The Factors Behind the Morphotropic Phase Boundary in Piezoelectric Perovskites

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The best piezoelectric materials are solid solutions in the vicinity of the steep morphotropic phase boundary (MPB) separating rhombohedral and tetragonal phases in the composition–temperature plane. A classical example is the lead zirconate titanate [Pb(Zr,Ti)O3, PZT] system, with x ≈ 0.52, where the two phases are separated by a boundary extending from the lowest temperatures up to several hundred degrees. The origin of the boundary has been under keen studies for 40 years. Recent interest is largely due to the need to develop new, lead-free piezoelectrics, for which a natural starting point is to understand the properties of the present systems. Here, we demonstrate, through high-pressure (up to 8 GPa) neutron powder diffraction experiments and density functional theory computations on lead titanate (PbTiO3, PT), that it is the competition between two factors which determines the MPB. The first is the oxygen octahedral tilting, giving advantage for the rhombohedral R3c phase, and the second is the entropy, which in the vicinity of the MPB favors the tetragonal phase above 130 K. If the two factors are in balance over a large temperature range, a steep phase boundary results in the pressure–temperature plane.

Introduction

Piezoelectric applications, such as the atomic force microscope cantilever moving the tip in a precisely controlled manner on a sample surface, are often based on solid solutions in the vicinity of the phase boundary. An example is the phase boundary between the tetragonal and rhombohedral perovskite phases in the Pb(Zr,Ti1−x)O3 (PZT) system, where x ≈ 0.52. Due to the first-order phase boundary, rather small changes in the pressure or electric field results in a large response. For a stable performance, it is an advantage to have an almost vertical boundary in the composition–temperature plane; in the case of PZT, the boundary extends from the lowest temperatures up to 500 K, whereas the corresponding change in x is only about 0.03. This phase boundary is frequently termed the morphotropic phase boundary (MPB).1 In solid solutions, the MPB is characterized by two competing, coexisting phases. However, the factors responsible for the vertical line are not well understood, and there has been considerable interest toward systems possessing a MPB. Notably, the monoclinic phase observed in the PZT system has been under keen studies as it is often suggested that it explains the large electromechanical response near the MPB compositions via the polarization rotation model. However, solid solutions are somewhat difficult systems to study as the local disorder obscures the determination of the structure, not to mention the resulting difficulties in first-principles computations. Correspondingly, many high-pressure studies were dedicated to a more simple but isostructural PbTiO3 (PT).2–7 The early Raman scattering study reported a room-temperature continuous-phase transition between the ferroelectric and paraelectric phases to occur at 12.1 GPa,2 consistent with the synchrotron X-ray diffraction studies.3,4

Hydrostatic pressure mimics the “chemical pressure” due to the cation substitution (such as Zr for Ti in PZT) and also eliminates complications due to the configurational entropy. Density functional theory (DFT) computations predicted a first-order phase transition to appear between the P4mmm and R3c phases at T = 0 K at around P = 9 GPa of pressure.2 Analogously to the case of PZT, this type of transition would be characterized by two-phase coexistence. On the basis of the high-pressure X-ray synchrotron diffraction study, the symmetry of PT at 22 GPa of pressure and 10 K was assigned to be rhombohedral,5 which suggests that there would be a similar MPB in PT in the P–T plane as that found in PZT in the x–T plane. The transition between the P4mmm and rhombohedral phases was interpreted to occur via monoclinic phases; however, this assignment is questioned in ref 8. For clarity, we note that a monoclinic symmetry, commonly observed in solid solution systems, does not mean that piezoelectric properties can be understood by the polarization rotation model (see, for instance, ref 9). According to a more recent X-ray synchrotron study, the room-temperature phase transformation sequence was reported to possess only tetragonal, (pseudocubic) tetragonal, and tetragonal structures with tilted oxygen octahedra, with no MPB.6 This suggests that attention should be paid to the influence of temperature on phase stabilities. Since X-rays do not allow a reliable determination of the oxygen positions! The octahedral tilts, neutrons are necessary. Octahedral tilting occurs often in perovskites as it allows energy minimization by changing the bond lengths and angles. Most clearly, the effect is seen in the case of low-symmetry rhombohedral phases, R3c and its subgroups since the octahedral tilting resulting in changes in bond lengths and angles is accompanied by an efficient
volume compression.\textsuperscript{10} The present study was dedicated to study the phase stabilities as a function of temperature and pressure. The DFT computations correspond to the 0 K temperature, and thus, the thermal energy must be separately estimated. Our hydrostatic high-pressure neutron powder diffraction studies and the first-principles DFT computations reveal that temperature plays an important role. As we show, the Gibbs energy $G = U - TS + PV$ contains two competing terms, determining the phase boundary in the $P-T$ plane; the entropy term $TS$ favors the tetragonal structure at the phase boundary at elevated temperatures, whereas the pressure $P$ times volume $V$ term favors the oxygen octahedral tilting of the rhombohedral phase.

