Electron density distribution under high pressure analyzed

by MEM using single crystal diffraction intensities

FeTiO₃ ilmenite and others—

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Abstract

Most of ilmenites ABO₃ bearing transition elements have semiconductive and antiferromagnetic properties. In order to elucidate the electron conductivity change with pressure, electron density distribution of FeTiO₃ ilmenite have been executed by single-crystal diffraction intensities measurement at several high pressures up to 8.2GPa with synchrotron radiation at KEK using new DAC with large single-crystal diamond plate windows. The compression mechanism of Fe²⁺Ti⁴⁺O₃ ilmenite has been investigated by the structure analyses. All structure refinements converged to reliable factors R=0.05. The deformation of the FeO₆ and TiO₆ octahedra under pressure was parameterized by interatomic distances, site-volume ratio and Fe²⁺Ti⁴⁺ interatomic distance across the shared edges and shared face. The octahedral deformation is reduced by compression.

Maximum entropy method (MEM) based on F_{obs} (hkl) of $FeTiO_3$ was applied to reveal electron density in comparison with the difference Fourier synthesis based on F_{obs} (hkl)- F_{calc} (hkl). The radial distribution of the electron density indicates more localization of electron around the cation positions. The bonding electron density found in bond Fe-O and Ti-O is lowered with pressure. Neither charge transfer nor electron hopping in FeTiO₃ is possible under pressure. The isotropic temperature factors B_{iso} become smaller with increasing pressure. This is because the atomic thermal vibration is considerably restrained by the compression.

Introduction

Crystal structures analyses at high pressures under nonambient condition have been attractive subjects to understand physical properties of crystalline materials such as solid ionics, ferroelectrics, ferromagnetics and earth interiors. Since synchrotron facilities and miniature diamond-anvil pressure cell (DAC) were developed or improved, structure studies under high pressure have been intensively carried out. The observation of the pressure effects not only on the structure but also on the elastic properties and charge distribution has been executed by X-ray diffraction studies and by the measurements of those physical properties. Raman and infrared spectroscopy also take an advantage of DAC for lattice dynamical studies. The diffraction studies of single crystal or polycrystalline samples have been carried out at high temperatures or low temperatures by means of external electric resistance heater or laser and at low temperatures by cryostat.

Application of the synchrotron radiation (SR) has enhanced and accelerated the high-pressure

crystallography, because of their great advantages for diffraction studies under nonambient conditions. Many aspects of structure changes under compression, such as phase transformation, lattice deformation, cation ordering, decomposition, amorphization and solid reactions due to lattice instability including electronic state change have been elucidated by means of X-ray diffraction, absorption and resonance phenomena using DAC cell. Many beam lines were designed especially for high-pressure studies by means of XAFS, multi-axes diffractometer, powder diffractometer, inelastic scattering spectroscopy, infrared spectroscopy and Mössbauer systems.

High-pressure diffraction studies often encountered several difficulties for in situ observation but the significant progresses in the studies under extreme conditions have been made using SR facilities. The high intensity of SR has the following great advantages: intensive transmittance for anvil and window in the X-ray path, high signal-to-noise (S/N) ratio of the diffraction intensity, detection of the weak diffraction peaks, narrow peak profile and the short measuring period.

A²⁺B⁴⁺O₃ ilmenite and its related compounds have attracted material scientists and crystal chemists because of their practical applications. The compound with a large A cation (A: Mg, Fe, Mn, Co, Zn) and small B cation (B: Si, Ge, Sn, Ti) has many polymorphs, pyroxene, garnet, ilmenite, perovskite. The compression mechanisms of A²⁺B⁴⁺O₃ ilmenites of MgSiO₃ (stable at high-pressures), MgGeO₃ (stable at moderate-pressures) and MgTiO₃ (stable at ambient pressure) were investigated by single-crystal structure analyses under high pressure (Yamanaka, et al, 2005).

Ilmenite structure has the unique face-shared and edge-shared configurations of AO₆ and BO₆ octahedra. Cation-cation interactions in the structure have a significant meaning not only for the degree of disorder but also for physical properties, such as ferroelectric property and magnetism. The present in situ high-pressure investigations on ilmenite-type phase have been carried out using in SPring-8 and KEK synchrotron radiation and MoK α rotating anode X-ray generator. The present investigation aims to clarify the structure changes induced by lattice-electron interaction under high pressure. Pressure dependence of electron density distributions of FeTiO₃ has been elucidated by single crystal diffraction study using SR and maximum entropy method (MEM).

