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2008 J. Phys.: Condens. Matter 20 472203

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## FAST TRACK COMMUNICATION

# Evidence against the polarization rotation model of piezoelectric perovskites at the morphotropic phase boundary

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Received 15 October 2008, in final form 20 October 2008

Published 6 November 2008

Online at [stacks.iop.org/JPhysCM/20/472203](http://stacks.iop.org/JPhysCM/20/472203)**Abstract**

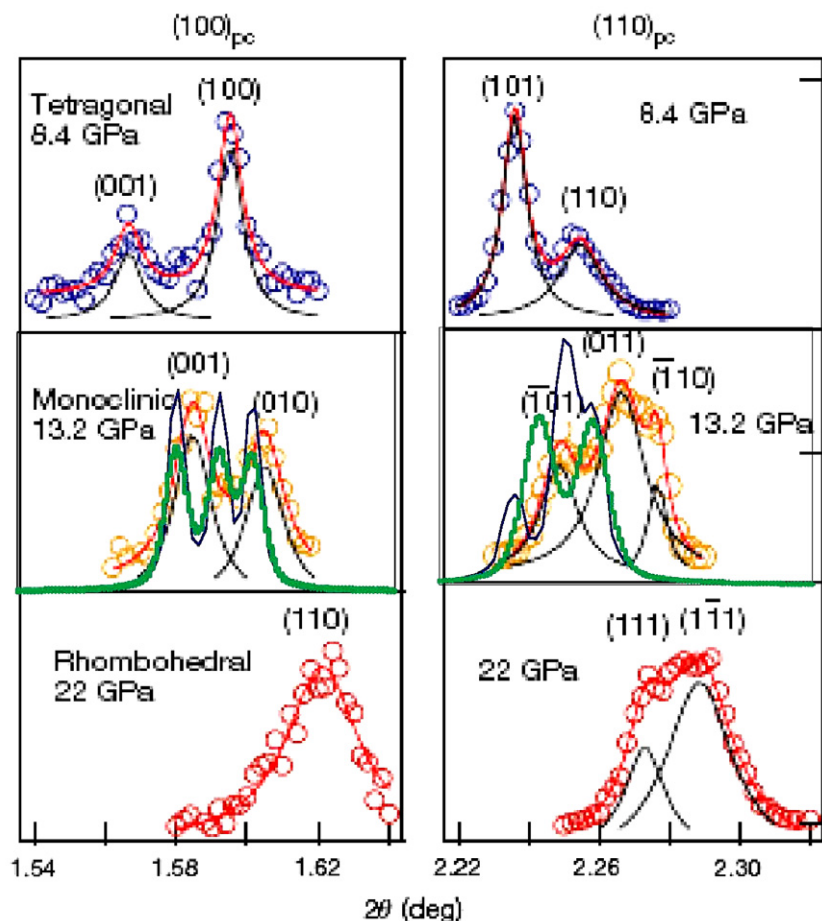
The origin of the very large piezoelectric response observed in the vicinity of the morphotropic phase boundary in perovskite lead zirconate titanate and related systems has been under intensive study. Polarization rotation ideas are frequently invoked to explain the piezoelectric properties. It was recently reported that lead titanate undergoes a phase transformation sequence  $P4mm \rightarrow Pm \rightarrow Cm \rightarrow R\bar{3}c$  at 10 K as a function of hydrostatic pressure (Ahart *et al* 2008 *Nature* **451** 545). We demonstrate that this interpretation is not correct (i) by simulating the reported diffraction patterns, and (ii) by means of density-functional theory computations which show that the  $Pm$ ,  $Cm$  and  $Pmm2$  phases are all unstable in the pressure range studied, and further show that octahedral tilting is the key stabilization mechanism under high pressure. Notes on more general grounds are given to demonstrate that a continuous phase transition between rhombohedral and tetragonal phases via an intermediate monoclinic phase is not possible. Thus, two-phase coexistence in the vicinity of the phase transition region is probable and has an important role as regards electromechanical properties.

