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Abstract

Electron density distributions of $PbTiO_3$, $BaTiO_3$ and $SrTiO_3$ were determined by synchrotron x-ray powder diffraction up to 55 GPa at 300 K and *ab initio* quantum chemical molecular orbital (MO) calculations together with a combination of maximum entropy method calculations. The intensity profiles of Bragg peaks reveal split atoms in both ferroelectric $PbTiO_3$ and $BaTiO_3$, reflecting the two possible positions occupied by the Ti atom. The experimentally obtained atomic structure factor was used for the determination of the deformation in electron density and the *d-p-π* hybridization between d_{xz} (and d_{yz}) of Ti and p_x (and p_y) of O in the Ti-O bond. *Ab initio* MO calculation proved the change of the molecular orbital coupling and of Mulliken charges with a structure transformation. The Mulliken charge of Ti in the TiO_6 octahedron increased in the ionicity with increasing pressure in the cubic phase. The bonding nature is changed with the decrease in the hybridization of the Ti-O bond and the localization of the electron density with increasing pressure. The hybridization decreases with pressure and disappears in the cubic paraelectric phase, which has a much more localized electron density distribution.

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Introduction

The prototype perovskite ferroelectrics $PbTiO_3$ (PTO) and $BaTiO_3$ (BTO) have been studied by both scientific and industrial communities because of their importance in modern ultrasonic and related devices [1-10]. The behavior of these materials raises fundamental questions in solid state physics. In particular, they serve as textbook examples of pressure- or temperature-induced soft phonon-driven structural transitions. In addition, because of the simplicity of their structures, they also serve as ideal tests for theory and first-principles calculations. Theoretical work has shown that the hybridization between the Ti 3*d* states and O 2*p* states is essential to the ferroelectric properties in both PTO and BTO [1], and that orbital hybridization exists between the Pb 6*s* state and O 2*p* states and plays a crucial role in the larger ferroelectricity observed in tetragonal PTO [11], whereas the interaction between Ba and O is almost ionic in tetragonal BTO [11][12]. One of the challenging tasks in this area of research is experimentally accessing the bonding electron distributions associated with the orbital hybridization in these materials.

First principles calculations proposed the transition from ferroelectric to antiferro- distortion in the tetrahedral phase [3][4][5]. *Ab initio* molecular orbital calculations [6][7] were undertaken to elucidate the electronic structure and dynamical structure change. The elastic properties of $SrTiO_3$ (STO) in the cubic, tetragonal and orthorhombic phases were also carried out using the *ab initio* pseudo-potential method [8] and reported a cubic ($Pm\bar{3}m$)-tetragonal ($I4/mcm$) transition at 6 GPa, a tetragonal-orthorhombic ($Cmcm$) at 14 GPa and an orthorhombic to monoclinic ($P2_1/m$) transition at 24 GPa. Here we examine experimentally the pressure dependence of the electron density (ED distribution in PTO and BTO using a combination of single crystal diffraction and maximum entropy method (MEM) calculation [13][14]. The present measurements and analysis reveal the pressure-induced changes in the *d*-*p*-π hybridization originally predicted for these materials.

Experimental

Single crystal diffraction measurements up to 12 GPa were performed using diamond anvil cells (DACs) and synchrotron single crystal x-ray diffraction facility at beam line BL-10A of the Photon Factory (KEK, Tsukuba, Japan) with a wavelength of λ=0.61907 Å (20.0137 keV). Intensity measurements were carried out with a four-circle diffractometer using a fixed ϕ-rotation and 100 μm collimator. A scintillation counter rather than imaging plate detector was used to measure diffraction intensities, because it is capable of much more precise intensity measurements and determination of the precise orientation matrix than an area detector. An orientation matrix (UB matrix) and unit cell parameters were determined by least-square fitting using the refined peak positions of 25 reflections.

The detailed specifications of this DAC is described in a previous report [15]. Mixture of ethanol, methanol and water of 16:4:1 used as the pressure-transmitting medium, which guarantees hydrostatic conditions up to 12 GPa. Pressure is measured by the ruby luminescence method [16]. The high-pressure experiment is described in detail in supplement [17].

