



# Electrical conductivity model of Al-bearing bridgmanite with implications for the electrical structure of the Earth's lower mantle



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## ABSTRACT

Electrical conductivity measurements of bridgmanite with various Al contents and a constant Mg# of 90 were performed at temperatures ranging from room temperature up to 2000 K at pressures of 26–28 GPa in a Kawai-type multianvil apparatus by impedance spectroscopy analysis. The incorporation of Al into bridgmanite raises its electrical conductivity significantly, but it is a small conductivity variation with respect to the quantity of Al. Synchrotron Mössbauer spectroscopy of recovered samples showed significant amounts of ferric iron in aluminous bridgmanite. The mobility of the charge carriers in bridgmanite was calculated based on the conductivity and the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio. The relationship between the logarithm of the electrical conductivity and the reciprocal temperature is consistent with  $\text{Fe}^{2+}$ – $\text{Fe}^{3+}$  electron hopping (small polarons) as the dominant conduction mechanism at low temperatures (<1400 K) and ionic conduction at higher temperatures (>1600 K). By taking various conduction mechanisms into account, we develop an electrical conductivity model for aluminous bridgmanite as a function of the Al and Fe contents. The small polaron conduction model indicates that the electrical conductivity of aluminous bridgmanite has a maximum at around 0.06 Al atoms per formula unit, and any further increase in the Al content in bridgmanite reduces the conductivity. In contrast, the ionic conduction model indicates that the electrical conductivity simply increases with increasing Al content. The resulting conductivity of Al-bearing bridgmanite first increases up to 0.06 Al atoms per formula unit and then remains constant or increases with increasing Al content at higher temperatures. The increase in conductivity observed in the uppermost part of the lower mantle by electromagnetic studies can be explained by the gradual decomposition of majorite garnet. The deeper lower mantle conductivity would be controlled by small polaron conduction because of the large positive activation volume required for ionic conduction.

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## 1. Introduction

Electrical conductivity measurements provide a useful method for constraining temperature, structure and composition of Earth's deep interior (e.g., see Yoshino, 2010; Yoshino and Katsura, 2013). Conductivity-depth profiles from Earth's surface to the deep mantle have shown that conductivity increases with increasing depth up to 800–1000 km, and becomes constant at greater depths (e.g., Olsen, 1999a, 1999b; Tarits et al., 2004; Kuvshinov et al., 2005; Kuvshinov and Olsen, 2006; Velínský, 2010; Civet et al., 2015). This increase in conductivity in the uppermost lower mantle cannot be explained by a major pressure-induced phase transforma-

tion, because the post-spinel phase transition occurs at approximately 23.5 GPa, and is related to the 660-km seismic discontinuity (Ito and Takahashi, 1989). Bridgmanite is a dominant constituent mineral in the lower mantle. Thus, knowledge of the electric conduction mechanism for bridgmanite is essential to understand the conductivity profile of the lower mantle. Bridgmanite is thought to store much of the Al and Fe content in the lower mantle (Irifune, 1994; Wood and Rubie, 1996). One plausible hypothesis that accounts for the increased conductivity in the uppermost lower mantle is that the increase in the Al content of bridgmanite with increasing depth is associated with the continuous decomposition of majorite garnet to depths of approximately 800 km in pyrolitic composition (Irifune et al., 2010). We report here on a systematic study of the effect of the Al content on the electrical conductivity of bridgmanite to investigate this hypothesis.

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Early studies involving electrical conductivity measurements of bridgmanite were performed using Fe-bearing and Al-free compositions at low temperatures (Peyronneau and Poirier, 1989; Shankland et al., 1993). This work indicated that small polaron conduction characterized by electron-hole hopping between the ferrous and ferric iron sites is a dominant conduction mechanism. Later, Katsura et al. (1998) measured the conductivity of Al-free bridgmanite at higher temperatures in a Kawai-type multi-anvil press, and found that ionic conduction with a strong temperature dependence is dominant at high temperatures rather than small polaron conduction. However, Xu et al. (1998) reported that Al incorporation in bridgmanite strongly enhances the small polaron conduction mechanism. There are large variations in the Al content of bridgmanite under lower mantle conditions. For example, the Al contents of bridgmanite in pyrolitic and mid-ocean ridge basalt (MORB) compositions are 3.5–6 and 15 wt%, respectively (Irifune et al., 2010; Ono et al., 2001). However, the electrical conductivity of aluminous bridgmanite has not previously been measured as a function of its Al content.

In this study, impedance spectroscopy measurements were performed at 26 or 28 GPa and at temperatures up to 2000 K in a Kawai-type multi-anvil apparatus to investigate the effects of the Al content on the electrical conductivity of bridgmanite. To understand the role of the small polaron conduction mechanism, the ferric iron content of the bridgmanite was determined by synchrotron  $^{57}\text{Fe}$  Mössbauer absorption spectroscopy. We then used the results of these measurements to construct a conductivity model of bridgmanite as a function of the Al and Fe contents. Finally, we will discuss the origin of the conductivity increments observed in the uppermost lower mantle and a conductivity-depth profile of the lower mantle based on the proposed conductivity model.

