Electron hybridization and anharmonic thermal vibration effect on structure transition of SrTiO₃ at high-pressure and low-temperature.

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Abstract

We execute electron density analysis of SrTiO₃ at low-temperatures up to 80 K and high-pressures up to 11.88 GPa using X-ray single-crystal diffraction experiment and *ab initio* quantum chemical molecular orbital (MO) calculation. The lattice constants of *a* and *c* of tetragonal phase are noticeably decreased with pressure above *P_c* in comparison with those at low temperature below *T_c*. The lattice constant ratio of *c/a* < 1 of the tetragonal phase becomes more extreme with increasing pressure. On the other hand, the ratio below *T_c* is *c/a* > 1 and increases with lowering temperature.

Difference Fourier (D-F) synthesis experimentally proves the residual electron densities $\Delta\rho(\text{xyz})$ are associated with two different effects: electron hybridization bonding electron and anharmonic thermal vibration atoms. The *d-p- π* hybridization between Ti(3*d*) and O(2*p*) orbitals is confirmed in the residual electron density, which is deformed from the ideal spherical density conducted by the atomic scattering factor *f_i* using Hartree-Fock (HF) approximation. MO calculation also reveals the electron hybridization. Anharmonic thermal vibration of atoms yields a large effect to the structure transition. Mulliken charges analysis of MO calculation indicates much smaller charges than their formal ionic charges. Their ionicity increases from cubic to tetragonal above *P_c* and below *T_c*.

30 Keywords

31 Structure transition at high-pressure and low-temperature; Anharmonic thermal vibration:

32 d - p - π hybridization electron density; Molecular orbital calculation

33

34 Introduction

35 Structure changes of ferroelectric crystals under extreme conditions are often induced from the
36 phonon-electron interaction. An antiferro-distortive phase transition of SrTiO₃ (STO) at 105 K was reported
37 [1][2]. At low-temperatures below around 37 K, soft phonon anomaly and quantum fluctuation for the transition
38 were suggested by electron paramagnetic resonance and dielectric measurement [3] [4][5][6]. A super
39 conducting state was confirmed [7]. Optical investigations by Raman and infrared spectroscopy have been also
40 executed for STO at low temperature [8][9]. First principles calculation proposed the transition from
41 ferroelectric to antiferro-distortion in tetrahedral phase [10][11][12][13]. *Ab initio* molecular orbital calculation
42 (MO) has been intensively undertaken to elucidate the dynamical structure change [14][15]. Evidence for a
43 phase transition of STO on (001) surface at low-temperature was proved by RHEED [16].

44 A cubic-tetragonal phase boundary is proposed by the Landau theory of phase transitions with the coupling
45 effect between the order parameter and the volume spontaneous strain [8]. The phase transition mechanism is
46 characterized by the distortion and tilt of the TiO₆ octahedra in the tetragonal phase with nonlinear couplings
47 between the structural order parameter and the volume strain as a function of the applied pressure [17][18][19].

48 Experimental determination of the charge density in cubic STO has been reported by studies employing
49 synchrotron [20], laboratory X-rays [21] and γ -ray diffraction at room temperature [22].

50 The topological analysis of the electron density of STO was discussed based on the X-ray diffraction study
51 at 145 K and theoretical calculation using the density functional formulae [23]. The analysis of the kinetic and
52 potential energy density, derived from the electron density, reveals the stabilizing crystal-forming role of the O
53 atoms in STO. The experimental electron density and the kinetic energy densities are observed [24].
54 Calculations of electron densities are carried out from X-ray diffraction data [25].

55 We aim to elucidate static atomic positional disorder using X-ray single-crystal diffraction experiment of
56 STO at low-temperatures and high-pressures. Difference Fourier synthesis discloses the residual electron
57 density distribution in consideration of bonding electrons and anharmonic thermal vibration. Quantum
58 chemical MO calculation is also undertaken to confirm the effective charge of atoms at the transition under
59 low-temperature and high-pressure conditions.

60

61 Experiment

62 Sample preparation of single crystal STO is described in **supplement**. Sample preparation gives large

63 effects on structure transition and Curie point.

64 Single crystal diffraction study was undertaken using four-circle diffractometer of RIGAK AFC7 with
65 point detector of scintillation counter on 18 kW rotated anode X-ray generator. The highly collimated beam
66 is applied for diffraction experiments under extreme conditions. Precise diffraction intensity measurement at
67 low-temperatures down to 80 K was undertaken. Diffraction studies at high pressures up to 11.88 GPa were
68 made using diamond anvil cell [DAC] designed for single crystal diffraction study [26]. Pressure is measured
69 by the ruby fluorescence system [27].