X-ray powder diffraction experiments were also executed using DAC at pressures up to 55 GPa at ambient temperature. The lattice parameters of the samples were determined by Rietveld profile fitting from the observed diffraction peaks. The Rietveld refinement was conducted using the RIETAN-2000 program [18]. First, the background intensity distribution was adjusted for the refinement. The lattice constants, atomic positional coordinates and temperature factors were then treated as variable parameters. Subsequently the profile parameters and site-occupancy parameters were varied in the refinement. The full width half maximum parameter, asymmetry parameters and peak profile function confirmed that the diffraction data guaranteed a reliable profile analysis.

Analysis and result

Structural Refinements

To determine effective charges of constituent atoms of ferroelectric materials by x-ray diffraction, a conventional structural refinement is first carried out using the full matrix least-squares program RADY [19]. Reflections observed up to 2θ= 75° and with intensities of $F_o>3\sigma(F_o)$ were used for the least-squares refinements. Observed intensities are converted to structure factors after correction for x-ray absorption by the DAC, x-ray extinction, and Lorentz and polarization effects. Structure factors for reflections *hkl* are calculated by the atomic position $(x_s\ y_s\ z_s)$ for atom *s* of element *j* and atomic scattering factor f_j together with displacement factor.

Atomic coordinates, site occupancy parameters, anisotropic displacement factors and isotropic extinction parameters were chosen as the variable parameters. The reliable parameter of the least square refinement is represented by R (= w$\Sigma||$Fobs$|^2$ - $|$Fcal$|^2|/\Sigma|$Fobs$|^2$). The factors of all present experiments were converged within R=0.05. Since ferroelectric phases have a non-centrosymmetric structure, the origin of the structure of PTO and BTO was fixed at Pb(0 0 0) and Ba(0 0 0), respectively. The results of least-squares refinements for PTO and BTO are presented in Tables 1 and 2, respectively.

Pb-O and Ti-O bond distances in PTO and Ba-O and Ti-O distances in BTO are presented in Table 3. Fig. 1 shows Pb-O and Ti-O bond lengths in PTO as a function of pressure. The difference in the two Pb-O2 and two Ti-O1 distances along the c axis becomes noticeably smaller in the tetrahedral ferroelectric phase with pressure. Their differences disappear in the cubic paraelectric phase. However, the four Pb-O1 and four Ti-O2 are not altered significantly by pressure. Above 12GPa, PTO adopts the cubic $Pm\bar{3}m$ structure, and all Pb-O and Ti-O bonds in the PbO_8 and TiO_6 polyhedra are respectively converged to equal values. For completeness, we also list the bulk modulus determined for the two materials [4][5]. The calculated data are K_0=101(6) GPa, K_0'=4 (fixed) for PTO, which are good agreement with K_0=107(3) GPa, K_0'=5.0(1) [9]; K_0=154 GPa, K_0'=4 for BTO, a little larger than K_0=135 GPa, K_0'=6.4 [8].

Maximum Entropy Method (MEM) Analysis

Highly resolved distributions and atomic positional displacements are essential for understanding the electric polarization in ferroelectric materials. The Fourier series of the structure factors provides the ED distribution ρ(xyz) in the real space:

$$\rho(xyz) = \frac{1}{V}\sum_h\sum_k\sum_l F(hkl)\exp\{-2\pi i(hx+ky+lz)\}. \qquad (1)$$

The difference Fourier synthesis $\{|F_{obs}(hkl)| - |F_{cal}(hkl)|\}$ is applied in order to disclose the deformation of the ED distribution. The residual ED $\Delta\rho(xyz)$ expresses the nonspherical deformation of the electron density, and is necessary, because the applied atomic scattering factor f_s is composed of the basically spherical distribution with sinθ/λ.

$$\Delta\rho(xyz) = \frac{1}{V}\sum_h\sum_k\sum_l \{|F_{obs}(hkl)| - |F_{cal}(hkl)|\}\exp\{-2\pi i(hx+ky+lz)\} \qquad (2)$$

The radial distribution of the ED distribution confirms the localization of electrons around atomic positions, which provides the dipole moment in a classical sense.

