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## Lower mantle electrical conductivity based on measurements of Al, Fe-bearing perovskite under lower mantle conditions



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#### ABSTRACT

Laboratory measurements of the electrical conductivities of minerals provide important constraints on the chemistry and structure of the Earth's interior. We have measured the electrical conductivity of Al, Fe-bearing perovskite (Pv), the most abundant lower mantle phase, using a laser-heated diamondanvil cell (LHDAC). The sample with composition  $Mg_{0.83}Fe_{0.21}Al_{0.06}Si_{0.91}O_3$  (Fe³+/ $\Sigma$ Fe ratio  $\sim$  0.4) was synthesized at 26 GPa and 2073 K using a multianvil press. Sample resistance was measured *in situ* at high pressure and high temperature up to 82 GPa and 2000 K, respectively. Results show a continuous increase in electrical conductivity with increasing pressure, in contrast to some previous studies of (Mg, Fe)SiO<sub>3</sub> perovskite and a pyrolite assemblage where a decrease in conductivity was observed at higher pressure. Our results suggest that (1) incorporation of aluminum in Pv has a strong effect on its electrical conductivity and evolution with pressure; (2) spin crossover of Fe³+ does not occur or its effect on the conductivity is small in Al, Fe-bearing Pv, and (3) the contribution of ferropericlase to the electrical conductivity of pyrolite may be significant. The electrical conductivity profile of the Earth's lower mantle derived from geomagnetic data can be better explained by a pyrolitic bulk chemical composition rather than a non-pyrolitic model such as one based solely on perovskite.

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#### 1. Introduction

As the largest layer in the Earth, the lower mantle and the physical properties of lower mantle minerals are important for understanding the Earth's bulk chemistry, structure and dynamics. It is widely believed that the lower mantle consists mainly of Al, Fe-bearing perovskite (Pv) and ferropericlase (Fp) with a small amount of Ca silicate perovskite, based on the comparison of physical parameters (e.g., density, sound wave velocity, and electrical conductivity) of observations with laboratory-based estimations (e.g., Ricolleau et al., 2009; Irifune et al., 2010; Chantel et al., 2012; Murakami et al., 2012). However, the proposed chemical composition of the lower mantle is still controversial. Several studies support a pyrolitic lower mantle (e.g., Irifune et al., 2010; Chantel et al., 2012), while other studies suggested a non-pyrolitic lower mantle (Ricolleau et al., 2009; Murakami et al., 2012).

Electrical conductivity is quite sensitive to temperature and iron content; hence laboratory-based electrical conductivity of

lower mantle phases can place constraints on the thermal/chemical structure of the lower mantle. The electrical conductivity of Pv has therefore been the subject of high-pressure and hightemperature studies for decades (Peyronneau and Poirier, 1989; Li and Jeanloz, 1990; Shankland et al., 1993; Katsura et al., 1998; Xu et al., 1998; Ohta et al., 2008, 2010a, 2010b; Potapkin et al., 2013). In their pioneering work, Peyronneau and Poirier (1989) studied the electrical conductivity of Pv and Pv + Fp aggregates using a diamond-anvil cell (DAC), and concluded that geophysical observations could be explained by an aggregate of Al-free (Mg, Fe)SiO<sub>3</sub> Pv + Fp. Katsura et al. (1998) performed electrical conductivity measurements of (Mg<sub>0.93</sub>Fe<sub>0.07</sub>)SiO<sub>3</sub> Pv at 23 GPa using a multianvil apparatus and obtained results that supported a pyrolitic uppermost lower mantle. A subsequent study (Xu et al., 1998) found that incorporation of aluminum greatly enhances the electrical conductivity of Pv (~3.5 times higher than aluminumfree Pv), based on data collected during multianvil experiments. The laser-heated diamond-anvil cell (LHDAC) study of Ohta et al. (2010b) involved electrical conductivity measurements of pyrolite and mid ocean ridge basalt (MORB) up to 133 GPa, and results indicated that the electrical conductivity of pyrolite did not match profiles based on geomagnetic observations below 1500 km. Instead, pyrolite + MORB bulk composition was found to be

