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High-Pressure Effect on PbTiO₃: An Investigation by Raman and X-Ray Scattering up to 63 GPaP.-E. Janolin,^{1,*} P. Bouvier,² J. Kreisel,² P. A. Thomas,³ I. A. Kornev,^{4,†} L. Bellaiche,⁴ W. Crichton,⁵
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We report a room-temperature high-pressure x-ray and Raman scattering investigation of lead titanate (PbTiO₃) up to 63 GPa. Three continuous phase transitions at 13, 20, and 45 GPa between tetragonal-like phases occur. As a result, no evidence is found for a pressure-induced morphotropic phase boundary. Our study provides experimental evidence that PbTiO₃ presents a complex sequence of phases accommodating pressure through mechanisms involving oxygen octahedra tilting and reentrance of ferroelectricity.

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In past years, there has been a renewed interest in understanding ferroelectrics with a focus on materials with an important piezoelectric response. One of the most extensively studied ferroelectrics is the perovskite PbTiO₃ (PTO), which is also an end member of technologically important piezoelectrics such as PbZr_{1-x}(TiO₃)_x (PZT) or Pb(Mg_{1/3}Nb_{2/3})_{1-x}(TiO₃)_x [1]. Ferroelectricity results from a delicate balance between long-range Coulomb forces and short-range interionic repulsions. The (in)stability of this balance has previously been extensively investigated as a function of temperature, pressure, or electric field, and new phase transitions in model ferroelectrics like PTO seemed, therefore, unlikely to be observed.

Following the pioneering work by Samara *et al.* [2], it was accepted that pressure reduces ferroelectricity in perovskites and even annihilates it for a critical pressure p_c at which the crystal structure is cubic (e.g., BaTiO₃ [3] and PTO [4]). Recent discoveries that, under high pressures, relaxor ferroelectrics do not stay or become cubic [5] and ferroelectric PZT displays a wealth of phase transitions without becoming cubic [6,7] were unexpected. Whether this absence of a cubic phase is related to the chemical complexity of these materials and if simple perovskites show similar features remained open questions.

Pursuing this query, the high-pressure behavior of a broad range of simple ABO₃ perovskites have then been studied with *ab initio* calculations [8–12]. While all authors agree that the behavior of ferroelectrics under pressure is more complex than initially anticipated, different scenarios have been proposed for PTO. Wu and Cohen [8] have predicted at 0 K a sequence of three ferroelectric phases ending by the cubic paraelectric one ($P4mm \xrightarrow{9 \text{ GPa}} Cm \xrightarrow{11 \text{ GPa}} R3m \xrightarrow{22 \text{ GPa}} Pm-3m$). This scenario was slightly modified recently [13], replacing the rhombohedral and cubic ending phases with a centrosymmetric nonferroelectric *R-3c* phase at 10 K and 20 GPa. The

morphotropic-phase-boundary-like low-symmetry monoclinic *Cm* phase was presented as having the potential to generate large electromechanical responses. The same *P4mm* to *R-3c* phases transitions with *R3c* bridging phase were predicted by Frantti *et al.* [11] as the result of an efficient compression through octahedral tilting. On the contrary, it has been proposed that ferroelectricity in perovskites and related materials [9,10,14] is first reduced or suppressed under pressure but then is enhanced or reappears at higher pressure through some original electronic effect. Most of the above-cited work was based on theoretical investigations only.

A great deal of confusion thus currently exists in perovskites under pressure in general and in PTO in particular: (1) What is the exact role (if any) of octahedral tilting in perovskites under pressure? (2) Can pressure really induce low-symmetry ferroelectric phases and a continuouslike morphotropic phase boundary? (3) What is the precise phase diagram of PTO under pressure? (4) Can ferroelectricity be indeed enhanced or reappear at high pressure?

Motivated to experimentally resolve such issues, we present here an x-ray and Raman scattering investigation of PTO up to 63 GPa, the highest pressure yet attained on this material. We demonstrate that, at room temperature, PTO undergoes three phase transitions leading to the following conclusions: (i) The tilting of oxygen octahedra plays a central role in an efficient compression of PTO. (ii) No evidence is found for monoclinic or rhombohedral structures. On the contrary, we observe (iii) *I4/mcm* and *I4cm* tetragonal structures where the tetragonality continuously increases above a critical pressure. (iv) The highest-pressure phase is ferroelectric and noncubic, confirming earlier calculations [9,10] and disproving others [8,11,13].