The Fourier synthesis inevitably has a termination effect as a result of the limitations on the number of measured reflections. However, the difference Fourier synthesis can remove the termination effect in the observed ED distribution. The deformation electron density is obtained from the difference Fourier synthesis $|F_{obs}(\boldsymbol{h})|$ - $|F_{cal}(\boldsymbol{h})|$ within the reciprocal space defined by $\sin\theta/\lambda<1.22$ at ambient pressure. However, the opening angle of the DAC restricts observed diffraction to small Q-values. $F_{obs}(hkl)$ in this limited reciprocal space cannot provide a precise residual electron density from the structure refinement by standard least-squares methods.

MEM statistically estimates the most reliable ED distribution from a finite set of observed structure factors, so the termination effect found in the Fourier synthesis is ignored. The method originated with Jaynes [20] and was subsequently applied to crystallographic problems from the standpoint of with several experiments and theories [21-26]. The calculation method is described in supplement [17]**.** A detailed discussion and procedure for using the single crystal diffraction intensity data under high pressure in a MEM analysis were also described in our two earlier papers [13][14]

The data used in the MEM calculation are the F_{obs} ($\boldsymbol{h}$). In a single crystal diffraction study these data are directly measured individually for all reflections. Consequently, the single crystal diffraction intensity measurement can provide a much more precise ED distribution than the MEM analyses using powder diffraction intensities, because the former has no ambiguity in the deconvolution of the overlapping intensities often found in the powder diffraction pattern, along with a much larger number of observed F_{obs} ($\boldsymbol{h}$).

The difference MEM calculation using $|F_{MEM}(\boldsymbol{h})|$ - $|F_{cal}(\boldsymbol{h})$ |results in a more precise deformation electron density than does the difference Fourier synthesis. The residual ED distribution can be derived from the aspherical ED distribution such as may be produced by *d*-electrons or anharmonic thermal vibration of atoms. The anharmonicity is ignored in the present refinements, because the Debye temperatures, Θ_D, for PTO and BTO are much higher than room temperature.

The deformation electron density is observed in the tetragonal site symmetries, even though no initial structure model is applied in the MEM calculation. Although the diffraction angle of the DAC is limited to 80° in 2θ, the MEM guarantees a sufficiently reliable electron density around the atomic positions.

Because the MEM approach is statistical, it provides probability distributions that show the two possible positions for Ti atoms. The generated electron density map is asymmetric features around these two positions of Ti and oxygen atoms of PTO and BTO. The split atoms are observed only in the direction of <001>. However, they are not found in any direction perpendicular to <001>, as presented in BTO (Fig. 2). The split atoms are generated by long range ordered atomic displacements. Localization of bonding electrons, lone-pair electrons and aspherical distribution of *d* electrons are considered. In the previous paper [10], the split atoms of Ti and O are proved in the Fourier synthesis for tetragonal PTO. The present experiment reveals the splitting of these particular atoms decreases with increasing pressure.

The MEM ED distribution between Ti and O on (010) plane of tetragonal phase is schematically presented with the split atoms in Fig. 3.

The difference Fourier map confirms *d*-electron orbit of Ti (3*d*) in the site symmetry of *m*2*m*, proving d_{xz} or d_{yz} in t_{2g} group at the octahedral site. The residual electron density around Ti is clearly observed indicating that hybridization of the *d* electron of Ti and *p* electron of oxygen construct *d*-*p*-π bond. Present MEM maps experimentally first prove the *d*-*p* hybridization between d_{xz} (and d_{yz}) of Ti and p_x (and p_y) of O1. However, a hybridization of d_{xy} of Ti and p_z of O2 of the coplanar atoms is not obviously observed at all pressures. From the split atoms in the tetragonal phase, an obvious deformation electron density is observed confirming the possible polarization in the direction perpendicular to <001>. But the superposed two domains indicate the opposite direction of the deformation. The cubic phase of PTO at 11.9 GPa has no polarization in any direction perpendicular to the <001> direction, as shown in Fig. 4. The ED distribution around Ti and O atoms are not contradictory to the centro-symmetric cubic site symmetries of $m\bar{3}m$, resulting in the paraelectric property without any deformation.