## 2. Experimental procedure

The starting materials were synthetic orthopyroxene ( $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{SiO}_3$ ) powders containing various amounts of aluminum ( $\text{Al}_2\text{O}_3 = 0, 4, 7$  and 11 wt.%). To measure its electrical conductivity, the sample powder was placed in an  $\text{Al}_2\text{O}_3$  sleeve with an inner diameter of 1.3 mm and a thickness of 1 mm. Molybdenum electrodes (1.3 mm-diameter) were then placed in contact with the sample; the measured conductivity included that of the electrodes in addition to that of the sample. The oxygen fugacity was controlled using a Mo/MoO<sub>2</sub> buffer, which is close to or slightly higher than an iron-wüstite buffer (Xu et al., 1998). Two sets of WRe<sub>3</sub>–WRe<sub>25</sub> thermocouples were mechanically connected to each of the Mo electrode in contact with the sample, and were insulated from the LaCrO<sub>3</sub> furnace using  $\text{Al}_2\text{O}_3$  and MgO insulators. The assembly consisted of a Cr<sub>2</sub>O<sub>3</sub>-bearing MgO pressure medium, a ZrO<sub>2</sub> thermal insulator and a cylindrical LaCrO<sub>3</sub> furnace. Tungsten carbide cubes with truncated edge lengths of 3 mm were used. The conductivity measurement cell design is described in detail elsewhere (Yoshino et al., 2008a).

Xu et al. (1998) found that the iron loss from the sample to the electrodes during synthesis of the high-pressure phase prior to performing the conductivity measurements leads to abnormally low conductivity values, and thus emphasized the importance of pre-synthesis of the high-pressure phase in a separate run. Therefore, a sample (4 wt%  $\text{Al}_2\text{O}_3$ ) was synthesized before the conductivity measurements were performed. The orthopyroxene powder was placed in a molybdenum capsule. The synthesis experiments were conducted at 25 GPa and 1873 K in the Kawai-type multi-anvil apparatus for 4 h within the stability field of bridgmanite. The retrieved samples were polished to remove the iron-poor part that existed close to the buffer material (Mo foil). Phase identifications were then carried out using a micro-beam X-ray diffractometer in reflection geometry. Finally, the polished samples were

**Table 1**  
Chemical composition of run products.

	5K1478 <sup>a</sup> n = 6	5K2629 n = 15	5K1485 n = 7	5K1488 n = 6
SiO <sub>2</sub>	57.40(98)	56.31(81)	58.20(139)	51.62(112)
Al <sub>2</sub> O <sub>3</sub>	4.06(20)	4.07(48)	6.48(58)	10.45(66)
FeO <sup>b</sup>	7.11(11)	7.09(62)	6.15(44)	7.07(89)
MgO	36.24(81)	36.20(63)	34.05(228)	31.41(116)
CaO	0.37(11)	0.25(15)	0.30(14)	0.31(12)
Na <sub>2</sub> O	0.04(3)	0.03(3)	0.06(4)	0.11(5)
Total	105.24(112)	104.63(32)	105.20(278)	100.11(160)
O = 3				
Si	0.94(1)	0.94(1)	0.95(1)	0.89(1)
Al	0.08(0)	0.08(1)	0.13(1)	0.21(1)
Fe	0.10(0)	0.10(1)	0.08(1)	0.09(1)
Mg	0.89(2)	0.90(1)	0.83(4)	0.81(3)
Ca	0.01(0)	0.00(0)	0.01(0)	0.01(0)
Na	0.001(0)	0.001(1)	0.002(1)	0.003(1)
Total	2.02(1)	2.02(4)	1.99(2)	2.01(1)
Mg#	90.1(1)	90.1(8)	90.8(1)	90.0(1)

The chemical compositions of melt were measured by an electron probe micro-analyzer under the operating condition of 15 kV and 12 nA.

<sup>a</sup> This run failed in the conductivity measurement by breakage of lead wire. Al-bearing bridgmanite was synthesized at 1900 K and 26 GPa, and was used for synchrotron Mössbauer spectroscopy.

<sup>b</sup> FeO is assumed that all Fe is ferrous iron.

prepared in the form of disks for use in the conductivity measurements.

Impedance spectroscopic measurements were carried out using a Solartron 1260 impedance gain-phase analyzer combined with a Solartron 1296 interface, which makes it possible to measure the properties of very high impedance materials (up to  $10^{14}$  Ω). Complex impedances were obtained at frequencies ranging from 1 MHz down to 0.1 Hz. The fundamental applied voltage is 1 V. The impedance spectra of Al-bearing bridgmanite measured at various temperatures generally showed a semicircular arc characteristic at low temperatures, suggesting that the equivalent circuit of the material is a sample resistance and capacitance in parallel (Supplementary Fig. 1). The sample resistance was calculated by fitting of the experimental data under the assumption that the equivalent circuit is a resistance–capacitance parallel circuit. At higher temperatures, the first arc disappeared and the induction component derived from the lead wire appeared. The conductivity values were computed from impedance values ( $Z'$ ) that were measured at the frequency where the phase shift is closest to zero.

In the case where orthopyroxene was used as the starting material, during heating to 1500 K, the nominal conductivity generally increased with increasing temperature and exceeded 1 S/m. During continuous heating to more than 1800 K, and following annealing at this temperature, the conductivity decreased until the orthopyroxene was completely transformed into bridgmanite, and then became nearly constant. After annealing for 1 h, heating and cooling cycles were repeated over a temperature range from 500 to 2000 K. During each cycle, the temperature was changed in 50–100 K increments and the electrical conductivity was measured at each temperature. Subsequent heating and cooling cycles were conducted until the reversibility of the conductivity behavior was confirmed.

After the conductivity measurements, the presence of bridgmanite was confirmed by micro-focused X-ray diffraction in all the samples. The samples were then polished to observe their microstructure by scanning electron microscopy and to determine their chemical compositions using electron microprobe analysis (EPMA), which was performed under operating conditions of 15 kV, 12 nA, a point beam and a 10-s counting time. The measured chemical compositions are summarized in Table 1. Finally, the samples were prepared in the form of doubly-polished thin

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