We have carried out room-temperature pressure-dependent experiments on PTO powder and ⟨001⟩- and ⟨111⟩-oriented single crystal samples. Hydrogen or argon

were used as pressure-transmitting media in diamond anvil cells. The experimental setups for Raman scattering and x-ray diffraction have been presented elsewhere [5]. The x-ray experiments were carried out on the ID09A and ID30 high-pressure beam lines at the European Synchrotron Radiation Facility (ESRF). The pressure-induced changes were checked to be reversible.

We first discuss our x-ray diffraction data which suggest three structural phase transitions between 0.1 and 63 GPa. Figure 1 presents the pressure evolution of the lattice parameters as determined from four experiments. At low pressure the $\{h00\}$ and $\{hh0\}$ reflections are split, whereas $\{hhh\}$ ones remain singlets. The diffraction pattern at ~ 2 GPa is consistent with the $P4mm$ space group. The initially large tetragonal distortion is considerably reduced with increasing pressure as illustrated by the coalescence of the $\{h00\}$ reflections (inset of Fig. 1). The evolution of the a and c parameters up to $p_{c1} \approx 13$ GPa is in agreement with earlier observations [15]. From $p_{c1} \approx 13$ GPa up to $p_{c2} \approx 20$ GPa, the structure appears metrically cubic. Above $p_{c2} \approx 20$ GPa, a careful inspection of the pattern reveals that the $\{h00\}$ and $\{hh0\}$ Bragg reflections are split whereas the $\{hhh\}$ ones remain single up to 63 GPa. This provides evidence for a tetragonal-like distortion from 20 to 63 GPa. The c/a ratio increases in this pressure range up to a small but significant value of 1.010 ± 0.005 at 63 GPa.

Within the high-pressure region of tetragonal distortion, we observe weak superstructure reflections (SSR) of the type $3/2$ $1/2$ $1/2$ above 43 GPa. They are due to the oxygen octahedron tilting as in SrTiO_3 (STO) at low temperature and correspond to the $a^0a^0c^-$ tilt system [16].

We have also performed quantitative Rietveld analysis on selected powder diffraction patterns. We first discuss the result for $p = 50$ GPa. We considered several doubled unit cells with different space groups including antiferrodistor-

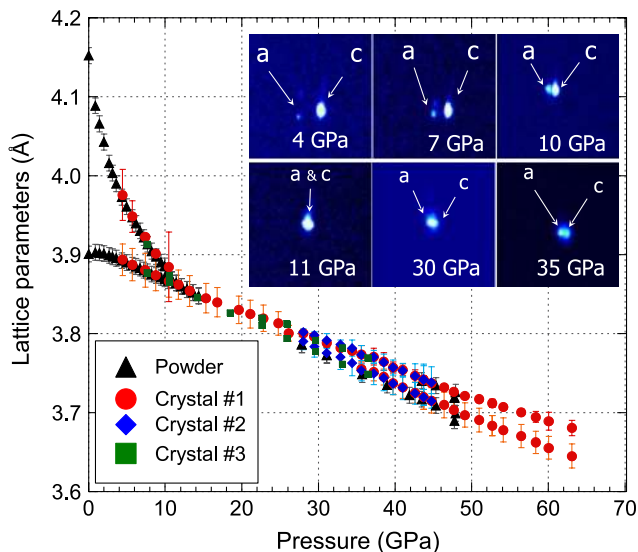


FIG. 1 (color online). Pressure evolution of the lattice parameters of PbTiO_3 from 0.1 to 63 GPa and of the $\langle 004 \rangle$ Bragg spot (inset).

sive motions and/or ferroelectric displacements, i.e., tetragonal $I4cm$, $I4/mcm$, etc., orthorhombic $Imma$, $Pnma$, etc., or monoclinic Pc , $C2/m$, etc. The tetragonal phases provided the best refinements. In particular, the $I4cm$ space group yields better agreement factors ($R_{wp} = 2.89\%$, $R_{\text{Bragg}} = 2.54\%$, goodness of fit (GOF) = 1.27) between the observed and calculated profiles (Fig. 2) compared with the nonferroelectric $I4/mcm$ space group ($R_{wp} = 2.96\%$, $R_{\text{Bragg}} = 2.71\%$, GOF = 1.35). Both phases have the same angle of oxygen octahedra tilt (1.8°). However, this tilt value has to be taken with care because of the uncertainty resulting from the weak SSR reflections. The polar displacement in the $I4cm$ space group is related to the Ti shift of $0.009(3)$ Å, comparable to the value calculated by Kornev *et al.* [9] and in agreement with the recently proposed reentrance of ferroelectricity under high pressures.