The ED maps of PTO (Fig. 4) and BTO (Fig. 5) with increasing pressure are given as projections on the (100) plane at $x = 0.5$ and the (001) plane at $z = 0.5$ in the region from 1 e/Å^3 to 10 e/Å^3. These maps show the split atoms and statistical positional disorder indicating polarization in the <001> direction. However, the maps projected on (001) at $z = 0.5$ indicate no polar character in the <100> and <010> directions. The Ti-O bond with the apical oxygen O1 in the (100) projection at z=0.5 reveals *d*-*p*-π bonding along z. In contrast, the four Ti-O bonds in the projection containing the co-planer oxygen O2 indicate no *d*-*p*-π bond character. The pressure dependence of the ED distribution is presented for the tetragonal ferroelectric phase of PTO at 0.0001, 6.0 and 9.3 GPa and cubic paraelectric phase at 11.9 GPa in Fig. 4. The split atom feature reflects the two possible positions occupied by the Ti atom. The splitting decreases with increasing pressure, and disappears in the cubic paraelectric phase and accompanied with the more localized electron density. The radial ED distribution on the O-Ti-O bonds parallel to the *z*-axis shown in Fig. 6 indicates that the localization of electron density around Ti atoms is enhanced with pressure.

Effective Charges

Atomic-scattering factors $f_i(\boldsymbol{h})$ are obtained from the Hartree-Fock wave functions (*i.e.*, one-particle model). Thus, $f_j(\boldsymbol{h})$ gives an ideally spherical ED distribution for an isolated atom. $f_j(\boldsymbol{h})$ includes anomalous dispersion: $f(\boldsymbol{h}) = f_0 + \Delta f' + i\Delta f''$. Effective charges of atoms are obtained from the least-squares calculation by the shell model in which the core and valence electrons are separated. Inner-core electrons are frozen with respect to bonding effects according to the pseudo-potential model, and only valence electron densities are deformed due to coordination and thermal vibration of atoms. They are more sensitive to the interatomic potential affected by the coordination of the adjacent atoms.

A monopole refinement was applied instead of the multipole deformation density in this analysis. The κ-parameter [27][28] was applied to the atomic scattering factor to provide an indicator of the valence electron distribution around a given atom. The κ-parameter used in this analysis is expressed as $\rho_{\mathrm{valence}}(\mathbf{r})=\mathrm{P}_{\mathrm{valence}}\kappa^{3}\cdot\rho_{\mathrm{valence}}(\kappa\cdot\mathbf{r})$, where $\rho_{\mathrm{valence}}(\mathbf{r})$ is the ground state density of the free atom. $\mathrm{P}_{\mathrm{valence}}$ indicates the valence-shell population, which is the occupancy parameter of valence electrons. The perturbed valence electron density is

$$f(\mathrm{s}/2) = \Sigma[\mathrm{P}_{j.\mathrm{core}} f_{j,\mathrm{core}}(\mathrm{s}/2) + \mathrm{P}_{j,\mathrm{valence}} f_{j,\mathrm{valence}}(\kappa_j,\mathrm{s}/2) + \Delta f'_j + i\Delta f''_j\,] \qquad (3)$$

The valence scattering of the perturbed atom at s/2 (= $\sin\theta/2\lambda$) is given by

$$f_{\text{M-core}}(\kappa_j, s/2) = f_{j,\text{ M-core(free atom)}}\,(\sin\theta/\lambda \cdot 1/\kappa_j). \qquad (4)$$

The κ-parameter was determined by the minimization of least-squares refinement using diffraction intensities of all reflections within $2\theta < 120^\circ$ at ambient conditions. The least-squares calculation starts from the neutral scattering factor (κ=0.0) to determine the κ-parameter.

In the case of $\kappa = 1$, the atomic-scattering factor is the radial distribution of neutral balance, which is the same as the factors found in the *International Table for Crystallography* [29} . A value $\kappa > 1$ designates a localized valence electron density, implying more ionic bonding. On the other hand, $\kappa < 1$ characterizes a broad radial distribution of electron density, indicating more covalent bonding.

The effective charge q of atom j is the equivalent valence-shell population P_j, which is derived from the κ-refinement.

$$q = -\int \Delta\rho(r)\,dr = -4\pi\int r^2\rho(r)\,dr \qquad \mathbf{(5)}$$

The effective charges at ambient conditions are:

$q_{\text{Pb}} = +1.74$, $q_{\text{Ti}} = +2.92$ and $q_{\text{O}} = -1.55$ for $PbTiO_3$,

$q_{\text{Ba}} = +1.91$, $q_{\text{Ti}} = +2.79$ and $q_{\text{O}} = -1.57$ for $BaTiO_3$.

