



Electrical conductivity of wadsleyite as a function of temperature and water content

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ABSTRACT

Electrical conductivity of wadsleyite was measured at 16 GPa using a KAWAI-type multi-anvil press under controlled oxygen fugacity. Water-doped and -undoped samples were used to examine the effect of water on conductivity. Two water-doped wadsleyite samples used for the conductivity measurements contained 0.3 ± 0.01 and 1.2 ± 0.02 wt.% water. The temperature ranges for the conductivity measurements were 500–2000 K for water-undoped samples and 500–1000 K for water-doped samples. Above 1500 K, the electrical conductivity values are essentially the same among different runs with an average activation enthalpy of 1.5 eV, suggesting that small polaron conduction should dominate. Below 1000 K, the conductivity systematically increases with increasing water content, suggesting proton conduction as a dominant conduction mechanism. Electrical conductivity of anhydrous wadsleyite in the mantle transition zone should be about 3×10^{-2} S/m in the normal geotherm. Hydration enhances the conductivity of wadsleyite; by containing 0.1 wt. % water, the conductivity of wadsleyite increases by 0.3 log units. The conductivity jump associated with the dry olivine–wadsleyite transition is only 0.7 log units. A dry olivine–wadsleyite conductivity model well agrees with the current semi-global conductivity–depth profiles, thus the concept of a globally hydrated mantle transition zone is not necessary in view of electrical conductivity. The high conductivity observed in the wedge mantle cannot be explained by hydrous wadsleyite. Alternatively, the presence of either phase E or supercritical fluids in the wedge mantle is proposed.

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1. Introduction

Electromagnetic studies have shown that electrical conductivity changes greatly within the upper mantle. Some current reports (Neal et al., 2000; Utada et al., 2003) show an electrical conductivity of 2×10^{-3} S/m at 100 km depth, reaching 1 S/m at the bottom of the transition zone. In the lower mantle, however, a large change in conductivity has not been observed. A variety of phase transitions occur in major minerals in the upper mantle, and therefore, it is expected that the large change in electrical conductivity could be explained by phase transitions.

In addition to such a global scale phenomena, another anomalous increase in conductivity in the upper mantle has been reported. Electrical conductivity profiles at the mantle transition zone beneath northeast China (Ichiki et al., 2001) indicated higher conductivity than that for the stable continental areas (Neal et al., 2000). Although such high conductivity has been attributed to the presence of water in the wedge mantle (Ichiki et al., 2001), there

have been insufficient laboratory experiments to fully quantify the effect of water on mantle minerals.

Olivine transforms to wadsleyite at a depth of 410 km, the latter mineral should be significantly more conductive than olivine to explain the large conductivity increase in the upper mantle. In addition, wadsleyite can contain significant amounts of water (Kohlstedt et al., 1996), so the high conductivity in the wedge mantle could be due to enhancement of electrical conduction by wadsleyite hydration. If this is the case, it may be possible to estimate the water content in the wedge mantle from the electrical conductivity.

The pioneering work of Omura (1991) showed that electrical conductivity of wadsleyite in its stability field is around 10^{-2} S/m. However, this study has been criticized by Duba and von der Gonna (1994) for the lack of control of the chemical environment. Xu et al. (1998) presented the conductivity of wadsleyite and attributed their conduction data purely to small polaron conduction (electron–hole hopping between Fe^{+2} and Fe^{+3} ions). However, Huang et al. (2005) reported the presence of 0.08 wt.% water in Xu et al.'s (1998) wadsleyite sample, and attributed Xu et al.'s conductivity data to proton conduction. Thus, experimental data on the small polaron conduction of wadsleyite is not available. Even though

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Huang et al. (2005) claimed they determined the effect of water on electrical conductivity of wadsleyite, their improper experimental procedure could cause possible formation of fluid phases which may affect the conductivity of hydrous minerals (Yoshino et al., 2006). Hence, electrical conductivity of wadsleyite should be re-investigated with proper experimental techniques.

This paper presents comprehensive new data on small polaron and proton conductions in wadsleyite under appropriate mantle conditions. In this study, electrical conductivity of wadsleyite is measured as a function of water content, which is determined in recovered samples. To investigate the effect of sample water content on electrical conductivity, both water-doped and -undoped samples were used. Small polaron conduction is overshadowed over a wide temperature range by proton conduction and is estimated by subtracting proton conduction from the experimental data.

A conductivity-depth profile is calculated down to 550 km depth using the present experimental data with previously published conductivity data on anhydrous olivine (Constable et al., 1992) and hydrous olivine (Yoshino et al., 2006). This laboratory-based conductivity profile is compared with geophysical observations to discuss temperature and water content in the transition zone.

