Electrical conductivity of mantle peridotite at the uppermost lower mantle condition

T Yoshino, T Katsura, D Yamazaki and E Ito

Institute for Study of the Earth’s Interior, Okayama University, 827 Yamada, Misasa, Tottori 682-1093, Japan

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

Abstract. Electrical conductivity of mantle peridotite was measured at 25 GPa and temperature up to 1800 K in a Kawai-type multi-anvil apparatus. The starting material was gel with a composition of fertile spinel lherzolite (KLB1). After the conductivity measurement, mineral phases of run products are composed of magnesium silicate perovskite, ferro-periclase and Ca perovskite. The conductivity value of the peridotite is distinctly higher than those of post-spinel and magnesian silicate perovskite with a composition of (Mg$_{0.9}$Fe$_{0.1}$)SiO$_3$, but lower than that of ferro-periclase. Both absolute values and change in activation enthalpy for the conductivity of the mantle peridotite are similar to those for the silicate perovskite. A presence of aluminous perovskite with substantial amount of ferric iron in crystal structure would enhance bulk conductivity of the lower mantle.

1. Introduction

The lower mantle except for the D” layer is believed to be composed of magnesium silicate perovskite (~80 vol.%) and ferro-periclase (~20 vol.%) with a smaller amount of calcium silicate perovskite [e.g., 1]. In Al-free olivine composition system (post-spinel), iron preferentially partitions into ferropericlase in comparison with the silicate perovskite [e.g., 2]. Thus high iron content in the ferropericlase phase leads to higher conductivity than in the silicate perovskite. Although silicate perovskite is volumetrically the major phase in lower mantle rocks, if ferropericlase is interconnected in lower mantle rocks, lower mantle conductivity could be higher than that expected from perovskite [3].

Yoshino et al. [4] demonstrated that the ferro-periclase in post-spinel cannot interconnect in silicate perovskite matrix. Volume fraction of ferro-periclase in the pyrolitic mantle is around 18 vol.%, which is lower than that of postspinel. Although interconnection of ferro-periclase seems to be more difficult to establish in the lower mantle rocks, addition of Al and Ca to the post-spinel system changes microstructure and phase composition because of appearance of Ca perovskite and decrease in volume proportion of ferro-periclase. As a result, the bulk conductivity behavior would be different from that of the simple system. In this study, we expand upon the work of Yoshino et al. [4] by investigating the interconnection of ferro-periclase in polycrystalline solid silicates of primitive mantle peridotite, KLB-1, by an in situ electrical conductivity measurements. Further, we investigate the effect of Al in silicate perovskite on the bulk conductivity to construct a reference conductivity-depth model in the lower mantle.

1 To whom any correspondence should be addressed.
2. Experimental methods

The starting material was gel with a chemical composition of a fertile spinel lherzolite from Kilbourne’s Hole, New Mexico (KLB1). High pressure and temperature were generated using an octahedral pressure cell without edge in a Kawai-type multi anvil apparatus. A schematic of the cell assembly used in an experiment is shown in Fig. 1. The sample was loaded into a sintered Al₂O₃ sleeve with outer and inner diameters of 2.5 and 1.3 mm, respectively, and sandwiched between two molybdenum disks (1 mm diameter, 0.3 mm thickness) that served as electrodes. Mo electrodes were used so that the oxygen fugacity would be close to the Mo/MoO₂ buffer, which is similar to that of iron-wüstite buffer [5]. The pressure medium was composed of Cr-doped MgO. A LaCrO₃ heater was surrounded by a ZrO₂ sleeve. Two sets of WRe₇-WRe₂₅ thermocouples insulated from the heater by Al₂O₃ sleeves were mechanically connected to each Mo electrode in contact with the sample.