Figure 1. The structural parameters from the first-principles computations as a function of hydrostatic pressure at 0 K. (a) Tetragonal $a_T$ and $c_T$ and rhombohedral $a_R$ and $c_R$ lattice parameters and (b) the fractional coordinates of the titanium and oxygen ions in the $P4mm$ phase; the lead ion was fixed at the origin, titanium was at (1/2, 1/2, $z_{Ti}$), and the oxygen ions were at (1/2, 1/2, $z_{O1}$), (1/2, 0, 1/2 + $z_{O1}$) and (0, 1/2, 1/2 + $z_{O1}$).

Figure 2. (a) Phonon densities of states of the $P4mm$ and $R3c$ phases at 5 and 8 GPa pressures. (b) The phonon free-energy difference between the $R3c$ and $P4mm$ phases as a function of temperature at fixed pressures. It is seen that phonon entropy favors the $P4mm$ phase at elevated temperatures in the vicinity of the phase boundary. The lowest and second lowest curves correspond to 5 and 6 GPa pressure data.
In the case of insulators, the phonon contribution to the internal energy \( U \) and the entropy \( S \) is significant at finite temperatures.

**Methods Section**

Lead titanate powder was prepared through the solid-state reaction technique by mixing the PbO and TiO\(_2\) oxides in desired proportions. The phase purity and crystal structure were checked by X-ray powder diffraction measurements. High-pressure neutron powder diffraction experiments were carried out at the Los Alamos Neutron Scattering Center using the toroidal anvil press (TAP-98) equipment\(^{13,12}\) set on the high-pressure-preferred orientation (HIPPO) diffractometer.\(^{13,14}\) Pressure was generated using the high-pressure anvil cells. Sodium chloride was used as a pressure calibrant material. Data were collected at 300 and 600 K as a function of pressure. Rietveld refinements were carried out using the program General Structure Analysis System (GSAS).\(^{15}\) The pressure was estimated from the reflection positions of the NaCl phase through the equation of state\(^ {16} \) up to 4 GPa. At higher pressures, no signal from the NaCl crystals was observed, and the pressure was estimated through the equation of state, based on the Birch–Murnaghan equation,\(^ {17,18} \) of PbTiO\(_3\) reported in ref 3. It was necessary to include the reflections from the diamond anvils at high pressures in the refinement model. Typically, data sets from data banks 2 and 3 were used in order to get better statistics. The advantage of neutron diffraction over the X-ray diffraction is its ability to detect oxygen positions, which is a crucial factor when possible oxygen octahedral tiltings are studied.

The density functional theory code ABINIT\(^ {19,20} \) was used to compute the total energies, phonon frequencies and eigenvectors,\(^ {21} \) and the phonon entropies for tetragonal and rhombohedral phases at different hydrostatic pressures. We have earlier considered other space group symmetries and found the \( P4mm \rightarrow R3c \rightarrow R3c \) phase transformation chain to be the most favorable one at 0 K temperature, with the transition pressures at 9 and 27 GPa, correspondingly.\(^ {7,22} \) We tested the \( Cmcm, Cm, Pm, I4cm, \) and \( R3m \) symmetries and found that they had higher enthalpy values and often also phonon instabilities in the vicinity of the transition pressure.\(^ {7,8} \) Thus, the computationally expensive phonon contributions to the entropy and internal energy as a function of temperature were dedicated to the \( P4mm \) and \( R3c \) phases between 5 and 8.5 GPa of pressures. The computations were carried out within the standard local density approximation\(^ {23} \) and using a plane wave basis. Norm-conserving pseudopotentials were generated using the OPIUM package.\(^ {24} \) The estimation of the phonon contribution necessitates that a subset of \( k \) points within the Brillouin zone be selected and the corresponding eigenvalues (phonon energies) be computed. The phonon frequencies were computed by using the nonshifted \( 6 \times 6 \times 6 \) \( k \) point mesh (with the gamma point included) for the \( P4mm \) and the \( 4 \times 4 \times 4 \) for the \( R3c \) phase. For the phonon entropy and density-of-state computations, additional frequencies were estimated at intermediate \( k \) points through the Fourier interpolation scheme. Within the harmonic approximation, the temperature-dependent changes in internal energy and entropy were estimated.\(^ {25} \) We note that though the temperature dependences of the internal energy, entropy, or equilibrium volume are not solely determined by the phonons, it explains, to a first approximation, the temperature-dependent behavior of insulators. The computations must be limited to the pressures at which no phonon instabilities exist.

**Ground-State Phases**

Figure 1 shows the tetragonal and rhombohedral lattice parameters at 0 K as a function of hydrostatic pressure, as obtained from the DFT computations. In the tetragonal phase, the characteristic feature is the fast decrease of the \( c \)-axis parameter, which was also observed in experiments.\(^ {4} \) It is seen that the distortion from the centrosymmetric structure decreases with increasing pressure. Earlier computations showed that, also, the spontaneous polarization diminishes with increasing pressure.\(^ {7} \) It was reported that at room temperature, synchrotron measurements revealed weak superlattice reflections at 47 GPa\(^ {3} \) and above 43 GPa.\(^ {6} \) As noted...
above, the $I4cm$ phase was not found to correspond to the minimum enthalpy at 0 K when $P \leq 40$ GPa. These reflections were assigned to the oxygen octahedra tilting in ref 6. This pressure range is beyond the one discussed in the present study, which focuses on the lowest-pressure phase boundary. At 0 K, the $R3c$ phase was found to be energetically favorable above 9 GPa due to the more efficient compression allowed by the oxygen octahedra tilting, which can largely be understood by considering the Madelung energy term. These results were confirmed by computing the enthalpies and phonon instabilities and phonon symmetries, which were remarkably consistent.

