

Electrical conductivity of FeTiO₃ ilmenite at high temperature and high pressure

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Electrical conductivity measurements were carried out on synthetic FeTiO₃ ilmenite with a KAWAI-type multianvil high-pressure apparatus (USSA-5000). The temperature range was 300–600 K and the pressure range was 8–16 GPa. The activation energy and the activation volume were calculated to be 0.21 eV and -0.22 cm³/mol, respectively. The low value of the activation energy and the small negative activation volume are consistent with conduction by hopping of small polarons, suggested to be an intervalence charge transfer $\text{Fe}^{2+} + \text{Ti}^{4+} \rightarrow \text{Fe}^{3+} + \text{Ti}^{3+}$. In comparison with the electrical conductivity of (Mg_{0.93},Fe_{0.07})SiO₃ ilmenite with a larger activation volume of -0.90 cm³/mol, we suggest that $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ hopping conduction is the dominant conduction mechanism in (Mg,Fe)SiO₃ ilmenite and significant lattice disorder was involved at high temperature.

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I. INTRODUCTION

Ilmenite, FeTiO₃ is a naturally occurring mineral commonly found as an inclusion in kimberlites, a type of igneous rocks derived from the upper mantle down to depths of some 400 km and thus pressures of 12–13 GPa.¹ The ilmenite structure was determined by Barth and Posnjak,² and has been investigated at high temperature and high pressure.^{3–5} Under ambient conditions, FeTiO₃ has a stable ilmenite structure. Above 16 GPa, the ilmenite phase transforms to orthorhombic perovskite structure.^{6,7} The ilmenite structure may also be an important one for metasilicates undergoing high-pressure transformations in the Earth's mantle because (Fe,Mg)SiO₃ adopts this structure at pressures of the transition zone in the mantle.^{8,9} Thus, the measurements of electrical conductivity of ilmenite FeTiO₃ at high temperature and high pressure can help in understanding the electrical conductivity of a structural analogue (Mg,Fe)SiO₃ ilmenite and the conductivity structure of transition zone in the mantle.

FeTiO₃ ilmenite is one of mixed-valence transition metal-bearing minerals, in which Fe may be in two different oxidation states Fe²⁺ and Fe³⁺, similarly Ti may be in Ti³⁺ and Ti⁴⁺. Thus the complexities of conduction mechanism in FeTiO₃ arise^{4,5} because the transfer of electrons can occur between the two valence states such as $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ and $\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$, the charge transfer or intervalence transition can also occur between different metal cations such as $\text{Fe}^{2+} \rightarrow \text{Ti}^{4+}$. The corresponding conduction process is, often loosely, termed “hopping,” “hopping of small polaron,” or “charge transfer.” Some authors have studied the electrical conductivity of ilmenite FeTiO₃ at high pressure or at high temperature. Andreozzi *et al.*¹⁰ carried out the conductivity measurements on synthetic FeTiO₃ and the mineral ilmenite in the temperature range 400–1273 K at different oxygen partial pressure, obtaining activation energy in the range 0.10–0.40 eV for synthetic FeTiO₃ and 0.13–0.21 eV for the natural ilmenite mineral. Resistance-pressure studies¹¹ on

synthetic samples of ilmenite show that there is a decrease in resistance (i.e., conductivity increase) as a function of pressure, Seda¹² showed a similar trend that the resistance value at 3.1 GPa is ~ 2.3 times the value at 11.5 GPa at room temperature. However, to our knowledge, the electrical conductivity of FeTiO₃ ilmenite has not been investigated at high temperature and at high pressure so far, as a result the conduction mechanism at high temperature and high pressure has not been well resolved. In this study, we carried out the measurements of electrical conductivity on FeTiO₃ ilmenite under pressure up to 16 GPa and temperature up to 600 K. The values of conductivity measurements were fitted to the formula $\sigma = \sigma_0 \exp(-\Delta H/kT)$ using a nonlinear Levenberg-Marquardt procedure,¹³ where $\Delta H = \Delta E + P\Delta V$. Then the activation volume ΔV was determined for the first time which usually pertains to conduction mechanism. On the other hand, our previous measurements¹⁴ on (Mg_{0.93},Fe_{0.07})SiO₃ ilmenite at pressures of 25, 30, and 35 GPa and temperatures of 300 to 1200 K showed a very large pressure dependence of the electrical conductivity, the determined activation volume of -0.90 cm³/mol was much larger than those of other Fe-bearing silicates minerals. It was another motivation to measure the electrical conductivity of the structural analogue FeTiO₃ ilmenite at high temperature and high pressure in this study.

