ , is  $\sim 0.4$  meV above the  $Cm$  phase at 9 GPa in the MPB region, while the  $R\bar{3}c$  phase is close in energy to the cubic phase (also see figure 2). This clearly shows the existence of an MPB region, and also explains why multiple monoclinic phases could be observed experimentally. We find that the  $Cm$  is closely followed by the  $R3m$  phase at  $P \sim 10$  GPa. At 25 GPa and beyond, the zone-boundary modes become stable. The energy differences between the two zone-boundary structures are very small,  $\sim 0.01$  meV at 25 GPa and above. There is an  $R3m$ – $R3c$  phase transition around 20–25 GPa, and an  $R3c$  to  $R\bar{3}c$  phase transition between 35 and 45 GPa.

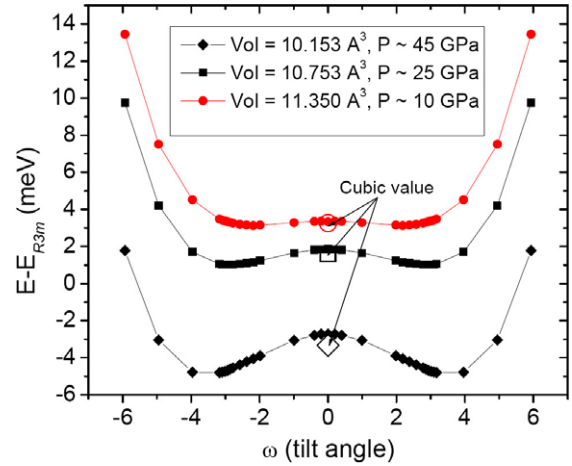
First-principles calculations using WC-GGA (figure 1(b)) also show a  $Cm$  phase between the T and R phases. The  $P4mm$ – $Cm$  transition occurs around  $\sim 9$  GPa, and the energy differences are again very small. The R phase appears to be  $R3c$  instead of  $R3m$  as observed in LDA calculations. This is in fact in better agreement to experimental observation [11] than the  $R3m$  phase predicted using LDA, since the Raman scattering indicates presence of a zone-boundary instability after the monoclinic phases. The phase transition pressures



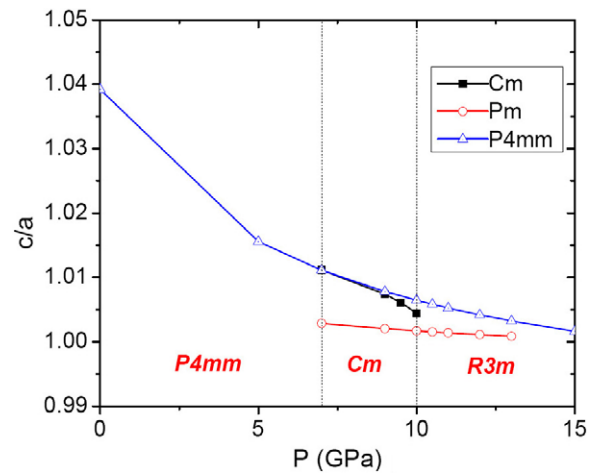
**Figure 1.** (a) Enthalpy differences per formula unit with respect to the cubic phase versus pressure using LDA. One can clearly see that the zone-boundary modes are only stable at pressures of  $\sim 25$  GPa and above. At moderate pressures of  $\sim 7$ – $10$  GPa one observes a monoclinic phase. (b) Preliminary calculations using WC-GGA clearly shows existence of an MPB region between 9–10.4 GPa. The rhombohedral phase following the  $Cm$  phase is  $R3c$ , with both polar and zone-boundary distortion. This is in better agreement with experimental results which did not seem to observe any  $R3m$  phase. Experiments cannot distinguish between the  $R3c$  and  $R\bar{3}c$  phase. We expect to see a  $R3c$  to  $R\bar{3}c$  transition between 30 and 37 GPa. This result clearly establishes the existence of an MPB region in  $PbTiO_3$ .

are  $P4mm$ – $Cm$  around 9 GPa,  $Cm$ – $R3c$  around 10.9 GPa and a  $R3c$  to  $R\bar{3}c$  transition around 30–37 GPa. Again the  $Pm$  phase is very close in energy to the  $Cm$  phase, consistent with multiple monoclinic phases observed experimentally [11].

