Effect of iron content on electrical conductivity of ferropericlase with implications for the spin transition pressure

The lower mantle constitutes more than 50% of the Earth's volume and plays an important role in the evolution and dynamics of the Earth's interior. The lower mantle is believed to be composed of two main minerals: $MgSiO_3$-rich perovskite (Mg-Pv) and ferropericlase (FP). Since Badro *et al*. [1] experimentally observed the pressure-induced electronic high spin (HS) to low spin (LS) transition of iron in FP under lower mantle conditions, recent experimental and theoretical studies have demonstrated that an electronic HS to LS transition of Fe^{2+} occurs in iron-rich FP at high pressures exceeding 50 GPa. The electronic spin-pairing transition of iron affects many physicochemical properties such as volume, density, incompressibility, optical absorption spectra, sound velocity, electrical conductivity, and Fe-Mg partitioning.

The pressure at which the HS-LS transition occurs would depend on the iron content in FP. Fei *et al*. [2] suggested that the spin transition pressure largely decreases with decreasing iron content in FP, on the basis of the compression curve at room temperature. At the top of the lower mantle, the iron content in FP coexisting with Al-bearing Mg-Pv would be considerably low. Therefore, the accurate determination of the spin transition pressure for iron-poor FP is fundamental in understanding the current mantle structure and mineralogy. However, the low iron content in FP makes it difficult to detect the spin transition because of the weak signal from the electronic state of iron. Electrical conductivity measurement would be a powerful tool for detecting the spin transition pressure of FP as a function of iron content, because electrical conduction in FP occurs through electron hole hopping between ferrous and ferric iron sites. Although high-pressure studies exceeding 30 GPa have been performed using the diamond anvil cell (DAC), the very small sample volume precludes the electrical conductivity measurement of high-resistance materials. In this study [3], the electrical conductivity of FP, $(Mg_{1-x},Fe_x)O$, was measured using the Kawai-type multianvil apparatus (large volume). The recent technical development of high-pressure generation using sintered diamond anvils [4] can allow the accurate electrical conductivity measurement of FP with a lower iron content, because of the use of larger volume samples than in the DAC.

The starting materials were sintered aggregates of FP with various amounts of iron content (x = 0.07, 0.10, 0.13, 0.17, 0.24). The high pressures and high temperatures were generated using a Kawai-type multianvil apparatus with a DIA-type guide block system, SPEED mkII, installed at beamline **BL04B1**. We used sintered diamond cubes with an edge length of 14 mm as a second stage anvil. The anvil truncation was 1.5 mm. The generated pressures were calibrated by *in situ* X-ray diffraction with the Au pressure scale. The cell assembly for the electrical conductivity measurement and X-ray radiography are shown in Fig. 1. One side of the rectangular-shaped sample with a thickness of 0.5 mm was connected to the $W_{97}Re_3$–$W_{75}Re_{25}$ thermocouple and the other side was in contact with a Au electrode electrically connected to the heater through the sintered diamond anvil and guide block. The sample was heated using a pair of TiB_2 sheet heaters. The sample temperature was measured using a thermocouple. Electrical conductivity was measured by a 2-wire method with an alternating current signal with an amplitude of 1 V and a frequency range of 0.1–1 Hz. The samples were once heated to 500 or 600 K and then cooled to room temperature while measuring the conductivity.

All samples examined in this study behaved as a semiconductor. Figure 2 shows the electrical conductivity of FP with various iron contents at 300 K as a function of pressure. At lower pressures, the electrical conductivity of all FP samples increases with increasing pressure. For the FP with higher iron

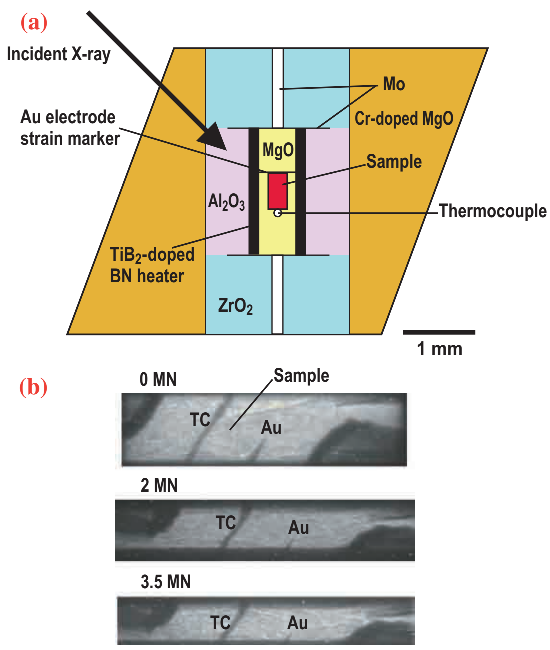

Fig. 1. **(a)** Schematic cross section of the cell assembly used in our experimental runs. **(b)** X-ray radiography images of the sample and the thermocouple through the TiB_2 heater at various press loads (in MN).