Experiment

Synchrotron radiation for single-crystal diffraction study

In the present experiment we used an optimum wavelength for the high-pressure diffraction study from the SR beam emitted from the bending magnet at BL-02B1 SPring-8, and at BL-10A, KEK. The SR source was monochromated to λ =0.40772Å (E=30.388keV) by Si (111) double crystal monochromater in SPring-8 with 8GeV operation and λ =0.61907Å (E=20.0137keV) in KEK with 2,5GeV. Since a small aperture of DAC window gives a limited diffraction angle, a short wavelength has an advantage for a large reciprocal space, providing a large Q-value. For the intensity integration of the stepping counts, at least hundred steps for each diffraction peak are designed with a pulse motor with 1/1000 per degree in 20. The divergence of the beam from the bending magnet has an advantage from the crystalline mosaicness in comparison with the radiation from the insertion devices, such as wiggler or undulater, which provide too sharp peak profiles for the accurate profile analysis.

The incident beam was converged by Pt-coated mirror and practiced through the evacuated guide pipe. HUBER Eulerian cradle (512.1) seven-circle goniometer and scintillation counter in BL-02B1 were utilized for the present high-pressure diffraction study in SPring-8. A collimator of 100µm in diameter was adopted, because the gasket hole was 200µm and the sample size was several ten microns cross.

A receiving slit of 1° angle was used. An evacuated collimator through the guide pipe approached quite near to the DAC.

Diamond anvil cell for single-crystal structure analysis

The high-pressure single-crystal X-ray diffraction study on ruby (AI_2O_3) and pyrope ($Mg_3AI_2Si_3O_{12}$) have been made up to 31 GPa and 33 GPa respectively by Kim-Zajonz et al. (1998) and Zhang et al. (1998). Single-crystal structure analyses under pressure often encounter the following difficulties for the intensity measurement: hydrostaticity, large blind region due to pressure cell, X-ray absorption, small sample space and sample centering in the beam. Our DAC solves these difficult problems and enables us to discuss electron density distribution under pressures up to 50 GPa (Yamanaka et al., 2002).

Generally beryllium hemispheres or plate windows have been used as the backing plates for single-crystal diffraction measurement, because beryllium has a very low X-ray absorption. However, the backing plate gives many broad and fairly strong spotty powder rings. These rings are often overlapped with diffraction peaks of sample and make profiles of those peaks ambiguous. These obstacle rings interrupt the intensity measurement.

We have tried to find much more efficient window instead of beryllium. Our DAC consists of large single-crystal diamond plates supporting diamond anvils and corn-shaped angle adjusting steel disk. The (100) plates of large single-crystal diamonds of about two carats have a size of 6mm x 6mm wide and 2mm thick. The thickness is almost same height as 1/8-carat diamond anvils. The plate windows are directly fixed on the (100) table plane of diamond anvil. The diamond plate windows have a quite small absorption effect on the intensities of incident and diffracted beams. And the absorption correction for diffraction intensities becomes much simple because both backing plates and anvils are diamond.

Beryllium plates or disk windows cannot permit diffraction studies under pressures higher than 20 GPa because of their softness. Diamond plate windows are allowed to achieve the diffraction studies over 50 GPa in case of diamond anvil with table and culet plane of 1mm and 400µm in diameter.

A large diamond plates perform a wide window with maxim diffraction angle of 70° . Since single-crystal diamond plates are transparent widows, these plates are very convenient for the alignment of opposed diamond anvil and setting sample in the DAC. The present DAC can be easily installed on the four-circle diffractometer. The specification of the DAC is detailed in Yamanaka et al., (2001).

Pressure transmitting media is used in order to preserve hydrostatic pressures. A mixture of ethanol and methanol is used as pressure transmitting media at pressures up to 15 GPa. The FeTiO₃ single crystal of $40\mu m \times 60\mu m \times 20\mu m$ was placed in the gasket hole of $250\mu m$ in diameter together with pressure marker (ruby chips) and pressure transmitting media. A spring steel gasket was preindented to $80\mu m$ in thickness beforehand. Pressure measurement was carried out on the ruby fluorescence system (Mao et al., 1978, 1986).