Figure 2 shows the  $E$  versus  $\omega$  for the  $R\bar{3}c$  phase at three different volumes, where  $\omega$  is the octahedral tilt angle [25]. The energies have been plotted with respect to the ground state energies at the respective volumes, obtained from the equation of state. The ground state structure has the zone-center  $R3m$  phase at two of the volumes, and zone-boundary  $R\bar{3}c$  phase at  $V = 10.153 \text{ \AA}^3$ . The rhombohedral angle was kept fixed to that of relaxed  $R\bar{3}c$  structure at the corresponding volumes ( $60.04^\circ$  at  $V = 11.35 \text{ \AA}^3$ ,  $60.09^\circ$  at  $V = 10.753 \text{ \AA}^3$  and  $60.17^\circ$  at  $V = 10.153 \text{ \AA}^3$ ). Even though the  $R\bar{3}c$  phase



**Figure 2.** Energy of the  $R\bar{3}c$  phase per five atom formula unit versus octahedral tilt angle [28]. Even though the  $R_{25}$  mode is unstable in cubic perovskite, the well depth is larger only at pressures above 25 GPa and very shallow, almost close to the cubic value (shown in open symbols) around 10 GPa (also see figure 1 at 10 GPa). This explains why it is more likely to stabilize zone-boundary distortions at higher pressures above 25 GPa than at moderate pressures  $\sim 10$  GPa. In fact this is what is observed experimentally.



**Figure 3.**  $c/a$  ratio for the tetragonal and the monoclinic phases selected pressures using LDA. The  $Pm$  phase has a relatively lower strain, and the polarization lies very close to the orthorhombic  $[x0x]$  direction.

( $R_{25}$  zone-boundary mode) is energetically favorable relative to the cubic phase in cubic  $PbTiO_3$  [18], the energy surface is very shallow at a volume of  $11.35 \text{ \AA}^3$  (pressures  $\sim 10$  GPa), and it is less stable than the zone-center instabilities. Density functional perturbation theory (DFPT) phonon calculations also show that the  $R_{25}$  zone-boundary mode is unstable relative to cubic at zero pressure, but the ferroelectric instability is more unstable [18]. Only at pressures above 25 GPa ( $V = 10.753 \text{ \AA}^3$ ) the well is deep enough to stabilize the zone-boundary mode. The tilt angle at a volume  $V = 10.753 \text{ \AA}^3$  is about  $\sim 3^\circ$ , while it is less than  $2^\circ$  at  $V = 11.350 \text{ \AA}^3$ .

Figure 3 shows the  $c/a$  ratio of the  $P4mm$  and the two monoclinic phases,  $Cm$  and  $Pm$ , at selected pressures.

While the ratio for  $Cm$  phase at 7 GPa is very close to that of  $P4mm$ , with larger pressure it deviates to values below that of  $P4mm$ . The  $Pm$  phase where the polarization is along  $[x0z]$  at 9 GPa has  $\mathbf{P} = (0.24904, 0, 0.24905) C/m^2$ . This is close to an  $Amm2$  phase (polarization along  $[x0x]$ ). So a separate calculation of a structure with perfect  $Amm2$  symmetry at this pressure was performed and it showed that  $Amm2$  is *not* energetically preferred and lies even above the  $Pm$  phase in the MPB region. Such proximity of the polarization in  $Pm$  symmetry along that of  $Amm2$  phase is not surprising, since the 12th-order Landau–Ginsberg–Devonshire (LGD) theory [12] does predict a phase boundary between the  $Pm$  and the  $Amm2$  phase about which one can continuously rotate the polarization in the monoclinic  $[x0z]$  plane.

#### 4. Discussion

We find that both the LDA and WC functionals give an MPB under pressure. The WC functionals give better agreement with the experiments as expected. The energy differences are very small near the phase transition regions (sometimes about  $2 \mu\text{V}/\text{atom}$ ), and effects of zero-point motion may affect details of the phase diagram. Differences in transition pressures from previous LDA calculations [10] could be because of our higher plane-wave energy cutoff as compared to the one used in the paper. This does not affect the main conclusion that there is a pressure induced MPB region in  $\text{PbTiO}_3$ , confirming previous first-principles calculations and experiments [11].