Electrical conductivity was measured by means of a pseudo 4-wire method using alternating current. A sample reference resistance ranging from 10² to 10⁶ ohm was connected to the sample in series. Sinusoidal signals with an amplitude of 1V and frequency of 0.1 Hz were applied to the circuit from a function generator (for detail, see [6-7]). The conductivity measurements were carried out from room temperature (300 K) to the desired temperature (up to 2000 K) with heating and cooling cycles. After the first heating, temperature was kept at the desired temperature for the desired duration to synthesize the post-spinel phase and achieve textural equilibrium. The temperature was changed in a 50–100 K increments or decrements. Electrical conductivity was measured at each temperature step. In the subsequent heating path, reproducibility was confirmed. The conductivity was calculated from sample resistance and the average thickness and length of the sample.

The phase and composition of the samples were checked using micro-focus X-ray diffraction (XRD). Microstructure of samples was observed on the polished section using scanning electron microscopy (SEM).

3. Experimental results

The recovered sample was composed of mainly magnesium silicate perovskite and ferro-periclase with small amount of Ca perovskite. The presence of the small volume fraction of Ca perovskite should have little influence on bulk conductivity because Ca perovskite crystals with an idiomorphic shape are isolated in a matrix composed of magnesium silicate perovskite and ferro-periclase. The perovskite crystals with rounded shape show equigranular texture. Because mean grain size of the magnesium silicate perovskite is less than 1µm, the chemical composition of each phase cannot be determined by a conventional electron microprobe analyzer. There is no reaction zone between sample and Al₂O₃ capsule. In the part adjacent to the Mo electrode, iron loss to the electrode was not observed by high contrast back-scattered image. Chemical composition of the magnesian silicate perovskite is characterized by higher iron and aluminum contents in comparison with that in post-spinel.

Figure 2 shows the electrical conductivity of peridotite sample as a function of reciprocal temperature. The absolute conductivity increases with increasing temperature, and the temperature dependence of conductivity (σ) can be expressed according to the Arrhenian relation:
Table 1. Summary of runs

| Run No. | Sample | T (K)            | Log $\sigma_0$ (S/m) | E (eV) | Remarks               |
|---------|--------|------------------|----------------------|--------|-----------------------|
| 5K903   | KLB1   | 400-1400         | 0.83 (1)             | 0.36 (0) | This study            |
|         |        | 1500-1800        | 3.44 (23)            | 1.12 (7) |                       |
| 5K906a  | PV     | 350-1100         | 0.91 (2)             | 0.46 (0) | Mg#90                 |
|         |        | 1750-2000        | 2.64 (6)             | 0.93 (2) |                       |
| 5K946a  | PS     | 500-1200         | 0.55 (6)             | 0.45 (1) | Fo90                  |
|         |        | 1800-2000        | 2.50 (9)             | 1.01 (3) |                       |
| 5K1014a | FP     | 500-1000         | 1.76 (2)             | 0.35 (0) | Mg#83                 |
|         |        | 1200-1600        | 3.94 (5)             | 1.12 (1) |                       |
| KSI98b  | Al-free PV | 400-900   | 0.60                | 0.41    | Mg#93                 |
|         |        | 1500-2000        | 2.30                | 0.92    |                       |
| XSPR98c | Al-free PV | 1673-1873     | 1.12 (12)           | 0.62 (4) | Mg#91.5               |
|         | Al-bearing PV | 1673-1873   | 1.87 (11)           | 0.70 (4) | Mg#91.5               |

All experiments were conducted above 25GPa.

\(^a\)Yoshino et al. [4]
\(^b\)Katsura et al. [8]
\(^c\)Xu et al. [5]

\[ \sigma = \sigma_0 \exp \left( -\frac{H}{kT} \right) \]  (1)

where $\sigma_0$ is the pre-exponential factor, $H$ is the activation enthalpy, $k$ is the Boltzmann constant, and $T$ is the absolute temperature. The logarithm of the conductivity in higher temperature regions has a steeper slope than that of sample in relatively low temperature regions. The two temperature regions were fitted separately by Eq. (1), the pre-exponential factor ($\sigma_0$) and activation enthalpy ($H$) are summarized in Table 1. The activation enthalpy of the sample in the high temperature region above 1500K is 1.1 eV, showing a constant activation enthalpy up to 1800K. In the low temperature range (400-1400K), the activation enthalpy is 0.36 eV.