II. EXPERIMENTAL

A. Sample synthesis

Starting materials were Fe₂O₃ and TiO₂ powders, with a ratio of Fe₂O₃:TiO₂=1:1.01 to ensure a small amount of excess TiO₂ than iron oxide. The reagents of Fe₂O₃ and TiO₂ were dried at 1100 °C for 24 h, then mixed and ground in a mortar for about 40 min. The mixture was compressed to a cylinder with 10 mm in diameter and 5–10 mm in length, and heated at 1200 °C for 3 h with oxygen fugacity controlled to be $f_{\text{O}_2} = 10^{-6}$ bar by a CO₂:H₂ gas mix of 152:248.

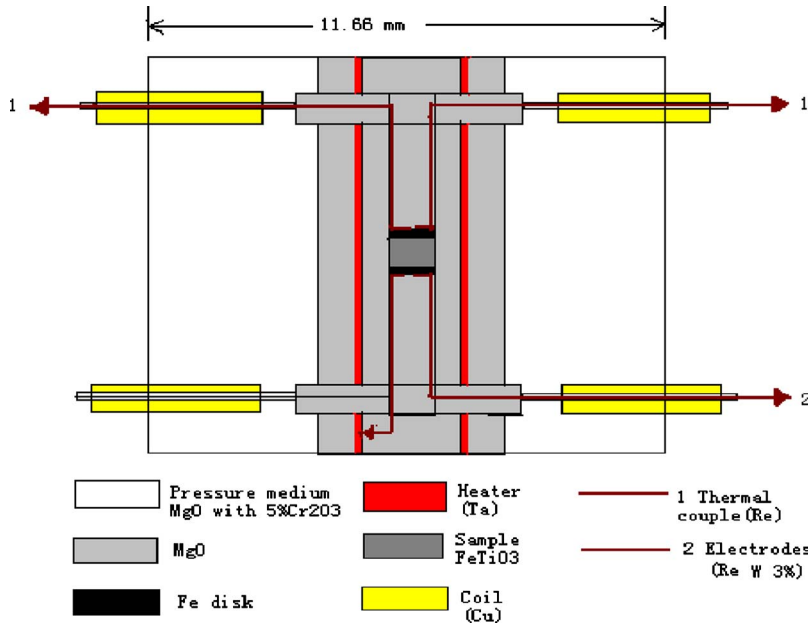


FIG. 1. (Color online) The sample assembly for resistance measurement at simultaneous high temperatures and high pressures.

Then the sample was quenched in water. Powder x-ray diffraction indicated that the core of the cylinder sample is composed of FeTiO_3 only and the rim is $\text{FeTiO}_3 + \text{Fe}_2\text{TiO}_5$. FeTiO_3 is found in nature as a primary component of ilmenite with a normal rhombohedral crystal system, lattice parameters are $a = 5.087 \text{ \AA}$ and $c = 14.042 \text{ \AA}$. The core part was used for measurements of electrical conductivity.

B. Electrical conductivity measurements

The high-pressure and -temperature experiments were performed with a KAWAI-type multianvil high-pressure apparatus (USSA-5000) at the Institute of the Earth’s Interior, Okayama University. The sample assembly for the electrical conductivity measurement is schematically shown in Fig. 1. The edge length of tungsten carbide anvils was 32 mm and their truncated edge length was 7.0 mm. A pyrophyllite gasket of 3.30 mm in thickness was used. The octahedral pressure medium was composed of $\text{MgO} + 5\% \text{ Cr}_2\text{O}_3$ with 14 mm edge length, a 3.0 mm diameter hole was drilled in it to accommodate a heater of Ta foil with $13.5 \times 18.0 \text{ mm}$ width and 0.02 mm thickness. Temperature was measured using a $\text{W}_{97}\text{Re}_3 - \text{W}_{75}\text{Re}_{25}$ thermocouple with 0.76 mm diameter. The thermocouple junction was placed on one end of the sample, another W_{97}Re_3 wire was placed on the other end of the sample for electrical conductivity measurement. The pressure was calibrated at ambient temperature using phase transition of Bi (2.5 and 7.7 GPa) and GaAs (18.8 GPa). It is known that pressure may drop by heating to some degree; however, the pressure drop mainly occurs above 1000 K from our experience of *in situ* x-ray diffraction. The temperature was only increased to 600 K in this study, thus the pressure drop by heating was negligible. In our measurements of electrical conductivity, the temperature was increased from 300 to 600 K with a step of 50 K or 100 K, and the pressure was increased from 8 to 16 GPa with a 4 GPa step. The experimental processes for electrical