Electrical conductivity data obtained in this study is used in Yoshino et al. (2008) to constrain the transition zone conductivity structure beneath the oceanic mantle. However, detailed accounts of all experimental procedures are described here. In addition, this paper discusses the conductivity structures in the wedge mantle transition zone and transition zones beneath the stable cratonic regions with the view point of wadsleyite hydration.

2. Experimental procedures

2.1. Sample preparation

Three kinds of starting samples were prepared in the following procedures, namely a single crystal of natural olivine and water-doped and -undoped pre-synthesized wadsleyite.

Initially crack free and visually homogeneous olivine single crystal from China with an average composition of $(\text{Mg}_{0.91}\text{Fe}_{0.09})_2\text{SiO}_4$ (Table 1) was used to prepare disks with a thickness and diameter of 1 mm. In each run, the olivine single crystal was converted to polycrystalline wadsleyite by heating to 1700 K at 16 GPa immediately before the electrical conductivity measurement. Orientation of the single crystal was not considered because the starting material of olivine and the transformed wadsleyite had no relation in crystallographic orientation (Kubo et al., 1998). Although the single crystal olivine was initially water free, a certain amount of water was always found in the recovered wadsleyite samples after conductivity measurements.

Table 1
Composition of single crystal olivine

Oxides	wt.%
SiO ₂	39.86
Al ₂ O ₃	0.00
FeO _(total)	9.47
CaO	0.14
MgO	49.72
MnO	0.13
TiO ₂	0.00
Cr ₂ O ₃	0.16
NiO	0.32
P ₂ O ₅	0.00
K ₂ O	0.00

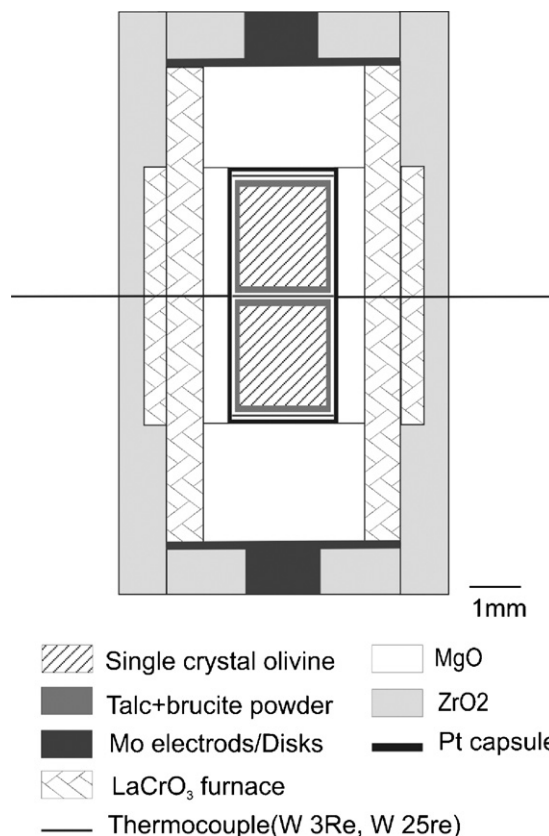


Fig. 1. Schematic cross section of the high-pressure cell assembly for the synthesis of hydrogen-doped samples.

Water-doped wadsleyite was prepared in a separate hot-pressing run prior to the conductivity measurement. This procedure produced controlled water content in the sample and minimized the interference from free water on the conductivity measurement. A mixture of talc and brucite powder, with a 1.4:1 weight ratio, was used as a water source. The water content of the wadsleyite was controlled by changing the amount of talc + brucite mixture. Olivine single crystals and the talc + brucite powder were loaded into Pt tubes with an outer diameter of 2.2 mm and wall thickness of 0.1 mm (Fig. 1), and then sealed by welding. Mo disks were also loaded in the capsule to fix the oxygen fugacity of the sample on the Mo–MoO₂ buffer, whose fugacity is close to that of the Fe–FeO buffer (McCammon, 2005). Two single crystals were loaded into a single Pt capsule, so that one is used for electrical conductivity measurements while the other is for water content measurements.

Hot-pressing experiments were carried out using a KAWAI-type multi-anvil apparatus. The second stage anvils were tungsten carbide (WC) cubes with a truncated edge-length of 6 mm. The sample assembly (Fig. 1) consisted of a pre-sintered MgO + 5% Cr₂O₃ octahedron with an edge-length of 14 mm. A ZrO₂ sleeve surrounding the LaCrO₃ furnace was used as a thermal insulator. The stepped geometry of the furnace was used to reduce the thermal gradient in the cell. A thin MgO sleeve was placed between the heater and Pt capsule to electrically insulate the capsule from the furnace. A W3% Re–W25% Re thermocouple was located on the outside of the Pt capsule to measure the sample temperature. The assembly was compressed to about 16 GPa, and kept at 1370 K for 2 h before quenching. A retrieved sample from the synthesis experiment was then cut into a section 1 mm in thickness and 1 mm in diameter.

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