More reflections used in the least-squares calculation gives a better reliable κ-parameter. Because of the limited number of reflections accessible experimentally as a result of the limited opening angle of the DAC, the κ-parameter was not precisely able to resolve effective charges at high pressure.

The sum rule $\sum_i q_i = 0$ is fulfilled to within the error of 0.01 for both materials. The values are very similar to the Mulliken charges determined by *ab initio* calculations using Hartree–Fock (HF) and density functional theory [30], and suggest that BTO is slightly more ionic than PTO. Mulliken effective charge of BTO and PTO obtained by seven different calculation methods [12] all indicates noticeably covalent character; the present experimental results are similar to the HF calculations. For comparison, we also list effective charges obtained in the current work and relevant theoretical calculations by Evarestov et al (2003) [31] in Table 4. Effective charges of Pb and Ba are compared.

Discussion

The difference Fourier map $|F_{obs}(\boldsymbol{h})|$ - $|F_{cal}(\boldsymbol{h})|$ for BTO and PTO at ambient conditions has been determined by x-ray single-crystal diffraction [4], and ED distributions for PTO and BTO have been computed by first-principles calculations [11][12][31]. These theoretical results allow a visualization of the local ED distribution in an ideal unit cell and correspond to a case, in which the ferroelectric pseudo-particle occupies one of the well of double-well potential. In our case, because we employed a statistical method, which provides statistical average, therefore we observed split atoms, in fact the split atoms indicate there are two possible positions for Ti atom in the ferroelectric phase and consistent with theory [31]. The present experimental results are consistent with the first-principles calculation [1], which first predicted a hybridization between d_{xz} (and d_{yz}) in the t_{2g} orbitals on Ti and the p_x (and p_y) orbitals on the apical oxygen. The present experimental x-ray diffraction studies using the single crystals of BTO and PTO elucidate the ferroelectric behave ours of the real bulk crystal.

The present investigation of the split-atom makes a comparison with the previous 8-site model [32],[33][34] which has been used to explain the successive ferroelectric transitions in BTO and $KNbO_3$ with temperature (see supplement [17]). They observed strong streak-type diffuse-scattering in the their cubic phases$_3$; they also observed drastic changes in the diffuse scattering accompanying the relevant structural transitions with temperature. The eight-site model was proposed and used to explain observed streak-type diffuse-scattering$_3$. According to this model, the Ti cation in BTO can occupy eight sites in its cubic phase at high temperature. With decreasing temperature BTO undergoes a paraelectric to ferroelectric transition. In our case, we focused on the intensity profile of each Bragg peak within the accessible reciprocal lattice space. We did not scan the space between Bragg peaks, thus we would not observe the streak-type diffuse scattering in our measurements.

According to the modern definition of polarization, spontaneous polarization arises from the flow of polarization currents in solids, which corresponds to the Berry phase of electronic wave functions, and can be interpreted as a displacement of the center charge of the Wannier functions (see example Refs. [35][36]). The spontaneous polarization cannot be calculated directly from diffraction measurements, because information about the electronic wave functions is required. We obtained statistical average of space and time of atomic vibrations and displacements and from this calculate the effective charge (*q*) and polarized deviation ($\Delta\mathbf{r}$) of bond distances. Effective charges of atoms were obtained from the least-squares calculation based on the shell model.

In general, heavy atoms such as Pb and Ba in oxides show a small temperature factor in comparison with oxygen atom. In this study, however, we observed the time and space average of dynamical phenomena due to atom disorder or micro domain disorder of PTO and BTO bulk structure. We found a large ED deformation around Pb atom found along particular directions in the MEM maps. The displacement of Pb atoms is more noticeable than those of Ti and O atoms, but these deformations disappear at higher pressures, where the ferroelectric structure transforms to paraelectric. The transformation probably turns out, because the domain disorder or atomic displacement is homogenized or disappear above 11.9 GPa for PTO and 2 GPa for BTO.

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Fig. 1 Pressure dependence of Pb-O and Ti-O bond distance of two $PbTiO_3$ polymorphs: tetragonal phase at lower-pressure region and cubic phase at higher-pressure region. The observed errors are smaller than the symbols.