4. Discussion

The present study demonstrated that mantle peridotite shows higher conductivity than post-spinel. There are two considerable reasons to explain high conductivity of mantle peridotite. One is interconnection of iron-rich ferropericlase in mantle peridotite and the other is increase of Fe$^{3+}$ in (Mg,Fe)SiO$_3$ perovskite due to Al incorporation to perovskite structure.

The former interpretation is more unlikely based on the following arguments. Because volume fraction of ferro-periclase in the mantle peridotite is much smaller than that of post-spinel, it is more difficult to establish interconnection of ferro-periclase. In addition, the activation enthalpy of conductivity of a bulk rock should correspond to that of a conductive phase if the conductive phase establishes interconnection in the resistive matrix [9]. The fact that conduction mechanism of ferro-periclase changes from

![Figure 2](image-url)
small polaron to large polaron migration around 1000 K [4,10] is inconsistent with the observation showing a change of activation enthalpy around 1500 K from the present study. Rather, the switching temperature of activation enthalpy for mantle peridotite is close to the temperature at which the dominant conduction mechanism switches from small polaron to ionic conduction for magnesium silicate perovskite [11]. The activation enthalpy (~0.4 eV) in the low temperature region (400-1400K) is similar to those of the silicate perovskite [4]. In this temperature region, transportation of small polarons (electron hole hopping between Fe$^{2+}$ and Fe$^{3+}$) has been interpreted as the dominant conduction mechanism. Relatively high activation energy (>1.0 eV) observed at high temperatures (>1400 K) may be derived from another intrinsic mechanism such as ionic conduction, which occurs at higher temperatures through the creation of cation vacancies. Therefore, the conductivity of silicate-perovskite would control the electrical conductivity of the mantle peridotite under the lower mantle condition.

The more probable interpretation to explain higher conductivity of mantle peridotite is the Al incorporation to (Mg,Fe)SiO$_3$ perovskite, leading to higher Fe$^{3+}$ concentration due to the charge couple substitution even if the oxygen fugacity is low [12,13]. The mantle rocks are thought to contain significant amount of Al. Al enters the MgSiO$_3$ perovskite structure in amounts well above the mantle aluminum content, making the presence of other aluminous phases unlikely [14]. In Al$_2$O$_3$-bearing systems there is a marked increase in the degree to which Fe (Fe$^{2+}$ + Fe$^{3+}$) partitions into perovskite [15]. In peridotitic mantle, where the perovskite phase should contain 4 to 5% Al$_2$O$_3$ by weight, the perovskite has essentially the same Fe/(Fe$^+$+Mg) ratio as coexisting ferro-periclase [e.g., 16]. Xu et al. [5] reported a significant effect of aluminum on the conductivity of perovskite. The (Mg,Fe)SiO$_3$ perovskite containing 2.89 wt.% Al$_2$O$_3$ has an electrical conductivity about 3.5 times higher than that of Al-free perovskite. The conduction mechanism in perovskite has been interpreted to be small polaron conduction, because the Al-bearing perovskite has about 3.5 times the amount of Fe$^{3+}$ as the Al-free sample. Therefore, high conductivity obtained from this study can be explained by a dominant presence of Al-bearing perovskite in the mantle peridotite. In summary, Al-bearing perovskite is likely to govern the bulk electrical conductivity of the lower mantle.

Acknowledgments
This work was supported by Grant-in-Aids for Scientific Research, No. 18740280 and 13440164 to TY and TK, respectively, from the Japan Society for Promotion of Science.

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