conductivity were described in detail by Katsura and co-workers.^{15,16}

The electrical circuits for measurement are shown in Fig. 2. The reference resistance was 100Ω . A sinusoidal signal with amplitude of 1.0 V and frequency of 0.1 Hz was applied to the circuit. Sample resistance was obtained by dividing the voltage applied on the sample by the circuit current. The circuit current was obtained from the voltage applied on the reference resistance connected to the sample in a series. The details have been given elsewhere.^{14,15} To obtain high quality and stable data, background noise was always monitored during the data acquisitions and, to avoid bias in the data, several data acquisitions were repeated.

III. RESULTS

After the experiments, the sample was embedded in epoxy, and polished to examine the length and diameter of the sample. The electrical conductivity was calculated with the following equation:

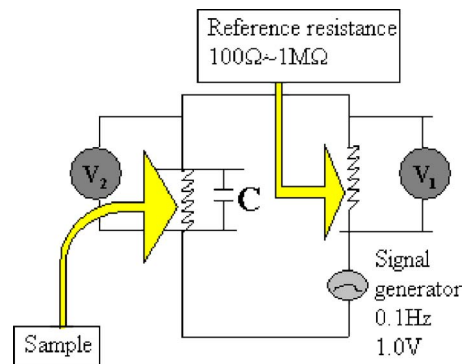


FIG. 2. (Color online) The diagram of electrical circuits for the measurement of sample’s conductivity.

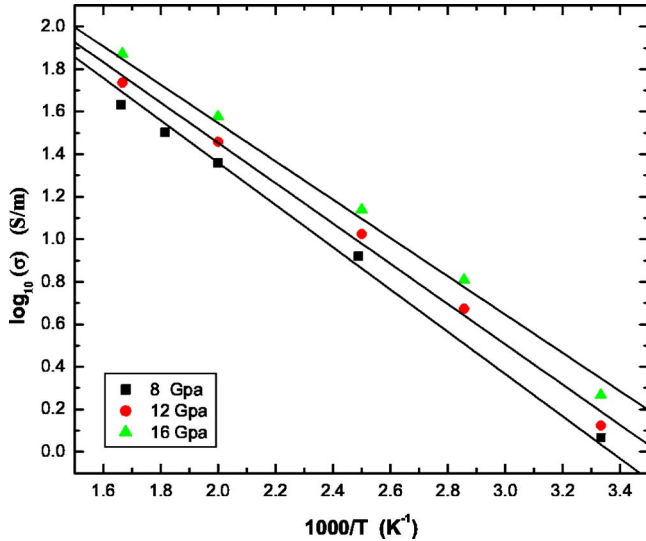


FIG. 3. (Color online) Logarithm of electrical conductivity vs reciprocal temperature for FeTiO₃ ilmenite, fitting data at 8, 12, and 16 GPa yields the parameters in Eq. (2).

$$\sigma = \frac{L}{R \times S} \text{ (S/m)}, \quad (1)$$

where L is the length of sample, R is the direct current resistance and S is the section area. The changes of L and S under pressure are negligible in Eq. (1) for the calculation of the electrical conductivity, because L and S change only by order of several percent under pressure in this study, on the other hand, the conductivity changes by orders of magnitude.