Fig. 2 MEM ED of $BaTiO_3$ derived from the all reflections within $2\theta<80°$ at ambient conditions. MEM $F_{MEM}(\boldsymbol{h})$ is shown on plane (010) at y=0.0 with a contour of 1.0 eÅ^{-3} up to 10.0 eÅ^{-3} with origin at Ba (000). The red arrows represent the positional disorder of Ti and O atoms. The red arrow indicates the splitting of atoms.

Fig. 3 *d-p-π* bond in two domains. Figure A indicates the π-bond in the single domain. Figure B shows the individual *π*-band in the split atom model. Figure C represents the apparent *π*-bond in the statistically distributed domains, which proved in the observed MEM map shown in Fig. 4. The upper C and lower C maps present the electron density under low pressure and high pressure.

Fig. 4 MEM ED distribution of $PbTiO_3$ at $x = 0.5$ on the (100) plane with increasing pressure. Statistically split atoms of Ti and O are clearly found in the tetragonal phase, indicating the polarization in the <001> direction. The deformation of the electron density is generated from *d-p-π* hybridization between Ti and apical O. In contrast, the Ti-O bonds with four co-planer O show no hybridization.

Fig. 5 MEM ED distribution of $BaTiO_3$ at x=0.5 on (100) plane with increasing pressure. Split atoms are observed only in the ED distribution at 0.4 GPa. The splitting is not found at pressures above 2.5GPa. Tetragonal phase ($P4mm$ z=1) transforms to the cubic paraelectric phase ($Pm\bar{3}m$ z=1) at about 2 GPa. A contour of the projection is same in Fig. 2.

Fig. 6 Localization of electron density of Ti atom in $BaTiO_3$.

The radial distribution in O-Ti-O bond in the MEM map is derived from the all reflections within $2\theta<80°$ with increasing pressure. The radial distribution in the Fig. 5 shows the localization of electron density of the cubic paraelectric phases is enhanced with pressure in the direction of <001>. But almost no change in the localization is observed in the direction of <100> and <010>.

Table 1

PbTiO$_3$ Structure refinement

	'etragonal						Cubic
	0.0001	1.0	3.3	6.0	9.3	10.3	11.9
a (Å)	3.9014(5)	3.9094(4)	3.8997(7)	3.8871(5)	3.8736(9)	3.8691(8)	3.861(1)
c (Å)	4.1466(7)	4.081(2)	4.026(2)	3.945(1)	3.890(2)	3.8797(9)	
V (Å^3)	63.11(2)	62.69(3)	61.22(9)	59.61(4)	58.37(20)	58.08(8)	57.5(1)
No$_{obs}$	2020	358	119	336	183	202	105
No$_{used}$	331	60	66	99	99	101	52
Pb x	0	0	0	0	0	0	0
Y	0	0	0	0	0	0	0
Z	0	0	0	0	0	0	0
B$_{iso}$ (Å^2)	0.938	0.906	0.889	0.783	0.809	0.770	1.826
Ti x	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Y	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Z	0.5455	0.5386	0.5309	0.5292	0.5278	0. 5151	0.5
B$_{iso}$ (Å^2)	0.374	0.233	0.312	0.349	0.399	0.378	0.396
O1 x	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Y	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Z	0.1218	0.1131	0.0942	0.0805	0.0652	0.0164	0.0
B$_{iso}$ (Å^2)	0.619	0.543	0.665	0.675	0.686	0.582	2.090
O) x	0.5	0.5	0.5	0.5	0.5	0.5	-
Y	0	0	0	0	0	0.0	-
Z	0.6282	0.6202	0.5998	0.5848	0.5724	0.5424	-
B$_{iso}$ (Å^2)	0.863	0.782	0.790	0.842	0.811	0789	-
R (%)	4.13	4.32	5.06	3.22	3.84	4.81	6.77
wR(%)	4.75	2.48	4.20	3.14	3.43	4.04	8.00

The numbers in parentheses denote errors of the last decimal.

Atomic coordinate of Pb in the tetragonal phase is fixed to (0 0 0), because it is a noncentric structure. The position is placed for the origin of the structure of PTO.

R(%) indicates the reliable factor ($R= \Sigma||Fobs|^2 - |Fcal|^2|/\Sigma|Fobs|^2$).