We proceeded similarly with $p = 37$ GPa. Again, better refinements were obtained with tetragonal phases but now $I4/mcm$ and $I4cm$ gave similar agreement factors with a tilt angle of 1.6° and nearly zero Ti cation displacement [$0.002(3)$ Å] in the $I4cm$ phase. This suggests that a phase transition from $I4/mcm$ to $I4cm$ occurs between 37 and 50 GPa. Further refinements located this phase transition at $p_{c3} \approx 45$ GPa, above the highest pressure of our Raman data. Finally, we refined the diffraction pattern at 18 GPa. It was not possible to determine any distortion as very good agreement factors and matching between the observed and calculated diffraction patterns are obtained within the cubic $Pm-3m$ phase.

Figure 3 presents Raman scattering spectra of a PTO powder sample at selected pressures between 0.1 and 44 GPa. At ambient conditions, the spectral signature and

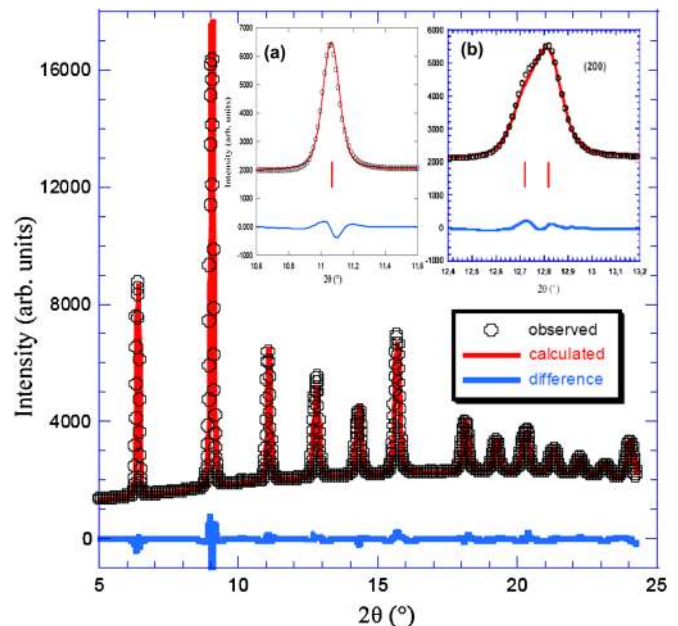


FIG. 2 (color online). Rietveld refinement ($I4cm$) of a powder diffraction pattern obtained at 50 GPa. Insets: blowup of the (a) (111) and (b) (200) pseudocubic Bragg peak.

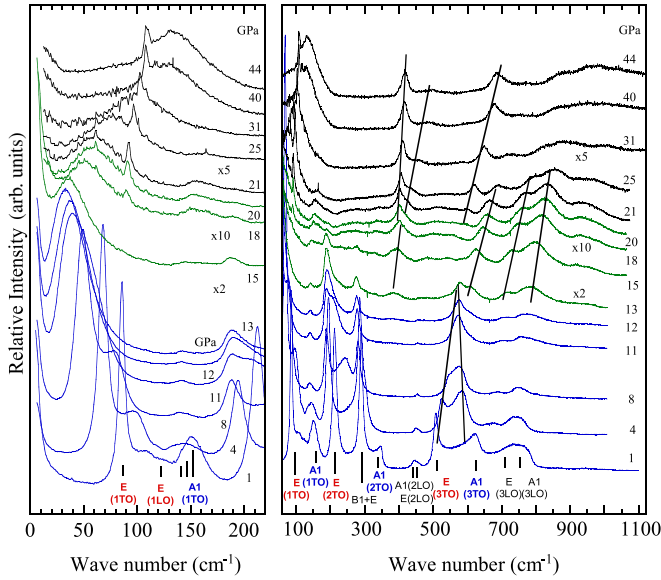


FIG. 3 (color online). Selected Raman spectra of PbTiO_3 as a function of pressure up to 44 GPa. Symmetry attribution according to Ref. [17].