The electrical conductivities of FeTiO₃ ilmenite at 8, 12, and 16 GPa are shown as a function of reciprocal temperature in Fig. 3. The temperature and pressure dependence of electrical conductivity is usually expressed as¹⁷

$$\sigma = \sigma_0 \exp(-\Delta H/kT), \quad (2)$$

where σ_0 is a pre-exponential factor, activation enthalpy $\Delta H = \Delta E + P\Delta V$, in which ΔE is the activation energy and ΔV is the activation volume; P is pressure, k is the Boltzmann constant, and T is absolute temperature. All measured conductivities from 300 K to 600 K at 8, 12, and 16 GPa were fitted to Eq. (2) using a Levenberg-Marquardt nonlinear procedure,¹³ obtaining the pre-exponential factor, activation energy, and activation volume to be $\sigma_0 = 2231.08$ S/m, $\Delta E = 0.21$ eV, and $\Delta V = -0.22$ cm³/mol, respectively.

IV. DISCUSSION AND CONCLUSIONS

Figure 3 shows the electrical conductivity of FeTiO₃ ilmenite increases by a factor of around 40 with increasing temperature from 300–600 K at the same pressure, in agreement with suggestion of Andreozzi *et al.*¹⁰ that FeTiO₃ ilmenite is semiconductor. The determined activation energy 0.21 eV also matches their results of activation energies in the range 0.10–0.40 eV for synthetic FeTiO₃ and 0.13–0.21 eV for the mineral ilmenite. In general, the conclusion that conduction is due to hopping of small polarons

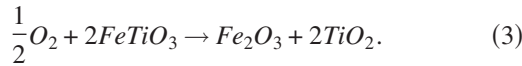
is drawn from the small value of the activation energy and a small negative activation volume (i.e., conductivity increases with increasing pressure).¹⁸ According to our results with the activation energy $\Delta E = 0.21$ eV and activation volume $\Delta V = -0.22$ cm³/mol, the electrical conductivity of FeTiO₃ ilmenite are obviously compatible with conduction by hopping of small polarons. The ionic conduction is eliminated as it usually has a larger activation energy (typically of more than 1 eV) and a positive activation volume, i.e., the electrical conductivity decreases as pressure increases due to more difficult formation of vacancies at high pressure.¹⁸

As to the pressure effect on conductivity of FeTiO₃ ilmenite, the conductivity is expected to increase due to a decrease in atomic distances and an increase of atomic orbital overlap under pressure. The electrical conductivity at 11.5 GPa is ~ 2.1 times the value at 3.1 GPa at 300 K calculated from Eq. (2), in good agreement with Seda¹² that the resistance value at 3.1 GPa is ~ 2.3 times the value at 11.5 GPa at room temperature. Compared to the temperature dependence of conductivity discussed above, the electrical conductivity of FeTiO₃ ilmenite is primarily determined by the temperature but not pressure. A weak pressure effect also supports the small polaron model as the dominant conduction mechanism.¹⁷

Although the Ti⁴⁺ oxidation state is far more common in terrestrial minerals than Ti³⁺, and the existence of Fe²⁺-Ti⁴⁺ assemblages is potentially very common,¹⁹ however, Fe²⁺-Fe³⁺ and Fe²⁺-Ti⁴⁺ coordination clusters may coexist in the same structure, and give rise to homonuclear Fe²⁺ \rightarrow Fe³⁺ and heteronuclear Ti²⁺ \rightarrow Ti⁴⁺ intervalence transitions, thereby complicating the conduction process in FeTiO₃ ilmenite.^{4,5,19,20} There are several lines of evidences pointing to Ti²⁺ \rightarrow Ti⁴⁺ intervalence charge transfer for the conduction mechanism in FeTiO₃ ilmenite: (1) Ti²⁺ \rightarrow Ti⁴⁺ intervalence transition has been assigned in molecular orbital calculations by Sherman²⁰ for FeTiO₃, the calculated energy of Fe²⁺ \rightarrow Ti⁴⁺ charge transfer is 18 040 cm⁻¹ and experimental determined Fe²⁺ \rightarrow Ti⁴⁺ charge-transfer energy is 20 200 cm⁻¹ for ilmenite,²¹ in reasonable agreement with the optical absorption energies that occur in the visible-region (15 000–21 000 cm⁻¹) spectra of numerous Fe-Ti oxides and silicates.^{12,19,21,22} A recent study¹² on ilmenite also found a pressure-induced charge transfer Fe²⁺ + Ti⁴⁺ \rightarrow Fe³⁺ + Ti³⁺, explaining the increase in the ferric component and corresponding decrease in the ferrous component in FeTiO₃ as a function of pressure from ⁵⁷Fe Mössbauer study. (2) A Mössbauer study of the (1-x)Fe₂O₃-xFeTiO₃ series²³ showed that all Fe²⁺ ions in Fe₂O₃-rich samples participate in electron transfer with an equal number of Fe³⁺ ions, this electron transfer continues for the value of x as great as 60%. But no electron transfer between Fe²⁺ and Fe³⁺ cations is observed in the compositional range 0.75 < x < 1.0. In the range 0.75 < x < 1.00, Ti efficiently blocks electron transfer between Fe²⁺ \rightarrow Fe³⁺ ions. Thus, the mechanism of electron transfer in FeTiO₃ ilmenite was attributed to a Fe²⁺ \rightarrow Ti⁴⁺ intervalence transition.^{12,19} (3) An alternative explanation is a pressure-induced chemical reaction