**1. Introduction**

The polarization rotation (PR) model [1, 2] has been proposed for explaining the large electromechanical coupling coefficients observed in ferroelectric perovskites in the vicinity of the morphotropic phase boundary (MPB). The MPB region separates tetragonal and rhombohedral phases; these do not have a group-subgroup relationship and thus no continuous transition between the phases is possible. The most intensively studied systems are solid solutions, prime examples being lead zirconate titanate,  $Pb(Zr_xTi_{1-x})O_3$  (PZT), and  $xPb(Mg_{1/3}Nb_{2/3})O_3-(1-x)PbTiO_3$  (PMN-PT). The essential feature of the PR model is the insertion of one (or more) low-symmetry phase(s) to continuously (via group-subgroup chains) connect the tetragonal and rhombohedral phases separated by the MPB in order to continuously rotate the polarization vector by means of an electric field or pressure between the pseudo-cubic [001] and [111] directions along

the  $(1\bar{1}0)$  plane. This rotation path was predicted to be accompanied by a large electromechanical response [3]. There are, however, several ambiguities related to the PR model (see, e.g., [4]) and experimental studies interpreted in terms of this idea. As an example, the pressure induced phase transitions of lead titanate ( $PbTiO_3$ , PT) are considered below. Hydrostatic pressure induces similar structural changes, which are observed to occur due to the substitution of Ti by a larger cation, such as Zr, causing so-called 'chemical pressure'.

At high temperatures PT undergoes a phase transition between the  $P4mm$  and  $Pm\bar{3}m$  phases [5]. At room temperature PT transforms to a cubic phase through a second-order transition at 12.1 GPa [6], whereas it was predicted through density-functional theory (DFT) computations that a phase transition between  $P4mm$  and  $R\bar{3}c$  phases occurs at 9 GPa at 0 K [7]. Notably the latter phase transition is similar to the phase transition observed in PZT as a function of Zr composition. In simplest terms, one expects to have three



**Figure 1.** X-ray diffraction data collected for PT at 10 K. The figure is adapted from [8]. The green and blue lines (middle panels) were added by us. The green line shows the simulated  $Pm$  pattern using the lattice parameters given in [8]. The model where the  $a$  and  $b$  axes are switched (blue line) does not improve the fit<sup>1</sup>. Neither of the one-phase  $Pm$  structure models fits the peak (black lines) positions and intensities (e.g., the reflection labeled as  $(\bar{1}10)$  is not modeled, and cannot be explained by preferred orientation).

(This figure is in colour only in the electronic version)

different phase boundaries in the pressure–temperature plane of PT, separating the  $P4mm$  and  $Pm\bar{3}m$ ,  $P4mm$  and  $R\bar{3}c$  and  $R\bar{3}c$  and  $Pm\bar{3}m$  phases. A very different interpretation was recently given in [8], according to which the phase transition from the  $P4mm$  to  $R\bar{3}c$  phase would occur via monoclinic phases, which was further claimed to give support to the PR model. We (i) demonstrate that the single-phase model is incorrect in the vicinity of the phase transition, (ii) demonstrate that the monoclinic distortions reported earlier are not stable, (iii) summarize the arguments which show that the phase transition must be of first order and (iv) outline the method for determining the piezoelectric properties in the vicinity of the phase boundary.

## 2. Computational methods

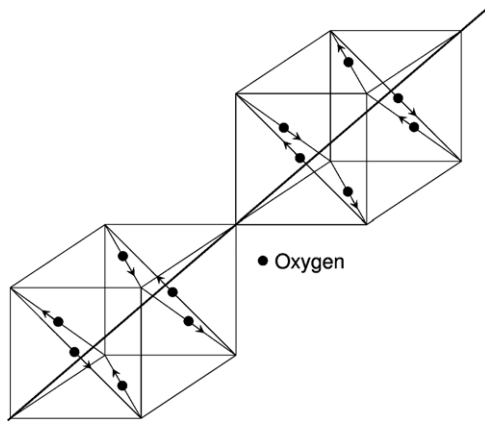
The DFT code ABINIT [9, 10] was used to compute the total energies and phonon frequencies and eigenvectors [11] at different pressures. The computations were carried out within

<sup>1</sup> According to the authors of [8], ‘ $a$  and  $b$  were inadvertently switched for  $Pm$ ’. Information obtained through Nature Editorial Office.

the local-density approximation and using a plane wave basis. Norm-conserving pseudopotentials were generated using the OPIUM package [12]. A more detailed description of the computational approach is available in [7]. For the simulation of the x-ray diffraction patterns the Powder Cell program was used [13]. The lattice parameters were adapted from [8]. The asymmetric unit was not given in [8], and thus the atomic positions were estimated using the values found from the DFT computations, which are close to the values estimated from our high-pressure neutron powder diffraction experiments at few GPa pressures [14].