band positions correspond to those for the space group $P4mm$ with its expected $3A_1 + 4E + B_1$ Raman active modes. The common notation $A_1(jTO)$, $A_1(jLO)$, $E(jTO)$, $E(jLO)$, with $j = 1, 2, 3$, is used to identify these modes. Because our unpolarized spectra are recorded on powder with random orientations, we observed some additional poorly defined oblique or quasimodes as expected for ferroelectric samples [17]. In good agreement with our x-ray data, two critical pressures are evidenced as bands appear or disappear (Fig. 4). Up to p_{c1} the softening of some Raman modes is in agreement with the earlier reports [4]. For $j = 2, 3$ $E(jTO)$ - $A_1(jTO)$ pairs tend to merge under pressure, indicating the reduction of the tetragonal anisotropy. Note that the observed splitting between $A_1 + E$ modes and the elastic order parameter ($\sqrt{c/a} - 1$), determined by x rays, are linearly correlated. The pressure evolution of the soft $E(1TO)$ mode yields the first critical pressure, $p_{c1} \approx 13$ GPa, from the intersection of the linear interpolations below and above p_{c1} (Fig. 4). The softening of $A_1(1TO)$ mode is not directly observed because of a Fermi resonance with an overtone ($2TA$) mode which might originate from zone boundary acoustical phonons. These states could interact with the $q = 0$ soft phonons and become Raman active through mechanism similar to that found in quartz [18].

We now consider the Raman signature above 13 GPa. For symmetry reasons, first-order Raman scattering is forbidden in the $Pm-3m$ perovskite structure expected from x-ray data. We indeed observe that the Raman intensity is significantly reduced when crossing p_{c1} , but Fig. 3 shows that the Raman signature is, nevertheless, not totally suppressed and maintains a significant fine structure: (i) the low-frequency soft mode persists and hardens with pressure, (ii) some bands persist at 200, 280 cm^{-1} , and

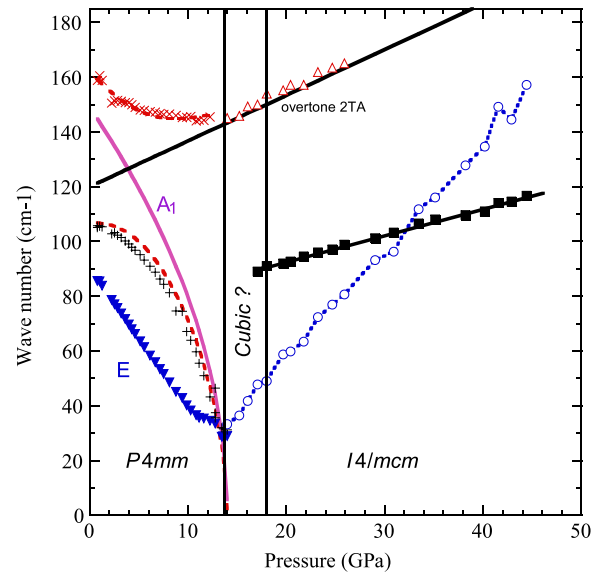


FIG. 4 (color online). Pressure dependence of PTO low wave number phonons up to 44 GPa. The solid lines represent the dependence expected for the uncoupled excitations A_1 and $2TA$. Typical Landau dependence of A_1 wave number is obtained with $p_c \approx 13$ GPa and an exponent of $1/2$.

(iii) new bands appear at 380, 620, 710, and 790 cm^{-1} and increase in intensity between 13 and 20 GPa.