TABLE I. Parameters of the activation energy ΔE and activation volume ΔV for $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ small polarons conduction in silicate minerals.

Sample	P (GPa)	T (K)	ΔE (eV)	ΔV (cm^3/mol)	References
$(\text{Mg}_{0.84}\text{Fe}_{0.16})_2\text{SiO}_4$ olivine	1.2, 40	293–673	0.40	–0.18	24
$(\text{Mg}_{0.89}\text{Fe}_{0.11})_2\text{SiO}_4$ olivine	1.2, 40	293–673	0.42	–0.10	24
$(\text{Mg}_{0.89}\text{Fe}_{0.11})\text{SiO}_3$ perovskite	1.2, 40	293–673	0.48	–0.26	24
Single crystal San Carlos olivine 2013	4, 7, 10	1273–1673	1.35	0.96	17
Al-free perovskite H852	25	1673–1873	0.68		26
Al-bearing perovskite H858	25	1673–1873	0.70		26
$(\text{Mg}_{0.93}\text{Fe}_{0.07})\text{SiO}_3$ Perovskite	23	500–900	0.41		16
(Mg, Fe)O magnesiowüstite	5, 10	<1000	0.3–0.4	–0.60	25
Assemblage of $(\text{Mg}_{0.92}, \text{Fe}_{0.08})\text{SiO}_3$ perovskite and $(\text{Mg}_{0.76}, \text{Fe}_{0.24})\text{O}$	2–40	300–673	0.288	–0.129	18
$(\text{Mg}_{0.93}\text{Fe}_{0.07})\text{SiO}_3$ perovskite	30, 35	300–1400	0.39	–0.06	14
$(\text{Mg}_{0.93}\text{Fe}_{0.07})\text{SiO}_3$ ilmenite	25, 30, 35	300–1200	0.69	–0.90	14



Seda¹² eliminated the possibility of the above oxidation reaction taking place under pressure in their FeTiO_3 samples since there was no evidence of an increase in TiO_2 content suggested by the above reaction. We used two Fe disks to prevent oxygen from reacting with sample FeTiO_3 and kept the phase of FeTiO_3 ilmenite stable during our measurements, thus the above oxidation reaction is also unlikely to occur in our experiment.

The behavior of the electrical conductivity in silicate ilmenite mineral seems quite different. Yokoshi *et al.*¹⁴ first measured the electrical conductivity of $(\text{Mg}_{0.93}, \text{Fe}_{0.07})\text{SiO}_3$ ilmenite at pressures of 25, 30, and 35 GPa and temperatures of 300 to 1200 K, obtaining the activation energy and activation volume of 0.69 eV and $-0.90 \text{ cm}^3/\text{mol}$, respectively. Thus the electrical conductivity of $(\text{Mg}_{0.93}, \text{Fe}_{0.07})\text{SiO}_3$ ilmenite has large pressure dependence. Note the previous studies on olivine $(\text{Mg}, \text{Fe})_2\text{SiO}_4$,^{17,24} magnesiowüstite $(\text{Mg}, \text{Fe})\text{O}$,²⁵ silicate perovskite $(\text{Mg}, \text{Fe})\text{SiO}_3$,^{14,16,24,26} as well as assemblage of perovskite and magnesiowüstite¹⁸ have showed the electrical conductivity of many Fe-bearing mantle silicate minerals are due to hopping of small polarons $\text{Fe}_{\text{Mg}}^\bullet$ (Fe^{3+} at Mg sites) operated in $\text{Fe}_{\text{Mg}}^x \rightarrow \text{Fe}_{\text{Mg}}^\bullet + e'$ ($\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$), we suggest that the conductivity in silicate ilmenite is also due to $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ small polarons conduction consequently. Table I lists parameters of the activation energy and activation volume for $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ small polarons conduction in these silicate minerals. Although the activation energy of 0.69 eV for conductivity in silicate ilmenite is much larger than that of FeTiO_3 ilmenite, the value is much close to the activation energy of 0.68 eV and 0.70 eV of perovskite,²⁶ so the activation energy of 0.69 eV is not in contradiction with conduction by small polaron. Actually, Sherman²⁷ found that $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ transitions are unsymmetrical (Fe^{2+} and Fe^{3+} cations occupy crystallographically different sites) in most silicates, and the larger activation