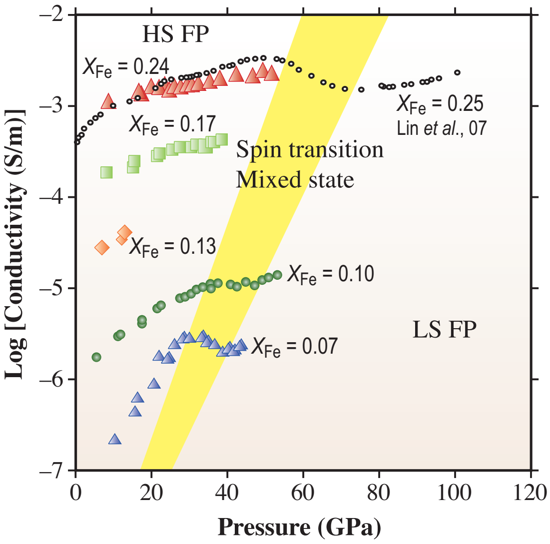

Fig. 2. Electrical conductivities of $(Mg_{1-x},Fe_x)O$ as a function of pressure at a constant temperature of 300 K. At low pressures, the conductivity constantly increases but the conductivity of FP with relatively lower X_{Fe} drops or becomes constant from 30 to 45 GPa. Large symbols denote the data obtained in this study. Small open symbols denote the electrical conductivity of $(Mg_{0.75},Fe_{0.25})O$ obtained from the DAC study.

content (x = 0.17 and 0.24), the electrical conductivity monotonically increases with pressure up to 38 and 53 GPa, respectively. For the FP with lower iron content (x = 0.07 and 0.10), the electrical conductivity slightly decreases or becomes constant with increasing pressure. Further increase in pressure leads to an increase in electrical conductivity. This trend is consistent with that of the electrical conductivity of FP through the HS-LS transition measured at room temperature in the DAC. This conductivity change suggests that the spin transition pressure would decrease with decreasing iron content in FP. FP with lower iron content prefers a smaller ionic radius in the Mg site compared with high-Fe FP. The ionic radius of Fe^{2+} in the HS state is much larger than that of Mg^{2+}, whereas the ionic radius of Fe^{2+} in the LS state is smaller than that of the Mg ion. Therefore, the spin transition of low-Fe FP is likely to occur at lower pressures.

In the present study, we demonstrated that low iron content in FP yields significantly lower spin transition pressure, as shown in Fig. 3. The spin transition of FP affects the nature of Fe-Mg partitioning between Mg-Pv and FP [$K_D = (Fe/Mg)_{Mg\text{-}Pv}/(Fe/Mg)_{FP}$]. Recent laser-heating DAC studies demonstrated a decrease in K_D in San Carlos olivine with a composition of $(Mg_{0.9}Fe_{0.1})_2SiO_4$ from 50 to 100 GPa. For the Al-free system, the iron content (X_{Fe}) in FP coexisting with Mg-Pv is around 0.2. The HS-LS transition in FP should start above 50 GPa. Pyrolite, which is a hypothetical rock composition of the mantle, contains a considerable amount of Al. The effect of alumina on K_D decreases X_{Fe} in FP in association with the incorporation of Fe^{3+} to Pv. On the basis of the present results, the spin transition pressure is expected to be around 35–40 GPa, which is consistent with that at which the K_D determined from rocks with pyrolite composition considerably decreases [5]. Our experimental results suggested that the spin transition in FP occurs at pressures lower than the 50 GPa predicted from FP with high iron content (x > 0.17).

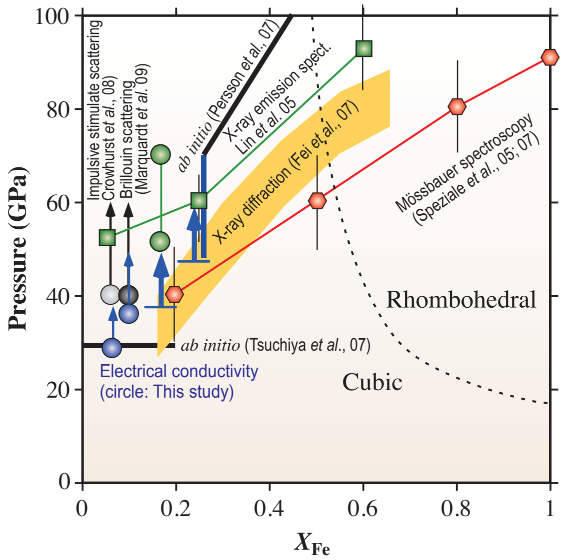

Fig. 3. Spin transition pressures as a function of X_{Fe} in the $(Mg_{1-x},Fe_x)O$ solid solution at 300 K. Blue solid circles indicate the spin transition pressure determined in this study and the arrow represents the mixed spin state. Blue horizontal bars indicate the minimum transition pressure. The other symbols represent the spin transition pressure or crossover predicted by different experimental techniques (modified after [2]).

Takashi Yoshino

Institute for Study of the Earth's Interior, Okayama University

E-mail: tyoshino@misasa.okayama-u.ac.jp

References

[1] J. Badro *et al.*: Science **300** (2003) 789.
[2] Y. Fei *et al.*: Geophys. Res .Lett. **34** (2007) L17307.
[3] *T. Yoshino, E. Ito, T. Katsura, D. Yamazaki, S. Shan, X. Guo, M. Nishi, Y. Higo, K. Funakoshi: J. Geophys. Res.* ***116*** *(2011) B04202.*
[4] E. Ito *et al.*: Earth Planet. Sci. Lett. **293** (2010) 84.
[5] T. Irifune *et al.*: Science **327** (2010) 193.