70 The structure factor F_{obs} is expressed by

71
$$F_{cal}(\vec{h}) = K \sum_j a_j f_j(\vec{h}) \sum_{js} T_{js}(\vec{h}) \exp\{2\pi i(hx_{js} + ky_{js} + lz_{js})\} \quad (1)$$

72 Atomic scattering factor f_j of j atom was provided by Hartree-Fock approximation. Anomalous dispersion
73 parameters were taken into account in $f = f_o + \Delta f' + i\Delta f''$. The least-squares refinement is conducted by

74 minimization of Δ :
$$\Delta = \sum_h w(\vec{h}) \left\{ \left| F_{obs}(\vec{h}) \right| - \left| F_{cal}(\vec{h}) \right| \right\}^2$$

75 Result and discussion

76 The lattice constants were determined by least-square calculation based on the peak refinement of 25
77 reflections of the single-crystal diffraction. The lattice constant changes as a function of temperature and
78 pressure are presented in **Table A.1 and A.2 in appendices**. The transition pressure (P_c) from cubic to
79 tetragonal phase is at about 7 GPa and in the low-temperature experiments the transition temperature (T_c) is
80 about 100K. These P_c and T_c are in a good agreement with previously reported data [7].

81 In order to clarify the pressure and temperature dependence of the lattice constants, two compression curves
82 are presented in **Fig. 1**. The compression of a and c of the tetragonal phase are noticeably decreased at
83 high-pressures in comparison with those at low-temperature. The ratio of c/a of the tetragonal phase in
84 high-pressure with $c/a < 1$ becomes more extreme with increasing pressure above P_c . On the other hand, the ratio
85 at low temperature below T_c is $c/a > 1$ and increases with lowering temperature. The observed lattice constants
86 and atomic positions of two phases at high-pressure and low-temperature are listed in **Table A.1 and A.2 in**
87 **appendices** respectively. The tetragonal structures are formed by rotation of TiO_6 octahedron around the c axis
88 due to the displacement of oxygen atoms.

89 Two Ti-O1 distances enormously decrease in the tetragonal structure at both low-temperature and
90 high-pressure. On the other hand, four Ti-O2 increases with pressure. The rotation of four O2 in the (001) plane

with keeping the four-fold rotation axis is more extended with increasing pressure. The bond distance ratio of Ti-O2/Ti-O1 of the tetragonal phase induces the distortion of octahedron of TiO₆. The bond distance ratio of the tetragonal phase at high-pressure is much larger than at low-temperature, as shown in **Table 1**. Since the rotation induced by the compression is related to $c/a < 1$ in the tetragonal phase, the more rotation promotes the distinct changes. The bond distance changes with pressure and temperature are presented in **Fig. A.1 in appendices**. Every four Sr-O1 and Sr-O2 distances in the tetragonal phase remarkably decreases with pressure above P_c , although Sr has twelve coordinations with O in the cubic phase.

Pressure effect to the structure is much more remarkable than thermal effect. Average bond $\langle \text{Sr-O} \rangle$ is much more compressed than $\langle \text{Ti-O} \rangle$ under the both conditions. The measurable tolerant factor of

$$t = \frac{\langle \text{Sr-O} \rangle}{\sqrt{2} \langle \text{Ti-O} \rangle} \text{ using the average bond lengths in Table 1 decreases with compression and cooling. The}$$

factor proves a more deformation of tetragonal lattice with these conditions.

Electron density distribution

Difference Fourier synthesis (D-F) of $\{|F_{obs}(hkl)| - |F_{cal}(hkl)|\}$ discloses the deformation electron density (ED) distribution. The residual ED $\Delta\rho(xyz)$ expresses the nonspherical deformation electron cloud by

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

The atomic scattering factor f_i in the structure factor $F(hkl)$ applies Hartree-Fock approximation, which is composed of the spherical ED distribution model without any interaction from the nearest or second neighbor atoms. D-F maps based on the harmonic oscillator model show the deformation of ED around Sr and Ti atomic positions in the projection on to (001). Aspherical residual ED distributions are recognized around the Ti position at ambient conditions. The distributions show the non-spherical bonding electron and anisotropic anharmonic thermal vibration of atoms. The ED along the Ti-O bond is good agreement with the first principles calculations and molecular orbital calculations at ambient conditions [10][11][13][14][28].