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consistent with observed conductivity profiles in the deeper part of the lower mantle. The mismatch of pyrolite properties to conductivity profiles was attributed to the drop of electrical conductivity induced by spin crossover of Fe<sup>3+</sup> in Pv. More recently, Potapkin et al. (2013) reported the pressure evolution of the electrical conductivity of Mg<sub>0.60</sub>Fe<sub>0.40</sub>Si<sub>0.63</sub>Al<sub>0.37</sub>O<sub>3</sub> Pv, relevant to Pv in a bulk MORB composition. Results indicated that the electrical conductivity of Al, Fe-rich Pv did not decrease up to  $\sim$ 120 GPa, in contrast to the behavior of (Mg, Fe)SiO<sub>3</sub> Pv and pyrolite material (Ohta et al., 2010a, 2010b). However, the conductivity data of Potapkin et al. (2013) could not be compared directly with lower mantle profiles, because their composition of Pv was not representative for the Earth's lower mantle. Laboratory-based data on the behavior of Pv at high-pressure and -temperature with composition relevant to the lower mantle are limited so far. Notably, no study has yet reported the electrical conductivity of Pv with pyrolitic composition up to high-pressure and -temperature conditions that simulate the deeper part of the lower mantle.

Experimental studies have shown that iron in Pv and Fp undergoes spin crossover at high pressures and high temperatures corresponding to the middle part (~2000 km depth) of the lower mantle (Badro et al., 2004; Lin et al., 2007a; Potapkin et al., 2013; McCammon et al., 2013). It is widely believed that high spin to low spin crossover of Fe<sup>2+</sup> in Fp occurs at around 30-80 GPa depending on the iron content and temperature (Lin et al., 2007a; Fei et al., 2007; Komabayashi et al., 2010; Yoshino et al., 2011). Fe<sup>2+</sup> in Pv has been postulated to undergo crossover from high spin to intermediate spin (McCammon et al., 2008; Lin et al., 2008; Potapkin et al., 2013), although theoretical calculations have failed to find a stable intermediate-spin state of  $Fe^{2+}$  in Pv (e.g., Hsu et al., 2011; Metsue and Tsuchiya, 2012). There is also some dispute as to whether spin crossover of Fe<sup>3+</sup> in Pv occurs in the lower mantle (see review by McCammon et al., 2013). There is, however, a general consensus that the Fe<sup>3+</sup> remains in the high spin when it occupies the A-site of Pv (Catalli et al., 2010, 2011; Fujino et al., 2012; Lin et al., 2012; Potapkin et al., 2013), and that it undergoes high spin to low spin crossover at 50-60 GPa when it occupies the B-site of Pv (Catalli et al., 2010, 2011; Fujino et al., 2012; Lin et al., 2012). Although spin crossover is considered to strongly affect electrical conductivity (Lin et al., 2007b; Ohta et al., 2007, 2010b; Yoshino et al., 2011), only one study so far has conducted a simultaneous investigation of the electrical conductivity and electronic state of iron in Pv (Potapkin et al., 2013).

In this study we report the electrical conductivity of Al, Febearing Pv up to 82 GPa and 2000 K using the LHDAC technique on a well characterized sample with composition relevant for the lower mantle (Mg<sub>0.83</sub>Fe<sub>0.21</sub>Al<sub>0.06</sub>Si<sub>0.91</sub>O<sub>3</sub>). Results show a monotonic increase in electrical conductivity with increasing pressure with no drop in contrast to previous studies of (Mg, Fe)SiO<sub>3</sub> perovskite and pyrolite. Such differences from previous data can be attributed to the effect of aluminum and Fp. Overall the conductivity of Al, Fe-bearing Pv is significantly higher than geomagnetic observations, which is consistent with a pyrolitic lower mantle rather than a non-pyrolitic composition such as a perovskitic model.