We have also shown that the energy surface with respect to octahedral tilt is very flat and close to that of cubic at moderate pressures of  $\sim 10$  GPa, and only at pressures above  $\sim 25$  GPa do we find a stable zone-boundary phase. Our results contradict those of Frantti *et al* [26], who computed a tetragonal  $P4mm$  to a zone-boundary  $R3c$  phase transition at 9 GPa. They suggest that it is the phase coexistence between the  $P4mm$  and the  $R3c$  phase that gives rise to the large piezoelectric response in  $\text{PbTiO}_3$ , and not the polarization rotation through an intermediary low symmetry phase. Our results clearly show that the oxygen octahedral tilt has energies close to cubic near the MPB region, and only at pressures above 25 GPa do zone-boundary instabilities become stable. In fact we do not find any unstable zone-boundary modes in our  $Cm$  phase in the MPB region using LDA. We have also clearly shown the generality of the existence of MPB using different exchange–correlation functionals. We believe that the results by Frantti *et al* are incorrect due to some technical error.

Our results also show strong evidence against the nanotwin theory for the monoclinic phases at MPBs, which asserts that the observed monoclinic phases [3] are actually nanotwinned tetragonal and rhombohedral nanodomains [27–29]. Our first-principles calculations clearly establish a  $T \rightarrow M \rightarrow R$  phase transition sequence, as do recent experiments [11],

which show not one, but two monoclinic phases. Observation of microstructures need not be interpreted as evidence against monoclinic symmetry. The monoclinic phase has up to 24 possible domain orientations, compared to six for tetragonal, so nanodomains are completely consistent with monoclinic ground states.

Our present results are consistent with our previous theoretical [10] and experimental [11] work, and emphasize the small energy difference among the various phases. It is a triumph of DFT that such low energy phase transitions can be predicted reliably, although the exact pressures of these transitions is outside the accuracy of first-principles methods, at least without considering zero-point and thermal contributions.

#### Acknowledgments

We thank Z Wu, M Ahart, M Somayazulu, R Caracas and Pierre-Eymeric Janolin for useful discussions. This research was supported by the US Office of Naval Research.

#### References

- [1] Park S E and Shrout T E 1997 *J. Appl. Phys.* **82** 1804
- [2] Fu H and Cohen R E 2000 *Nature* **403** 281
- [3] Noheda B *et al* 1999 *Appl. Phys. Lett.* **74** 2059
- [4] Guo R *et al* 2000 *Phys. Rev. Lett.* **84** 5423
- [5] Noheda B *et al* 2001 *Phys. Rev. Lett.* **86** 3891
- [6] Slater J C 1950 *Phys. Rev.* **78** 748
- [7] Cohen R E 1992 *Nature* **358** 136
- [8] Singh D J *et al* 2005 *J. Physique IV* **128** 47
- [9] Ghosez Ph *et al* 1999 *Phys. Rev. B* **60** 836
- [10] Wu Z and Cohen R E 2005 *Phys. Rev. Lett.* **95** 037601
- [11] Ahart M *et al* 2008 *Nature* **451** 545
- [12] Vanderbilt D and Cohen M H 2001 *Phys. Rev. B* **63** 094108
- [13] Sergienko I A, Gufan Y M and Urazhdin S 2002 *Phys. Rev. B* **65** 144104
- [14] Budimir M, Damjanovic D and Setter N 2006 *Phys. Rev. B* **73** 174106
- [15] Bellaiche L, Garcia A and Vanderbilt D 200 *Phys. Rev. Lett.* **84** 5427
- [16] Wu Z and Krakauer H 2003 *Phys. Rev. B* **68** 014112
- [17] Rouquette J *et al* 2004 *Phys. Rev. B* **70** 014108
- [18] Rouquette J *et al* 2005 *Phys. Rev. B* **71** 024112
- [19] Catalan G *et al* 2006 *Phys. Rev. Lett.* **96** 127602
- [20] Gonze X *et al* 2002 *Comput. Mater. Sci.* **25** 478
- [21] Wu Z and Cohen R E 2006 *Phys. Rev. Lett.* **73** 235116
- [22] Tran F *et al* 2007 *Phys. Rev. B* **75** 115131
- [23] Rappe A M *et al* 1990 *Phys. Rev. B* **41** 1227
- [24] Singh D J 1994 *Planewaves, Pseudopotentials, and the LAPW Method* (Boston, MA: Kluwer–Academic)
- [25] Megaw H and Darlington C N W 1975 *Acta Crystallogr. A* **31** 161
- [26] Frantti J *et al* 2007 *J. Phys. Chem. Lett.* **B 111** 4287
- [27] Jin Y M *et al* 2000 *Phys. Rev. Lett.* **91** 197601
- [28] Schonau K *et al* 2007 *Phys. Rev. B* **75** 184117
- [29] Rao W F *et al* 2007 *Appl. Phys. Lett.* **91** 052901