Electron density distribution expressed by Maximum Entropy Method (MEM)

In order to comprehend the bonding or nonbonding character, we need a more precise determination of the electron density distribution. The difference Fourier synthesis encounters the problem of the ambiguity in the observed electron density distribution induced from the termination effect of Fourier series. Electron density distribution analysis by Maximum-Entropy Method (MEM) conquers the problem and presents a much more reliable electron distribution. MEM statistically estimates the most reliable electron density distribution from the finite observed structure factors. The problem caused by the

termination effect in the difference Fourier synthesis would be ignored.

In order to understand the bond nature and electronic state under high pressure, diffraction intensity measurements are conducted using DAC but it has a limited diffraction angle. Hence the number of $F(\vec{h})$ in the limited reciprocal space lowers the result of structure refinement by the least-squares method based on $F(\vec{h})$.

The ideal entropy (S) of MEM was basically originated from Jaynes (1968) and the theory of MEM was applied for structure analysis by Collins (1982); Sakata and Sato (1990); Sakata et al., (1992) and Yamamoto et al., (1996). S is represented by

$$S = -\sum_{j} \rho'(\vec{r}_{j}) \ln \frac{\rho'(\vec{r}_{j})}{\tau'(\vec{r}_{j})}$$
⁽¹⁾

where the electron density $\rho'(\vec{r}_i)$ and the preliminary electron density $\tau'(\vec{r}_i)$ are

$$\rho'(\vec{r}_j) = \frac{\rho(\vec{r}_j)}{\sum_j \rho(\vec{r}_j)}$$
(2)
$$\tau'(\vec{r}_j) = \frac{\tau(\vec{r}_j)}{\sum_j \tau(\vec{r}_j)}$$
(3)

j is a minimum pick cell in the unit cell. $\tau(\vec{r}_i)$ indicates an electron density one cycle before the iteration

of least-squares calculation of $\rho(\vec{r})$. Fourier transform of the estimated $\tau(\vec{r}_j)$ provides $F_{cal}(\vec{h})$:

$$F_{cal}(\vec{h}) = V \sum_{j} \tau(\vec{r}_{j}) \exp(-2\pi i \vec{h} \cdot \vec{r}_{j})$$
(4)

where V is the unit cell volume. $\rho(\vec{r})$ is defined by

$$\rho(\vec{r}_j) = \tau(\vec{r}_j) \exp\left[\frac{\lambda F_0}{N} \sum_{h} \frac{1}{\sigma^2(\vec{h})} \left\{ F_{obs}(\vec{h}) - F_{cal}(\vec{h}) \right\} \exp(-2\pi i \vec{h} \cdot \vec{r}_j) \right]$$
(5)

where *N* is the number of the observed $F_{obs}(\vec{h})$; λ is a Laguerre's undermined coefficient. Fo is a total number of electrons. The calculated $\rho(\vec{r}_j)$ replaces $\tau(\vec{r}_j)$ in the next cycle and calculates $F_{cal}(\vec{h})$ again by eq. 2 and 3. The least-squares calculation is repeated up to the cycle where $\sigma(\vec{r}_j)$ satisfies the condition of $\rho(\vec{r}_j) \cong \tau(\vec{r}_j)$. And finally the calculation is converged to obtain the most reliable

$$F_{\scriptscriptstyle mem}(h) \, {\rm and} \, \, \rho_{\scriptscriptstyle MEM}(\vec{r}_{\scriptscriptstyle j}) \, .$$

Pressure dependence of electron density distribution of FeTiO₃ ilmenite

A large attention has been given to the structure transformations of oxides bearing transition elements from the industrial use of ferroelectrics, ferromagnetics and solid ionics. The structure changes are often induced from the lattice-electron interaction under compression. The electron density distribution of Fe²⁺Ti⁴⁺O₃ ilmenite (R3, Z=6) has been investigated as a function of pressure by X-ray single-crystal diffraction study at high pressures up to 8.2 GPa using Maximum-Entropy Method (MEM). FeTiO₃ has an antiferromagnetic property at ambient conditions. The structure has face-shared and edge-shared configurations of the FeO₆and TiO₆ octahedra. The cation-cation interactions in the structure have a significant meaning not only for the degree of disorder, such as corundum or LiNbO₃ type structure, but also for physical properties of magnetism. Diffraction intensity measurements at high pressures of 3.6, 5.3 and 8.2 GPa were made using wavelength λ =0.61907Å of SR at BL-10A, KEK with the above mentioned DAC. The intensities observed by stepping count mode are converted to the structure factor after the several aforementioned corrections.