energies in mixed-valence silicates may result from the asymmetric charge transfer.

In addition, the radius r_p of the small polaron in $(\text{Mg}_{0.93}, \text{Fe}_{0.07})\text{SiO}_3$ ilmenite also supports our suggestion. According to the theory of polaron,^{18,28} if r_p is smaller than, or of the same order as, the lattice parameter, the polaron is a small polaron. Otherwise, it is a larger polaron. We calculate the polaron radius from expression^{18,28}

$$r_p = \frac{1}{2} \left(\frac{\pi}{6} \right)^{1/3} \left(\frac{N}{V} \right)^{-1/3}, \quad (4)$$

where N/V is the number of sites per unit volume. Taking the molar volume of $(\text{Mg}_{0.93}, \text{Fe}_{0.07})\text{SiO}_3$ ilmenite to be 26.354 cm^3 from Smyth and McCormick,²⁹ the number of iron sites per unit volume is $N/V = (1/26.354) \times 0.07 \times 6.02 \times 10^{23} = 1.599 \times 10^{21} \text{ cm}^{-3}$. The radius r_p of the polaron is therefore $r_p = 3.45 \text{ \AA}$, smaller than the lattice parameter of silicate ilmenite ($a = 4.73 \text{ \AA}$). This value is consistent with the definition of a small polaron.

Then we discuss the activation volume of electrical conductivity. Generally, conduction due to hopping of $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ small polarons relates to a small negative activation volume as the most cases listed in Table I; however, there are also several exceptions therein. Xu *et al.*¹⁷ obtained relatively large positive activation volumes of $0.96 \text{ cm}^3/\text{mol}$ for the single crystal olivine electrical conductivity, they eliminated an ionic conduction mechanism which has a positive activation volume of the order of an ionic volume in the range of several cm^3/mol , and suggested that some lattice deformation was involved. Also little disorder was observed in synthetic FeTiO_3 in the experiments using x-ray diffraction at $1050 \text{ }^\circ\text{C}$ ³ and neutron powder diffraction below $1100 \text{ }^\circ\text{C}$,³⁰ being consistent with the small activation volume of $-0.22 \text{ cm}^3/\text{mol}$ for FeTiO_3 ilmenite in this study. It certainly shows the relationship between the activation volume and the lattice deformation. However, a significant amount of disorder was observed above $1100 \text{ }^\circ\text{C}$, $900 \text{ }^\circ\text{C}$, $700 \text{ }^\circ\text{C}$, and $200 \text{ }^\circ\text{C}$ in members of $(\text{FeTiO}_3)_x(\text{Fe}_2\text{O}_3)_{1-x}$ solid solution

with compositions $x=1.0, 0.9, 0.8, 0.7$, respectively.³⁰ On the other hand, comparison of temperature and pressure effects on crystal structure of ilmenite FeTiO₃ at high temperature and high pressure³ showed that the unit cell compression is quite anisotropic at high pressure and the structure changes are smaller, whereas the high-temperature behavior is characterized by nearly isotropic expansion of the unit cell and significant structural distortion. Therefore, we suggest the activation volume of $-0.90 \text{ cm}^3/\text{mol}$ for the electrical conductivity of a structural analogue (Mg_{0.93},Fe_{0.07})SiO₃ ilmenite¹⁴ may be due to large disorder at high temperature up to 1200 K, though further research is necessary to confirm it.