#### 2. Experimental procedure

The sample of Al, Fe-bearing Pv was synthesized using a multianvil apparatus and was synthesized in the same run as the sample S4949 in our previous study (Potapkin et al., 2013). Fine grained SiO<sub>2</sub>, MgO,  $^{57}$ Fe<sub>2</sub>O<sub>3</sub> (90% enriched) and Al<sub>2</sub>O<sub>3</sub> were ground well for 1 h. The mixture was heated at 973 K for one day in a H<sub>2</sub>–CO<sub>2</sub> gas-mixing furnace, where oxygen fugacity was controlled at log fO<sub>2</sub> = -21 to reduce Fe<sup>3+</sup> to Fe<sup>2+</sup>. The starting material was loaded into a rhenium capsule and then packed into a MgO container. The multianvil synthesis used LaCrO<sub>3</sub> for the heater, and was run for 30 min at pressure and temperature conditions of 26 GPa and 2073 K, respectively. The synthesized sample was examined using a field-emission-type scanning microscope (SEM) (Leo Gemini 1530) and the chemical composition was determined using an electron microprobe (JEOL JXA-8200) operated at 15 kV and 15 nA. The sample was determined to have the composition  $Mg_{0.828(18)}Fe_{0.208(13)}Al_{0.059(2)}Si_{0.911(23)}O_3$ . Phase identification was performed by powder X-ray diffraction (XRD) using a FR-D high-brilliance Rigaku X-ray diffractometer with Mo-K $\alpha$  radiation operated at 55 kV and 60 mA. The XRD pattern showed the sample to be single phase Pv. The  $Fe^{3+}/\Sigma Fe$  ratio was determined by Mössbauer spectroscopy with a nominal <sup>57</sup>Co high specific activity source in a rhodium matrix. The Mössbauer spectra were analyzed using the MossA software package (Prescher et al., 2012), and indicated a  $\mathrm{Fe^{3+}}/\Sigma\mathrm{Fe}$  ratio of 0.36(5). At ambient conditions the electrical conductivity could not be measured because of the high resistance.

Electrical conductivity measurements were carried out using a diamond anvil cell (DAC). After characterization, the sample was prepared by double polishing so that the top and bottom surfaces were parallel to each other. Diamonds with 250  $\mu m$  culet diameter were used for anvils. A 250  $\mu m$  diameter hole was drilled in a rhenium plate, which was pre-indented to a thickness of  $\sim\!50~\mu m$ . A mixture of cBN + NaCl was filled into the hole in the rhenium plate and subsequently compressed to 50  $\mu m$  thick. After compaction, a  $\sim\!100~\mu m$  diameter hole was drilled in the cBN + NaCl mixture using a pulsed laser. Platinum foils with 5  $\mu m$  thickness were placed underneath the sample as electrodes, and the sample + electrodes were sandwiched between two layers of SiO2 glass, which served as a thermal insulator (Figs. 1, 2).

Determination of electrical conductivity from measured resistance values requires knowledge of the thickness, width and length of the sample. The width and length were determined by optical observation using a microscope with higher accuracy compared to the thickness. The uncertainty in the width and length is small, since it can be accurately measured throughout the entire procedure (compression, heating and decompression). In order to estimate the thickness of the sample, the thickness of the sample chamber (SiO<sub>2</sub> glass + sample + electrode) was directly measured using a micrometer and assuming that the diamonds were not deformed. From the results, we estimated the relationship between pressure and thickness ratio (Fig. 3). In calculating the thickness of individual components (SiO<sub>2</sub> glass, sample or electrode), we further assumed that all components compressed uniformly. For example, the initial thickness of the platinum electrode was 5 µm and the estimated thickness ratio was roughly 0.5 at 20 GPa, hence the thickness of the platinum was estimated to be roughly 2.5 µm at 20 GPa. The validity of this assumption was justified by SEM observation of the recovered sample (Figs. 2a, 3). The relative uncertainty of the thickness determination is estimated to be  $\pm 50\%$ (see discussion for details).

During the DAC experiments the pressure was determined at 300 K using the Raman spectra of diamond (Akahama and Kawamura, 2004), and at higher temperatures assuming a thermal pressure of +15% (Sinmyo and Hirose, 2013). The electrical conductivity was determined by the two-terminal method using a multimeter. For run #1, the electrical conductivities of the sample were measured up to 77 GPa without heating (Table 1, Fig. 4). For runs #2–5, the electrical conductivities of the samples were measured at high-pressure and -temperature conditions. The samples in runs #2–5 were heated by a portable laser heating system using the double-sided heating technique in order to reduce temperature gradients (Kupenko et al., 2012). The laser-heated spot was expanded sufficiently in order to heat the entire sample located between electrodes. The temperature was determined during laser

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