Figure 1



The measurement at ambient pressure was executed using the laboratory X-ray source with MoK α radiation. Structure parameters including anisotropic thermal parameters are in **Table 1**.

 Fe^{2+} (3d⁶) and Ti⁴⁺ (3d⁰) cations across the shared face are alternatively located along the *c* axis. The FeO₆ and TiO₆ octahedra are respectively located in a plane parallel to (001) and linked with the adjacent octahedra with shared edge.

The cation positions move in the direction of the *c* axis with pressure and tend to approach the center of FeO_6 and TiO_6 octahedra with increasing

Table 1	
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Structure refinement of FeTiO₃ ilmenite at various pressures.

Pressure		1atm	3.6GPa	5.3GPa	8.2GPa
20		80	80	80	80
$\sin \theta / \lambda (\text{\AA}^{-1})$		0.91	0.90	0.90	0.90
a((Å)	5.08810(4)	5.0678(11)	5.0567(13)	5.0398(10)
c((Å)	14.0910(10)	13.9956(9)	13.8892(10)	13.7968(12)
	c/a	2.769	2.762	2.747	2.738
Vol	(Å ³)	315.93(5)	310.40(13)	307.57(16)	303.49(12)
No. re	ef.(used)	408	215	214	200
R	(%)	1.81	3.29	3.56	4.19
wF Fe (00z)	R (%) z	2.99 0.355430(9)	4.40 0.35570(5)	4.71 0.35568(5)	5.78 0.35611(7)
	$B_{eq}(Å^2)$	0.457(1)	0.390(9)	0.36(1)	0.22(1)
Ti (00z)	z	0.146429(9)	0.14641(5)	0.14641(6)	0.14695(8)
	$B_{eq}(A^2)$	0.352(1)	0.31(1)	0.28(1)	0.29(1)
O(xyz)	х	0.31717(9)	0.3169(5)	0.3169(5)	0.3185(8)
	У	0.02351(9)	0.0233(5)	0.0232(5)	0.0233(7)
	Z	0.24498(3)	0.24538(9)	0.24533(10)	0.24600(15)
	$B_{eq}(A^2)$	0.48(1)	0.33(11)	0.30(11)	0.35(15)
Fe	$U_{11}U_{22}$	0.00582(3)	0.0050(2)	0.0046(3)	0.0021(3)
	U ₃₃	0.005732(1)	0.004860(3)	0.004362(3)	0.004136(5)
	U_{12}	U ₁₁ /2	$U_{11}/2$	$U_{11}/2$	U ₁₁ /2
	$U_{13} U_{23}$	0	0	0	0
Ti	$U_{11} U_{22}$	0.00433(3)	0.0037(3)	0.0033(3)	0.0040(4)
U ₃₃		0.004709(1)	0.004430(4)	0.004123(4)	0.002976(6)
	U ₁₂	U ₁₁ /2	U ₁₁ /2	U ₁₁ /2	$U_{11}/2$
	$U_{13} U_{23}$	0	0	0	0
0	U_{11}	0.0050(1)	0.0037(10)	0.0027(10)	0.0043(16)
	U ₂₂	0.0057(1)	0.0043(10)	0.0043(11)	0.0051(14)
	U ₃₃	0.006784(1)	0.004844(7)	0.005017(7)	0.003313(10)
	U_{12}	0.00209(9)	0.0023(9)	0.0021(9)	0.0018(14)
	U_{13}	0.000221(8)	0.00055(8)	0.00028(8)	0.00025(12)
	U ₂₃	0.001462(8)	0.00039(8)	0.00024(9)	0.00025(12)
	$G_{iso}(x10^{-4})$	0.180	0.198	0.197	0.196

pressure. The regularity of TiO_6 octahedra is enhanced at higher pressure. Bond distances of Fe-O, Ti-O, O-O octahedral edges, selected bond angles, FeO_6 and TiO_6 volumes are presented as a function of pressure in **Table 2**. All oxygen atoms of O1 to O9 (indicated in **Figure 1**) occupy a crystallographic equivalent position. These octahedra have a pair of three equivalent bond distances, M-O (sh face) and

M-O (unsh face) (M: Fe and Ti). M-O (sh face) and M-O (unsh face) bond lengths are presented as a function of pressure. Bond angle \angle O-M-O (sh face) corresponds to the O1-O2-O3 shared face and \angle O-M-O (unsh face) to the O4-O5-O6 face for AO₆ and O7-O8-O9 for BO₆ opposite to the vacant space.