## 3. Notes on the x-ray diffraction and Raman scattering analysis

According to [8], PT undergoes a phase transformation sequence  $P4mm \rightarrow Pm \rightarrow Cm \rightarrow R\bar{3}c$  at 10 K as a function of hydrostatic pressure. We show that the x-ray diffraction (XRD) pattern collected at 13.2 GPa [8] is not consistent with the reported  $Pm$  symmetry, by simulating the corresponding pattern. Figure 1 shows that the reflection positions and intensities significantly deviate from the experimental ones and



**Figure 2.** The unstable normal mode of the  $R3m$  phase at the L  $(\frac{\pi}{a} \frac{\pi}{a} \frac{\pi}{a})$  point involves only oxygen ions. Two rhombohedral unit cells are shown: it is seen that the two octahedra are tilted about the threefold axes clockwise and anticlockwise. The condensation of this mode corresponds to the phase transition  $R3m \rightarrow R3c$ . All the modes had positive frequencies when the  $R3c$  phase was used. The bold line is the threefold rotation axis.

also from the fits (shown by black continuous lines). It is worth noting that in the case of PT the pseudo-cubic 110 reflections have the strongest XRD intensities. The 13.2 GPa XRD pattern shown in figure 1 more likely corresponds to a two-phase diffraction pattern. This is seen by studying the intensities of the 100 and 001 reflections: for tetragonal and pseudo-tetragonal structures the intensity ratio should roughly be 2:1 (as is seen from the diffraction pattern collected at 8.4 GPa, figure 1), whereas it is roughly 0.9:1 for the 13.2 GPa data.

It was stated that the Raman scattering data reflect the monoclinic  $M_C$  ( $Pm$  phase) to monoclinic  $M_A$  ( $Cm$ ) and the monoclinic  $M_A$  to rhombohedral phase transitions [8]. We find this assignment questionable, since the phonon symmetries, central for the phase transition studies, were not addressed. For example, the  $B_1$  symmetry normal mode in the  $P4mm$  phase breaks the fourfold symmetry [15], whereas the  $A_1$  symmetry modes preserve it. The spectral features below  $100 \text{ cm}^{-1}$  include several peaks from the  $A_1$  symmetry modes alone, due to the strong anharmonicity of the  $A_1$  (1TO) mode [16, 17], in addition to the E symmetry modes and Rayleigh scattering (which dominates the region close to the laser line, as was noted in [6]). It was rather recently that the  $A_1$  (1TO) mode was identified in PT [16, 17]: many earlier assignments dismissed this mode since the line shape was very asymmetric and turned out to be consisted of many subpeaks. In practice this means that, in the vicinity of the phase transition, it is hard to identify the number of modes in the low-frequency region—not to mention the difficulty of identifying their symmetries from the spectra collected without proper polarization measurements. This, in turn, prevents space group assignments.

#### 4. DFT studies

DFT computations predict that PT undergoes a phase transition from the  $P4mm$  phase to the  $R3c$  phase at around 9 GPa [7]. In contrast, a phase transition sequence  $P4mm \rightarrow Cm \rightarrow$

$R3m \rightarrow Pm\bar{3}m$  (phase transitions at 10, 12 and 22 GPa, respectively) was found in [18]. The high-pressure end of this transition was more recently modified to form the sequence  $R3m \rightarrow R3c \rightarrow R\bar{3}c \rightarrow R3c$  with phase transitions occurring at 18, 20 and 60 GPa, respectively [8]. We carried out similar computations for the  $Pm$  and  $Pmm2$  phases, in addition to the phases listed in [7]. For consistency, phonon frequencies of the  $R3c$  phase were computed at 9, 10 and 15 GPa pressures at the Brillouin zone center and boundary points.