B$_{iso}$(Å) is an isotropic temperature factor of atom

Table 2

BaTiO$_3$ Structure refinement

Pressure	Tetragonal			Cubic	
(GPa)	0.0001	0.4	2.5	4.3	5.8
a (Å)	4.0023(4)	4.0010(5)	3.9919(7)	3.9782(2)	3.9699(3)
c (Å)	4.0251(4)	4.0806(8)	3.9919(7)	3.9782(2)	3.9699(3)
V (Å^3)	64.48(1)	64.39(3)	63.61(3)	62.96(1)	62.57(2)
No$_{obs}$	1616	391	371	371	402
No$_{used}$	302	62	47	46	46
Ba x	0	0	0	0	0
Y	0	0	0	0	0
Z	0	0	0	0	0
B$_{iso}$ (Å^2)	0.447	0.494	0.390	0.381	0.377
Ti x	0.5	0.5	0.5	0.5	0.5
y	0.5	0.5	0.5	0.5	0.5
z	0.4854	0.4904	0.5	0.5	0.5
B$_{iso}$ (Å^2)	0.583	0.783	0.849	0.833	0.625
O1 x	0.5	0.5	0.5	0.5	0.5
y	0.5	0.5	0.5	0.5	0.5
z	0.1218	0.1131	0.0	0.0	0.0
B$_{iso}$ (Å^2)	0.710	0.691	0.796	0.768	0.604
O2 x	0.5	0.5			
y	0	0			
z	0.5145	0.5066			
B$_{iso}$ (Å^2)	0.624	0.717			
R (%)	1.32	4.66	4.88	4.90	3.87
wR (%)	2.15	3.36	3.80	3.79	3.99

All parameters in this table are same as those in Table 1.

Table 3

Bond distance of PbTiO_3

	tetragonal						cubic
Pressure	0.0001	1.0	3.3	6.0	9.3	10.3	11.9
Ti-O1	1.756(3)	1.73636)	1.758(8)	1.771(6)	1.800(9)	1.935(8)	-
Ti-O1	2.390(4)	2.344(9)	2.268(1)	2.175(8)	2.091(1)	1.945(1)	-
Ti-O2x4	1.981(2)	1.988(2)	1.970(3)	1.956(2)	1.945(1)	1.937(1)	-
(Ti-O)	2.012	2.005	1.984	1.962	1.945	1.938	1.931
Pb-O1 x4	2.805(2)	2.810(2)	2.784(3)	2.767(2)	2.751(5)	2.737(7)	-
Pb-O2 x4	2.486(3)	2.499(4)	2.529(5)	2.542(4)	2.553(7)	2.626(6)	-
Pb-O2 x4	3.254(4)	3.201(7)	3.113(9)	3.017(6)	2.951(9)	2.859(8)	-
(Pb-O)	2.848	2.836	2.809	2.775	2.752	2.740	2.730

Bond distance of BaTiO_3

	tetragonal		cubic		
Pressure	0.001 GPa	0.4 GPa	2.5 GPa	4.3 GPa	5.8 GPa
Ti-O1	2.152(2)	2.091(8)	-	-	-
Ti-O1	1.880(1)	1.930(8)	-	-	-
Ti-O2 x4	2.004(1)	2.001(2)			
(Ti-O)	2.008	2.004	1.996	1.989	1.985
Ba-O1 x4	2.830(1)	2.824(2)	-	-	-
Ba-O2 x4	2.799(1)	2.851(6)	-	-	-
Ba-O2 x4	2.8812)	2.817(6)	-	-	-
(Ba-O)	2.837	2.834	2.823	2.813	2.807

The numbers in parentheses denote errors of the last decimal.
(Ti-O), (Ba-O) and (Pb-O) are average values of these bonds.

Table 4

Effective charge defined by κ-refinement

$Ba Ti O_3$		$PbTiO_3$	
Effective charge		Effective charge	
Ba	+1.91	Pb	+1.74
Ti	+2.59	Ti	+2.92
O	-1.50	O	-1.55

Basis sets of DFT and HF are used in the present calculation method by Evarestov et al., (2003).

Mull and WTAO indicate Mulliken charge and Wannier-type atomic orbital (see their paper).