Numbers of 3d-electrons of Ti are reduced with more ionization. Sr has an outer shell electron (valence electron) orbitals of only 5s electron which is a spherical electron orbital. The D-F map at ambient conditions in

118 **Fig. 2** shows the $d-p-\pi$ hybridization between t_{2g} electron of Ti($3d$) and p_x electron of O($2p$). The ED
119 distribution around Ti with increasing pressure is presented in **Fig. A.2 in appendices**. These maps prove the
120 more localization of ED, resulting in more ionic character in the tetragonal phase. The localization is enhanced
121 with increasing pressure above P_c . The π bond character gradually disappears with successive pressure.

122 The same bonding nature of the $d-p-\pi$ bond in the octahedral site in the ferroelectric orthorhombic
123 perovskite KNbO_3 [29] and ferroelectric tetragonal perovskite PbTiO_3 were found by maximum entropy
124 method using the X-ray single crystal diffraction intensities. *Ab initio* model calculation [30] proves O valence
125 electrons in BaTiO_3 are strongly hybridized with Ti. The ED feature around Ti at ambient conditions accords
126 with the ED calculations [22][31]. Sr valence shell electrons do not exhibit asphericity and deformation of the
127 electron orbital, because of $5s$ electron.

128 The difference of Ti-O and Sr-O bond distances in the tetragonal phase can be explained by **Fig. A.1**, in
129 which the D-F maps of the tetragonal phase at 10.28 GPa and 80 K. The thermal vibration of the O1 atom
130 interprets two positive peaks along the c axis around O1 in the map at 80 K. Electron densities of both Ti and Sr
131 are elongated to the direction of the c axis. The $c/a > 1$ of the tetragonal phase at low-temperature can be
132 explained by the positional disorder in the direction of the c axis. The D-F map at 10.28 GPa proves the residual
133 ED is elongated to the a -direction. The two maps specify the difference in thermal dynamical vibration of atoms
134 of the tetragonal phases under low-temperature and high-pressure conditions.

135

136 **Anharmonic thermal parameter**

137 The distortion of ferroelectric substance is disclosed by the thermal vibration of atoms, which is introduced
138 as thermal parameters $T_j(hkl)$ in the structure refinement. The parameters are indicators of the atomic positional
139 disorder (lattice average) and dynamical disorder (time average) of the atomic vibration in the crystal structure.
140 Harmonic oscillation of atom cannot make any shift of the atomic position, because the harmonic potential do
141 not shift the minimum of the parabolic potential well. ED ascribed to the dynamical disorder can be discussed
142 only by anisotropic anharmonic thermal vibration of atoms in consideration of higher-order tensors than the
143 conventional second-rank thermal parameters.

144 From X-ray diffraction analysis, anharmonic thermal vibrations of all atoms are enhanced with thermal
145 energy and cause the deformation of the lattice [26]. On the other hand, the localization of the valence electron
146 around the cation position is more enhanced under higher-pressure.

147 Anharmonic thermal analyses of titanate and niobate perovskite have been performed using synchrotron
148 radiation and hot neutrons [32][33]. The motions of the split atom model and the rotator model are obtained in
149 the present phase transition.

150 We adopted a multimodal distribution in the probability density function using cumulant expansion and
151 Gram-Charlier series expansion [34][35]. We take into account of fourth-rank in $T_g(hkl)$ in eq. (1). Since the
152 factors above fifth-rank have a large correlation with each other, they are not reliable. Consequently they are not
153 applied in the calculation. The anharmonic equation of the cumulant and Gram-Charlier series expansions are
154 detailed in **Table A.3 in appendices**. They can be interpreted by the atomic positional disorder and atomic
155 vibration. Electron density in D-F maps of cubic STO based on harmonic model (left side) and anharmonic
156 oscillation model (right site) are presented in **Fig. 3**.

157 Anharmonic model in the tetrahedral phase at low-temperatures reveals a large anisotropy in both Sr and Ti.
158 Anharmonic thermal vibrations of O (including O1 and O2) in both cubic and tetragonal phases are more
159 obvious than Sr and Ti. O1 and O2 show noticeable anisotropic anharmonic parameters below T_c , as shown **Fig.**
160 **3**. O2 has a variable positional parameter and more flexibility than O1.

161

162 **MO calculation and Mulliken charge**

163 The electronic structures, (band structure, density of state and ED distribution), have been examined with
164 emphasis on the covalency effects of ferroelectrics. Structure studies of dynamical properties of perovskites
165 have been published by LDA [36] and the local spin density approximation was reported by GGA calculations
166 [37]. The electronic structure of a wide range of perovskites was examined using *ab initio* HF method [38]. A
167 number of different approximations correlation functional including hybrid exchange techniques have been
168 developed. Many methods are compared with previous quantum mechanical calculations [11][12][13][14].