The main outcomes of our present and earlier computations are: (i) the  $R3m$  phase is not stable (octahedral tilting makes the  $R3c$  phase favorable above 9 GPa), (ii) above 9 GPa tetragonal ( $P4mm$  and  $I4cm$ ), orthorhombic ( $Cmm2$  and  $Pmm2$ ) and monoclinic ( $Pm$  and  $Cm$ ) phases were revealed to be unstable by the Brillouin zone boundary modes and higher enthalpy values, (iii) no support for an intermediate phase was found, and (iv) no phonon instabilities were observed in the  $R3c$  phase. In contrast, one of the Brillouin zone corner point L  $(\frac{\pi}{a} \frac{\pi}{a} \frac{\pi}{a})$  modes of the  $R3m$  phase was unstable at 9 GPa pressure. The mode involved only oxygen displacements (this was the only mode which was found to be unstable: all modes at the  $(000)$ ,  $(00\frac{\pi}{a})$  and  $(\frac{\pi}{a} \frac{\pi}{a} 0)$  symmetry points were positive). The mode is depicted in figure 2. This corresponds to the mode where the upper and lower octahedra are tilted clockwise and anticlockwise about the threefold symmetry axis, thus again demonstrating that the octahedral tilting stabilizes the  $R3c$  phase. This is due to the fact that octahedral tilting allows a more efficient compression [7, 19, 20].

We note that since the  $R3m$  phase is not stable, it is somewhat hypothetical to consider the instability of an unstable phase. A more rigorous treatment, starting from the  $P4mm$  phase, is given in [7], with the same outcome. Thus, the energetically favorable phase was obtained by allowing the crystal to relax according to the normal mode displacements of the unstable modes seen in the  $P4mm$  phase. Thus the transition between  $P4mm$  and  $R3c$  phases is characterized by two-phase coexistence, in an analogous way to the phase transitions seen in PZT as a function of composition. This is an important prediction as it in turn suggests that the two-phase coexistence has a crucial role for the piezoelectric properties near the phase transition pressures in PT, in a similar way to what was demonstrated in [21] for PZT in the vicinity of the MPB.

#### 5. Symmetry considerations

Group-theoretical analysis indicates that, although the phase transition between monoclinic and tetragonal phases can be continuous, the transition between rhombohedral and monoclinic phases must be of first order [22]. Thus, even if one were to have a monoclinic phase, it would not make the transformation path continuous. First-order transitions are often characterized by the two-phase coexistence, one phase being metastable over a finite temperature or pressure range. This is consistent with the experimentally known features of PZT according to which there is two-phase coexistence [20, 23, 24]. Neutron and x-ray powder diffraction

studies revealed that the polarization vector in the monoclinic  $Cm$  phase is very close to the pseudo-cubic [001] direction, and hardly rotates from that direction [20, 24], in contrast to what one anticipates from the PR model. Thus the polarization vector changes discontinuously when the transition from the pseudo-tetragonal monoclinic to the rhombohedral phase occurs. As Li *et al* noted, ‘the availability of multiple phases at the MPB makes it possible for the polarization to thread through the ceramic’ [21].

## 6. How do we model the piezoelectric response?

The piezoelectric response can be divided into extrinsic and intrinsic contributions. The latter is due to the changes in electron densities as a response to an applied field or stress and can be computed through standard density-functional theory methods. The extrinsic part is significantly more challenging, as it involves domain wall motions and changes in the phase fractions in the vicinity of the phase boundary (e.g., between tetragonal and rhombohedral phases). In the case of poled ceramics one first computes the necessary angular averages of the piezoelectric constants and takes their dependence on temperature, composition or stress into account. This dependence is notable in the vicinity of the phase transition. For an intrinsic contribution such a computation is rather straightforward. However, obtaining the description of domain wall motion due to an applied electric field or stress for different compositions or at different temperatures is a nontrivial task.

## 7. Conclusions

In conclusion, evidence against the applicability of the polarization rotation model to perovskites is strong. Instead, the currently known best piezoelectric perovskites possess a so-called morphotropic phase boundary at which a first-order phase transition between rhombohedral and tetragonal (or pseudo-tetragonal) phases takes place. For the electromechanical properties it is important to note that this transition exhibits two-phase coexistence. Structural factors responsible for the stabilization of the rhombohedral phase, either at large hydrostatic pressures or at large chemical pressures (as occurs in  $Pb(Zr_xTi_{1-x})O_3$  with increasing  $x$ ), were addressed.

## Acknowledgments

YF is grateful for the Finnish Cultural Foundation and Tekniikan Edistämissäätiö foundation for financial support.

This project was supported by the Academy of Finland (Project Nos 207071 and 207501 and the Center of Excellence Program 2006–2011). The Finnish IT Center for Science (CSC) is acknowledged for providing computing resources.

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