Figure 4. Tetragonal $a$ and $c$ lattice parameters and the fractional coordinates of the titanium and oxygen ions at 600 and 300 K as a function of hydrostatic pressure. Space group $P4mm$ was used in the refinements. The lead ion was fixed at the origin, titanium was at $(1/2, 1/2, z_{\text{Ti}})$, and the oxygen ions were at $(1/2, 1/2, z_{\text{O}})$, $(1/2, 0, 1/2 + z_{\text{O}})$, and $(0, 1/2, 1/2 + z_{\text{O}})$ (here, a constraint $z_{\text{Oi}} - z_{\text{Oii}} = z_{\text{O}}$ was used). In the case of the highest-pressure structure at 600 K, all ions were relaxed to the inversion symmetry positions. Correspondingly, we switched to use the higher-symmetry space group $P4/mmm$ for which the ion positions are fixed by symmetry.
At high pressures, many parameters were refined alternatively since their effect on corrections were tested after the isotropic ADP parameters alone became physically meaningless. Anisotropic and anisotropic titanium and oxygen atomic displacements remained negative. Negative principal ADP parameters are often a sign of an incorrect structural model. In addition, the absorption due to the high-pressure chamber can affect the intensities. It is well-known that in many Pb-based perovskite oxides, the Pb ions are often significantly displaced from their ideal sites, which is assigned to the 6s² lone electron pair. This results in large ADP parameters for Pb. Also, the anomalous behavior of Ti ADP parameters is seen already at ambient pressures at low temperatures. However, other Pb-based perovskites, such as PZT, did not reveal anomalous oxygen ADP parameters. Since no signs of space group symmetry lowering were found and the use of subgroups (e.g., $4_1cm$) did not eliminate the problem, we finally decided to use the anisotropic ADP parameters with no symmetry constraints (this was done by using the P1 symmetry, by constraining the nuclei positions to correspond to the $P4_{2}mm$, and by setting no constraints to ADP parameters) and to constrain the displacements of oxygen along the c-axis to be the same. For simplicity, absorption correction was not refined. This model worked very well and gave reasonable structural parameters. Figure 3 shows a typical refinement. The lattice parameters and ionic positions as a function of pressure at 300 and 600 K are given in Figure 4. We note that they are similar to the structural parameters at 0 K (compare to Figure 1).

Though the ADP ellipsoids must be adopted with caution, we note that they were elongated along the (101) directions; see Figure 5. This again reveals that the oxygen octahedral tilting is still an important mechanism at the elevated temperatures, though it is no more able to turn the structure to rhombohedral within the pressure range studied. The $I4cm$ symmetry corresponds to the octahedral tilting in the ab plane, which in turn would suggest ADP ellipsoids elongated toward the (110) directions, in contrast to our observations. Synchrotron X-ray radiation experiments suggested that at room temperature, the $P4_{2}mm$ phase transforms to a pseudocubic phase at 12 GPa, though the detailed determination of the oxygen octahedral tilting through X-ray diffraction is often rather difficult. Our NPD data show that at high pressures, the oxygen displacements are anomalous, which offers an explanation for the reported deviations from the ideal cubic symmetry. We propose that also the aforementioned anomalous behavior of Ti ADP parameters as a function of temperature is related to this competition and explains the deviations from the ideal cubic or tetragonal. The DFT computations revealed the unstable octahedral tilting modes, which strongly supports the experimental observations.

### Conclusions

Our high-pressure neutron powder diffraction experiments and first-principles computations demonstrate that the phase boundary in the temperature—pressure plane is largely determined by the two competing factors, oxygen octahedral tilting allowing efficient compression and phonon entropy favoring the tetragonal phase. The first mechanism dominates at the lowest temperatures, whereas the entropy term dictates at elevated temperatures. Neutron powder diffraction data show that both mechanisms coexist even above room temperature at high pressures. If the two terms balance in the large temperature range at (nearly) constant pressure, a steep morphotropic phase boundary results. In the case of practical applications, on the basis of solid solutions, composition plays the role of pressure, and the configurational entropy term due to the substitutional disorder cannot be neglected.
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References and Notes

(22) Our phase transition sequence is different from the one suggested in Ganesh, P.; Cohen, R. E. J. Phys.: Condens. Matter 2009, 21, 064225, which they dismissed by a note “We believe that the results by Frantti et al. are incorrect due to some technical error”. This statement is unfounded; we checked the pseudopotentials and compiled newer version of the Abinit code, carried out computations again, and found no technical or other errors. The outcome was the same as that published in ref 7.