Before discussing this apparent discrepancy between Raman and x-ray scattering data, it is useful to discuss the spectra above $p_{c2} = 20$ GPa, where we observe the appearance of new bands at 410 and 620 cm^{-1} and an abnormally narrow peak at 90 cm^{-1} which persist up to 44 GPa. Above p_{c2} the bands are well-defined, suggesting that they originate from a long-range distortion. An important aspect of this signature is the relative sharpness of the band originally at 380 cm^{-1} ; such a sharp band in this spectral region is often encountered in perovskites presenting octahedral tilts. We also observe in this new phase a clear hardening of the low wave number soft mode. We note that this new phase has fewer modes than the phases below p_{c2} , suggesting an increase in symmetry. In fact, the Raman signature measured for PTO above 20 GPa is very similar to that observed for STO at low temperature in the $I4/mcm$ space group [19]. Thus, our Raman spectra and x-ray data provide concomitant arguments for a nonpolar tetragonal $I4/mcm$ structure for PTO above $p_{c2} = 20$ GPa and up to $p_{c3} = 45$ GPa.

Finally, we discuss the structure in the intermediate pressure range $p_{c1} < p < p_{c2}$. Diffraction suggests a metrically cubic structure while Raman scattering provides evidence for a deviation from a cubic structure. Three scenarios can be evoked. The first calls for the existence of a local polarity inside the TiO_6 octahedra without long-range correlation in line with what has been observed for KNbO_3 [20]. This model finds some support from a recent high-pressure x-ray-absorption near-edge structure technique study of PTO [21] where it was found that the Pb

displacement is reduced to zero above p_{c1} while the Ti atoms remain locally displaced. However, our observed spectral signature above p_{c1} is far better defined than the high-temperature or high-pressure Raman spectra of disordered cubic BaTiO_3 [22] or KNbO_3 [23]. A second scenario concerns the presence of a subtle long-range structural distortion, below the detection limit of diffraction. Space group determination from Raman spectroscopy alone is difficult without the spectral signature of a reference phase. Nevertheless, we know the two adjacent phases and our spectral evolution suggests rather second-order dominated phase transitions, implying a group-subgroup relationship with the adjacent phases should be considered. One possibility is that the prototypic $Pm-3m$ perovskite structure could act as a “bridge” between these two phases. The Raman signature observed in the cubic phase would then be of second-order type. The detailed fine structures being associated to variation in the second-order density of states as in cubic STO [19]. Another possibility is the tetragonal structure (with a space group $I4cm$) proposed from first-principle calculations [9,10] which is a common supergroup of the adjacent phases. This space group presents both cation displacements and antiferrodistortive octahedra tilts thus potentially acting as a natural bridge between $P4mm$ (only cation displacements) and $I4/mcm$ (only octahedra tilts). Third, it is worth emphasizing that a competition takes place in this pressure range between structures close in energy, including $Pm-3m$ and $I4cm$ [9,10]. Such a competition might give rise to a complex local structure where the cation displacements are not totally disordered but correlated on the nanoscale, similar to $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ which presents a cubic overall structure with local polar clusters. Although we cannot exclude such a situation for PTO, the existence and underlying mechanism of polar clusters without chemical disorder remains to be elucidated. Further investigations are therefore needed to determine unambiguously the structure between p_{c1} and p_{c2} .

In conclusion, we have presented complementary Raman and x-ray scattering investigations up to 63 GPa of the classic ferroelectric PbTiO_3 , which allows the clarification of the high-pressure behavior of ferroelectrics. Our experiments reveal the following phase sequence for PTO: $P4mm$ (polar) $\xrightarrow{13 \text{ GPa}}$ close to cubic ($I4cm$ or local distortions within $Pm-3m$) $\xrightarrow{20 \text{ GPa}}$ $I4/mcm$ (nonpolar) $\xrightarrow{45 \text{ GPa}}$ $I4cm$ (polar). Interestingly, the experimentally observed pressures are close to those theoretically determined in Ref. [10] for this phase sequence. While we cannot provide a definite assignment of the intermediate ($p_{c1} < p < p_{c2}$) phase, the structure above p_{c2} is well described by a non-ferroelectric and antiferrodistortive $I4/mcm$ phase. Above p_{c3} , the phase becomes ferroelectric, conserves its oxygen tilting motion, and can be described by the polar $I4cm$ space group which has also been observed in the piezoelectric PZT for Ti-rich morphotropic compositions [24]. Our study provides experimental evidence that multiple

phase transitions, tilting of oxygen octahedra, and reentrance of ferroelectricity take place in PbTiO_3 at high pressure. We hope that our study motivates further investigations beyond the prototype PbTiO_3 .

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