Three bonds of M-O (sh face) of FeO₆ and TiO₆ octahedra are longer than those of M-O (unsh face). The longer M-O (sh face) bonds are more shortened under pressure than shorter M-O (unsh face). Therefore, the cation shifts toward the center of octahedra. The compressions of Ti-O bond lengths Selected interatomic distances and bond angles of FeTiO₃ are smaller than those of Fe-O. The shared edge of octahedra, O-O (sh edge) has a less influence by compression than the O-O (unsh edge). With increasing pressure M-O (sh face) of the both octahedra is more compressive than M-O (unsh face). The FeO₆ octahedra exhibit a more obvious tendency than theTiO₆.

In order to clarify the polyhedral distortion and finite homogeneous strain, Robinson et al., (1971) proposed the quadratic elongation λ (= $\Sigma(\theta_r 90^\circ)/11$) and the bond angle variance σ^2 (= $\Sigma(I/I_o)^2/6$): λ indicates a deviation from the center-to-vertex distance I_o for an ideal octahedron with *mm* symmetry whose volume is equal to that of the distorted octahedron.



Table 2

Interatomic distances and bond angles

Pressure		1 atm	3.6 GPa	5.3 GPa	8.2 GPa	β.
Fe-Osh	x 3	2.2017(6)	2.185(2)	2.178(3)	2.170(4)	1.8(2)
Fe-Ounsh	x 3	2.0795(6)	2.064(3)	2.059(3)	2.041(4)	2.2(2)
<fe-o></fe-o>		2.1406	2.125	2.119	2.106	2.0(2)
Ti-Osh	х3	2.0867(6)	2.077(3)	2.069(3)	2.066(5)	1.3(2)
Ti-Ounsh	х3	1.8745(6)	1.868(3)	1.863(3)	1.859(4)	1.0(1)
<ti-0></ti-0>		1.9806	1.973	1.967	1.963	1.1(2)
Fe-Ti		2.9450(3)	2.9210(10)	2.9065(11)	2.8858(15)	2.47(7)
Fe-Fe₁ Fe-Fe₂		3.0029(2) 4.0743(3)	2.9918(7) 4.0275(9)	2.9850(8) 4.0091(10)	2.9769(8) 3.9704(14)	1.07(4) 3.09(6)
Ti-Ti₁		2.9925(2)	2.9800(7)	2.9732(8)	2.9602(8)	1.31(6)
Ti-Ti 2		4.1267(4)	4.0860(10)	4.0671(12)	4.0548(16)	2.18(3)
O-O 1		2.6975(9)	2.686(5)	2.680(5)	2.684(7)	0.7(3)
0-0 ₂ 0-0 ₃		3.2184(9) 3.0539(5)	3.205(5) 3.020(2)	3.198(5) 3.009(2)	3.180(8) 2.981(3)	1.4(2) 2.9(1)
O-O 4		3.0073(7)	2.975(3)	2.965(3)	2.930(5)	3.1(2)
O-O 5		2.9210(6)	2.911(3)	2.906(3)	2.886(4)	1.4(3)
O-O 6		2.6041(6)	2.593(2)	2.582(3)	2.586(4)	0.9(4)
O-O 7		2.8851(6)	2.872(3)	2.860(3)	2.857(5)	1.3(2)
∠O-Fe-O 1**	***	75.55(2)	75.84(10)	75.94(10)	76.40(15)	
∠O-Fe-O ₂ ∠O-Fe-O₃		89.20(2) 90.97(2)	88.83(8) 90.54(10)	88.78(8) 90.46(10)	88.15(11) 90.08(14)	
∠O-Fe-O₄		101.40(3)	101.75(10)	101.86(11)	102.34(15)	
∠O-Ti-O 1		80.54(2)	80.58(10)	80.72(11)	81.01(15)	
∠O-Ti-O 2		82.01(2)	82.02(8)	81.90(9)	82.23(13)	
∠O-Ti-O ₃		93.34(2)	93.30(9)	93.12(9)	93.27(13)	
∠O-Ti-O ₄		102.36(3)	102.28(11)	102.46(11)	101.90(15)	
∠Fe-O-Ti		86.70(2)	86.49(11)	86.33(11)	85.84(16)	