169 In the present study, *ab initio* calculation of the electronic structure is performed using the quantum
170 chemical MO calculation program package of Gaussian-09 [38]. Structural models were based on the atomic
171 coordinates experimentally determined by the precise structure analyses by single crystal X-ray diffraction study.
172 The results of the calculation are visioalized by program GaussianView [39], which is the graphical interface
173 available for Gaussian-09.

174 We applied HF and DFT for all calculations using program Gaussian-09 at different pressures and
175 temperatures with the 3-21G and 6-31G basis set. We applied several structure models including Sr, Ti and O

176 together with H atoms to avoid the lone-paired electrons of oxygen. The selected structure models are the
177 distribution of atoms perspective to $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ directions.

178 Surface of the highest occupied molecular orbitals surface at various pressures and temperature are
179 presented in **Fig. A.4** and **Fig. A.5 in appendices**. High-energy orbital surface indicates the $d-p-\pi$ bond between
180 Ti and O, which is shown in **Fig. 4**. The orbitals clearly show the π bond in the figure. The calculated MO
181 figures are in accordance with the D-F map observed by the residual ED distribution of the $d-p-\pi$ bond. No
182 bonding orbital is found in MO around Sr atoms, because valence electron of Sr is $5s$. Since MO calculation
183 reveals the static electron orbits, it does not disclose the atomic vibration of atoms.

184 Mulliken charges indicate the effective charges for Sr, Ti and O ions. The calculated charges are presented
185 at variable temperatures and pressure in **Table 2**. The charges of Ti, Sr and O are much smaller than their
186 formal ionic charges. The covalent nature of the Ti–O bond is proved, as already discussed from the residual
187 ED in the D-F map. However, the charge of Sr remains a little closer to the formal charge. In the tetragonal
188 structure at high-pressures above P_c , Ti and Sr increase their ionic characters. Mulliken charges of Ti, Sr and O
189 increase their ionicity with changing structure from cubic to tetragonal at high-pressures above P_c . The charge of
190 Ti ion increases with increasing pressure and lowering temperature. It infers the perovskite structure is
191 composed of the rigid octahedra of TiO_6 . But Sr atom seems to be placed in the open space. The ionicity is
192 accelerated in the tetragonal phase. Trigger of the rotation may be induced by the approach of the compression
193 toward the limit of the Ti–O bonds of antiferroelectric tetragonal phase.

194

195 **Conclusion**

196 Precise diffraction intensity measurement at extreme conditions can reveal ED in the D-F maps indicating
197 the electron hybridization of $d-p-\pi$ bond of Ti and O electron around Ti. ED ascribed to the dynamical disorder
198 can be discussed only by anisotropic anharmonic thermal vibration of atoms. The pressure dependence of ED is
199 more localized and more ionized with elevating pressure.

200 The compressions of the lattice constants of a and c of tetragonal phase are noticeably decreased at pressures
201 above P_c . The lattice distortion of $c/a < 1$ of the tetragonal phase becomes more intensified with increasing
202 pressure. On the other hand the ratio at low temperature below T_c is $c/a > 1$ and increases with lowering
203 temperature. The difference in the lattice constants is induced by rotation of O2 atomic positions in two phases
204 between high-pressure and low-temperature experiments.

205 Observed Mulliken calculated by *Ab initio* MO charges of Ti, Sr and O are much smaller charges than their
206 formal ionic charges. The increase in their charges indicates more ionic at the transition from cubic to tetragonal
207 above P_c and below T_c , which is coincident with the experimental results of the D-F observations.

208

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215

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260

261 **Figure caption**

262 **Fig. 1** Solid and open circles respectively indicate the lattice constants of a and c from the high-pressure and
263 low-temperature experiments. The lattice constants of a_t^* and c_t^* of the tetragonal phase are normalized to the
264 pseudocubic lattice ($a_t^* = 1/\sqrt{2} a_{\text{tetr}}$ and $c_t^* = 1/2 c_{\text{tetr}}$). The error in the lattice constant is less than the presented
265 circles and squares.

266 **Fig. 2** Residual electron density distribution in the D-F maps on the (001) plane of the SrTiO₃ cubic phase at
267 ambient conditions shows the d - p - π hybridization between t_{2g} electron of Ti(3d) and p_x electron of O(2p). TiO₆
268 octahedron in the cubic phase has the site symmetry of $m\bar{3}m$. Dotted lines show the d - p - π hybridization.