In summary, the measured electrical conductivity of FeTiO₃ ilmenite in this study is contributed to hopping of small polarons due to charge transfer $\text{Fe}^{2+} \rightarrow \text{Ti}^{4+}$, whereas

$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ small polarons conduction is the dominant mechanism in (Mg_{0.93},Fe_{0.07})SiO₃ ilmenite with significant lattice disorder involved at high temperature.

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¹S. E. Haggerty and V. Sautter, *Science* **248**, 993 (1990).

²J. D. Barth and E. Posnjak, *Z. Kristallogr.* **A88**, 265 (1934).

³B. A. Wechsler and C. T. Prewitt, *Am. Mineral.* **69**, 176 (1984).

⁴N. C. Wilson, J. Muscat, D. Mkhonto, P. E. Ngoepe and N. M. Harrison, *Phys. Rev. B* **71**, 075202 (2005).

⁵N. C. Wilson, S. P. Russo, J. Muscat, and N. M. Harrison, *Phys. Rev. B* **72**, 024110 (2005).

⁶A. Mehta, K. Leinenweber, A. Navrotsky, and M. Akaogi, *Phys. Chem. Miner.* **21**, 207 (1994).

⁷K. Leinenweber, W. Utsumi, Y. Tsuchida, T. Yagi, and K. Kurita, *Phys. Chem. Miner.* **18**, 244 (1991).

⁸L. G. Liu, *Earth Planet. Sci. Lett.* **36**, 237 (1977).

⁹A. E. Ringwood, *Earth Planet. Sci. Lett.* **5**, 401 (1969).

¹⁰G. B. Andreozzi, F. Cellucci, and D. Gozzi, *J. Mater. Chem.* **6**, 987 (1996).

¹¹C. Boekema, F. Van Der Woude, and G. A. Sawatzky, *J. Phys. Colloq.* **37**, c-603 (1976).

¹²T. Seda and G. R. Hearne, *J. Phys.: Condens. Matter* **16**, 2707 (2004).

¹³W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes* (Cambridge University Press, Cambridge, 1986).

¹⁴S. Yokoshi, T. Katsura, E. Ito, K. Kawabe, and M. Okube, *COE-21 International Symposium, MISASA*, March 5–6, 2005, Misasa, Japan (unpublished), lecture M13D.

¹⁵K. Fuji-ta, T. Katsura, and Y. Tainosho, *Geophys. J. Int.* **157**, 79 (2004).

¹⁶T. Katsura, K. Sato, and E. Ito, *Nature (London)* **395**, 493 (1998).

¹⁷Y. Xu and T. J. Shankland, *Phys. Earth Planet. Inter.* **118**, 149 (2000).

¹⁸A. Goddat, J. Peyronneau, and J. P. Poirier, *Phys. Chem. Miner.* **27**, 81 (1999).

¹⁹R. G. Burns, *Annu. Rev. Earth Planet Sci.* **9**, 345 (1981).

²⁰D. M. Sherman, *Phys. Chem. Miner.* **14**, 364 (1987).

²¹R. G. J. Strens and B. J. Wood, *Miner. Mag.* **43**, 347 (1979).

²²G. Smith, *Can. Mineral.* **15**, 500 (1977).

²³B. N. Warner, P. N. Shive, J. L. Allen, and L. Terry, *J. Geomagn. Geoelectr.* **24**, 353 (1972).

²⁴T. J. Skankland, J. Peyronneau, and J. P. Poirier, *Nature (London)* **366**, 453 (1993).

²⁵D. P. Dobson, N. C. Richmond, and J. P. Brodholt, *Science* **275**, 1779 (1997).

²⁶Y. Xu, C. McCammon, and B. T. Poe, *Science* **282**, 922 (1998).

²⁷D. M. Sherman, *Phys. Chem. Miner.* **14**, 355 (1987).

²⁸I. G. Austin and N. F. Mott, *Adv. Phys.* **18**, 41 (1969).

²⁹J. R. Smyth and T. C. McCormick, *Mineral Physics and Crystallography: A Handbook of Physical Constants*, edited by T. J. Ahrens (American Geophysical Union, Washington DC, 1995).

³⁰R. J. Harrison, S. A. T. Redfern, and R. I. Smith, *Am. Mineral.* **85**, 194 (2000).