* ≤(bx10-3GPa-1) : Coefficients of compressibility

** Metal-metal distances are indicated as follows:
 1: across shared edge between adjacent metal sites;
 2: across vacant octahedral position, along <001>.

*** Oxygen-oxygen distances are indicated as follows:

1: Fe-Ti shared face; 2: Fe site, face opposite the shared face;

3: Fe site, shared edge; 4: Fe site, unshared edge;

5: Ti site, face opposite the shared face; 6: Ti site, shared edge; 7: Ti site, unshared edge.

****Oxygen-matal-oxygen angles are indicated as follows;

1:shared face; 2:shared edge; 3:unshared edge; 4:unshared face

Fig. 2

Residual electron density distribution of FeTiO3 observed by diferenceFourier synthesis Fobs-Fcal.on the (010) plane at 0.1Mpa.The data set of $\sin \theta / \lambda < 1.22$ is used for the calculation. The contour lines are drawn from 0.2 to 4.0 eÅ-3 with 0.2 eÅ-3 intervals

Hence an ideal polyhedron is characterized by λ =1.0 and σ^2 =0. These terms of σ^2 and λ of FeO₆ and TiO₆ presented in **Table 3** indicate their anisotropic compressions. Since σ^2 and λ of TiO₆ are much smaller than those of FeO₆, the latter is much more distorted than the former. These deformations of both octahedra are not obviously changed with increasing pressure according to λ of FeO₆ and TiO₆. This is probably because the extremely large void space in the unit cell accepts the deformations of both octahedra. FeO₆ does not show a noticeable Jahn-Teller distortion induced from Fe²⁺ (3d⁶), because the site symmetry of the cation is $\overline{3}$.

In comparison with the difference Fourier synthesis, MEM calculation using $F_{mem}(\vec{h}) - F_{cal}(\vec{h})$ brings much more precise electron distribution which indicates the deformation electron density. Difference Fourier synthesis obtained from the $F_{abs}(\vec{h}) - F_{cal}(\vec{h})$ within the reciprocal space of $\sin\theta/\lambda < 1.22$ (Figure 2) indicates a vague electron density distribution, because of the errors in the observed intensities and the termination effect of data sets.

The $\sigma(\vec{h})$ of the error of $Fobs(\vec{h})$ in eq. (5) of the present MEM calculation empirically applied the least-squares of MEM using each data set at various pressures are summarized in Table 4. The Laguerre's undermined coefficient λ in eq. (5) is also presented in **Table 4**. The accuracy of the electron density analysis is tested by the various observed numbers of $F_{obs}(\vec{h})$ related with the reciprocal space in $\sin\theta/\lambda$, because the diffraction angle using DAC is limited up to 70 ° in 20. The test proves that the electron density distributions using $F_{obs}(\vec{h})$ are not so big different, but the localization of the electron distribution is a little clearly indicated by the data sets of a larger reciprocal space.

MEM analysis reveals the valence electron densities of Fe and Ti. Figure 3 shows the electron

	1 atm	3.6 GPa	5.3 GPa	8.2 GPa		
Pressure						
FeO ₆						
Volume($Å^3$)	12.575	12.327	12.183	11.955		
V/Vo	1	0.98	0.969	0.951		
λ	1.0273	1.0277	1.0274	1.0278		
σ^2	92.81	93.77	92.71	93.03		
height*(Å)	2.4899(9)	2.462(3)	2.445(3)	2.410(4)		
TiO ₆						
Volume(Å ³)	9.984	9.891	9.770	9.742		
V/Vo	1	0.991	0.979	0.976		
λ	1.0278	1.0276	1.0277	1.0258		
σ^2	86.52	85.97	86.45	80.00		
height(Å)	2.2071(9)	2.203(3)	2.185(3)	2.189(4)		
* octahedral height along <001>						