269 **Fig. 3** Harmonic oscillation model (left side) and anharmonic model (right side) in the D-F map on (001)
270 plane show the ED distributions at the TiO₆ and SrO₈ polyhedron at ambient conditions. Four positive peaks
271 near Ti and Sr atoms in the cubic phase found in harmonic model disappear in consideration of anharmonic
272 thermal vibration atoms.

273 **Fig. 4** MO calculation is executed using the method of HF and basis set of 3-21G. In the MO on the
274 projection perpendicular to the $\langle 010 \rangle$ direction, Red and green colors are positive and negative orbitals,
275 respectively. Hybridization between Ti(3d) and O(2p) at the TiO₆ octahedral site forms a d - p - π bond. Obvious
276 hybridization is not found around Sr atom.

277

278 **Table caption**

279 **Table 1** Bond distance

280 The numbers in parentheses denote errors of the last digit. Tolerant factors are obtained from the observable
281 average bond distances.

282 **Table 2** Mulliken charges

283 Mulliken charges of all atoms in STO are individually determined by using the model of HF/3-21G. The
284 calculated charge of O_{cal} is defined for the neutrality of the bulk crystal. Those of O1(-2e) and O2(-2e) are
285 different each other and they are not same as O_{calc}, because H atoms are imaginary added to O1 and O2 to
286 neglect the lone-paired coordination.

287

Table 1

Bond distance at high-pressure condition							
Press (GPa)	<Sr-O>	Sr-O1 x4	Sr-O2 x2	<Ti-O>	Ti-O1 x2	Ti-O2 x4	Tolerant
cubic <i>Pm3m</i>							
0.0001	2.761(2)			1.952(2)			1.000
1.35	2.757(2)			1.949(2)			1.000
5.10	2.736(3)			1.934(3)			1.000
tetragonal <i>I4/mcm</i>							
7.38	2.669(3)	2.612(3)	2.727(3)	1.931(3)	1.922(3)	1.935(3)	0.977
10.28	2.572(3)	2.431(2)	2.713(3)	1.945(3)	1.909(3)	1.963(3)	0.935
11.88	2.523(3)	2.339(2)	2.706(3)	1.957(3)	1.894(2)	1.988(3)	0.912

Bond distance at low temperature							
Temp (K)	<Sr-O>	Sr-O1 x4	Sr-O2 x2	<Ti-O>	Ti-O1 x2	Ti-O2 x4	Tolerant
cubic <i>Pm3m</i>							
300	2.761(5)			1.952(5)			1.000
190	2.761(5)			1.952(5)			1.000
120	2.760(6)			1.951(6)			1.000
100	2.758(6)			1.960(6)			1.000
tetragonal <i>I4/mcm</i>							
95	2.630(6)	2.759(6)	2.500(7)	1.977(6)	1.952(6)	1.989(5)	0.941
85	2.603(6)	2.755(6)	2.451(5)	1.986(6)	1.988(6)	2.003(5)	0.927

Table 2
Bond distance and Mulliken population change at high pressure

cubic <i>Pm3m</i>					
P (GPa)	Sr(2e)	Ti(4e)	O(-2e)	O _{calc}	
0.0001	1.174	1.786	-0.883	-0.987	
1.35	1.032	1.874	-0.850	-0.968	
5.10	0.949	1.883	-0.894	-0.944	
tetragonal <i>I4/mcm</i>					
	Sr(2e)	Ti(4e1)	O1(-2e)	O2(-2e)	O _{calc}
7.38	1.133	1.929	-0.934	-0.906	-1.021
10.28	1.141	1.948	-0.936	-0.914	-1.030
11.88	1.227	1.989	-0.935	-0.921	-1.072

Bond distance and Mulliken population change at low temperature

cubic <i>Pm3m</i>					
T (K)	Sr(2e)	Ti(4e)	O(-2e)	O _{calc}	
300	1.174	1.786	-0.883	-0.987	
190	0.925	1.830	-0.890	-0.918	
120	0.865	1.834	-0.895	-0.899	
100	0.864	1.834	-0.896	-0.899	
tetragonal <i>I4/mcm</i>					
	Sr(2e)	Ti(4e)	O1(-2e)	O2(-2e)	O _{calc}
95	1.131	1.886	-0.891	-0.904	-1.005
80	1.177	1.850	-0.894	-0.907	-1.009

Figure

Figure

Figure

Harmonic oscillator model

Anharmonic oscillator model

Fig. 3

Figure

Fig. 4