Octahedral quadratic elongation (λ) and angle variance (σ^2)

Table 3

bonds, respectively. The former two densities more increase in the bonding electron on their bonds with compression than the latter two. On the contrary, the compression reduces the bonding electron on both Fe-O(unsh) and Ti-O (unsh) bonds. The electron density between Fe²⁺(3d⁶) and Ti⁴⁺(3d⁰) cations across the shared face becomes smaller with pressure.

distribution on (010) plane at 0.0001, 3.6, 5.3 and 8.2 GPa. At ambient pressure the electron density distribution around Fe²⁺ (3d⁶) and Ti⁴⁺ (3d⁰) cations are not spherical but elongated along the direction of the c-axis due to d-electron orbital. The external compression by DAC give an effect on the Coulomb potential in M-O (M=Fe,Ti) bonds and a repulsive force is enhanced under high-pressure condition. The Electron densities on the Fe-O (sh) and Ti-O (sh) bonds are increased with pressure than those on the Fe-O (unsh) and Ti-O (unsh) Table 4

Maximum Entro	py Method c	calculation o	f FeTiO ₃
			0

				-	
Pressure	1 atm*	1 atm	3.6 GPa	5.3 GPa	8.2 GPa
No. of					
reflections	933	408	215	214	200
Maximum					
20	120	80	80	80	80
Maximum					
$\sin\theta/\lambda$	1.22	0.91	0.90	0.90	0.90
a [†]	1.0	1.0	1.2	1.2	1.5
b	1.5	1.5	3.5	4.0	4.5
λ (× 10 ⁻⁵)	0.2	0.5	0.3	0.35	0.35
No. of the MEM					
cycles	863	285	801	779	879
R-factor(%)	6.33	4.08	5.13	5.63	6.36

 σ (h)= a x (sin θ/λ) + b *Data without using diamond anvil cell

The localization of the valence electron around the cation position is more enhanced under higher pressure. MEM proves that the radial electron distribution between Fe and Ti is reduced with increasing pressure. The radial distribution shown in **Figure 4** indicates the localization of electron around cations is more intensified with increasing pressure. Then the electron conduction between Fe and Ti along <001> becomes lower with pressure. On the basis of MEM calculation, the pressure dependence of the electron radial distributions obviously shows the more localization of electron around cations with increasing pressure. However, the electron conductivity measurement using polycrystalline samples, which will be reported elsewhere, reveals the more conductive at higher pressure. It is probably because the conduction is more intensified by shortening the band gap under compression.



3.2GPa



Figure 3

The electron-density on the (010) plane calculated with the MEM at 0.1 MPa, 3.6, 5.3 and 8.2 GPa. The data sets of sin $\theta/\lambda < 0.90$ are used for the MEM calculations. The contour lines are drawn from 0.2 to 4.0 eÅ⁻³ with 0.2 eÅ⁻³ intervals.

Summery

X-ray diffraction study gives the electron densities distribution including the valence electron and the bonding electron. The charge density analysis based on the diffraction intensities provides the effective charge of ions and dipole moment. The charge distribution reveals a significant admixture of the covalency in the chemical bond and the appropriate charge state of the cations and turns out to be far from a formal charge. The significant *d*-electron population indicates that some degree of non-sphericity of the valence electron distribution around cation.



Figure 4

Pressure dependence of the electron density distributions of FeTiO3 ilmenite observed by MEM between Ti and Fe along the <001> direction at various pressures

The pressure dependence of the bonding electrons of FeTiO₃ is shown by MEM (**Figure 3**). It is clarified by the radial distribution shown in **Figure 4** that the electron density between Fe²⁺ (3d⁶) and Ti⁴⁺ (3d⁰) cations across the shared face becomes smaller with increasing pressure. This is because the repulsion of *d*-electrons between two cations is enlarged with the external compression. The FeTiO₃ valence electron localization around the cation position is more enhanced under higher. Neither charge transfer nor electron hopping in FeTiO₃ is possible under pressure. The deformation of FeO₆ and TiO₆ octahedra from the regular octahedron is reduced by compression. The isotropic temperature factors B_{iso} of FeTiO₃ in Table 1 are reduced with increasing pressure. This is explained by the reason that the atomic thermal vibration is considerably restrained by the compression.

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